

# Entrepreneur India

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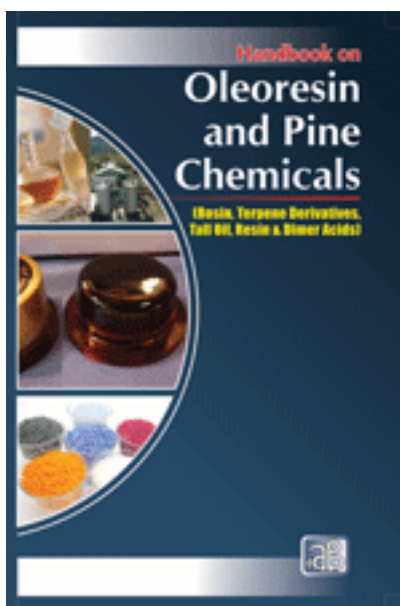
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Handbook on Oleoresin and Pine Chemicals (Rosin,  
Terpene Derivatives, Tall Oil, Resin & Dimer Acids)



<b>Code:</b>	ENI207
<b>Format:</b>	Paperback
<b>Indian Price:</b>	2200
<b>US Price:</b>	59
<b>Pages:</b>	608
<b>ISBN:</b>	8178330199
<b>Publisher:</b>	Pacific Business Press Inc. Asia

Oleoresin and pine chemicals are a fascinating group of substances derived from the sap of coniferous trees. This diverse family of products includes rosin, terpene derivatives, tall oil, resin, and dimer acids, each with their own unique properties and characteristics. Rosin, also known as colophony, is a sticky substance that is obtained by distilling the resin from pine trees. Terpene derivatives, on the other hand, are a broad class of compounds that are derived from terpenes, which are the primary components of essential oils in plants. Tall oil is a byproduct of the pulping process in the paper industry. It is obtained by extracting fatty acids from the black liquor, a waste stream generated during pulp production. Resin refers to the mixture of gum and resin obtained from pine trees. It is often processed to remove impurities and concentrated into a solid or liquid form. Dimer acids are a specific type of fatty acid derived from tall oil or other vegetable oils. They are created through a chemical reaction called dimerization, which involves the linking of two fatty acid molecules. Dimer acids are known for their excellent performance as raw materials in the production of various products such as coatings, adhesives, and synthetic lubricants.

The global oleoresin market size is anticipated to witness a compound annual growth rate (CAGR) of 6.9%. Growing demand from healthcare, pharmaceutical, food, and beverage industries are driving forces of the global oleoresin market. Oleoresins are made from varied ingredients and spices, which are found all around the world. It is usually found in semi-solid extract form. A variety of oleoresins has multiple characteristics based on the spice they are derived from. They exhibit numerous therapeutic as well as antioxidant properties as well and are utilized in the pharmaceutical, healthcare, food, and beverage industries. The European region led the market with a revenue share of more than 30%. This is attributed to the increasing demand for flavors and coloring agents from the food & beverage industry. Another factor contributing to increased demand for the product in the region is the demand from cosmetic, fragrance, and personal care products industries that act as a hefty end-use industry for oleoresins.

The Major Contents of the books are Pinus, Oleoresin Extraction, Processing of Oleoresin, Rosin Derivatives, Terpene Based Adhesives, Essential Oil, Wood Turpentine Oil, Turpentine Products, Tall Oil, Dimer Acids.

A comprehensive reference to manufacturing and entrepreneurship in the Oleoresin and Pine Chemicals products business. This book is a one-stop shop for everything you need to know about the Oleoresin and Pine Chemicals products manufacturing industry, which is ripe with potential for manufacturers, merchants, and entrepreneurs. This is the only comprehensive guide to commercial Oleoresin and Pine Chemicals products manufacture. It provides a feast of how-to knowledge, from concept through equipment purchase.

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**Sample Chapter:**

# Pinus

## Introduction

The genus *Pinus* L comprising evergreen trees has been known to mankind from time immemorial. Theophrastus (372-287 B.C.) in his early writings made a reference to the morphology and reproduction of pines. Its decorative value has been exploited in old Chinese paintings. Pine incense used to be burnt in the religious ceremonies of the Mayas, the Aztecs and the Romans.

The pines have been traced back in geological history to the Jurassic period (150 million years) though they reached their climax of distribution only in the Tertiary (60 million years). By the lower Cretaceous (125 million years) two distinct groups emerged viz. (i) Haploxylon or soft pines and (ii) Diploxylon or hard pines. The plants exhibit an exceptionally long life. In the Inyo National Forests of California, USA there is a tree of *Pinus aristata* which is more than 4600 years old still producing cones occasionally.

*Pinus* belongs to the family Pinaceae or Abietaceae of the order Coniferales. The other genera included in this family are *Abies* Mill., *Cathaya* Chun & Kuang, *Cedrus* Link., *Keteleeria* Carr., *Larix* Mill., *Picea* A. Dietr., *Pseudolarix* Gord., *Pseudotsuga* Carr. and *Tsuga* Carr.

Some of the characteristic features of the family are as follows: the plants are monoecious; the microsporophylls are spirally arranged with two abaxial sporangia per sporophyll; female cones with numerous spirally arranged pairs of scales (seed scale complex) viz. ovuliferous scales and the bract scales; the former free from the latter or only slightly fused at the base; ovules adaxial with their micropyles directed towards cone axis; and seeds generally winged.

## Distribution

The genus has a cosmopolitan distribution and is represented by about 105 species. Jackson however mentions c. 80 valid species. It is found mainly in the northern hemisphere: northern Europe, northern and central America, Bahamas, British Honduras, the subtropics of North Africa, the Canary Islands, Afghanistan, Pakistan, India, Burma and the Philippines, crossing the Equator in Indonesia. In the tropical countries like India it is found in the hills with subtropical or temperate climates though some pines are grown as ornamentals even at lower altitudes.

## Distribution in India

In the Indian subcontinent there are six species of *Pinus* of which four are distributed in the Himalayas. They are *P. roxburghii* Sarg., *P. wallichiana* A.B. Jacks., *P. insularis* Endl. and *P. gerardiana* Wall. ex Lamb. A few trees of *P. armandii* Franch. occur in the North East Frontier Agency (NEFA). *P. merkusii* Jungh. & de Vriese grows on the hills of Burma. The altitudinal range of these pines varies considerably. Apart from indigenous species, some exotic species also occur. These are listed below along with the areas where they were successfully planted.

## Morphology

In their general habit, young pine trees are pyramidal with their horizontal branches disposed in regular whorls. As the tree matures, this symmetry is lost and the crown becomes rounded, flat or even spreading. Under cultivation, when planted close, the trees lose their branches and thus have a considerably long bole.

The stem bears two types of branches: (i) branches of unlimited growth or long shoots, and (ii) branches of limited growth or dwarf shoots, also termed brachyblasts. The long shoots appear on the main stem as lateral buds in the axils of scale leaves. Each of these shoots terminates in an apical bud which is enclosed by a number of bud scales closely surrounded by a thick mat of hairs. The lateral buds grow more or less horizontally to a certain length and this growth has been termed nodal growth. In some pines this growth is

restricted to the production of a single internode every year (uninodal pines) but in some others there may be two to several internodes per year (multinodal pines).

The dwarf shoots or foliar spurs develop on the long shoots arising in the axils of scale leaves. Each dwarf shoot initially has two opposite scales termed prophylls followed by 5-13 spirally arranged scaly cataphylls. These are in 2/5 phyllotaxy. Finally depending upon the species 1-5 needle like leaves develop. Unlike the long shoot the dwarf shoot lacks a terminal bud. The leaves are of two kinds (i) the foliage leaves which appear only on the foliar spurs and (ii) the scale leaves which are developed as protective structures.

The male and female cones are borne on the same tree though on different branches. They become visible towards the end of spring or the beginning of summer. The male cones (the modified dwarf shoots) appear in clusters (catkin) on the lower branches of the tree whereas the female cones which replace the terminal buds of the long shoots are the modified long shoots. In most of the species including *Pinus roxburghii* and *P. wallichiana* the mature female cones open and release the seeds but in others the seeds are released only after the cones fall to the ground and rot. In a few species such as *P. flexilis* the cones remain on the tree for several years and open only when they are scorched by forest fire.

The pines are generally light demanders; a few can tolerate partial shade for several years but their growth is stunted. They do not thrive in areas which remain hot and humid throughout the year. Only a few species like *P. taeda* grow successfully on wet lands. Alternation of seasons dry and wet and warm and cold or often a combination of both is required for the normal development of pines.

There are several external characters which facilitate the identification of different pines. The number of needles per dwarf shoot their length the position of the umbo on the apophysis and the shape size and colour of the resting bud are some of the important ones.

*P. wallichiana* the blue or Bhutan pine commonly known in trade as Kail is found in the Himalayas mainly from Kashmir to Bhutan at altitudes of 1 500-3 000 m. It has also been recorded at as high an altitude as 3 600 m along the region of Namchebazar and Thengopoché. It is very common in the Western Himalayas in Kashmir valley Simla Chakrata and Mussoorie and in the eastern Nepal at altitudes of 1 500-2 135 m. In Bhutan it occurs along the valley above the river Tista (lower Rangeet valley). Though this species is sporadically distributed along the eastern part of the Kameng division of NEFA it is most dominant in the Khalaktang area Rupa valley and the Dirang Dzong valley at an altitude of 1 500 m covering an extensive area along the hill slopes. In the Subansiri division of NEFA the species is restricted to the mountain slopes surrounding the Apatanang valley at an altitude of 1 500-1 830 m. Here it appears to have been introduced since there is no trace of the species in the surrounding mountain slopes.

The species is found on a variety of geological formations growing best on well drained moist soil with an annual rainfall of 100-200 cm. Some of the best forests are found on mica schist which breaks down into ideal soil. It is frequently associated with *Cedrus deodara* (Roxb.) G. Don *Abies pindrow* (Royle) Spach and *Picea glauca* (Moench) Voss.

The blue pine is an elegant tree 30-90 m high with horizontally spreading branches. The young shoots are glaucous green. Each dwarf shoot has five needles 12.5-20.0 cm long and the leaf sheaths (scale leaf prophyll and cataphyll) are non persistent. The winter buds are cylindrical conic 0.6-1.2 cm long. The female cones are 15-30 cm long with rounded ovuliferous scales. The seeds are winged; wings membranous about thrice as long as the seed.

Under abundance of light and protection the blue pine regenerates profusely. The seeds germinate during rainy season. If artificially regenerated direct sowing is preferred to transplanting. The young trees grow fairly rapidly but on reaching maturity the girth increment becomes slow and growth in height may almost stop.

Kingdon Ward reported the occurrence of this species in the NEFA area. The tree attains a height of 18 m

and a diameter of one metre. The winter buds are cylindrical blunt and slightly resinous. The needles are 10-15 cm long. The female cones are subterminal in groups of 2-3; cone is 2.5 cm or more long broadly tapering into rounded apex. The wingless seeds are 1.3-1.6 cm long and are liberated soon after they ripen. The taxonomic status of *P. insularis* and *P. kesiya* Gord. is not satisfactorily settled. There is a strong possibility that these two names refer to the same species. Savory made a study of the morphology and anatomy of the wood of these two species. No significant difference was found between them to justify their separation. Accordingly *Pinus insularis* Endl. has been treated by some authors as a synonym to *P. kesiya* Royle ex Gord. in Loud Gard. mag. 16-8 1840.

The Khasi pine is restricted only to the eastern Himalayas where it is commonly found along the various ranges of the Garo, Khasi and Jaintia hills (800-2000 m). The species has been introduced successfully in the Aijal area of the Lushai hills (1220 m). In the northern part of Manipur and the Naga hills round about Kohima (1220-1830 m) it appears in isolated patches. The plant grows well in fairly moist regions free from extremes of heat and cold on loose textured soil like granitic or sandstone rocks covered with clay. The tree is 60-90 m in height and trunk up to 6 m in diameter. The bark is thick reddish grey and deeply fissured giving a reticulate appearance. The branches are arranged in whorls forming a rounded crown. The leaves are in fascicles of threes and are 15-25 cm long slender with acute apices. The old needles fall for the most part during April-May though the scale leaves are persistent.

The male and female cones appear on the new shoots during February-March. The mature male cones are light brown and 3-5 cm in diameter. The female cones are approximately 5.0-7.5 cm long and 4-6 cm in diameter and are the smallest amongst the Indian pines. They are ovoid and initially light green but turn brown as they mature. The prominent umbo is sharply mucronate in the centre. The seeds have long wings which are about four times the length of the seed.

The plants come up naturally in places of abandoned or shifting cultivation or in areas where undergrowth of forests has been burnt. For artificial regeneration the seeds are sown broadcast. The growth rate is fairly high.

Of all the Indian pines *P. roxburghii* is the most important and is known as the Himalayan long leaved pine or Chir pine. It is peculiar to the main valleys of the western Himalayas at altitudes of 460-1500 m and extends into Bhutan (Biswas 1933). Along the eastern Nepal this species is restricted to lower elevations. In NEFA along the Kameng Frontier Division it appears to be very sparsely distributed among the pure and extensive formations of *P. wallichiana*. It either forms a pure forest or occurs as a co-dominant species with other plants. At higher altitudes it is associated with *Cedrus deodara* (Roxb.) G. Don *Pinus wallichiana*, *Quercus inlana* roxb. and *Rhododendron arboreum* Smith whereas at lower altitudes it is found along with *Anogeissus latifolia* Wall. *Bauhinia latifolia* Cav. *B. variegata* L. and *Shorea robusta* Roxb.

*P. roxburghii* is a large evergreen tree with a spreading crown. The young shoots are grey to pale brown and the winter buds are ovoid and non resinous. Leaves 15-40 cm long three on a dwarf shoot. The mature female cones are 12-24 cm x 7.5-14.0 cm the ovuliferous scales having reflexed apices. The umbo is very prominent and the seeds are about 8-16 mm long with c. 2.5 cm long membranous wings.

Natural regeneration is normally through seeds. Mature cones are collected from healthy trees for artificial regeneration placed in hot sun to loosen the scales and then the seeds thrashed. This is normally practised where coniferous forests have been damaged by fire and is mostly done by direct sowing (With India Raw Materials VIII).

This species is the source of Chilgoza or Nioza seeds of commerce which are eaten as such or after roasting. It is found in northern Afghanistan and in the north western Himalayas occurring on the borders of Tibet, Kashmir and Pakistan. It also occurs in Kalpa (Kinnaur) and Pangi districts of Himachal Pradesh. The plant is an evergreen tree 18 m or more in height and 1.8-2.4 m in diameter. It grows on dry rocky

grows at an elevation of 1 830 3 600 m. It thrives best in areas where the rainfall is scanty but winter snowfall is heavy. The species can easily be identified by its bark which is shed in small flakes. The branches are ascending and are either obscurely whorled or not whorled. They are comparatively thin grey with mottled appearance. The shoots are glabrous and greyish green. The winter buds are spindle shaped and nearly 1.5 cm long. The stout short leaves are c. 5 10 cm long and occur in groups of threes on dwarf shoots. The male cones are visible during May June when pollination takes place. The female cones are large hard and woody having reflexed triangular umbos. Each cone is 15 20 cm × 10 13 cm.. The seed is c. 2.5 cm long with a very short rudimentary wing.

*P. merkusii* is the most tropical of all pines and is of common occurrence in the southern Shan States of Burma. It has been recommended for planting along the eroded hill slopes of the Andaman and Nicobar Islands. Commonly known as Tenasserim pine it normally attains a height of c. 20 m when mature. The bark is grey to brown thick and deeply fissured. The leaves are in pairs 17 33 cm long persisting for 1 ½ 2 years. The female cones are cylindrical borne in pairs and at maturity reach a length of c. 5.7 cm. The umbo is rhomboid and furrowed. The small seeds are winged.

## Anatomy

### Root

The plant possesses initially a primary taproot with a large number of laterals arising in an acropetal succession. In most cases the growth of the primary root soon becomes arrested while the laterals termed long roots continue to grow. Later the dwarf roots arise in clusters on the long roots. They branch dichotomously and form coralloid masses. Some of these harbour an ectotrophic mycorrhiza and are termed mycorrhizal roots.

**Long roots.** In a transverse section the epidermal cells appear more or less isodiametric and many of them are filled with tannin as in *P. roxburghii* *P. wallichiana* and *P. gerardiana*. The broad cortex is distinguishable into a peripheral zone of small and an inner zone of large parenchymatous cells.

Frequently the cells of both the zones are filled with starch. The endodermis is composed of suberized cells usually impregnated with tannin which gives them the brownish orange colour. It shows indistinct casparian strips followed by 6 7 layers of pericycle. The walls of the peripheral pericyclic cells are slightly thickened while those of the inner cells are thin. Many of them contain tannin.

The stele is generally diarch or tetrarch but may sometimes show pentarch condition. The number of protoxylem elements varies from 8 to 16. Each protoxylem point is associated with a resin duct and consists mostly of scalariform or scalariform pitted tracheids while the metaxylem is made up of pitted tracheids. The phloem which alternates with the xylem strands consists of parenchyma sieve and tannin cells. The pith cells contain a considerable amount of starch; some of them also contain tannin.

Secondary growth sets in when the primary tissues are still in the process of differentiation. A zone of cambium differentiates from the parenchymatous cells beneath the phloem. This by repeated periclinal divisions forms secondary xylem towards the pith and secondary phloem towards the cortex. In the region of the resin ducts the cambium cuts off only parenchymatous cells resulting in broad xylem rays. With subsequent development of the secondary wood the rays are reduced to the width of only a single cell. The secondary xylem is made up of tracheids with bordered pits on their tangential and lateral walls. Many tracheids get blocked with tyloses in older roots. The rays are either uni or multiseriate the latter being always associated with resin ducts.

The primary phloem soon gets crushed and is unrecognizable. The secondary phloem consists of radially oriented (disposed) rows of cells. Many of the parenchymatous phloem ray cells contain tannin.

## Pine Oleoresin Extraction Methods



# Introduction

Modern gum naval stores methods have been developed to benefit both the gum producer and the timber owner. Following the methods described in this booklet will bring maximum gum yields will reduce chipping labor requirements about 50 percent and will make the worked out tree saleable for other wood products. If these modern turpentine methods are used naval stores can be integrated in the management plan for pine timbered lands and timber owners can almost double the dollar value per tree by leasing or working for naval stores before they harvest.

The aim of this booklet is to bring together in one place all the best modern methods of producing gum and to describe the principal factors that affect gum flow.

The extraction methods and application techniques described here were developed during 15 years of research and testing by scientists at the Forest Research Institute with the cooperation of gum producers and timber owners throughout the gum naval stores belt.

## Cup the Larger diameter Trees for Increased Yields and Greater Profits

A crop of single faced trees 11 inches in diameter will produce 60 barrels more gum per year than 9 inch trees. The costs for installing tins and for chipping are about the same for 9 and 11 inch trees. The number of small diameter trees worked can be the difference between break even and profitable operation.

**Double Facing.** Only one face per tree should be installed on trees smaller than 14 inches in diameter. Simultaneous working of two faces installed on one tree does not mean that gum yields from that particular tree will double. The yield from two faces worked simultaneously is normally not more than 70 percent of the yield which could have been obtained from two faces worked one at a time.

Two faces should be installed on trees 14 inches d.b.h. and over for obtaining the greatest yield if the trees are to be worked out in 4 years.

The volume of gum produced is directly related to the width of the face. Good gum yields can be obtained with a face width equal to the diameter of the tree measured at breast height. For example a 10 inch tree should have a 10 inch face and a 12 inch tree a 12 inch face.

**Gum Yield from Shoulders.** With bark chipping and acid treatment 75 percent of the gum yields at each dipping flows from the shoulders of the face. If careless chipping extends the streak  $\frac{1}{2}$  inch beyond the range of the tins on each side of the face a barrel of gum is wasted during the season for every 310 trees worked.

**Use Correct Tin Lengths.** One piece tin assemblies or broadaxe inserted tins will not give full face widths on 12 inch trees and larger. For full face widths and good gum yields use 10 inch spiral gutters on trees 9 to 12 inches in diameter. Use 12 inch spirals on trees 12 to 16 inches in diameter. For an apron use a 7 or 8 inch straight or curved gutter with either length.

## First Year Installation of Spiral Gutters with Double Headed Nails

**Shaving the Bark.** Shave off the rough bark using double edge shove down scrape iron or a bark shave tool. Shave only the area where the tins will be nailed and the cup will sit. Shave a fairly flat seat for the apron and cup; keep the spiral gutter side of the tree round. Remove enough bark to get rid of the deep cracks.

**Attach the Apron First.** Drive the first nail at the middle of the apron. Level the apron and drive the second nail in the left shoulder. Set this nail close to the end of the tin so as to get full face width. Drive all nails near the top edge of the tins; this pulls the edge into the bark to prevent leakage behind the tins. Pound the inner lip of the right hand end of the apron so that it fits snugly against the tree. Do not nail the right hand end at this stage.

Use only double headed nails designed specially for attaching and removing naval stores tins.

**Attaching the Spiral Gutter.** Lap the lower end of the spiral gutter over the right hand end of the apron. Set

the angle of the spiral between 30 and 40 degrees around 30 for slash and steeper for longleaf pine. Drive the first nail in the middle of the spiral. Drive the next nail through both the spiral gutter and the apron at the overlap. Drive the shoulder nail last. Close any gaps between the gutter and the bark by pounding the inner edge of the gutter into the bark.

## Completed Installation

The double headed nails are numbered in the photograph to show the order in which they are driven. To support a large 2 quart cup a 30d flathead nail is used. A standard size cup takes a 20d nail. Drive the cup nail at a slight angle so outer edge of cup will snap over nail head. This holds cup snugly against tree.

## Use of the Advanced Streak

With bark chipping and acid treatment the familiar lead or advance streak is not necessary as it will not increase the volume of gum produced the first year from virgin installations. An advance streak applied 30 days before the regular chipping season begins will give good early season yields for the first 8 weeks of the season but yields for the remainder of the season will be reduced proportionally.

Producers may consider it desirable to produce an increased volume of gum during April and May. There may be a psychological effect in getting something in the cup quickly to spur the interest of chipping and dipping laborers.

The best type of advance streak for good early season yields is a bark streak  $\frac{5}{8}$  to  $\frac{3}{4}$  inch high treated with 50 percent sulfuric acid applied 30 days in advance of the regular chipping season.

## Turpentine and Growth

Measurement data covering a 2 year period from a plantation of 20 year old slash pine growing at the rate of 8 annual rings per inch with 15 x 15 foot spacing and worked with modern gum extraction methods showed that

The annual volume increment in cubic feet of turpented trees was 26 percent less than that of round unworked trees. This reduction in growth was correlated with the width of the face on the tree; the wider the face on a tree of given size the slower the growth. For normal face width equal to the diameter of the tree the annual deficit per turpented tree would be about 2 cents for pulpwood and 5 cents for saw logs at current stumpage prices. The gross value for naval stores per year would range from 15 to 25 cents per tree.

Growth loss from turpentine was not directly related to the volume of gum extracted from the tree annually. Thus the extent of growth loss is the same for indifferent work and poor gum yields as for skilled work and good yields.

## Bark Chipping

The bark hack removes the outer rough bark and the white inner bark exposing the gum ducts in the wood. Acid is then sprayed on the surface of the wood. The action of the acid holds these gum ducts open for a period of 2 weeks. It is the acid that makes the gum flow from the tree for the 2 week period. Chipping merely prepares the area for acid treatment. It is not necessary to cut into the wood with the bark hack because a wood streak  $\frac{1}{2}$  inch deep will not produce any more gum than a streak of bark depth both treated with acid.

**How Often to Chip and Treat.** Treating the streak with acid prolongs the flow of gum; therefore it is necessary to chip and treat only once every 14 days. Chipping and treating every 2 weeks during the chipping season will get practically all of the gum the tree can produce over a period of 4 to 6 years.

**Height of Streak to Chip.** For maximum gum yields over a 4 year period bark streaks  $\frac{3}{4}$  inch high are recommended for both slash and long leaf pine.

## Mounting and Sharpening the Bark Hack

The bark hack has been designed with a special flat bill square corners and high jaws to cut through two

thicknesses of bark. If it is correctly mounted and sharpened clean streaks can be chipped and blades will last several years.

The angle (called pitch ) at which the hack head is mounted in the wooden stock helps to prevent chipping into the wood. The best mounting angle for speedy bark chipping is shown below.

Proper sharpening of a bark hack blade contributes greatly to the chipping of a clean streak and actually determines how long a blade will last.

A steel cutter may be used to cut out and to thin the edges of a new blade as illustrated below but the final sharpening touches should be with a flat file. Do not use the cutter to resharpen the edges; use the flat file or whetstone.

Quite often laborers will file a long keen bevel at the bill to make woodcutting easier. But the corners will soon break leaving large gaps in the blade. The blade should be filed so that the corners are kept square at all times. A rounded or gapped corner will leave patches of inner bark in the streak. These patches of bark will stop the flow of gum from above the streak and reduce monthly yields.

In many instances poor gum yields from bark chipping and acid treatment have been traced directly to such a simple cause as improperly sharpened hack blades. To reduce the excessive breakage of blades for speedier bark chipping and for maximum gum flow from each streak producers should occasionally check with their laborers on the sharpening and mounting of bark hack blades.

## Treating the Streak

The difference between poor and good yields each month is directly related to the amount of acid properly sprayed on each freshly chipped streak.

A 50 percent solution of sulfuric acid is used on both slash and longleaf pine. The plastic bottle of the acid sprayer is filled only two thirds full and the sprayer is held at a 45 degree angle for obtaining good treatment. Keep the nozzle tip from 1 to 2 inches below the top of the streak and from 1 to 2 inches away from the tree. Move the sprayer in one steady motion across the streak spraying enough acid to wet the streak thoroughly from shoulder to shoulder.

The sprayer should be aimed so that the spray from the nozzle hits the streak at the line where bark meets wood. The acid should be discharged from the sprayer in the form of a spray. Normally a stream of acid does not give good treatment because a stream hits the streak with force spatters and the major portion runs down the face as waste.

Good treatment is of vital importance and laborers must be consistently supervised to assure quality treatment for profitable gum yields.

## Acid Penetration Above the Streak

For acid treatment to be effective the acid must penetrate the area above the exposed wood at the streak line. Acid penetration causes a reddish brown color in the white inner bark and on the surface of the wood. Penetration above the streak is necessary and is obtained only by good treatment in which the streak is wet thoroughly and evenly.

**Height of Acid Penetration.** The volume of gum produced by each streak is directly related to the distance the acid penetrates above the streak; the higher the penetration the greater the yield. The penetration line and the tissues killed by acid treatment can be seen when the next streak is chipped.

Normally 50 percent sulfuric acid properly applied in sufficient quantity will penetrate  $\frac{1}{2}$  to  $\frac{3}{4}$  inch above the streak in 14 days. Good penetration is obtained by using the acid sprayer correctly as the acid must be sprayed into the top portion of the streak. Through careless application most laborers waste more acid per streak than is needed for good treatment.

If the height of acid penetration is under  $\frac{1}{2}$  inch then treatment has been poor and maximum yields will not be obtained from that streak. Poor treatment can usually be traced to careless application.

For best gum yield the tissues killed by acid penetration should be removed and fresh green wood exposed with each streak chipped. Serious yield decline may result unless the chipping keeps up with the acid penetration.

## Pines for their Oleoresin

Pines besides being a source of valuable timber and pulpwood yield pitch tar rosin or colophony and turpentine collectively known as naval stores a term coined to these owing to their use for construction and maintenance of sailing vessels as sealing compounds for their wooden hulls. Rosin and turpentine are obtained by distillation of crude pine oleoresin exuding from the trunks of standing pine trees as a result of injury. Rosin and turpentine are also obtained by distillation or solvent extraction of felled pinewood and wood waste. In the paper pulp industry rosin and turpentine are obtained as one of the important by products. Pine rosin and turpentine as used in most varietal ways and form raw material to a number of industries all over the world. Rosin finds use in soap paper sizing wall board synthetic rubber adhesives paint driers varnishes lacquers paints water proofing compounds axle greases cements linoleum floor waxes pharmaceuticals inks etc; turpentine in paint and varnish thinning rosin solvent lacquers water proofing compounds synthetic pine oil insecticides terpene resins synthetic camphor flavours and perfumes refined terpenes and derivatives rubber pharmaceuticals polishes etc.

**Geographic distribution of pines.** The pines belong to 94 recognized species of the genus *Pinus*. Except one species *P. merkusii* (Merkus Pine) which crosses the Equator in Sumatra (Indonesia) in nature all the pines are confined to Northern Hemisphere extending from polar region to the tropics. A list of species represented in the natural flora of different countries is given in the Appendix I.

**Pines tapped for oleoresin.** The important pine species tapped for their oleoresin in different countries are *P. palustris* (Longleaf Pine) and *P. elliottii* (Slash Pine in U.S.A.; *P. pinaster* (Cluster or Maritime Pine) in France Portugal and Spain; *P. sylvestris* (Scots Pine) in U.S.S.R. Finland Norway Sweden Germany Poland Austria Yugoslavia Bulgaria and Hungary; *P. halepensis* (Aleppo Pine) in Greece France Spain and Algeria; *P. nigra* (Austrian or Black Pine) in Austria Albania Bulgaria Italy Spain Yugoslavia Greece and Turkey; *P. sibirica* (Siberian Stone Pine) in U.S.S.R. (Western and Central Siberia); *P. brutia* (Calabrian Pine) in Turkey; *P. peuce* (Balkan Pine) in Bulgaria; *P. pinea* (Italian Stone Pine) in Northern Italy; *P. heldreichii* in Yugoslavia; *P. ayacahuite* (Mexican White Pine) and *P. teocota* (Aztec Pine) in Mexico; *P. caribaea* (Caribbean Pine) in Honduras; *P. roxburghii* (Chir Pine) in India and Pakistan; *P. thunbergiana* (Japanese Black Pine) in Japan; *P. massoniana* (Masson Pine) and *P. tabulaeformis* (Chinese Pine) in China; *P. merkusii* (Merkus Pine) in Indonesia (Sumatra Island. In U.S.A. *P. taeda* (Loblolly Pine) and *P. ponderosa* (Ponderosa or Western Yellow Pine) are also tapped sometimes. More than three quarters of pine oleoresin are derived from *P. palustris* *P. elliotti* (U.S.S.) *P. sylvestris* (U.S.S.R. and Northern Europe) and *P. pinaster* (France Italy Portugal and Spain); oleoresin from the former three species comprising the most of it.

Besides following countries have also examined various pines that are growing naturally or introduced there to develop their naval stores resources. They are *P. pinea* in Spain; *P. pithyusa* *P. pallasiana* *P. nigra* var *caramanica* and *P. sylvestris* var. *hamata* in U.S.S.R.; *P. halepensis* in Cyprus Israel and Tunisia; *P. brutia* in Syria; *P. insularis* in Burma and Philippines *P. elliottii* in Argentina Brazil and South Africa; *P. radiata* in Australia Chile and New Zealand; *P. pinaster* and *P. caribaea* in Australia and South Africa; *P. roxburghii* in South Africa. *P. caribaea* var. *hondurensis* in British Honduras; *P. kesiya* (*P. khasya*) and *P. wallichiana* in India; *P. taiwanensis* in Taiwan and *P. densiflora* in Japan

**World production of pine rosin and turpentine.** Prior to World War II most of the world's supply of rosin and turpentine came from U.S.A. and even today it tops in naval stores production. But since then considerable advance has also been made by several other countries particularly U.S.S.R. and China

(People s Republic) Around 1959 about 1.72 million hectares of pine forest with an yield upto 100 Kg. crude oleoresin per hectare were tapped in U.S.S.R. Basing on the average of world s total production of 1964 to 1966 about 47.0% rosin and 42.5% turpentine is produced in U.S.A. 15.8% rosin and 13.3% turpentine in U.S.S.R. 8.6% rosin and 10.4% turpentine in China 7.2% rosin and 6.4% turpentine in Portugal 3.7% rosin and 2.9% turpentine in Mexico 3.0% rosin and 3.5% turpentine in Spain 2.9% rosin and 3.0% turpentine in France 2.8% rosin and 2.2% turpentine in India 2.2% rosin and 2.1% turpentine in Poland 1.9% rosin and 2.0% turpentine in Greece and rest of it i.e. about 4.9% rosin and 11.2% turpentine collectively by 14 other countries. The estimated production of rosin and turpentine in the different countries during late fifties and early sixties.

## Occurrence Formation and Exudation of Oleoresin in Pines

**Occurrence.** In pines the oleoresin is formed and translocated in the resin canals occurring in root wood and inner bark of the stem and leaves. The normal resin canals are longitudinal running parallel to axis or transverse running at right angle to it. Transverse canals are always included in the fusiform rays. The oleoresin in the longitudinal canals tends to reach the surface by means of transverse ones. The size of resin canals varies according to their orientation species age and growth rate of trees. The longitudinal canals are invariably larger in diameter than transverse ones. These are very large in diameter in species like *P. lambertiana* (average 175 255  $\mu$  maximum over 300  $\mu$ ) *P. roxburghii* (200 225  $\mu$  and *P. ponderosa*; large in *P. strobus* (average 135 150 $\mu$  maximum 200 $\mu$ ) *P. kesiya* (130 150 $\mu$ ) *P. palustris* *P. elliotii* *P. taeda* *P. rigida* and *P. echinata*; medium in *P. banksiana* (upto 100  $\mu$ ) *P. contorta* (60 105  $\mu$ ) and *P. wallichiana* (70 85  $\mu$ ) (106 196 210). Their proportion as per cent of wood volume is 0.3% in *P. ponderosa* 0.5% in *P. lambertiana* 0.7% in *P. strobus* and 0.8% in *P. palustris*. In *P. peuce* their number averages to 11 per linear cm. or 61 per sq. cm. and of these about 97% occur in the late wood whereas the early wood contains only 3%. In all the 3 Indian pines viz. *P. roxburghii* *P. kesiya* and *P. wallichiana* the number of both longitudinal and transverse canals has been recorded as 0 to 2 per sq. mm. except the longitudinal canals in *P. kesiya* where it is 0 to 3 per sq. mm. of wood; the diameters of radial canals which are smaller than the longitudinal ones are 40 to 5 $\mu$  30 to 35 $\mu$  and 30 to 40 $\mu$  respectively.

Traumatic resin canals arising as a result of injury may accompany transverse canals of normal type. They may be longitudinal or transverse but both seldom occur together. The longitudinal traumatic canals are generally arranged in a tangential row and usually restricted to early wood. The traumatic transverse canals are confined to rays and are larger in diameter than normal transverse canals. The epithelial cells of traumatic resin canals are thick walled whereas these are thin walled in normal canals.

In softwoods like pine resin is also contained in ray parenchyma cells in addition to the resin canals. The resin in epithelial cells of canals is generally fluid type whereas in parenchymatous cells adjacent to trachlieds it is more viscid. Direct analysis of parenchyma resin has not been carried out but the proportion of canal resin to total resin has been calculated to be 40% in *P. palustris*.

**Formation.** The oleoresin is produced in the epithelial cells of the canal and adjoining living parenchymatous cells which are especially active in the outer sapwood. The oleoresin is under pressure exerted by the epithelial cells into the lumen of canal; this pressure called oleoresin exudation pressure is responsible for the exudation of oleoresin when the trees are tapped. As the normal canals pass from sapwood into heartwood they cease to function and are frequently occluded with tylosoids and are gradually plugged entirely.

Evidence drawn from reciprocal grafts of *P. sabiniana* and *P. ponderosa* was that the oleoresin is formed locally and is not supplied from tree crown. The site of oleoresin synthesis in the epithelial and sheath cells of the canals was considered to be in the plastids and later on in the endoplasmic reticulum. A recent study in *P. halepensis* allocated the site in special organelles i.e. spherosomes in epithelial cells of canals and

adjacent living parenchymatous cells. These organelles were especially active in younger tissues which contained a higher proportion of resin acids than the older ones. The terpenes are suggested to be produced in the spherosomes at a later stage of their development into the oleoresin.

**Mechanism of oleoresin exudation.** Studies have been carried out on the anatomy of tapped faces and mechanism of resin flow in *P. pinea*. Wounding causes differentiation of traumatic resin canals at that level and the tissues surrounding the faces get soaked with resin more abundantly at the lower levels. The normal longitudinal resin canals reached by the wound become obstructed by tylosoids formed in the interior of the canals and also they get elongated tangentially with their orifices divaricated. In intact longitudinal canals the resin is always contained in the resiniferous cells and never runs into the lumen. The canals interrupted by traumatic lesions on the other hand the secretory cells react in one of the two ways either by turgescence which tends to immobilize the resin in the cytoplasm or in following sequence of processes the resin emulsifies in the cytoplasm the vacuole disappears the nucleus degenerates the cell membranes thicken and turn into lamellae the pits enlarge and the resin exudes through them into the lumen and perhaps only the cells reacting in the later fashion are able to feed the flow of resin from a wound. Resin flow from the wound is governed by three principal conditions a physiological defence mechanism consisting in a very rapid increase in cellular turgescence leading to the occlusion of the interior of the canal by swelling of its epithelial cells; this phenomenon which takes place relatively far from the wound in cells of live tissues is accompanied by a hyper secretion of resin; emulsifying of the resin in the water of cellular cytoplasm its displacement and its oozing through the pit membranes to the interior of canal total dehydration of cells and embalming of their membranes by the resin giving a characteristic laminated appearance. At the dehydration stage the resin flow appears to cease and it therefore seems that it is controlled by the water in the secretory cells.

## Oleoresin Tapping

The oleoresin tapping also called turpentine implies in general to several operations such as selection of trees making of blaze or face on the tree fixing of lips and pots to collect the resin exuding from the cut face freshening of the blaze collection of oleoresin and scrape (solidified oleoresin).

There are two methods of oleoresin tapping which in French are termed as *le gemmage a vie* (cautions or light tapping) and *le gemmage a mort* (tapping to death); former method aims at obtaining the oleoresin without causing the death to trees and is adopted for longer spells while the second method exhausts and kills them. The later method is adopted only when a tree is to be felled soon after. Before introduction of cups and lips oleoresin exuding from the blaze was allowed to run down to the foot of the tree where it was received in a little trough hollowed out in one of the roots in the sand. This practice resulted in much waste and contamination. Hugues method employing lips and pots was introduced in Landes (France) for the first time in 1844 which spread in the region by 1885. Hugues method soon formed the basis for oleoresin tapping in a number of countries. The salient features of principal resin tapping methods in vogue in different countries are described here in brief

### French Methods.

*P. Pinaster* is the principal oleoresin yielding species in France. Methods adopted for tapping are as follows.

**Hugues method.** (a) **Le gemmage a vie** This method suggests tapping of trees 110 cm. g.b.h. or above but often trees of 90 cm. g.b.h are also tapped. The initial blaze is made at the base starting a little above the ground level preferably on the eastern face and worked for 5 years. A second one is added on trees of 130 cm. g.b.h. or above. The season of tapping in France extends to about 8 months (1st March to 31st October). During this period about 30 streaks or freshenings are made at 8 day intervals with an adze (*abschott*) and with a *rascllet* when it reached higher. In a season about 6 to 7 crops are collected. Before

actual tapping starts gradual thinning of bark to a height of about 60 cm . and width of 15 to 20 cm. nearly reaching wood in the middle is made as early as the 2nd week of February.

Initially the blaze is 9 cm. wide and is extended upward to 60 cm. height during the freshenings by the end of first year. Depth of the initial blaze and freshenings increases from the sides inwards reaching a maximum of 1 cm. in the middle. Similarly in subsequent years freshening is made upward in continuation of the previous years s blaze (face).

**Le gammage a mort** This method of tapping to death is used in the last 5 years of felling. The blazes are made as close as possible in the 1st year and worked for 4 years. Generally one blaze is made on trees of 50 60 cm. g.b.h. and a blaze is added for increase of every 20 cm. The blaze width and height is not actually restricted in a mort tapping. Freshening of blazes is done once or twice a week.

**Bellini s method.** Bellini around 1930 introduced a new method. In this a circular incision about 5 cm. in diameter and 2 to 3 mm. deep is made just sufficient to pierce below the outer bark by a special drill like tool. The cut is gradually enlarged during the season upto 10 cm. diameter and 1 cm. in depth. The face is protected by a sort of cover protector . The oleoresin from the blaze is led through a tube receptacle into the container (bottle). This method though facilitated working of many faces on a tree at a time and collection of oleoresin in pure and liquid form retaining much more turpentine content did not gain wide attention owing to high labour costs.

### **Spanish Method**

In Spain *P. pinaster* is the principal species constituting about 94% of the total pine stands tapped for oleoresin; the other two species viz. *P. halepensis* and *P. nigra* var. *calabrica* constituting 5 and 1% respectively. Tapping is done on Hugues pattern however the Spanish faces differ from French faces being 12 cm. wide 3.4 m. high (final height in 5 years) and 1.5 cm. deep. A new method called Spanish narrow face was recommended for stands to be tapped for 20 to 25 years. In this system 5 narrow faces 2.2 cm. wide 2.2 cm. apart and 1 cm. deep are started near the base of the tree and worked upwards giving 19.8 cm. combined width of face i.e. 11 cm. width of actual tapping surface and total 8.8 cm. untapped space leftover between 1st to 5th blazes. The method is reported to be better than standard faces used in Spain as it results in rapid healing of faces 8 to 10% greater oleoresin yield and easier to work. However it takes longer time in freshening. Trials are also being carried out to tap Spanish pines employing herringbone (Mazek) system with or without chemical stimulation and American bark chipping method with acid stimulation

### **Greek Method**

In Greece *P. halepensis* and *P. halepensis* var. *brutia* are tapped for oleoresin. Tapping schedules follow Hugues pattern but the standard Greek face is about 31 cm. long (annual height) and 11.5 to 12.5 cm. wide; freshening of blaze is done at 7 day intervals. Narrow face of about 4 to 7 cm. (Angistri Islands) or 7 to 10 cm. (Sofika) are also employed for long term tapping of stands where regeneration is slow.

## **Hydrogenless Hydrogenation of Resin Acids**

Hydrogenation of resin acids at low pressure with palladium on carbon or platinum oxide catalysts has been reported to yield dihydro compounds rapidly with the formation of tetrahydro compounds requiring more rigorous conditions. Reduction with lithium in liquid ammonia has also been reported; the major products are different from those of catalytic hydrogenation as expected. Homogeneous hydrogenation of the abietic type acids using tris(triphenylphosphine)rhodium chloride as the catalyst was not successful but the pimelic and isopimelic type resin acids were partially hydrogenated to the dihydro compounds.

Under very mild conditions and in the presence of stoichiometric amounts of water and a palladium on carbon catalyst alkali metal formates have been reported to be effective hydrogen donors.

This method has been used to successfully hydrogenate soybean oil methyl esters. We herein report that

resin acids can be hydrogenated using this method at ambient condition to form the dihydro derivatives

## Experimental

The resin acid methyl ester (0.1 mmol) was dissolved in 0.3 ml solvent in a 3 ml screwcap reaction vial. Appropriate amounts of deionized water and sodium formate (99%) were then added following conditions used for the transfer hydrogenation of soybean oil methyl esters<sup>5</sup>. The reaction vial was placed in a vortex test tube mixer to ensure mixing of all the components before adding 5 mg of 10% palladium on carbon catalyst. The instant of palladium addition was used as the zero reaction time. The temperature rose slowly from ambient to 33°C 34°C over the course of the reactions. Aliquots (2 to 3  $\mu$ l) were withdrawn periodically diluted with Me t Bu ether and analyzed with an Hewlett Packard 5880 gas chromatograph (FID) using a 14 m thin film. DB1 column at 190°C and a 30 m BDS column at 190°C. Components of the reaction products were identified by their relative retention characteristics.

For the reactions at controlled temperatures and at 5x scale. vortex mixing was replaced by magnetic stirring.

The influence of variables on the reactivity of the transfer hydrogenation was determined by comparing of the initial reaction rate (ro initial slope of the molar fraction) as a function of time.

## Results and Discussion

Resin acids were used as the methyl esters to facilitate direct monitoring of the product composition by gas chromatography (GC) during the course of the reaction. Because the reaction is heterogeneous an efficient stirring method was needed for the small solution volumes used in most of this study a vortex mixer was found to be more efficient than ultrasonic mixing. In scaling up the reactions however mixing could be accomplished with a magnetic stirrer.

Methyl isopimarate which has an exocyclic double bond was chosen as the substrate for determining optimum reaction conditions because it reacted quickly and the expected hydrogenation products are well resolved in GC analysis. Using an amount of catalyst so that Pd > 0.4% and toluene as the solvent the effect of the proportion of water and sodium formate was determined. Like Arkad et al. we found that 3 mol of water per mole of sodium formate gives the most efficient reaction whether using toluene or a more polar solvent (50% toluene Me t Bu ether) (Figure 1). Accordingly all further reactions were carried out with this water content. Sodium formate is most efficient when used in a ratio of 2 mol per mole of resin acid methyl ester which also agrees with the results of Arkad et al.

**Transfer Hydrogenation of Isopimaric/Pimaric Acids.** Under the conditions described and using toluene as the solvent methyl dihydroisopimarate was the only reaction product from methyl isopimarate. Attempts to drive the reaction by increasing the acidity of the system (2.1 formic acid Na formate) were not successful. Contrary to expectations not only were tetrahydroisopimarates not formed but the reaction rate slowed considerably probably because the solubility of formic acid in water effectively made some water unavailable. Solvent polarity was then increased with a water insoluble solvent Me t Bu ether (Figure 2). Although a slight increase in polarity had a negative effect on the reaction rate about 1:1 toluene Me t Bu ether provided the best reaction conditions. The conversion of methyl isopimarate to dihydroisopimarate as the only product was complete in about 1.5 h. Reaction at the ring double bond occurred to a very small extent even after 40 h (about 5% methyl 18 isopimaranoate was formed). However 20% of methyl dihydroisopimarate was isomerized during this 40 hour period to a mixture of methyl 8(14) isopimaren 18 oate and methyl 8 isopimaren 18 oate.

Because ultrasonic waves have been reported to accelerate many heterogeneous reactions we tried the isopimarate transfer hydrogenation under the most efficient reaction conditions and ultrasonic mixing. The reaction was approximately 6 times slower than the reaction with mechanical stirring. This was probably a result of the deleterious effect of ultrasound on ion exchange kinetics.



The conditions found to be most efficient for isopimarate hydrogenation transfer were then applied to methyl pimarate and methyl sandaracopimarate. These esters reacted slower than isopimarate but pimarate reacted unexpectedly faster than sandaracopimarate (Table I). Whereas isopimarate followed a zero order reaction path up to 95% conversion transfer hydrogenation of sandaracopimarate and pimarate deviated from a straight line reaction path earlier in the conversion.

**Transfer Hydrogenation of Abietic Acids.** The best reaction conditions for hydrogen transfer for the abietic type methyl esters were not the same as those found for methyl isopimarate. Both the polarity of solvent and the formate resin acid ester ratios were different. Optimum conditions were 4 mol of sodium formate per mole of resin acid with a solvent composition of 3 : 1 toluene : Me t Bu ether. The water : sodium formate ratio was maintained at 3 : 1. As with isopimaric and pimaric type methyl esters only one double bond was hydrogenated for all four abietic type esters as in disproportionation of rosin over Pd/C. The reaction was complete in 5 to 6 h.

For methyl abietate transfer hydrogenation the major reaction products were 13b abiet 8(14) en 18 oate (64%) and 13b abiet 7 en 18 oate (25%) (Table II). This is consistent with the results of platinum oxide reduction of 12 hydroxyabietic acid in which the proportion of the 13 b 8 (14) en isomer to the 13b 7 en isomer was nearly 3. Only very small amounts of the 13 a isomers were formed.

Although methyl neoabietate hydrogenates faster than abietate the initial rate of formation of the dihydro compounds is practically the same; some isomerization to methyl abietate (maximum about 25%) and a slight dehydrogenation to methyl dehydroabietate occur. The reaction product distribution is essentially the same as for abietate; only trace amounts of 13(15) abietenolate are produced.

For methyl levopimarate the side reactions of isomerization and dehydrogenation are more prevalent (Figure 3). They do not occur if either catalyst sodium formate or water are absent which suggests that a catalyst water/formate complex is involved. Although a change in solvent polarity or in temperature does not affect selectivity in the formation of specific dihydro compounds it does affect the extent of dehydrogenation 21% of dehydroabietate is formed in toluene 13.5% in 1 : 1 toluene : Me t Bu ether and 20% at 0°C (45% at 80°C) in 3 : 1 toluene : Me t Bu ether. Although the reaction is much faster in 3 : 1 toluene : Me t Bu ether at 80°C ( $E_a = 11$  kcal/mol) the yield in hydrogenated products is much lower. The optimum temperature is about 20°C. Reducing the amount of catalyst decreased the reaction rate which is in agreement with the results of Arkad et al for soybean oil methyl esters. The amount of catalyst had no significant influence on the selectivity of the dihydro compounds but the proportion of dehydroabietate increased slightly with increasing amounts of catalyst.

The major hydrogenation products of methyl palustrate are the 8 abieten isomers. Isomerization of palustrate to abietate (maximum about 4%) and dehydrogenation occur to a very small degree compared with that of levopimarate. Because the hydrogenation products have a similar distribution for all abietic type esters except methyl palustrate the reaction mechanism for palustrate may be different.

## Terpene Resins

Pale amber transparent thermoplastic polyterpene hydrocarbon resins of the type formula  $(C_{10}H_{16})_n$  have been produced and sold on a commercial scale since 1938. These resins are characterized by ring and ball softening points (S.P.) ranging up to about 135°C.; they are soluble in a great variety of organic solvents including hydrocarbon solvents and are of good color stability. They are used in conjunction with other materials in the formulation of a wide variety of end products including adhesives adhesive tapes rubber goods and coating compositions. Depending on the nature of the end use the terpene resins are supplied either in solid form or in solution in hydrocarbon solvents; the solid forms are made in a wide range of softening points or molecular weights.

These polyterpene resins are derived primarily from the catalytic polymerization in solution of the bicyclic

monoterpene pinene C<sub>10</sub>H<sub>16</sub> principally the β isomer (nopinene) and may be regarded as essentially polymers from β pinene. The pinene in turn is derived from gum and sulfate turpentines from both of which it is recovered by fractional distillation.

This article is concerned only with these hydrocarbon resins and does not cover other terpene derived resinous substances such as rosins (q.v.) and the terpene phenol resins. The latter are produced by reacting terpene hydrocarbons or alcohols with phenol in the presence of acid catalysts followed by catalytic resinification of the resulting substituted phenol with a reactive substance such as formaldehyde. Such terpene modified phenolic resins exhibit among other properties increased solubility in drying oils. They are useful in adhesives and in various types of coatings including particularly wax emulsions varnishes paints and heat setting printing inks. Certain resins are also antioxidants for rubber.

## Physical Properties

The commercially available polyterpene resins are produced with a variety of softening points (measured by the A.S.T.M. ring and ball method E28 51T) ranging from + 10 to + 135°C. corresponding to a range from viscous liquid to hard brittle solid polymers at ordinary temperatures. The average molecular weights of these polymers increase as the softening points increase. A molecular weight of about 1200 to 1250 measured cryoscopically in benzene is characteristic for a polymer of 125 to 135°C. softening point. In common with polymers generally the polyterpenes are mixtures of polymers of various molecular weights and chain lengths. A characteristic molecular weight distribution obtained by fractionation for a commercial 135°C. softening point polyterpene resin is shown in Table 1. The fractionation was accomplished by partial precipitation from amyl alcohol the general procedure involving solution of the resin in hot amyl alcohol followed by cooling decanting the amyl alcohol solution from the precipitated higher molecular weight polymers and steam distillation of the decanted solution to remove the alcohol. Fractions 1-10 were so obtained increasing amounts of amyl alcohol being required for the successive fractions because of the decreased solubility associated with increased molecular weight.

These polymers are typically thermoplastic and merely soften or harden as they are heated or cooled no irreversible change occurring as long as the heating temperature is kept below that at which pyrolytic reactions set in. In common with other amorphous hydrocarbon resins these polymers show no sharply defined liquefaction or solidification temperatures and their softening points are therefore measured by arbitrary standard test methods.

The polymers are slightly less dense than water resulting in a relatively high bulking value compared to other polymeric materials. Values for the specific gravity of these resins range between about 0.97 and 1.00 depending on the softening point or molecular weight the exact composition of the monomeric terpene mixture polymerized and the method of production.

The resins exhibit solubility in or compatibility with a wide range of materials. Complete miscibility exists with liquid paraffinic naphthenic and aromatic hydrocarbons chlorinated hydrocarbons higher alcohols higher ketones esters and drying oils. Compatibility is exhibited with rosin ester gum waxes including paraffin wax polyisobutylenes petroleum residues and pitches mineral oils and certain types of petroleum hydrocarbon polymers. Under appropriate conditions compatibility is exhibited with rubber and modified rubbers including synthetic rubbers such as GR S. Compatibility with cellulose ethers and esters is however quite limited.

Inasmuch as these resins are entirely hydrocarbon in nature they are moisture resistant and possess good dielectric properties.

## Chemical Properties

As essentially pinene polymers principally polymers from β pinene the terpene resins exhibit properties typical of polymeric hydrocarbons including chemical inertness. They are inert to dilute mineral acids

alkalies and salt solutions and are characterized by acid numbers and saponification numbers less than four and approaching zero. Similarly they are resistant to heat over a wide range of temperatures varying only in fluidity with temperature.

The detailed chemical structure of the terpene resins cannot be regarded as satisfactorily elucidated. Published data in the chemical literature and patented art have indicated these polymers to be susceptible to both halogenation and catalytic hydrogenation and to reaction with ozone to give polymeric ozonides. For example the reported weight of hydrogen absorbed by a catalytic polymer made from  $\beta$  pinene was 1.2%. This is equivalent to 0.82 mole of hydrogen per  $C_{10}H_{16}$  recurring unit in the polymer chain. Based in part on these considerations and in part on physical properties Roberts and Day speculated that the catalytic polymerization of  $\beta$  pinene involved more than a simple chain addition reaction of monomer molecules and that isomerization occurred during the polymerization to give a polymer comprising a chain of recurring monocyclic  $C_{10}H_{16}$  terpene units each containing a carbon double bond. Powers has also suggested the recurring unit of polymers pinene to be monocyclic and unsaturated proposing a formula different in detail and in point of linkage.

More recent studies of these polymers by infrared spectrophotometric techniques have indicated that the polymers contain notably less unsaturation that would be required for a chain of recurring monocyclic terpene units but more than would be the case for a simple addition polymerization of  $\beta$  pinene molecules yielding a polymolecule containing only a single terminal double bond. Part but not all of the unsaturation observed by infrared examination appears to represent terminal double bonds in the polymolecules inasmuch as it decreases with increasing molecular weight.

These observations imply that the pinene polymerization is as postulated by Roberts and Day more complex than simple addition but that the final recurring unit structure is not solely monocyclic. Pending further elucidation it seems preferable to avoid the term poly  $\beta$  pinene insofar as the latter may imply simple addition polymerization.

# Terpene Based Adhesives

## Introduction

Terpene resins are low molecular weight hydrocarbon polymers prepared by cationic polymerization of terpenes. These products used by the adhesives sealant wax coating and investment casting industries are separated into three major categories pressure sensitive adhesives hot melt adhesives and coatings and elastomeric sealants. The pressure sensitive adhesives category includes solvent emulsion and hot melt pressure sensitive adhesives and rubber cements. The hot melt adhesives category includes hot melt adhesives coatings and investment waxes while the elastomeric sealants category includes sealants caulks and can end cements. Specific types of tackifying resins are required for each use.

Terpene resins are old in fact the oldest reference to polymerization was recorded in 1789 where in turpentine was treated with sulfuric acid. More modern milestones are a U.S. patent issued to Emile Rouxville in 1909 for subjecting hydrocarbons such as turpentine to sulfuric acid to produce a resin and to resemble various Indian rubbers. Twenty four years later aluminium chloride catalysis was patented for terpene polymerization by the Gulf Refining Company. Later in 1950 an excellent fundamental publication by Roberts and Day appeared in the chemical literature. Commercial terpene resins produced for adhesive applications resulted from modification of disclosed processes catalysts and terpene feed stocks.

## Chemistry

Commercial tackifying resins are prepared from the monoterpenes (Figure 1). Beta pinene alpha pinene and dipentene (limonene) are derived from turpentine by fractional distillation. The supply of dipentene is augmented by by product linonene collected during processing citrus fruit to frozen concentrate.

Commercial beta pinene typically ranges from 72-95% purity. Beta pinene resins are prepared from the lower assay material and flavour fragrance chemicals from the higher. Dipentene and alpha pinene resins are generally prepared from 92-98% pure feedstreams. Smaller quantities of modified terpene resins are produced from mixed feeds of terpenes, phenols and hydrocarbon monomers.

## Beta pinene resins

### Initiation

The effective catalyst for terpene polymerization is a complex protonic acid derived by the interaction of a Lewis acid typically  $\text{AlCl}_3$  and a cocatalyst or promoter such as adventitious water. The initiation step is completed when the hot proton produced attacks the exocyclic methylene group of a beta pinene monomer (Figure 2).

### Propagation

The tertiary carbenium ion rearranges prior to its attack on another monomer which begins the propagation step (Figure 3). The main repeating unit in a beta pinene resin is a ring having 1,4-disubstitution.

The resin can be visualized as a perfectly alternating copolymer of isobutylene and cyclohexene. Its chemistry can be explained on this basis.

Ozonolysis or peracid oxidation indicates one olefinic group per mer unit. Infrared analysis shows the expected gem-dimethyl group of the repeat unit and the single methyl of the end unit.

### Termination

The overriding determinant of molecular weight is chain transfer. This limits molecular weight to the 1000-2000 unit range as determined earlier by Roberts & Day. Figure 4 depicts the rearrangement of the end mer through ring expansion to a (2,2,1) bicyclic system and loss of a proton to form a camphenic end group. The camphenic carbenium ion depicted in Figure 4 will be non-propagative for steric reasons. Good analogy for this rearrangement mechanism to a non-propagative camphenic end cited above is seen in the acid-catalyzed Wagner-Meerwein isomerization of alpha or beta pinene which expands the four-membered rings to the (2,2,1) bicyclo ring system (Figure 5). A second minor chain transfer step to aromatic solvent also occurs during commercial manufacture. In this case the growing end attacks the solvent with elimination of a proton to produce the end group shown in Figure 6.

## Dipentene Resins

The initiation step is similar to that described previously for beta pinene resins. Propagation through the terminal methylene group would be predicted (Figure 7). However, the determination of olefin content by NMR, ozonolysis and perbenzoic acid oxidation indicates that only one half of the mer units have the expected unsaturation. The endocyclic or ring double bond is involved in the polymerization and is consumed in some manner. To explain these facts and elucidate the polymerization pathway, the structurally similar model compound 8-9 p-menthene (Figure 8) was subjected to polymerization conditions. Only dimer was obtained, therefore the presence of a double bond in the ring is required for a successful polymerization. Armed with this fact, we may theorise that the polymerisation of dipentene proceeds by initiation at the tri-substituted olefinic ring position with the carbenium ion undergoing cyclic polymerization to yield a structural unit as shown in Figure 9.

Butler has shown that the polymerization of the related 1-methylene-4-vinylcyclohexane proceeds partially by cyclization (Figure 9). More likely, the terminal isopropyl carbenium ion attacks the residual double bond of the penultimate mer unit and thus forms a ring with subsequent polymerization proceeding from the penultimate mer unit.

A structural representation based on this postulation is presented in Figure 10. The dotted bonds are those formed during polymerization, the Arabic numerals indicate the sequence of bond formation, and the letters the dipentene mers. By invoking either of the above mechanisms, we can satisfactorily explain the

presence of only one double bond per every two to three mer units. Further evidence of the polycyclic nature of the resin is the high density of the dipentene resins.

#### Alpha pinene resins

This monomer is the most difficult of the common terpenes to polymerize since it does not possess an exocyclic methylene group. Although alpha pinene easily forms the same initial carbenium ion as beta pinene (1) the propagation step Figure 11 is difficult for steric reasons. The presence of an adjuvant is required to eliminate the formation of large amounts of dimer which otherwise would form during the polymerization.

The presence of the adjuvant (also referred to as a synergist) is thought to stabilize the growing carbenium ion and thus give it a longer lifetime during which it can attack another alpha pinene monomer. Chain transfer to monomer is thus suppressed with its accompanying formation of dimer (Figure 12). The peracid oxidation of alpha pinene resin shows that approximately two thirds of the mer units contain an olefin indicating that in the remaining one third the four membered ring probably expands and results in a saturated mer unit possessing the (2 2 1) bicyclic system. Accordingly the two proposed mer structures (a) and (b) in an alpha pinene resin are illustrated in Figure 13.

#### Physical characteristics of resins

The number average molecular weights and molecular weight distributions of representative commercial terpene resins determined by vapor pressure osmometry and gel permeation chromatography are presented in Table 1.

The molecular weight is the most important single property of a polyterpene resin. It may be correlated to physical properties and utility. When a polymer property is plotted versus molecular weight there occurs a leveling off in the property at a particular molecular weight which varies for each resin or polymer. In most instances it is necessary to attain this minimum molecular weight range to get the desired physical properties e.g. polypropylene has to have a molecular weight of 50 000 and acrylonitrile 35 000 to be useful in common polymer applications. By contrast the relatively low molecular weights of terpene resins at which properties plateau coupled with their narrow molecular weight distribution and excellent solubility in elastomers makes them unique and useful for adhesives.

An adhesive consisting of a high polymer and a low molecular weight tackifier takes advantage of the properties of each component. The high polymer contributes strength through entanglements of extremely long chains and reinforcement with secondary valence bonds whereas terpene resins attain their utility from low molecular weight rapid change in viscosity with temperature Newtonian liquid behaviour and good solubility which provides high polymer segmental motion and wetting of substrates. It is recognized that the preferred tackifiers for pressure sensitive tapes are beta pinene resins having ring and ball softening points from 115°C to 135°C. This maximum utility appears on the bend or leveling off of the softening point molecular weight curve (Figure 14). At this bend the beta pinene resins are transparent amber glasses. Recently water white versions have been introduced.

Since initiation propagation and chain transfer process are all proceeding simultaneously we observe a distribution of molecular weights. This can be determined by gel permeation chromatography. During a typical batch polymerization the molecular weight distribution was observed to change during the course of the monomer addition. This is not surprising in view of the multitude of physical changes that are occurring e.g. the heterogeneous to near homogenous catalysis the increase in dilution. In order to better control the polymerization process most commercial operations employ a continuous process where a steady state ration of initiation/propagation/chain transfer is present. (cf. Commercial Production).

For a specified softening point dipentene and alphapinene resins have lower molecular weights than a betapinene resin indicating that the former polymer structures are more rigid and more compact than that of

a beta resin. The density of dipentene resins is higher than that of beta resins 0.998 to 0.974 corroborating the presence of rigid fused ring moieties. Although dipentene resins have a higher softening point/mer unit they have a smaller hydrodynamic volume and hence form solutions of low viscosity. The semi ladder structure is confirmed by greater thermal stability than betapinene resins. The density of alpha resins at 0.976 is very close to that of beta resins; more importantly the molecular weight and hydrodynamic volume are closer to those of dipentene resins than beta resins. For this reason the bulk properties of alpha resins resemble those of dipentene resins with the exception of thermal stability. The thermal stability of alpha resins is poorer because of the partial steric interaction due to the 1,3-disubstitution of the cyclohexene ring and absence of any double stranded placements.

### Pressure sensitive adhesives

A pressure sensitive adhesive is one which is permanently tacky requires no activation by heat solvent or moisture and which will adhere strongly to most surfaces upon application with a minimum of pressure. Tack is defined as instant low order adhesion developed by mere contact with a variety of dissimilar surfaces. The major components of a pressure sensitive formulation are elastomer and tackifier. The latter can be polyterpene hydrocarbon or rosin ester based. The elastomers generally rubbers have molecular weights between 60 000 and 350 000 which correspond to degrees of polymerization of 1 000 to 5 000. Because of their extreme chain length they provide the cohesive strength to formulation and in addition possess a latent tackiness. Their high molecular weights allow modification with large amounts of other substances without serious loss of cohesive strength. The terpene resins because of their chemistry and physical characteristics combine with the elastomer to produce formulations with the characteristics of tack adhesion and cohesion required of a successful pressure sensitive adhesive.

The tackifying resin can be thought of as a solid solvent for the rubber elastomer. Usually solubility is affected by molecular weight; the smaller the molecule the higher the solubility. While low molecular weight in a tackifying resin is desirable there is a practical limit to this feature. As molecular weight drops semisolid resin is produced which imparts tack but adhesives formulated with such a resin then fail cohesively. Conversely adhesives made with resins having a softening point beyond 135°C lack in tack. Empirically beta pinene resins of 115°C softening point impart the best balance of adhesive properties. The tackifying resin appears to operate by bringing out the smaller tack bestowing molecules from their dispersion in the mass of the rubber. The solubility of the longest chains of a rubber is at best limited so we can speculate that the tackifying resin exhibits a gradient solvent effect totally solubilising the shortest chains partially solubilising those of intermediate large size. In the case of the longest elastomer chains the tackifier probably operates by solubilizing segments thereby allowing wetting of the substrate and adhesion.

## Ozonolysis of Alpha Pinene

The discovery that the esters of pinic acid (2,2-dimethyl-3-carboxy-cyclobutylacetic acid) have excellent lubricant and plasticizer properties has stimulated interest in this compound and in its precursor pinonic acid (2,2-dimethyl-3-acetylcyclobutylacetic acid). The cost of producing these acids by permanganate oxidation of a pinene to pinonic acid and further oxidation to pinic acid with hypochlorite is expensive. On the other hand an ozonolysis process might be developed which would be economically attractive. Harries and coworkers made a cursory investigation of the ozonolysis of a pinene and reported about 25% yields of a liquid pinonic acid. Subsequently Brus obtained low yields of solid optically active pinonic acid by decomposition of an ozonide of a pinene. More recently Spencer and coworkers have reported that vapor phase ozonization of a pinene yields an ozonide containing five atoms of oxygen which yields pinonic acid. They question the validity of Harries' identification of pinonic acid.

Prior to the initiation of the research reported here workers at the Naval Stores Station of the United States Department of Agriculture Southern Utilization Research Branch had verified the fact that pinonic acid is actually obtained by liquid phase ozonolysis of a pinene using low concentrations (2%) of ozone and had increased the yield of pinonic acid to about 50%. This work consists of a broad screening program of the effect of a number of variables on the production of pinonic acid and pinic acid by the ozonolysis of a pinene in the liquid phase using concentrations of ozone up to 100%. The structural formulas of the principal compounds are

Effect of solvent ozone concentration and temperature on yields were investigated

**Solvent Screening.** The data obtained from an evaluation of the effect of solvent are listed in Table 1.

Except for those from experiments involving the use of acetic acid and carbon tetrachloride acetic acid as solvents all data in Table 1 resulted from single experiments unless otherwise indicated. The best of several experiments with each of five selected solvents involving changes in concentration of ozone ratio of ozone to pinene and ozonization temperature are listed in Table 1 with the footnote about multiple runs. In view of the apparent superiority of the carbon tetrachloride acetic acid solvent system this system was investigated in some detail.

**Ozone Concentration.** The ozonization of a pinene in carbon tetrachloride acetic acid solvent was studied as a function of ozone concentration in order to ascertain the possible advantages of the use of high concentrations of ozone. The technical literature does not contain any references to the use of high concentrations of gaseous ozone in the controlled oxidation of organic compounds.

A series of ozonolyses was made with 7.5 15 and 100 mole % gaseous ozone during the ozonization phase followed by a 0.5 hour reflux treatment. The data for these runs are presented in Table 2. The fact that the yields for all these runs are so nearly the same strongly suggests that the yield of desired products is independent of the concentration of gaseous ozone used.

**Effect of Temperature.** The effect of temperature on the ozonization of pinene in carbon tetrachloride acetic acid solvent was investigated. These data comprising a part of Table 3 suggest that there is only a slight increase if any in the yield of pinonic acid caused by changing the temperature of ozonization from 25° to 5° or 40° C.

Carbon tetrachloride acetic acid solvent composition and ratio of pinene to ozone during ozonization do not substantially affect yields

The data acquired on the effects of solvent composition and the ratio of pinene to ozone on the ozonization of pinene in carbon tetrachloride acetic acid solvent is presented as part of Table 3. These data suggest that changes in these variables do not effect any pronounced changes in the yield of pinonic acid. It appears that slightly better yields are obtained when a large excess of ozone is used.

**Post Ozonization Use of Dilute Ozone.** An investigation was made of the post ozonization use of a very dilute ozone (1000 p.p.m.) in oxygen at the reflux temperature of the liquid phase compared with simple refluxing. The data for these experiment are listed in Table 4.

In five of the six comparisons made between the use of simple refluxing and the use of 1000 p.p.m. ozone the use of ozone slightly increased the yield of desired products. The results of three series of experiments designed to test the effect of using dilute ozone over a long period of time suggests that little or no increase in the yield of desired products is obtained by using 1000 p.p.m. ozone for more than 2 hours. The results of a single pair of experiments designed to explore the advantages of using more concentrated ozone for post ozonization treatments suggests that the use of 2000 p.p.m. ozone may be more beneficial than 1000 p.p.m. ozone.

Experimental conditions are discussed

**Analysis for Products.** An aliquot of the final ozonolysis system stripped of solvent was dissolved in

chloroform and chromatographically analyzed by the method of Marvel and Rands. Department of Agriculture Olustee Fla. and our own study of known mixtures of pinonic acid terebic acid and pinic acid. The percentage of butanol in chloroform for the three elution solvents used were 0 1 and 2 respectively. To each 10 ml. fraction eluted 15 ml. of 95% ethanol was added prior to titration with standard alkali to the phenol red end point.

**Ozonization with Dilute Ozone.** Dilute ozone of known concentrations was prepared by vaporizing a known quantity of 100% liquid ozone in an evacuated reservoir of known volume and adding pure nitrogen or pure oxygen until 2 atmospheres pressure (absolute) was obtained. A given amount of the dilute ozone was then bled through a grooved stopcock and rotameter at 10 liters per hour through the reactor containing the solution of pinene. The reactor (for runs with an excess of pinene over ozone) was essentially a 28 × 200 mm. test tube with a short 45° side arm about 125 mm. above the bottom of the reactor with a 24/40 standard taper joint permitting connection with a reflux condenser and exhaust gas tube. An 8 mm. outside diameter glass gas inlet tube was concentrically sealed to a male 24/20 standard taper joint which fitted the top of the reactor tube. The gas inlet tube terminated about 15 mm. from the bottom of the reactor with a coarse fritted borosilicate glass pencil 12 mm. outside diameter or a finely perforated endsealed glass tube.

During ozonization the reactor was surrounded by 530 ml. of water (or other appropriate coolant) held in a open widemouthed Dewar flask. The jacketing water was stirred intermittently during the ozonization period and a temperature rise of approximately 4° C. was usually observed for each 0.95 gram of ozone passed into the reactor.

**Ozonization with 100% Ozone.** Liquid ozone and high concentrations of gaseous ozone are highly reactive with iron brass mercury rubber ordinary greases and many organic and inorganic compounds. Glass stainless steel aluminum concentrated sulfuric acid and perhalogenated hydrocarbons are compatible with ozone. Ozone handling apparatus must be cleaned scrupulously before using.

The apparatus for conducting ozonizations with 100% ozone is as follows The liquid ozone tube is connected to one arm of an inverted U tube by a ball and socket joint. The shallow U tube is made of 1 mm. capillary tubing and is approximately 2 ft. long in the horizontal direction. The other arm of the U tube terminates in a male standard taper 24/40 joint concentrically ring sealed about the capillary tube which extends about 3 cm. beyond the joint. An outlet or exhaust tube made of 0.5 mm. capillary tubing extends from the upper side of the 24/20 joint about a centimeter below the ring seal. Standard round bottom flasks are attached to the 24/40 joint.

## w Bromolongifolene

Abstract By analogy with w bromocamphene w bromolongifolene on fusion with alkali but at a comparatively higher temperature gives several monomeric and dimeric products as a result of ring enlargement. The monomeric products have been characterized as longihomocamphenilone (VIII) and longi isohomocamphenilone (IX). The dimeric products are composed of a mixture of longifolenyl ethers and the kinetic dimers. Lead tetraacetate oxidation of longifolene according to the method of Ourisson has been found to yield not only longihomocamphenilone and longidione but also a crystalline alcohol identified as isolongifolol (XI).

Base induced ring enlargement of w bromocamphene was first studied by Lipp. He observed that potassium hydroxide fusion of w bromocamphene affords a six membered ring ketone and divinyl ether as dimeric product. Later Huckel also investigated these reaction products but only recently Wolinsky after reinvestigation characterized the constituents as I to V.

Longifolene (VI) which in many reactions is similar to camphene also forms w bromolongifolene (VII).

Ourisson attempted alkaline fusion of the w bromo compound (VII) without success. A reinvestigation of the



alkali fusion of *w* bromolongifolene has produced interesting results which we wish to place on record. During the initial alkali fusion of *w* bromolongifolene using the method described by Wolinsky for *w* bromocamphene the bromo compound was recovered unchanged. Considering the structure of longifolene and its general inertness it was felt that the conditions for alkali fusion mentioned by Ourisson might not be applicable and hence certain modifications in the reaction were employed. After several attempts by varying the temperature of fusion it was found that a temperature range of 380 to 400° is required. Instead of glass tubes a stainless steel tube fitted with a long air condenser was found necessary for the drastic conditions employed.

As in the case of the camphene series the fusion products were steam distilled and the distillate and the residue worked up separately.

### Steam distilled products

By judicious application of GLC and TLC the product was found to be a mixture of four components the identification of which was carried out by employing both physical and chemical methods. Actual separation of these components was achieved by elution chromatography. Of the four two were identified as longifolene and unreacted *w* bromolongifolene. The other two were found to be ketones (5.7% yield). IR spectra of these showed close similarity and indicated that both are six membered ring ketones with a CH<sub>2</sub>CO linkage but they are different as shown by GLC, TLC and NMR studies.

One of the ketones (IR spectra Fig. 1; NMR spectra Fig. 3) agrees perfectly with the ring enlarged ketone longihomocamphenilone (VIII) prepared by Ourisson<sup>6</sup> by lead tetraacetate oxidation of longifolene. On the basis of chemical and NMR spectral evidence he proved the structure as being VIII the second ketone (obtained by us) must therefore have the structure IX and the name longi isohomocamphenilone (IR spectra Fig. 1; NMR spectra Fig. 4) is proposed. In conformity with this both these ketones give longidione (X) on treatment with selenium dioxide.

While preparing standard longihomocamphenilone (VIII) for comparison purposes by lead tetraacetate oxidation of longifolene according to the procedure of Ourisson together with longihomocamphenilone (VIII) and longidione (X) substantial amounts (5%) of another compound an alcohol which has been characterized as iso longifolol (XI) was isolated. Its identity was further confirmed by oxidation to iso longifolic acid (XII).

### Residue

The residue from steam distillation of the alkaline fusion product was purified by repeated chromatography and distillation under diffusion pump vacuum and the purity examined by TLC using silica gel impregnated with silver nitrate.

The product was found to be mostly dilongifolenyl ether dimer (XIIIa and b) since it has an absorption maximum at 6.05 $\mu$  (1653 cm<sup>-1</sup>) which supports the presence of a vinyl ether revealing that the alkaline fusion of VII predominantly produces a unique ring expansion. The ketone dimers (XIVa and b) which as in the camphene series might also be present could not be isolated. Although their presence is not supported by UV absorption a positive indication comes from ozonolysis of the dimeric product when both the ketones (VIII and IX) and the diketone (X) are produced. The presence of a divinyl ether was established by chromic acid oxidation to furnish longihomocamphenilone (VIII) longi isohomocamphenilone (IX) longidione (X) and longifolic acid (XV).

All m.p.s and b.p.s are uncorrected. Rotations were taken in CHCl<sub>3</sub> solution. IR spectra were taken as liquid films for liquids and in *n*-ujol for solids on a Perkin Elmer Model 137B Infracord spectrophotometer by Ms. Gopinath and Deshpande. The NMR spectra were taken in CCl<sub>4</sub> solution using tetramethylsilane as internal standard on a Varian A 60 spectrometer by Dr. Nair and Mr. Mulla. GLC analyses were carried out on a Griffin George instrument on polyester column using H<sub>2</sub> under pressure as the carrier gas by Ms. Bapat

and Sankpal Anhydrous Na<sub>2</sub>SO<sub>4</sub> was used for all drying purposes. Microanalyses were carried out by Mr. Pansare and colleagues.

w Bromolongifolene (VII). This was prepared according to the procedure of Ourisson with some modifications. To a mechanically stirred solution of longifolene (100 g) in dry ether (300 ml) Br<sub>2</sub> in dry ether (500 ml) was added at 10° during 3 hr and further kept at the same temp for ½hr. The mixture was then kept in a freeze for overnight. The ether was removed in vacuum at 20° dimethylaniline (200 g 3 equivs) added and the mixture heated for 7hr at 180°. It was acidified with HCl aq (1 1) extracted with ether washed thoroughly with water until free of acid dried the ether removed and the residue fractionally distilled to yield pure (GLC TLC) w bromolongifolene (43 45%) b.p. 150°/6 mm m.p. 40 41°. (Found Br 27.94. C<sub>15</sub>H<sub>23</sub>Br requires Br 28 02%).

Fusion of w bromolongifolene with potassium hydroxide. w Bromolongifolene (2 5 g) and KOH (6 15 g) were placed in a stainless steel tube (length 8 diameter 1 ) fitted with a long air condenser. The contents were heated on a sand bath and the temp slowly raised to and kept at 380 400° for 1½ hr. After cooling the tube the contents (dark brown) were poured into water. Several such fusions (from 90 g of VII) were combined together and steam distilled. The distillate and the residue were worked up separately.

Longihomocamphenilone (VIII) and longi isohomocam phenilone (IX). The steam distillate was extracted with ether washed dried and the ether removed. The residue (22.5g) was chromatographed on alumina (gr. 1 675 g) and eluted successively with pet. ether benzene and ether.

Pet ether eluate (15.5 g) was found to contain a mixture of longifolene and unreacted w bromolongifolene which were separated by repeated chromatography and characterized by GLC TLC. and IR analyses.

The earlier fractions of the benzene eluates and the later fractions of the ether eluates were rich in the ketones (IX and VIII) respectively. The intermediate fractions were a mixture of these two ketones. By careful and repeated chromatography of the appropriate fractions these two ketones were obtained in the pure form (GLC and TLC) and were further purified by sublimation.

Longihomocamphenilone (VIII; yield 2 g). It had m.p. 55 57° (a)D + (91.26° (c 7.15). (Found C 82.04; H 10.64. C<sub>15</sub>H<sub>24</sub>O requires C 81.76; H 10.98%). 2 4 DNP derivative m.p. 144° (Found N 14 23. C<sub>21</sub>H<sub>28</sub>O<sub>4</sub>N<sub>4</sub> requires N 14.01%).

The same ketone prepared from longifolene by treatment with lead tetraacetate according to the method of Ourisson showed the same m.p. (55 57°) but a higher specific rotation (141.6°). The m.ps of the DNPs of our ketone (144°) and the Ourisson s ketone as obtained by us (144 145°) were also somewhat lower than observed by Ourisson (156 158°). However GLC and TLC behaviour and the IR and the NMR spectra of our ketone were identical with Ourisson s ketone thus proving their identity. It may be possible that partial racemization has taken place during high temp alkali fusion which will explain the lower optical rotation.

Long isohomocamphenilone (IX yield 2 g). It had m.p. 52.53° (a) D + 64.13 (c 1.45). (Found C 82.08; H 10.79. C<sub>15</sub>H<sub>24</sub>O requires C 81.76; H 10.98%). 2 4 DNP derivative m.p. 166°. (Found N 14.45. C<sub>21</sub>H<sub>28</sub>O<sub>4</sub>O<sub>4</sub> requires N 14.01%).

Selenium dioxide oxidation of longihomocamphenilone (VIII) and longi isohomocamphenilone (IX) to longidione (X). A solution of SeO<sub>2</sub> (150 mg) in a few drops water and acetic acid (2 ml) was added to a solution of longi isohomocamphenilone (56 mg) in glacial acetic acid (2ml) at 80° and the mixture heated on a water bath for 24 hr. It was then diluted with water extracted with ether the ether extract washed with water dried and the ether removed. The solid diketone was crystallized from pet. ether as fine yellow crystals; yield 50 mg m.p. 93 94° mixed m.p. with authentic sample undepressed IR bands at 2960; 1730 and 1700 (doublet) 1497 and 1370 cm<sup>-1</sup>. (Found; C 77.05; H 9.61. C<sub>15</sub>H<sub>22</sub>O<sub>2</sub> requires; C 76.88; H 9.46%).

The similar oxidation of longihomocamphenilone (VIII) gives the same product.

Dilongifolenyl ether (XIII a b). The residue from steam distillation of the alkaline fusion products was

extracted with ether washed with water till neutral dried and the ether removed to yield a viscous dark brown product (35g). It was chromatographed over alumina (Gr.II 1kg). On distillation it afforded a viscous light yellow oil b.p. 215° (bath)/1.54 × 10<sup>-2</sup> mm; IR bands at 2941 1653 1449 1370 1205 1176 1156 1130 1093 1036 980 926 830 and 820 cm<sup>-1</sup>. (Found C 85.92; H 11.18. C<sub>30</sub>H<sub>46</sub>O requires C 85.24; H 10.97%).

### Chromic acid oxidation of dilongifolenyl ether

The ether (2.5 g) and CrO<sub>3</sub> (1.7 g) in acetic acid (18 ml) were heated on a water bath for 1 hr. Potassium carbonate (20g) was added to the green solution and the mixture steam distilled. The distillate was extracted with ether affording a yellowish oil (0.7 g) shown to be a mixture of longihomocamphenilone longi isohomocamphenilone and longidione by GLC and TLC analyses and further confirmed by actual isolation via chromatography over alumina.

The residue left after steam distillation of the product of chromic acid oxidation was made slightly acidic. The organic material was extracted with ether and divided by treatment with alkali into acidic and neutral portions. The former which was composed of longiforic acid (XV) was crystallized from ethyl acetate m.p. 220-221°.

Ozonolysis of dilongifolenyl ether. A solution of the ether (1.14 g) in CCl<sub>4</sub> (20 ml) was ozonized at 0° for 4 hr. Carbon tetrachloride was removed under vacuum and the residual ozonide was heated with water (20 ml) for 2 hr extracted with ether. The ether extract was separated into acidic and neutral portions by treatment with KOH. There was very little acidic material. The neutral portion a yellow oil (1 g) was shown to be a mixture of longihomocamphenilone longiisohomocamphenilone and longidione by GLC and TLC analyses and further confirmed by actual isolation via chromatography over alumina.

## Peroxides from Turpentine

Excellent activity of pinane hydroperoxide as a catalyst for 5°C.GR S polymerization was reported in the first article in this series. At that time attention was called to the fact that unusually high conversions and yields of the hydroperoxide can be obtained from pinane. This article discusses in greater detail methods of producing technical grades of pinane hydroperoxide from gum turpentine in good yields. The preparation and properties of pure cis-1-pinane-2-hydroperoxide have been described.

From gum turpentine or pinenes four steps are involved in producing technical grades of pinane hydroperoxide

Conversion of pinenes to pinane by hydrogenation

Purification of the pinane usually by distillation

Oxidation of purified pinane with molecular oxygen to give an oxidate having a peroxide content of about 50%

Stripping of the oxidate under vacuum to remove unoxidized pinane and leave the pinane hydroperoxide as the residue.

The product prepared on a 20 mole scale had a purity of 85 to 90% A conversion of at least 40% per pass and a yield based on pinane not recovered of 80 to 90% was obtained.

Peroxide number and degree of unsaturation are tests of product quality

**Peroxide Number.** The peroxide content of the various oxidates was determined by a slight modification of the iodometric method of Wheeler. The reaction time was 5 minutes and the results are expressed as peroxide number in milliequivalents per kilogram. The peroxide number of pure pinane hydroperoxide is 11760.

**Unsaturation.** The quantitative hydrogenation method of Joshel and coworkers was used to determine unsaturation in the various products. The results are calculated in terms of moles of hydrogen absorbed per

136 gross of sample. For convenience these values are referred to double bonds per mole in the case of turpentine and are converted to percentage of olefins in the case of crude pinanes.

**Sulfuric Acid Test.** For rapid control the purposes purity of freshly prepared pinane was estimated by shaking a portion with an equal volume of 85% sulfuric acid for 1 minute and examining the acid layer. Samples that give a cloudy acid layer or a straw color darker than 0.05N potassium dichromate solution will generally be unsatisfactory.

**Catalytic hydrogenation of pinene to pinane is first step in hydroperoxide production**

Pinane is prepared by catalytic hydrogenation of either a or b pinene. In the work reported in this article a commercial catalyst containing 16% nickel supported on filter aid and suspended in coconut oil was used. Both high pressure (20 to 100 atm.) and low pressure (15 to 30 pounds per square inch absolute) hydrogenations were made using this catalyst at a 1% nickel level and temperatures in the range of 60° to 150° C.

**High Pressure Hydrogenation.** In a representative high pressure hydrogenation 1275 grams of fresh gum turpentine = 1.4715 = 12.60 (10 cm. neat) = 0.8618 containing an average of 1.03 double bonds per mole were charged to a 3 liter rocker type autoclave. Commercial nickel hydrogenation catalyst (70 grams 14 grams of nickel) was added and the autoclave was closed flushed with hydrogen and charged with hydrogen at about 100 atm. The shaker was started and the autoclave was heated electrically to about 60° C. over a period of about 20 minutes by means of an electric furnace. At this point the hydrogenation caught and heat was cut off. The hydrogen pressure was permitted to drop to about 20 atm. and then recharged to about 100 atm. The temperature rose to 130°C. during the next 40 minutes and about 0.9 mole of hydrogen was absorbed per mole of turpentine. The heater was then adjusted to maintain this temperature for about 4 hours to complete the hydrogenation. Total hydrogen uptake was about 1 mole per mole of turpentine. Filtration after the reaction mixture was cooled yielded 1312 grams of crude pinane containing about 30 grams of coconut oil from the catalyst. Distillation of this product through a short Vigreux column at atmospheric pressure yielded 1020 grams of pinane boiling below 170° C.  $n_{20D} = 1.465 = 0.8546 = 9.0$  (10 cm. neat) which gave only a light yellow color when it was shaken with 85% sulfuric acid. This represents a yield of about 80% based on the gum turpentine charged.

The recovered catalyst was still fully active and was re used three times to produce yields of 88 89 and 87% of pinane. The low yield in the first run was due to the difficulty in removing the last of the pinane from the residual coconut oil.

**Low Pressure Hydrogenation.** Low pressure hydrogenations were carried out in stirred autoclaves designed for the hydrogenation of fats. The largest single charge was a 400 pound drum of gum turpentine. This hydrogenation was carried out at 22 pounds per square inch gage and 280° F. for 18.5 hours. At this time the run was stopped because of severe leakage at the agitator shaft bearing caused by the action of hot turpentine on the packing. This hydrogenation was only 84% complete that is quantitative hydrogenation indicated about 0.17 of a double bond remained per mole of terpene. The original gum turpentine had about 1.05 double bonds per mole indicating the presence of 5% of monocyclic terpenes which yield p menthane on hydrogenation. Small scale runs indicated that substantially complete hydrogenation of gum turpentine can be attained at 60 pounds per square inch and 150° C. when a suitable packing is used in the agitator shaft seal.

A portion (2400 grams) of this crude pinane was distilled through an efficient column at about 50 1 reflux ratio to give about 1500 ml. of pinane containing only about 1% of residual olefins.

**Small and large scale techniques of pinane oxidation are investigated**

**Method A.** Small samples (2 ml.) of pure pinane were oxidized with oxygen in 50 ml. Erlenmeyer flasks attached to gas burets. The reaction temperature was controlled by immersing the reactors in a constant

temperature oil bath. The samples were not stirred. The progress of the reaction was followed by observing the volume of oxygen absorbed. At the conclusion of each experiment the peroxide content of the sample was determined.

Method A was used to study the effect of light on the oxidation of pinane. For runs in the dark the reactors were completely covered with tin foil. A 200 watt incandescent light was used to illuminate the reactors for runs in the light. The results of these experiments are given in Table I.

Method B. Samples of pinane (0.1 mole) were oxidized in 125 ml. Erlenmeyer flasks immersed in a constant temperature oil bath. The samples were stirred by means of a glass encased magnetic stirring bar and wet oxygen from calibrated gas reservoir was passed over the surface of the liquid at the rate of 1 liter per hour. The exit gas was passed through a Dean Stark trap and condenser to remove entrained vapors and was then collected in a calibrated gasholder. Samples for use in determining peroxide number were withdrawn by interrupting the oxidation for a few seconds and using the oxygen inlet tube as a pipet to withdraw the sample.

Method B was used to investigate the effect of oxidation temperature on the peroxidation reaction. The results of these experiments are presented in Figure 1 and in Tables II and III. In calculating the data for Tables II and III allowance was made for the moisture content of the oxygen for the removal of samples and for the loss through the condenser by evaporation. Since such calculations involve a number of approximations the results are only semiquantitative.

Method C. This method was the same as Method B except the reactor was simply connected to an oxygen reservoir and the oxidation was carried out in a closed system. In Table IV results obtained by this method are compared with those obtained by method B.

Method D. Oxidations were made using 100 ml. samples of pinane containing 1.4% of olefins in a 250 ml reactor with a fritted glass false bottom for introduction of oxygen and equipped with the usual moisture trap and condenser. A temperature of 110° C. was maintained by means of a constant temperature oil bath and the oxidation time was 6 hours in each case. The crude oxidates were stripped at 0.3 mm. of mercury pressure to a pot temperature of 78°C using water vapor as a carrier gas to remove unoxidized pinane. Oxygen absorption was not measured but peroxide content was determined before and after stripping. To evaluate the effect of iron on the peroxidation duplicate runs were made with and without 1 gram of iron filings in the sample and iron turnings in the head space and trap. The runs with iron gave light yellow oxidates having peroxide numbers of 6200 and 6400. Stripping in the presence of iron gave a product having peroxide number of 10 600. The runs without iron gave similar oxidates having peroxide numbers of 5800 and 6600; the stripped product had a peroxide number of 10 800.

Method E. For larger scale runs (10 to 20 moles) using various grades of pinane the reactor consisted of a 3 or 5 liter three necked flask which was fitted with an efficient mechanical stirrer a fritted glass gas inlet tube a thermometer and a modified Dean Stark moisture trap and reflux condenser. The reactor was heated with a heating mantle at the start of the oxidation and was cooled with an air blast or with a wet cloth during the latter stages of the reaction. The oxidation was initiated at 120° to 130° C. and the temperature was lowered as the oxidation progressed. Samples were removed from time to time and the peroxide content was determined. Upon completion of the oxidation the peroxide was concentrated by stripping off the unreacted pinane under vacuum using water vapor as a carrier gas.

Oxygen flow rates of 200 to 400 liters per hour were used depending on the size of the charge. Oxygen absorption was not measured directly but in some experiments an efficient trap cooled with solid carbon dioxide was used to condense the volatile material from the exit gas. The amount of oxygen absorbed was then estimated from the total weight of products recovered. Results of experiments using this method are given in Tables V VI and VII.

The over all length of the reactor is about 1 meter. Neck A is fitted with a long stemmed glass

thermoregulator. The simple regulator shown in Figure 2 is satisfactory and convenient for this purpose. It is readily set simply by opening the stopcock until the desired temperature is attained and then closing it. Necks B and C are used for insertion of a thermocouple well (or thermometer) and a sampling tube. Neck D is the gas outlet and is fitted with a Dean Stark moisture trap and reflux condenser.

The coolant maybe any suitable high boiling liquid such as turpentine and is recirculated through a heat exchanger reservoir system by means of a centrifugal pump. The flow is controlled by means of a magnetic valve actuated through a relay by the thermoregulator. Heat for initiation of the reaction is provided by wrapping the reactor with electrical heating tape.

Oxygen input and exhaust were measured by means of wet test meters. Samples were withdrawn at suitable intervals for determination of peroxide content. Table VIII presents data for a typical run by this method.

Cold Rubber Polymerization. Samples of a crude pinane oxidate and a pinane hydroperoxide concentrate were tested by the Government Laboratories of the University of Akron for use in 5° C. copolymerization of butadiene styrene. For this evaluation in amine formula II (Formula A) and the low sugar iron formula (Formula B) previously reported and a sugar free formula (Formula C) were used. The sugar free formula was identical with the low sugar formula except for the omission of the sugar and part of the pyrophosphate from the activator. All peroxides were tested simultaneously at a given level. Representative data from these tests are given in Table IX.

Decomposition of Pinane Hydroperoxide. The general technique used in this work consisted of weighing a sample of pinane hydroperoxide (Approximately 0.1 gram) into a small glass ampoule adding the decomposing agent being tested flushing the ampoule thoroughly with nitrogen and sealing it. The sealed ampoules were immersed in a constant temperature bath and removed at suitable intervals chilled cleaned thoroughly and opened. The sample was transferred to a flask by means of the peroxide number solvent and the peroxide content was determined. Decomposition conditions were chosen on the basis of work on the pure peroxide.

Results of these experiments are given in Tables X XI and XII.

Over all yield of 85% is realized in production of high purity hydroperoxide

Preparation of Pinane. Although gum turpentine was used as the starting material in the work reported either a or b pinene can be used. b pinene hydrogensters more readily than turpentine or a pinene and can be hydrogenated at a little lower temperature. When gum turpentine is used instead of pure pinenes the product may contain up to 5% of p menthane and small amounts of other saturated terpenes but these do not interfere in the oxidation step.

If the hydrogenation step is carried out properly the product can be filtered distilled to remove the last traces of the catalyst and the carrier and used for the production of pinane hydroperoxide without further purification. If the hydrogenation step is not carried to completion purification of the crude pinane may be necessary. As shown in Tables V and X the presence of excessive amounts of residual olefins decreases the purity and stability of the product and the yield of hydroperoxide.

The residual olefins can be removed by efficient fractional distillation by washing with concentrated sulfuric acid or with chromic acid sulfuric acid mixtures by passage through activated silica gel or by a combination of these processes. Obviously such methods are relatively time consuming and expensive. In some cases it has been found satisfactory to oxidize the impure pinane for a short time at 130° to 140° C. and recover the unoxidized pinane by simple distillation. The olefins are more easily oxidized than the pinane. As a general rule it is much better to take adequate precautions to ensure complete hydrogenation than to have to remove residual olefins from the crude pinane. However the hydrogenation conditions should be fairly mild since high temperatures favor the production of trans pinane which is more resistant to oxidation than is cis

pinane. Furthermore vigorous hydrogenation conditions may convert the pinane to monocyclic hydrocarbons.

## Sylvestrene and some of its Derivatives

With the discovery of sylvestrene in Swedish pine oil derived from *Pinus sylvestris* probably the most intriguing chapter was opened in the chemistry of *m*-menthadienes. We now know for certain that sylvestrene is not a naturally occurring hydrocarbon but an artifact originating from D3 or D4 carene during the process of isolation through the dihydrochloride. However during the past one hundred years the structures of sylvestrene and its derivatives were the subject of innumerable inconclusive investigations. In recent times there has been great interest in the sylvestrene problem and the purpose of this review is to focus attention on the salient developments in this field.

### Sylvestrene

**Structure** Usually sylvestrene is obtained from sylvestrene dihydrochloride (1) by splitting off two molecules of hydrogen chloride using aniline sodium acetate and acetic acid or diethylaniline. Theoretically six *m*-menthadienes can arise by the dehydrochlorination process. However by precise fractionation the hydrocarbon mixture has been resolved into the isomers designated as sylvestrene isosylvestrene and sylveterpinolene with tentative formulae (II) (III) and (IV) respectively. That formula (II) represents sylvestrene is firmly established by the n.m.r. analysis of sylvestrene tetrabromide (V) which is obtainable only from sylvestrene. It was therefore proposed that the name sylvestrene should be confined to the D6 8(9) *m*-menthadiene which alone furnishes sylvestrene tetrabromide.

**New method of preparation** Whereas the earlier methods of obtaining sylvestrene depended on the fractionation of the hydrocarbon mixture derived from sylvestrene dihydrochloride recently it was prepared in about 47% yield by heating an ethanol ether solution of sylvestrene tetrabromide with zinc dust. This sylvestrene afforded copiously the tetrabromide and nitrosochloride derivatives but did not respond to the acetic anhydride sulphuric acid colour test.

### Sylvestrene nitrosochloride

Wallach who was the first to prepare the bimolecular sylvestrene nitrosochloride considered the monomeric form to be (VI) (VII) or a mixture of the two on the assumption that sylvestrene was a mixture of (II) and (III). If this view is accepted then the dimeric form is either (VIII) (IX) (X) or a mixture of these. In order to distinguish between these possible structures, the n.m.r. spectrum of the bimolecular nitrosochloride was studied. The results obtained favoured the formula (VIII) for the derivative which in turn would suggest that the correct formula for the monomer is (VI).

### Sylvestrene oxide

The epoxidation of sylvestrene with peracetic acid at temperatures below 0° has resulted in about 70% yield of sylvestrene oxide (XI). It is a colourless mobile liquid with a camphor menthol smell. The physical constants for the camphor menthol smell. The physical constants for the purest sample are b.p. 90°/20 mm  $n_{29} 1.4671$   $d_{20} 0.9307$  and  $(\alpha)_D^{20} + 54.1^\circ$ . On hydration with dilute sulphuric acid it gave the crystalline diol (XII) m.p. 135°. As will be seen in the sequel sylvestrene oxide is a useful raw material for synthesis of oxygenated derivatives in the *m*-menthane series.

## Recovery of 3 carene from Chinese Turpentine and Synthesis of Acetylcarenes

Fractions containing 56~72% 3 carene were recovered by two stage fractional distillation of Chinese wood and sulfate turpentines. Acetylation with acetic anhydride using zinc chloride as catalyst produced a mixture

of acetylated carenes with 4 acetyl 2 carene as the main product. The optimal condition for the acetylation was determined to be reaction temperature 70°C reaction time 6h amount of ZnCl<sub>2</sub> 3.8% and the ratio acetic anhydride 3 carene 2.0 1

## Introduction

The monoterpene 3 carene (3,7,7-trimethylbicyclo[4.1.0]heptane) is one of the major components in wood and sulfate turpentines produced in north China. Its content is about 10% in this turpentine. 3 Carene also occurs in essential oil such as oil from needles and barks of arborvitae (*Thuja* species). 3 Carene has been used for the synthesis of perfumes and raw materials for perfumes for example 4 acetyl 2 carene and 4 hydroxymethyl 3 carene. However there is no report about the utilization of 3 carene in China. The aim of this study was to recover fractions rich in 3 carene from Chinese turpentines and to synthesize 4 acetyl 1 carene. The synthesis conditions were optimized and the reaction mechanisms were elucidated.

## Distillation of wood and Sulfate Turpentines

### Material and Methods

Turpentine samples Wood turpentine was obtained in March 1987 from the Dunhua wood Rosin Factory in Dunhua city Jilin Province China using Korean pine (*Pinus koraiensis*). Sulfate turpentine was obtained in March 1987 from the Jiamusi Pulp and Paper Plant in Jiamusi city Heilongjiang Province China using wood of the following species; 70% Dahurian larch (*Larix dahurica*) and 30% of a mixture of Korean pine (*P. koraiensis*) Yeso spruce (*Picea jezoensis*) Khingan fir (*Abies nephrolepis*).

Fractional distillation the turpentines were distilled using a silverplated glass column with a vacuum jacket.

The distillation conditions were as follows

### Distillation Results

After the first distillation a distillate rich in a pinene was obtained (Table 1). The yield of a pinene in the distillate was 82% of the amount in the wood turpentine and 74% in the case of sulfate turpentine.

Practically all 3 carene was left in the residue.

The residues from the first distillation were subjected to a second distillation. Two fractions rich in 3 carene were recovered from the wood turpentine residue (Table 2). The total yield of 3 carene was 74% of that originally present in the wood turpentine.

The sulfate turpentine residue yielded a first fraction rich in pinene containing 70% of the amount present in the crude sulfate turpentine the second distillate was rich in 3 carene and contained 79% of the original amount in the crude turpentine.

It was thus possible through two fractional distillations to recover fractions containing 56~72% 3 carene with a recovery of 74~79% of the 3 carene present in the crude turpentine.

## Synthesis of Acetyl Carene

### Materials and Methods

Synthesis experiments were carried out with the two carene rich distillates from the wood turpentine and the carene rich one from the sulfate turpentine.

Carene rich distillate acetic acid anhydride and anhydrous zinc chloride were placed in a three necked flask equipped with a stirrer a thermometer a reflux condenser and a calcium chloride drying tube. The mixture was kept at a certain temperature for a certain time under stirring. After the reaction water was added and the organic phase was separated. The aqueous phase was extracted with three portions of diethyl ether. The ether solutions were combined with the organic phase the solution was washed with sodium bicarbonate until free of acid then dried by addition of sodium sulfate and the ether was removed. The residue was vacuum distilled and the fraction recovered in the range 118 ~120°C at 1333.22Pa containing mainly acetylated carenes was collected.

The synthesis products were characterized by GC GC 1R and GC MS. GC IR spectra were recorded with



a Hewlett Packard 5890A GC coupled a PRGLIB FTS 60 FTIR instrument using a HP 5 fused silica capillary column. The GC MS instrument was a JEOL D300 with a SE 30 fused silica capillary column. EI spectra were recorded at 70 eV.

## Results and Discussion

The yield of products is dependent on the type and the amount of catalyst the reaction temperature the reaction time and the ratio of reactants. Each factor was investigated and orthogonal experiments were carried out in order to establish the optimal conditions for the reaction.

Effect of catalyst Tin tetrachloride ( $\text{SnCl}_4$ ) and zinc chloride ( $\text{ZnCl}_2$ ) gave rather similar catalytic effects. Zinc chloride was preferred because it is less costly. The optimal amount of zinc chloride is around 3.8% (Table 3). With higher amounts polymerization of 3 carene seems to take place. With lower amounts the reaction is considerably slowed down.

Effect of temperature. The yield of acetylated products decreased considerably with increasing reaction temperature probably because of polymerization reactions (Table 4).

Determination of the optimal reaction conditions. According to the above results and earlier reports we decided to study the four factors reaction temperature reaction time amount of catalyst ratio of 3 carene and acetic anhydride in an orthogonal experiment utilizing three levels and nine experiments coded L9 (34) (Table 5 6).

The average yield for every level of each factor was calculated. Because the yields of products were nearly the same when the added amounts of catalyst were 2.1% and 3.8% (C1 and C2) the experiments of group A2B1C1D3 and A2B1C2D3 were repeated and compared with the highest yield of Table 6.

Under A2B1C2D3 conditions the yield of products was the highest and identical to the conditions and results of No.4 experiment (Table 7). So the optimal conditions were reaction temperature 70°C reaction time 6h added amount of catalyst 3.8% acetic acid anhydride 3 carene 2.0 1. Under these conditions the yield of products was 74~75%.

# Homopolymers and Copolymers of Acrylates

## Introduction

In continuation of the studies on the preparation of polymers containing terpenes and various terpene derivatives two new derivatives from a pinene have been investigated (1) homoterpenylmethyl carbinol 6 hydroxy 2 (1 hydroxy 1 methylethyl) heptanoic acid g lactone (I) and (2) a campholenol 2 (2 2 3 trimethyl 3cyclopentenyl) ethylalcohol (II). I was prepared by Howell and Hedrick by the platinum oxide reduction of homoterpenylmethyl ketone in sodium hydroxide solution; H was obtained by reduction of the corresponding aldehyde a campholene aldehyde. The properties and reactions of II and a campholene aldehyde have been described. Synthesis of various esters of II conversion of the esters to epoxides and evaluation of the epoxides as plasticizer stabilizers for poly (vinyl chloride) have also been described.

The work here describes the preparation and polymerization of the acrylates and methacrylates of I and II. In addition studies on the epoxidation curing and hydrolysis of some of the polymers of II were conducted. Polymers containing the unit I would be expected to undergo the lactone ring opening to yield water soluble polymers. Polymers of II would be expected to undergo an epoxidation readily. The reaction products of epoxidized polymers with for example fatty acids could find applications in the coatings field.

## Results and Discussion

### Monomers

Samples of a campholene aldehyde I and II were provided by Dr. G.W. Hedrick of the Naval Stores Laboratory of the Southern Utilization Research and Development Divisions Agricultural Research Service. In the preparation of additional II a campholene aldehyde was reduced with lithium aluminum hydride. The

physical constants of the three materials are given in Table 1.

The acrylates and methacrylates of II and I were prepared according to the procedure of Marvel and Schwen. However instead of distilling the products chromatography on silicic acid with diethyl ether hexane mixtures as eluent was used for purification of the monomers. Physical characteristics of the monomers and their analytical data are given in Table 2. Infrared analysis showed the presence of a trace of hydroxyl containing material in the acrylate and methacrylate of I. Although there was a good agreement in analytical data between the calculated and experimental values it is possible that a minor amount of the hydrolyzed lactone was still present in the derivatives of I or the hydroxyl band may have been due to absorbed moisture. The residue found in the analysis of the methacrylate of II was probably due to colloidal silicic acid introduced inadvertently during the chromatography of the monomer.

#### Homopolymerization

The experimental conditions and polymerization results for the various polymers are given in Table 3. Homopolymerizations were conducted in an emulsion system with the use of a detergent (Siponate DS 10) rather than soap as the emulsifier. The detergent gave better latices and conversions. The low inherent viscosities for the homopolymers of methacrylate of I and acrylate of II were unexpected. The polymers were isolated as white powders which could be molded (at about 150°C) into water clear brittle films. On one occasion the acrylate of I gave a material which could be molded into a strong film. In the homopolymerization of the acrylate of II whenever the conversion exceeded 35% some insoluble polymer began to form. Similarly long drying periods insolubilized the material probably by oxidative coupling at the allylic position. The polyacrylates of I were soluble in ethyl methyl ketone and chloroform. The polyacrylates of II were soluble in tetrahydrofuran ethylmethyl ketone and methylene chloride. Whereas only a trace of a hydroxyl containing material was indicated in the acrylate and methacrylate of I monomers the corresponding homopolymers appeared to contain more of the hydroxy acid despite the fact that their analytical data agreed with the calculated. A tightly bound water of hydration cannot be ruled out as the infrared analysis is not conclusive on this point.

#### Copolymerization

Copolymers of the acrylate of I. The acrylate of I was copolymerized with the acrylate and methacrylate of II and with acrylonitrile. The acrylate copolymers were isolated as white hard solids soluble in ethyl methyl ketone whereas the acrylonitrile copolymer was a yellow solid soluble in N methylpyrrolidone. The acrylate copolymers had inherent viscosities below 1.0; acrylonitrile copolymer had the exceptionally high viscosity of 4.4. The acrylates could be molded (at about 150°C.) into water clear brittle films whereas the acrylonitrile copolymer gave an extremely tough somewhat soft film.

The properties of all the copolymer films are given in Table 4. All of the copolymers gave transparent films. Prolonged drying of the copolymers of the acrylate and methacrylate of II insolubilized them. In general the copolymers of acrylate of I exhibited adhesion to a copper foil in varying degrees. This may have been due to the hydroxy acid component present in the polymers.

Copolymers of the methacrylate of I. The methacrylate and acrylate copolymers were isolated as white hard solids soluble in ethyl methyl ketone; the acrylonitrile copolymer was a yellow solid soluble in N methylpyrrolidone. None of the methacrylate of I copolymers possessed adhesive properties.

Copolymers of the acrylate and methacrylate of II. The acrylate/acrylonitrile copolymer was isolated as a yellow solid in a 95% yield of which only 30% was soluble in N methylpyrrolidone. The insolubility was probably due to the crosslinking of the acrylate portion.

The methacrylate/acrylonitrile copolymer was isolated in a quantitative yield; however only about 20% of it was soluble in N methylpyrrolidone.

The solution methacrylate/fumaronitrile copolymer was isolated as a dark tan solid soluble in tetrahydrofuran.

## Terpolymerization

Terpolymers of the acrylate of I. Two series of terpolymers involving the acrylate of I have been prepared. One of the series involved BD/AN comonomers. The terpolymers were isolated as water clear to white rubbery masses which could be molded (at about 130°C.) into clear tough films. Whereas the 30/61/9 acrylate BD/AN terpolymer was essentially insoluble in hot tetrahydrofuran and chloroform only 10% of the 60/33/7 acrylate BD/AN terpolymer was not soluble and the 78/17/5 acrylate/BD/AN terpolymer was soluble in chloroform and tetrahydrofuran.

The other series involved BD/Sty comonomers. These materials again were isolated as water clear to white rubbery masses which could be molded (at about 130°C.) into clear tough films. A film prepared on copper foil of the 80/14/6 acrylate/BD/Sty terpolymer adhered strongly to the foil. Of the four compositions only the 80/14/6 and 66/24/10 acrylate/BD/Sty terpolymers were partially (~70%) soluble in hot ethyl methyl ketone. Terpolymers of the acrylate of II. Another terpolymer series identical to the one described but with the acrylate of II was attempted. However with both the BD/AN and BD/Sty comonomers only low conversions were realized. The best yield (33%) was obtained with the 75/20/5 acrylate BD/AN terpolymer. The two terpolymers 75/20/5 and 58/34/8 on which inherent viscosities were run were soluble in tetrahydrofuran and had good viscosity values. The films pressed (at about 130°C.) from these materials were clear rubbery and strong.

## Epoxidation

Epoxidation of several polymers was explored to increase their functionality. Development of adhesive properties was also sought. The following polymers were investigated (1) polyacrylate of II (2) 60/40 acrylate of I/acrylate of II copolymer and (3) 66/24/10 acrylate of I/BD/Sty terpolymer. The in situ method<sup>11</sup> with hydrogen peroxide/glacial acetic acid with a resin catalyst (Amerlite IR 120) was explored. This method was preferred over the ones involving use of preformed peracids because it gave higher oxirane oxygen content in a shorter time and less contamination in the final product. Ethyl methyl ketone was used as a solvent for the polymers. Normally in epoxidations of polymers secondary reactions products such as glycol derivatives ketones and ether derivatives would be expected.

According to the infrared analysis of the epoxidized materials only a trace amount of unsaturation was observed in the epoxidized homopolymer of acrylate of II and no unsaturation was detected in the other two materials. Furthermore absorption bands attributed to epoxides (1250-840 cm.<sup>-1</sup>) were observed in the epoxidized polymers.

Analytical data calculated on the basis of one oxygen atom addition across the double bond indicated that for the polyacrylate of II only 10% of the theoretical addition had taken place for the copolymer 38% and for the terpolymer 25%. A more accurate determination could be probably achieved by the ether HCl method.

Although the epoxidized copolymer was isolated as a soluble product from the reaction mixture drying it at 39°C. for 26 hr. insolubilized it completely.

In the epoxidation of the terpolymer (66/24/10 acrylate of I/BD/Sty) two products were produced in about equal amounts. One of the materials was water soluble the other was water insoluble. The water soluble material was also insoluble in hot ethyl methyl ketone was extremely tough and a good film could not be molded. Hence an infrared spectrum could not be obtained. The water soluble material was pressed into a film; the infrared spectrum showed it to be the hydroxy acid and contained absorption bands characteristic of epoxides. Analytical data on the water soluble material could also be accounted for by assuming opening of the lactone ring. It is surprising that the lactone ring was opened under these acidic conditions.

## Curing

Epoxy polybutadienes cured with polyamines or anhydrides are good adhesives to metallic substrates. Accordingly the epoxidized polyacrylate of II and the acrylate of I/acrylate of II copolymer were mixed with

p phenylenediamine placed between copper foils and compressed and heated at 160°C. for 2 min. The film from the polyacrylate of II was extremely hard and completely nonadhesive; the copolymer film was partially adhesive.

### Hydrolysis of Polymethacrylate of I

The lactone ring in polymers of I should be susceptible to basic hydrolysis. A sample of the methacrylate homopolymer was hydrolyzed with 3.5% ethanolic potassium hydroxide at room temperature. After a period of about 2 hr. the infrared spectrum showed that most of the lactone ring had been opened; the product was soluble in ethanol and water. In water the hydrolyzed polymer formed a light blue very viscous solution. Evaporation of water yielded a transparent strong film. Infrared analysis on the film showed the presence of a strong absorption band for the carboxylate anion at 1565 and 1390  $\text{cm}^{-1}$  and only a minor absorption band at 1775  $\text{cm}^{-1}$  indicative of the lactone carbonyl. Thus the potassium hydroxide treated polymer is essentially all potassium salt of the polycarboxylate. The extremely facile opening of the lactone ring suggests an easy preparation of water soluble polymers.

## Polymers and Copolymers of Vinyl Pinolate

### Preparation of Vinyl Pinolate

The preparation of vinyl pinolate from pinolic acid has been described previously. More recent work has shown that the product formed from the reaction of pinolic acid vinyl acetate and mercuric sulfate is probably an acetoxyacetal which can be hydrolyzed at room temperature with mineral acid. Infrared absorption for a hydroxyl group was completely absent in the unhydrolyzed product. Hydrolysis however gave the expected vinyl pinolate.

### Polymerization

Polymerization of vinyl pinolate has been accomplished by free radical initiation in bulk solution suspension and emulsion systems. The conditions for polymerization and some properties of the samples of poly (vinyl pinolate) are summarized in Table I. Preparation of poly (vinyl pinolate) in suspension was unsuccessful until neutral buffered solution was substituted for distilled water in the polymerization recipe. In contrast polymerization of vinyl pinolate in buffered and unbuffered emulsion systems produced the same results.

All the samples of poly (vinyl pinolate) are colorless glasslike solids that melt between 70 and 105°C. Except for sample 31 B which is poly (vinyl pinolate) prepared in emulsion the samples are soluble in methanol acetone and tetrahydrofuran slightly soluble in benzene and insoluble in petroleum ether. Sample 31 B is soluble in acetone and tetrahydrofuran until it is dried. Then it is insoluble in acetone tetrahydrofuran and several other solvents.

Because poly (vinyl pinolate) contains one hydroxyl group per repeating unit reaction with a diisocyanate would be expected to produce a high degree of crosslinking. To prepare low molecular weight polymers that contain relatively fewer hydroxyl groups than poly (vinyl pinolate) and might therefore be more suitable for extending with diisocyanates vinyl pinolate was copolymerized in solution with vinyl acetate and vinyl chloride. Table II contains information concerning the preparation and properties of several vinyl pinolate vinyl acetate copolymers and Table III vinyl pinolate vinyl chloride copolymers. Transparent colorless films can be cast from both vinyl pinolate vinyl chloride copolymers. Transparent colorless films can be cast from both vinyl pinolate vinyl acetate and vinyl pinolate vinyl chloride copolymers but the films are brittle indicating that the vinyl pinolate units do not produce any appreciable internal plasticization.

Vinyl pinolate was copolymerized with vinyl acetate and vinyl chloride in emulsion as well as in solution.

The data resulting from the copolymerization experiments are compiled in Table IV.

Poly (vinyl acetate) and poly (vinyl chloride) prepared in emulsion are soluble in acetone and

tetrahydrofuran and so are the copolymers of vinyl pinolate prepared in solution and listed in Tables II and III. In contrast the copolymers of vinyl pinolate with vinyl acetate and vinyl chloride prepared in emulsion are soluble in acetone and tetrahydrofuran only until they are dried at room temperature. Attempts to dissolve the dried copolymer in benzene acetone tetrahydrofuran and dimethyl sulfoxide resulted in the slow softening and swelling of the copolymer. Apparently even small amounts of vinyl pinolate as small as 0.5 mole % copolymerized in emulsion with vinyl acetate or vinyl chloride produce a marked decrease in the solution of the dried copolymer.

Vinyl pinolate fails to copolymerize with vinylidene chloride under the emulsion polymerization conditions. Under similar conditions the relative reactivity ratios of vinylidene chloride (0.08) and the vinyl ester of a long chain fatty acid e.g. vinyl stearate (3.80) were determined and are unfavorable for copolymerization.

### Reaction of vinyl pinolate copolymers with Isocyanates

To learn something of the reactions of vinyl pinolate and its vinyl chloride and vinyl acetate copolymers with isocyanates a method was used based upon spectral analyses. By determining infrared absorbancies of a stretching vibration arising from the isocyanate group at  $4.5\mu$  of solutions of vinyl pinolate and its copolymers reacted with toluene diisocyanate and phenyl isocyanate it was possible to estimate the decrease in isocyanate concentration caused by the reaction. The change in concentration as represented by change in absorbancy gave a convenient method for measuring reactivity. Poly (vinyl acetate) and poly (vinyl chloride) homopolymers exhibited little or no reaction with either isocyanate at  $75^{\circ}\text{C}$ . (Table VI). One of the isocyanate groups of toluene diisocyanate was less reactive than the other group since almost half the isocyanate was unreacted when equivalent quantities of vinyl pinolate and the isocyanate were reacted. Phenyl isocyanate reacted completely. Similar results were obtained with the vinyl acetate vinyl pinolate copolymer 123 A. Copolymers 44 2 and a mixture of 121 A 123 A from which excess toluene diisocyanate was removed after reaction by precipitating and washing with hexane contained free isocyanate groups. With 0.1N solutions of the copolymers based on vinyl pinolate content the residual isocyanate content was 0.07N for the vinyl chloride copolymer and 0.064 for the vinyl acetate copolymer.

The results of a rate study involving reactions of the copolymers 44 2 and 123 A and phenyl isocyanate are tabulated in Table V. After about 6 hr. the isocyanate concentration with both polymers was about 0.07N (calculated 0.07N) and did not change much after an additional 8 hr. heating.

## Experimental

### Preparation of Vinyl Pinolate

Pinolic acid 372 g. (2.0 moles) freshly distilled vinyl acetate 2200 ml. copper resinate 1.0 g. and mercuric acetate 8.0 g. were mixed in a 3 l flask. Concentrated sulfuric acid 1.0 ml. was added and agitation continued at  $0-5^{\circ}\text{C}$ . until the pinolic acid was in solution. The batch was stored in a refrigerator ( $10^{\circ}\text{C}$ .) for two days. The sulfuric acid was neutralized with sodium acetate and the excess vinyl acetate and acetic acid distilled below  $30^{\circ}\text{C}$ . The residue was dissolved in 1500 ml. ether and washed with vigorous agitation for 15 min. with three 500 ml. portions of 1.5N hydrochloric acid. The solution was washed at  $10^{\circ}\text{C}$ . with cold water cold 0.5N sodium carbonate and dried. The ether was removed and the product distilled bulb to bulb; b.p.  $106^{\circ}\text{C}/1.0$  mm.; 334 g. 81%. The crude ester was redistilled through a column packed with glass helices b.p.  $84^{\circ}\text{C}/0.2$  mm. 1.4656.

### Polymerization of Vinyl Pinolate in Solution

A 250 ml. three necked flask equipped with a spiral condenser thermometer magnetic stirring bar and nitrogen inlet tube was charged with vinyl pinolate azobisisobutyronitrile (2% of weight of the monomer) and 150 ml. of A.R. grade benzene. The solution was stirred at reflux temperature under nitrogen for the desired number of hours. Then the benzene was removed by aspiration and the polymer was purified by repeatedly dissolving it in acetone and precipitating it in petroleum ether ( $35-75^{\circ}\text{C}$ .). Finally the polymer was

dissolved in benzene and freeze-dried.

#### Polymerization of Vinyl Pinolate in Suspension

Into a 100 ml. two-necked flask fitted with a spiral condenser, magnetic stirring bar, and nitrogen inlet tube was placed 3.0 g. of vinyl pinolate, 0.03 g. of Duponol C (du Pont's sodium lauryl sulfate), 0.3 g. of azobisisobutyronitrile, and 10 ml. of neutral buffered solution. The suspension was stirred under nitrogen at 60°C. for 48 hr. The poly(vinyl pinolate) which had coalesced into a single lump was dissolved in acetone and precipitated first in water and then in petroleum ether. Then the polymer was dried at 60°C. in a vacuum oven at 20 mm. of mercury.

#### Polymerization of Vinyl Pinolate in Emulsion

A 2 oz. screw-capped bottle was charged with 0.3 g. of Triton X 301 (Rohm and Haas sodium alkylaryl polyether sulfate 20% aqueous dispersion), 1.5 g. of vinyl pinolate, 0.75 ml. of 25% aqueous potassium persulfate, and 3 ml. of distilled water. After the air had been flushed from the bottle with a stream of nitrogen, the bottle was capped and tumbled in a water bath at 60°C. for 48 hr. A sulfuric acid salt solution (5% H<sub>2</sub>SO<sub>4</sub> saturated with salt) was used to break the emulsion. The poly(vinyl pinolate) was washed with water and purified by the same procedure described for suspension polymerization. After it has been dried, the poly(vinyl pinolate) was insoluble in dimethylformamide, methanol, acetone, 2-butanone, tetrahydrofuran, dioxane, benzene, toluene, chloroform, and carbon tetrachloride.

#### Copolymerization of Vinyl Pinolate and Vinyl Acetate in Solution

The same procedure described for solution polymerization of vinyl pinolate was used with the exception that a calculated amount of freshly distilled vinyl acetate was added to the solution.

#### Copolymerization of Vinyl Pinolate and Vinyl Chloride in Solution

Polymerization bottles (110 ml. Ace Glass T 1506) were charged with calculated amounts of vinyl pinolate, 0.2 g. of azobisisobutyronitrile, 40 ml. of A.R. grade benzene, and then cooled in a Dry Ice acetone bath. Vinyl chloride was condensed in the bottles until slight excess was present. When the excess vinyl chloride had been allowed to evaporate, the bottles were sealed with crown-type bottle caps and tumbled in a water bath at 60°C. for 48 hr. The copolymers were coagulated by pouring the benzene solutions into 400 ml. of methanol and purified by repeatedly dissolving them in tetrahydrofuran and precipitating them in rapidly agitated methanol. After the copolymers had been dried at room temperature for 48 hr. they could be dissolved easily in acetone and tetrahydrofuran but only with difficulty in benzene.

#### Copolymerization of Vinyl Pinolate and Vinyl Chloride in Emulsion

The calculated amounts of vinyl pinolate, 40 ml. of oxygen-free water, 3.0 g. of Triton X 301, and 4 ml. of 2.5% potassium persulfate solution were placed into 110 ml. polymerization bottles. While the bottles were being cooled in a Dry Ice acetone bath, a slight excess of vinyl chloride was condensed into it. When the excess had been allowed to evaporate, the bottles were capped and tumbled at 50°C. for 72 hr. The copolymers were coagulated with 400 ml. of saturated salt solution and collected on filter paper. After being washed with water and then with methanol, the copolymers were repeatedly dissolved in tetrahydrofuran and precipitated in methanol. Finally, the copolymers were dried at room temperature for 48 hr. If the copolymers are overheated on drying, they become insoluble in acetone, tetrahydrofuran, dimethyl sulfoxide, dimethyl formamide, and benzene.

#### Reaction of Polymers with Isocyanates

Exploratory experiments were made to select a solvent and to determine a suitable temperature and time for running the reactions. Tetrahydrofuran was a good solvent for the polymer; however, the isocyanates, toluene diisocyanate (a mixture of 2,4 and 2,6 isomers in a 4:1 ratio) and phenyl isocyanate were not stable in this solvent at 75°C. since this solvent did not affect the isocyanate adversely.

In instances indicated, the benzene was replaced with tetrahydrofuran for reasons of solubility. The benzene was removed in vacuo at room temperature and the residual polymer dissolved in the

tetrahydrofuran. In other instances also as indicated the polymers crosslinked and became insoluble in the latter solvent.

The substances investigated are tabulated in Table VI.

Benzene solutions (0.1N with respect to vinyl pinolate) of each of the copolymers 123 A and 44 2 were made up containing 0.3N phenyl isocyanate. These were heated to 75°C. for periods of 1 2 4 6 and 14 hr. After each heating period 1 ml. samples were removed and diluted with 2 ml. of tetrahydrofuran. The results are tabulated in Table V. The concentration of the hydroxyl and isocyanate initially in the diluted samples were about 0.03 and 0.1N respectively.

In another experiment benzene solutions containing 0.93 g. (0.1N) of a mixture of copolymers 121 A and 123 A in equal amounts and 0.87 g. (1.0N) toluene diisocyanate diluted to 10 ml were heated to 75°C for 2 hr. The polymers were precipitated by pouring into hexane washed by decantation redissolved and reprecipitated to remove excess isocyanate. The polymers were dissolved in tetrahydrofuran and diluted to 10 ml. The isocyanate concentrations after removal of excess isocyanate were 0.064N for the 121 A 123 A polymer mixture and 0.07N for the 44 2 polymer.

## Homopolymerization of Hydronopyl Vinyl Ether

### Discussion

The work reported in this paper was undertaken to determine the optimum conditions for polymerizing hydronopyl vinyl ether (Ia) and 2 hydronopoxyethyl vinyl ether (Ib) and to investigate the properties of the resulting polymers.

Samples of hydronopyl vinyl ether (HVE) and 2 hydronopoxyethyl vinyl ether (HEVE) were provided by the Naval Stores Division of the Southern Utilization Research and Development Division of the Agricultural Research Service and were prepared by published methods. During the course of the investigation the preparation of additional HEVE became necessary. Bissel reported a yield of 38% (based on sodium) for the preparation of HEVE. He allowed sodium to react with a large excess of hydronopol and then treated the resulting suspension with 2 chloroethyl vinyl ether. We have found that HEVE can be prepared in 93% yield (based on hydronopol) by mixing hydronopol and sodium hydride in an excess of 2 chloroethyl vinyl ether.

The polymerization of HVE and HEVE by initiation with free radical cationic and coordination catalysts was investigated. In accord with the report that most vinyl ethers do not polymerize well by free radical initiation neither HVE nor HEVE polymerized appreciably by free radical initiation in bulk or emulsion systems.

Under the conditions studied the order of effectiveness of cationic initiation of the polymerization of HVE is stannic chloride > boron fluoride etherate > titanium tetrachloride > vanadium oxychloride. Vanadium trichloride does not catalyze the polymerization of HVE. For polymerization of HEVE the order of effectiveness is boron fluoride etherate >>> stannic chloride. Titanium tetrachloride vanadium oxychloride and vanadium trichloride do not catalyze the polymerization.

Polymerization of HEVE by initiation with boron fluoride etherate at 78°C. produces the highest conversion and molecular weight of any method investigated. The poly (HEVE) is a tough slightly tacky rubber with a specific rotation of  $\alpha_D^{20} = 20.1^\circ$ . It is soluble in petroleum ether benzene toluene carbon tetrachloride and tetrahydrofuran but insoluble in methanol acetone and 2 butanone.

Okamura and Higashimura report that poly (isobutyl vinyl ether) can be separated into crystalline and noncrystalline fractions because the crystalline fraction is less soluble in 2 butanone. The insolubility of poly (HEVE) in 2 butanone may indicate the presence of some crystalline portions.

At best coordination catalysts prepared by mixing triisobutylaluminum with titanium tetrachloride or vanadium oxychloride or vanadium trichloride produce poor yields of poly (HEVE). Poor results were also

obtained when attempts were made to polymerize HVE with catalysts prepared by mixing triisobutylaluminum with vanadium oxychloride or vanadium trichloride. Conversely catalyst prepared by mixing triisobutylaluminum and titanium tetrachloride in a mole ratio of 2.7 : 1 produces poly (HVE) in the highest conversion and with the highest molecular weight of any catalyst investigated by us.

The poly (HVE) prepared with triisobutylaluminum titanium tetrachloride catalyst is hard and brittle but becomes rubbery at temperatures above 45°C. It has a specific rotation of  $[\alpha]_D^{25} = -26.2$  and is soluble and insoluble in the same solvents as poly (HEVE). An x ray diffraction pattern indicates considerable crystallinity in this polymer.

## Experimental

### Materials

Hydronopol vinyl ether (HVE) b.p. 80-81°C./2 mm.  $n_D^{20} = 1.4788$ ;  $d_4^{20} = 2.3.8^0$  (0.3882 g. in 25 ml. of benzene); 2 hydronopoxyethyl vinyl ether (HEVE) b.p. 87-88°C./0.5 mm.  $n_D^{20} = 1.4760$   $d_4^{20} = 18.1^0$  (0.418 g. in 25 ml of benzene) and hydronopol b.p. 126-128°C./10 mm.  $n_D^{20} = 1.488$  were provided by the USDA Naval Stores Laboratory Olustee Florida. The vinyl ethers contained 0.2% of hydroquinone and were purified by the method described by Schildknecht Zosc and McKinley and passed through alumina (Merck chromatographic grade) just before they were used. 2-Chloroethyl vinyl ether was obtained from Monomer Polymer Laboratories and distilled before use. Hexane (Phillips 99%) was refluxed over sulfuric acid washed dried with potassium carbonate and distilled from over sodium. A dispersion of sodium hydride (50.6% by weight) in mineral oil was procured from Metal Hydrides Inc. The boron fluoride etherate was obtained from Eastman Organic Chemicals stannic chloride from Baker Chemical Company triisobutylaluminum from Texas Alkyls titanium tetrachloride (99.5%) from Matheson Coleman and Bell and vanadium trichloride and vanadium oxychloride from Anderson Chemical Company.

### Preparation of 2-Hydronopoxyethyl Vinyl Ether

Into a 5 liter four necked flask fitted with a stirrer reflux condenser that was protected with a calcium chloride drying tube addition funnel and nitrogen inlet tube were placed 321 g. (6.68 moles) of NaH in mineral oil (50.6% dispersion by weight) and 650 g. (6.1 moles) of 2-chloroethyl vinyl ether. While the mixture was stirred rapidly 460 g. (2.7 moles) of hydronopol was added over a period of 1 hr. Stirring was continued for 2 hr. at room temperature and for 48 hours at reflux temperature. The reaction mixture was allowed to cool to room temperature and 500 ml. of methanol followed by 1500 ml. of water was added slowly. Six 250 ml. portions of ether were used to extract the organic material. The portions were combined washed with 500 ml. of water and dried over anhydrous magnesium sulfate. The ether and methanol were removed by distillation and the residue was distilled under reduced pressure through a 100 × 1 cm. spinning band column. A total of 580 g. (93% yield based on hydronopol) of 2-hydronopoxy ethyl vinyl ether b.p. 109°C./0.75 mm.  $n_D^{20} = 1.4730$  was collected.

### Polymerization of HVE and HEVE

Attempted free radical initiation in bulk. A 6 × 1 in. polymerization tube was charged with 2.0 g. of HVE and 0.02 g. of azodiisobutyronitrile. To purge the reaction mixture of oxygen the pressure in the tube was reduced to 0.1 mm. Hg with a vacuum pump and then nitrogen was admitted to the tube. Then the pressure was reduced to 0.1 mm. Hg and the tube was sealed and heated in an oil bath at 65°C. At the end of 40 hr. the contents of the tube was a thin liquid that was completely soluble in methanol. Similar results were obtained when 2.0 g. of HEVE was substituted for HVE.

Attempted free radical initiation in emulsion. Into a 2 oz. screwtopped bottle were placed 0.2 g. of Triton X 301 (a 20% aqueous dispersion of Rohm and Haas sodium alkylaryl polyether sulfate) 1.0 g of HVE 5 ml. of distilled water and 0.5 ml. of 2.5% potassium persulfate solution. The bottle was flushed with nitrogen capped and tumbled in a water bath at 55°C. for 36 hr. After the emulsion had been broken with saturated



sodium chloride solution two layers formed. The organic layer was a free flowing liquid completely soluble in methanol. The same results were obtained when 2.0 g. of HEVE was substituted for HVE.

Initiation with boron fluoride etherate. A method similar to the one reported by Sorenson and Campbell<sup>6</sup> was used. A 250 ml. three necked flask was fitted with a stirrer nitrogen inlet tube and rubber serum bottle cap and charged with 10 g. of vinyl ether in 40 ml. of n hexane. While the solution was kept under a nitrogen atmosphere and stirred it was cooled in Dry Ice acetone to  $-78^{\circ}\text{C}$ . A hypodermic needle was inserted through the serum cap and four drops of boron fluoride etherate were added to the solution. After 30 min. another four drops were added and the mixture was stirred for the desired length of time. A 10 ml. portion of methanol was poured into the reaction mixture which was allowed to warm to room temperature. The resulting solution was poured into 800ml. of methanol that was being rapidly stirred. The polymer that precipitated was removed from the supernatant liquid. Further purification of the polymer was effected by dissolving it in benzene and repeating the precipitation step. Finally the polymer was dissolved in 200 ml. of benzene. The solution was filtered and the polymer isolated by freeze drying. Inherent viscosities were calculated from flow times of the benzene solution taken at  $30^{\circ}\text{C}$ . in a number 50 Cannon Fenske viscometer. Data for polymerization of HVE and HEVE are collected in Tables I and II.

Initiation with boron fluoride etherate (Flash polymerization). Into a 250 ml. four necked flask fitted a stirrer nitrogen inlet tube Dry Ice acetone cooled dropping funnel and Dry Ice acetone cooled condenser was placed 30 ml. of n hexane and eight drops of boron fluoride etherate. While a nitrogen atmosphere was maintained the solution was cooled to  $-78^{\circ}\text{C}$ . and a solution of 10 g. of vinyl ether in 20 ml. of n hexane that was also at  $-78^{\circ}\text{C}$ . was added rapidly. After the reaction mixture had been stirred for 30 min. 10 ml. of methanol was added and the resulting solution was allowed to warm to room temperature. The poly (vinyl ether) was purified and isolated by the same method described in the preceding section. Data for the polymerization of HVE and HEVE are collected in Tables I and II.

Initiation with stannic chloride titanium tetrachloride and vanadium oxychloride. Inside a dry box that was continually flushed with nitrogen a 4 oz. screw topped bottle was charged with a weighed amount of vinyl ether and 15 ml. of n hexane. The bottle was sealed with a screw cap that had a hole punched in it and had been lined with a neoprene gasket. When the bottle had been cooled to the desired temperature a measured volume of n hexane solution containing a known amount of metal chloride or oxychloride was injected through the gasket into the bottle. Cooling was continued until polymerization was terminated by addition of 10 ml. of methanol. The poly(vinyl ether) was purified by the same method described previously. Data concerning the polymerization of HVE and HEVE with cationic initiators are collected in Tables I and II.

Attempted initiation with vanadium trichloride. In general the procedure was the same as described in the preceding section although the order in which the reagents were added was different. The vanadium trichloride was weighed directly into the polymerization bottle and mixed with n hexane. Then after the bottle was sealed and cooled the vinyl ether was injected into the bottle. Tables I and II contain data for the attempted polymerization of HVE and HEVE with vanadium trichloride.

Initiation with Coordination Type catalysts. A 4 oz. screw topped bottle was charged in a dry box and under nitrogen with hexane (10 ml./g. monomer) a measured volume of a hexane solution of triisobutylaluminum (0.1. g. i Bu<sub>3</sub>Al/ml.) and a measured volume of hexane solution of titanium tetrachloride (0.084 g. TiCl<sub>4</sub>/ml.) or vanadium oxychloride (0.03 g. VOCl<sub>3</sub>/ml.) or a weighed amount of vanadium trichloride. The bottle was sealed with a neoprene gasketed cap and the catalyst mixture was allowed to age.

If the polymerization were to be performed at room temperature a measured volume of vinyl ether was injected into the polymerization bottle which was shaken occasionally while it stood for 24 hr. For polymerization at  $-78^{\circ}\text{C}$ . the catalyst mixture after aging was cooled in a Dry Ice acetone bath for 30 min.

and a measured volume of vinyl ether was injected slowly into the bottle. Cooling was maintained for 24 hr. during which time the reaction mixture was swirled occasionally. Then the contents of the bottle were poured into rapidly stirred methanol. The precipitated polymer was purified by the same method previously described. Data for the polymerization of HVE and HEVE are collected in Tables III V.

#### X Ray Analysis of Poly (HVE)

A thick film was obtained by repeated casting of thin layers of a benzene solution of the poly (HVE). After the portions had dried over water the film was removed from the water and allowed to remain at room temperature for two weeks to remove residual solvent.

A Phillips x ray diffraction instrument (operated by Dr. M.L. Corrin) was used. The major machine settings were 35 Kv. 20 ma. B1 200 SF 16 TC 4 and M 0.8.

The scan of diffracted x rays (Fig. 1) indicates two maxima ( $2q = 13.5$  and  $19.0$ ). Using  $l = 1.54$  and Bragg's Law  $q = 2d \sin \theta$  the spacing distances are 6.55 and 4.66 Å. The sharpness of the recorded scan and the short distance ( $d$ ) indicate considerable crystalline polymer structure.

#### Evaluation of Poly (HEVE)

Preparation of sample. A 150 g. sample for evaluation was prepared by polymerizing 10 30 g. lots of 2 hydronopoxyethyl vinyl ether in dry n hexane solution by boron fluoride initiation in a Dry Ice acetone cooling bath. The polymerization mixture was stirred for the first 4 hr. and then allowed to stand for 14 hr. Then methanol was added the mixture stirred well and then allowed to warm to room temperature. The polymer was dissolved in benzene the solution was filtered and then the polymer precipitated by adding this solution to excess methanol with stirring. Solution in benzene and reprecipitation in methanol was repeated two more times and then the polymer was dried under reduced pressure. On the average conversion was 96% and the inherent viscosity of the polymer varied from 1.5 to 2.1 with the average for the 150 g. sample being 1.8.

## Terpolymers of Ethylene and Propylene with d Limonene and b Pinene

### Introduction

Ethylene propylene terpolymers (EPT) have recently enjoyed a great deal of research activity due to their remarkable oxidation and ozone resistance and their desirable elastomeric properties. The practical utilization of these materials has been hindered somewhat by the economic considerations involved in producing them and also the cost of the nonconjugated diene as the third monomer. In order to circumvent the latter problem limonene and related monoterpenes obtained from citrus oils were chosen as suitable third monomers. Limonene and a and b pinenes have been previously homopolymerized by a number of catalysts. Obviously in the case of EPT rubbers the Ziegler Natta catalysts were the catalysts of choice. Modena Bates and Marvel found that when optically active d limonene was homopolymerized the resulting polymer was optically inactive. Their work indicated that limonene polymerized into a bicyclic structure (I) as well as the desired structure II. The bicyclic structure was favored over the monocyclic structure by a factor of 1.5 2. In the case of a B pinene the expected structure (III) was obtained.

### Results and Discussion

An experimental program was undertaken to evaluate a series of EPT elastomers from a variety of Ziegler Natta type catalysts. The terpene monomers were introduced into the reaction vessel containing catalyst and solvent by vapor entrainment in the ethylene propylene gas stream. This method was found superior to injecting the terpene into the reaction vessel by means of a hypodermic syringe.

The resulting polymers were purified in the usual manner and freeze dried from a benzene solution. The

purified product was analyzed for unsaturation by the method of Kolthoff, Lee, and Maris and for methyl group content by infrared analysis. The intrinsic viscosity (0.4% solution in benzene) and gel content were also determined prior to vulcanization. (Gel content was determined by cyclohexane extraction at 23°C. over a 24 hr. period.)

The polymers sent for vulcanization are reported in Table I. All experimental conditions were kept constant except the types of catalysts employed and the ratio of aluminum alkyl to coordination compound.

The results of vulcanization tests gave highly undercured vulcanizates. The poor results were attributed to high gel content and acidic residues in the polymers. Samples I 49, I 58, I 66, I 69 and I 71 were examined by the testing laboratory for gel content, ash content, and spectrographic analysis on the ash residues. The results of these tests are reported in Table II. All attempts to obtain satisfactory vulcanizates on samples I 62, I 72, I 73, I 74, and I 79 were also unsuccessful. Analogous results were obtained with the *b*-pinene terpolymers, samples II 23, II 24, II 25 and II 28. In all cases, du Pont's Nordel EPT rubber was run as a control. The recipes employed in the vulcanization studies are reported in Table III.

Typical polymerization experiments performed in this study are reported in the experimental section. Where an insufficient amount of polymer was obtained for vulcanization studies, it is so noted. The following catalyst systems were examined: triethylaluminum with vanadium oxytrichloride, titanium tetrachloride, and titanium tetraiodide; triisobutylaluminum with vanadium oxytrichloride, and titanium tetrachloride, and diisobutylaluminum chloride with vanadium oxytrichloride and vanadium triacetylacetonate.

It is difficult to explain why structures II and III (from limonene and *b*-pinene, respectively) which are those incorporated in the terpolymers do not lend themselves readily to vulcanization, even though adequate unsaturation is indicated by titration with perbenzoic acid.

## Experimental

### Materials

Samples of chemical dipentene and *d*-limonene were furnished by Newport Industries Division of Heyden Newport Chemical Corporation. The *b*-pinene was furnished by the Glidden Company. Unless otherwise noted, the monomers were used without further purification. Ethylene and propylene were Matheson C.P. grade and were used directly after passing through two towers of magnesium perchlorate. Heptane, Phillips 99 mole % was purified by extraction with sulfuric acid, dried over sodium sulfate, distilled from sodium hydride, and stored over sodium ribbons. Triethylaluminum, triisobutylaluminum, and diisobutylaluminum chloride (Texas Alkyls); vanadium oxytrichloride and vanadium triacetyl acetate (Alfa Inorganics, Inc.); titanium tetrachloride (Matheson, Coleman and Bell) were all used without further purification. Inherent viscosities were determined as a 0.4% benzene solution in a No. 50 Cannon Fenske viscometer at 31°C.

### Preparation of EPT Rubber

**General procedure.** A 1 liter reaction flask equipped with efficient stirrer, condenser, and inlet tube was flame dried under a vigorous stream of prepurified nitrogen. Apiezon grease N was used throughout the system. The solvent was introduced and saturated with an ethylene-propylene gas mixture. The source of third monomer was then connected into the system and the appropriate amounts of catalyst (dissolved in solvent) were introduced into the reaction flask by means of hypodermic syringes.

Immediately, the appropriate rates of flow of ethylene and propylene gases were begun and the reaction allowed to run, with vigorous stirring, for the noted period of time and at the stated temperature.

Upon completion of the reaction, 10% hydrochloric acid in methanol (200 ml.) containing a small amount of 2,6-di-*tert*-butyl-*p*-cresol (du Pont Antioxidant No. 29) was introduced under a nitrogen atmosphere to destroy the catalyst, and the resulting mixture was thoroughly mixed with excess methanol in a high speed Waring Blendor. The resulting polymer was collected on a filter and purified by repeated precipitation in methanol from benzene. After five precipitations, the resulting polymer was lyophilized from a benzene

solution (approximately 10% in polymer) containing about 0.1% du Pont Antioxidant No. 29. The various physical properties were determined on the dried polymer.

Reaction parameters. Reaction parameters are listed in Table IV.

## Analysis of Unsaturation

Preparation and standardization of sodium thiosulfate solution. In a dark bottle was placed 13.22 g. (0.09 equiv.) of reagent grade sodium thiosulfate and 900 ml. of freshly boiled distilled water. The resulting solution was allowed to stand at least 24 hr. prior to standardization. The sodium thiosulfate was standardized by titration of the iodine liberated from a solution containing an accurately weighed amount of potassium iodate (0.1015g. reagent grade previously dried at ~ 110°C. for 24 hr. and stored in a desiccator) 1 g. of potassium iodide and 50 ml. of 0.4M acetic acid solution to a starch endpoint.

# Base catalysed isomerisations of terpenes

The panorama of base catalysed isomerisations of terpenes is an important part of aroma chemistry. Major contributions in this area are presented here under sections on hydrocarbons alcohols aldehydes ketones acids esters and epoxides.

## Hydrocarbons

*p* Menthenes. Pines and Eschinazi introduced sodium organosodium catalysts for example sodium benzylsodium catalyst (prepared by treating an excess of sodium in toluene with *o*-chlorotoluene) for isomerising the title compounds. One of their main findings is that when (+) *p* menth 1 ene (1) *trans* *p* menth 2 ene (2) or *p* menth 3 ene (3) is refluxed at 168–175° for 20–22 hrs with the catalyst the isomerisate is an equilibrium mixture of (3) (63%) (1) (32%) and *p* menth 8 (9) ene (4) (5%). The rate of racemisation of (+) (1) is relatively faster than that of its rate of isomerisation and (+) *trans* (2) reorganised to (+) (1).

There is no formation of *p* cymene (5). The mechanism proposed involves intermediate carbanions.

More recently Ferro and Naves studied the isomerisation of (1) (3) (4) (*cis* and *trans*) and *p* menth 4(8) ene (6) with sodium organosodium catalyst (catalyst S prepared according to Pines and Eschinazi xylene replacing toluene) and analysed (by GC) the products formed at reflux temperatures. Under these experimental conditions there is no equilibrium of the *p* menthenes. Thus (3) is obtained from (+) (1) and *cis* (4) in 52.1 and 78.6% in 48 and 6 hrs respectively; *trans* (4) however is less reactive than its stereoisomer.

Further the behaviour of the *p* menthenes toward *n*-lithioethylenediamine (catalyst L) at 50° and potassium *tert* butoxide (*t*-BuOK) in dimethylsulfoxide (DMSO) (catalyst B) at 100° was evaluated. By a 4 hr treatment with catalyst L (+) (1) only a small amount of the racemate resulted and with catalyst B the racemisation rate increases of 16% in 2 hrs without isomerisation. Reaction of *cis* (4) and *trans* (4) with catalyst L furnishes (6) in 76.9 and 48.6% (in 4 hrs) and with catalyst B 77.0% (in 8 hrs) and 64.3% (beyond 12 hrs) respectively. Use of catalyst S is recommended for the preparation of (3) from (1) and of catalysts L and S to obtain (6) from (4) (*cis* and *trans*).

Kinetically controlled regrouping of *p* menthenes with calcium amide catalyst in the liquid phase gives equivalent mixtures of isomers with *exo* and *endocyclic* double bonds.

*o* Menthenes. Rearrangements similar to *p* menthenes are observed in the interaction of the sister *o* isomers with calcium amide catalyst.

*p* Menthadienes. Investigations on base catalysed rearrangements of this family of hydrocarbons were reported by Pines and Eschinazi. On refluxing (+) limonene (7) with sodium benzylsodium or sodium hydride catalyst rapid racemisation occurs with evolution of hydrogen providing *p* cymene (5). Interruption of the reaction when the optical rotation drops to ~20% gives a catalysate that includes 20% of (+) (7) 50% of (+) (7) and 20% of a mixture consisting of *p* mentha 2 4(8) and *p* mentha 3 8(9) diene (8) and (9) in the

approximate ratio 4:1 and 1% of (5). Without a promoter but in the presence of sodium at reflux temperature (+) (7) only undergoes racemisation without aromatisation. With the catalyst the intermediates (8) and (9) are reversibly isomerised; on the other hand ( ) a phellandrene (10) loses optical activity and gets dehydrogenated to (5) with no signs of conversion to (8) and (9). Invoking carbanions these changes have been explained.

Swiss investigators have also tracked in the same way as p-menthenes the transformations of p-menthadienes. When reacted for 1 hr with catalyst L at 50° (+) (7) gives an equilibrium mixture of (8) (9) g-terpinene (13) and a terpinene (14) in the proportion 14:50:30:3 with increasing conversion to (5) depending on the reaction time. On processing with catalyst B the substrate is practically effected in 5 hrs at 100° and equilibrium is realised. Under refluxing conditions catalyst S generates (8) and (9) in the proportion 11:1.

Terpinolene (11) isolimonene (p-mentha-2,8-diene) (12) and g-terpinene (13) with the exception made for the latter in the case of catalyst S respond in a similar manner. With catalyst L the equilibrium of (11) (12) and (13) is attained in 30 min and with catalyst B in 15 min. Complete isomerisation is achieved in 6 hrs with catalyst S leading to (8) and (9) in the approximate proportion 11:1. As against these with catalyst S (13) changes completely to p-cymene (5) in 15 hrs.

The study with the conjugated dienes (8) (9) (14) and p-mentha-2,4-diene (15) has led to interesting results. Equilibrium between (8) (9) and (14) is attained by the action of catalysts L and B. Divergent behaviour is displayed with catalyst S; the cyclic dienes (14) and (15) only give (5) (100 and 90% in 24 hrs); (8) equilibrates with (9) in the approximate ratio 11:1. A modified carbanion mechanism has been advanced to explain this reaction.

Using pines and Eschmazi catalyst isoterpinolene (8) has been synthesised from (+) limonene (7).

A kinetic study of the action of t-BuOK/DMSO system on (±) limonene indicates that the initial products of isomerisation is a 5:3:1 mixture of (8) (13) and (14) and that the pseudo first order rate constant of 55° is  $4.5 \times 10^6 \text{ sec}^{-1}$ . Under the experimental conditions (8) and (14) afford the same products in 30 min. Hence the slow step in the isomerisation is the migration of the double bond to the exo-position.

From the above synthetic mixture derived from (±) limonene by precise fractionation (8) is recoverable in 11% yield. Since the sister isomers can also be reverted to this mixture and recycled this is an elegant method for the large scale preparation of this unusual hydrocarbon.

Whereas (±) p-mentha-2,4-diene (8) is convertible to (±) menthol isomers it is the (±) 8 that is higher priced being a possible precursor in the synthesis of ( ) menthol. Technically a facile route to this hydrocarbon is from (±) isolimonene (12) by contact with t-BuOK/DMSO combination at room temperature. In the rearrangement of p-menthadienes catalysed by t-BuOK/DMSO at 55° only three constituents of the isomerisate have been identified. A fuller picture of the equilibrium composition conditions for achieving it with 76.2%) with lesser amounts of m-mentha-1,8-diene (19) m-mentha-6,3-diene (20) m-mentha-1,7,8-diene (21) and m-cymene (22); at 100° aromatisation is complete. By reaction with t-BuOK/DMSO system at  $82 \pm 2^\circ$  for 3 hrs sylvestrene (17) affords (18) (45.0%) (19) (3.0%) (20) (5.5%) and (21) (0.9%) 13. With the same catalyst the hydrocarbon (18) largely resists rearrangement but the sister isomer (20) smoothly conjugates to (18).

(+) Car-3-ene. Ohloff and coworkers accomplished the base catalysed conversion of (+) car-3-ene (23) to (+) car-2-ene (24). The reaction of (23) with N-lithioethylenediamine for 1 hr at 100° results in an equilibrium mixture of the 3- and 2- isomers in the ratio 3:2 accompanied by cymenes equivalent to 2%. From the catalysate enriched (+) car-2-ene (80%) is obtained by fractionation. Others have followed this trail.

Theoretical reasons have been advanced to account for the greater stability of the 3- over the 2- isomer.

From the equilibrium constant 1.50 the free energy difference is extracted as 240 cal/mol at 25°.

A disadvantage of the above technique is the concurrent release of the cymenes. However under

regulated conditions use of *t* BuOK DMSO catalyst eliminates this defect and the reaction generates a clean equilibrium mixture consisting of 40% (+) car 2 ene and 60% (+) car 3 ene.

While today more advanced and different syntheses for ( ) menthol are used patents granted to Booth combined with that to Webb are classics of the technical exploitation of (+) car 3 ene for a ( ) menthol synthesis. The outstanding step in the chain of reactions is the rearrangement of the terpene to the 2 isomer. In general basic catalysts recommended consist of strong bases applied under conditions when carbanions of a hydrocarbon can be formed and these include simple or complex alkali metal alkyls also strong bases such as alkali metal alkoxides and alkali metal amides which are advantageously used in media that encourage the maturing of their basicity. Examples of the catalysts are activated sodium of the Pines type sodium and/or potassium derivative of  $\gamma$  picoline *t* BuOK in DMSO N lithioethylenediamine and Na or K metal on Al<sub>2</sub>O<sub>3</sub>.

Here we may digress a little. Above 180° in the presence of the basic catalyst (+) car 2 ene (24) decyclises to (+) isolimonene (12) and the latter conjugates to (+) p mentha 2 4(8) diene (8) the pivotal hydrocarbon in a ( ) menthol synthesis. The next stage is the migration of the exo double bond of (8) to give an equilibrium mixture of a terpinene (14) (50%)  $\gamma$  terpinene (13) (20%) isoterpinolene (8) (25%) and p mentha 3 8 diene (9) (5%). Finally the p menthadienes get dehydrogenated to p cymene (5). For these reasons the correct temperature and time must be chosen to terminate the reaction at the isoterpinolene stage. Catalysts which rearrange (+) car 3 ene to (+) car 2 ene will also perform this function.

Ferro found that Ohloff's reaction when conducted at 110° for 5 hrs gives an equilibrium mixture of (+) car 3 ene (23) and (+) car 2 ene (24) (55:45) with cymenes (12%); an 18 hr run augments aromatisation (20.4%). Also the findings of Acharya and Brown using *t* BuOK DMSO have been fully substantiated.

There are valuable data on the isomerisation of (+) car 3 ene (23) over basic catalysts such as MgO Cao SrO<sub>2</sub> Y<sub>2</sub>O<sub>3</sub>. La<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> by the pulse method. The reaction has been tracked in detail over MgO (I) and MgO (II) and CaO (II) catalysts. Rearrangement of (23) to (24) is the dominant change by synchronised two way decyclisation leads to a terpinene (14) and m mentha 1 5 diene (25) and further dehydrogenation to p cymene (5) and m cymene (22). From a tracer study with deuterium it is inferred that the double bond shift is most likely to proceed via II allylic anion (26).

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