THERMAL REACTIONS OF TERPENE HYDROCARBONS[1]

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I. INTRODUCTION

The terpenes are among the more important substances present in essential oils, the complex mixture of cyclic and acyclic compounds obtained from many plants and trees.

A detailed discussion of the composition of a great number of essential oils is outside the scope of this paper, but it is of interest to note some recent studies to illustrate their complexity. Rutovski and Vinogradova (125) have found that the essential oil of *Nepeta Cataria* contains tiglic acid, α- and β-citral, limonene, dipentene, a levorotatory sesquiterpene, geraniol, citronellol, nerol, and acetic, butyric, and valeric acids. Ikeda and Fujita (82a) report that the essential oil of *Cunninghamia kinoshi Hayata* contains pinene, sabinene, limonene, α-terpenol, *l*-borneol, and *d*-cedrol.

TABLE 1

Turpentine and rosin produced in the United States

YEAR	TURPENTINE	ROSIN
	gallons	*barrels*
1929	35,600,000	2,453,000
1930	35,837,000	2,455,000
1931	27,100,000	1,900,000
1932	22,000,000	1,600,000

Crude mineral oils from which terpenes have been isolated include those from Galicia, Rumania, Grozny, Baku, Canada, Beaumont, Texas, and Java. Engler and Hofer (45) state that Java oil is particularly rich in terpenic compounds. A South Africa crude oil consisted almost entirely of acyclic compounds with limonene and sylvestrene predominating. Upon evaporation the gasolines yielded a product much like gum arabic in appearance.

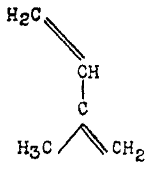
However, the only major industry engaged primarily in the production of terpenes is that of turpentine and rosin (115), which started many centuries before Christ when the natives of Asia manufactured pitches and oils from the gum of trees which grew along the shores of the Mediterranean. In the United States the production of crude resin from pines and the making of pitch and tar began in the early part of the seventeenth century. At that time, the gum was gathered from the pines of Virginia and North Carolina. Today, about two-thirds of the world's turpentine and rosin are produced in the southern states. Table 1 (177) shows the amount of these materials produced in the United States.

The importance of the industry is apparent upon consideration of the everyday uses into which turpentine enters. As a thinner of oil varnishes and gloss paints, for example, gum spirits of turpentine has no superior. It may be an ingredient of printing inks and is used for color-printing processes in lithography; in the manufacture of cotton and woolen print goods; in the manufacture of patent leathers; a thinner for waxes in shoe and leather polishes, and floor, stove, and furniture polishes; a solvent for waterproofing compositions, and for rubber and similar substances; an ingredient in belting greases; an insecticide; in laundry glosses, in washing preparations, in sealing wax and in pharmaceuticals, including disinfectants, liniments, soaps and ointments; and a raw material for producing synthetic camphor, and, indirectly, celluloid and explosives.

II. GENERALIZATIONS

The substances ordinarily considered in a discussion of the terpenes are the hemiterpene, isoprene (C_5H_8), the true terpenes, having the general formula $C_{10}H_{16}$, the sesquiterpenes of formula $C^{15}H_{24}$, the higher or polyterpenes, $(C_5H_8)_n$, and their various derivatives.

Simonsen (155) points out the relationship existing between isoprene and the higher terpene hydrocarbons, simple and complex. The latter may be considered as being made up of two or more isoprene molecules. Thus two molecules of isoprene, C_5H_8 (I) are contained in the molecule of the true terpenes, e.g., myrcene (II) and limonene (III), while the sesquiterpenes represented by formula IV contain three, and the higher terpenes contain more such nuclei.



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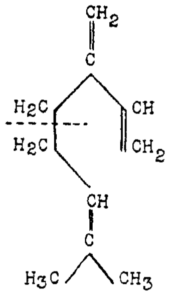

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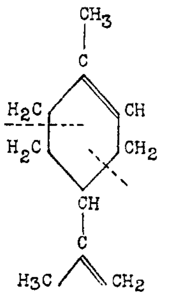

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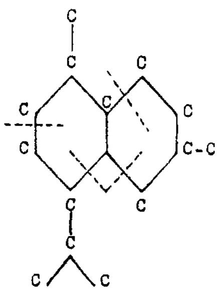


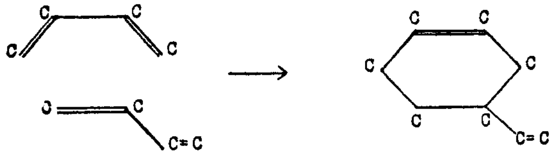
IV

Isoprene, a hemiterpene, is diolefinic and its thermal reactions are those to be expected of such a compound. At lower temperatures the principal change that it undergoes is one of polymerization to higher terpenic compounds. As the temperature is increased, decomposition takes place with the formation of ethylene, propylene, butadiene, etc., and at still higher temperatures aromatic compounds appear. Staudinger, Endle, and Herold (158) consider that the formation of aromatic substances is due to the polymerization of isoprene to hydroaromatic derivatives which, by further polymerization or condensation with isoprene, give products of high molecular weight. These mixtures of terpenes and polyterpenes then decompose into the aromatic compounds.

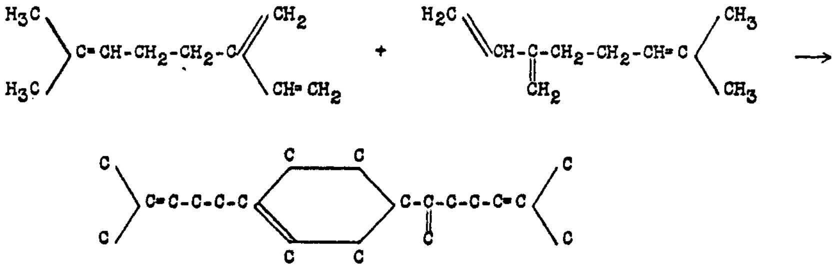
The polymerization of isoprene results in a complex mixture of terpenic substances ranging from simple terpenes to rubber. Some of the many simpler intermediates, which have been isolated and identified, are the same as naturally occurring terpenes, but others are not.

Whitby and Katz (190) have suggested that the most plausible mechanism for the polymerization of unsaturated compounds is "best represented as proceeding stepwise by the addition regularly of successive molecules of monomer to the double bond present at each stage of the polymerization immediately preceding." This, of course, applies to any olefinic compound.

The dimerization of isoprene, according to Wagner-Jauregg (182), proceeds as shown below:



This represents 1,4-addition and is of "general significance for the polymerization of hydrocarbons with conjugated double bonds. As a further example, the polymerization of myrcene to α-camphorene may be cited" (152).



Gapon (52), discussing the mechanism of polymerization of diolefinic hydrocarbons, draws the following conclusions, based upon the assumption that activation, in the presence of polymerization, consists essentially in the breaking of a double bond and the transformation of quadrivalent carbon atoms into tervalent carbon atoms: (1) The theoretical value of the energy of activation is the energy required to break one double bond, in the absence of chain reactions. (2) Activated molecules react with normal ones to give products of polymerization, although they can not react among themselves.

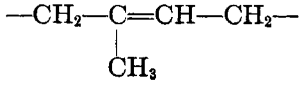
He also claims to have differentiated three second-order reactions in the polymerization of isoprene at 100–105°C. that occur simultaneously; two dimers, dipentene, and 1,3-dimethyl-1-vinyl-3-cyclohexane are formed together with a complex polymer. These three processes are seemingly so clearly differentiated that he further gives as the activation energies for the three reactions, 22,400, 21,500, and 18,800 calories, respectively.

The contention of Kassel (87) that the formation of polyatomic molecules by a second-order association process is possible at a relatively large fraction of all collisions has received support from the experiments of Vaughan (178) on measurements of the hydrogenation of ethylene and the dimerizations of ethylene and of 1,3-butadiene. Evidence was also obtained indicating that the orientation of the properly activated particles at the moment of impact is highly important for the achievement of reaction, and that the more complex the molecules the more precise must be their mutual locations.

Later experiments by Vaughan (179) on the dimerization of isoprene have served to bear out the above conclusions. In addition, working in the temperature range of 286.5°C. to 371°C. at pressures varying from 212 to 739 mm. the principal process, dimerization, was interpreted as a bimolecular association reaction.

The mechanism of polymerization of olefins which seems to be regarded the more favorably is that which involves the dissociation of hydrogen and comparatively simple addition to the double bond of another molecule. For example, Carothers (35) discusses the polymerization of ethylene as follows: "In effect at least this reaction involves in the first step the addition of ethylene, as H— + —CH=CH$_2$, to the double bond of another molecule of ethylene, and then a similar addition to butylene."

Although the structural unit in the polymeric chain from isoprene appears to be



$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-$$

and Midgley and Henne (104) obtained three dimers of isoprene, each of which contains two such units, Carothers has pointed out that Midgley's results "by no means prove that the actual mechanism of the reaction consists in the direct union of radicals corresponding in formula with the structural unit. The 1,4-addition of H— + —$CH{=}C(CH_3)CH{=}CH_2$ to isoprene, for example, would lead to the same result."

The reactions of myrcene, an acyclic terpene, should be quite similar to those of isoprene and, in so far as they are known, this seems to be true. However, the present status of our knowledge of the thermal behavior of myrcene leaves much to be desired.

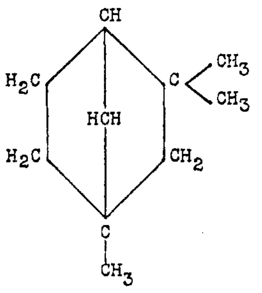
A glance at the structure of any of the cyclic monoterpenes would indicate that their thermal reactions are very complex, for these compounds are cycloölefins with unsaturated side chains. It would be interesting to compare the results of the studies of monocyclic monoterpenes with those of other substituted cyclic olefins, but a survey of the literature has shown that no study of the non-catalytic decomposition of cyclohexene or cyclohexadiene at a temperature above 300°C. has been published. Only one case has been reported in which the ring was broken, and this was a catalytic decomposition to hydrogen, paraffinic gases, and aromatics. One study is insufficient to use as a basis of comparison, but it is interesting to note how frequently isoprene, which must result from ring breaking, has been reported as a product of decomposition of monocyclic terpenes. Little is known of the other decomposition products.

Like other cyclohexene derivatives, the monocyclic terpenes undergo simultaneous hydrogenation and dehydrogenation in the presence of catalysts, yielding cyclohexyl and aromatic compounds.

In the case of dicyclic and tricyclic monoterpenes which may contain tri-, tetra-, or penta-methylene rings as well as a cyclohexene ring, the primary reactions would be expected to be dependent upon the relative stability of the two rings. In the case of the pinenes, the thermal decomposition products are quite similar to those of monocyclic terpenes. For example, Mahood (99) has pointed out that pinene yields considerable quantities of terpenic substances when "cracked" at temperatures below 400°C., while aromatic hydrocarbons and olefins, including isoprene, are the chief constituents of all fractions obtained at higher temperatures. This seems to indicate that the cyclobutane ring breaks before other reactions set in.

On the other hand, thujene, which contains a trimethylene ring, appears to be decomposed in the presence of catalysts in such a way that both the tri- and hexa-methylene rings are broken by the severing of one linkage, the product being a pentamethylene derivative.

Fenchane (I), isobornylane (II) and α-fenchene (III), all of which contain a pentamethylene ring, remain unchanged under conditions which result in the decomposition of thujene and pinene.



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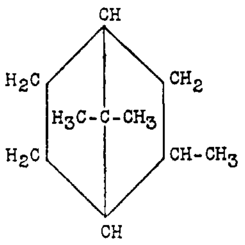

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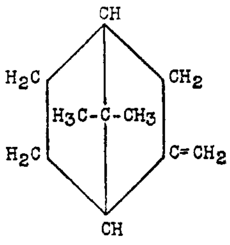


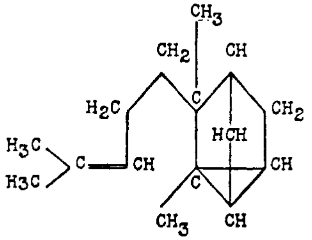
III

As a result of their work on the catalysis of bi- and tri-cyclic systems, Zelinsky and Lewina (199) make the following generalizations: "On catalytic hydrogenation, the bi- and tri-cyclic systems of terpene hydrocarbons are easily broken and hydrogen is absorbed. On catalytic dehydrogenation, however, the breaking of these rings leads to the formation of unsaturated hydrocarbons, and in case these form an unsaturated hydroaromatic compound, complete dehydrogenation occurs; if the unsaturated hydrocarbon is a cyclopentane derivative, no further dehydrogenation takes place."

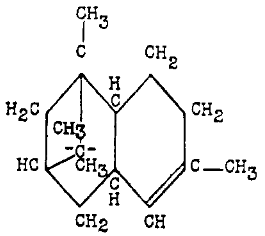
Of course, the sesquiterpenes and diterpenes present an even more complex picture than the monoterpenes, for they may have several rings, or one ring with a long unsaturated side chain, or they may be acyclic. However, no work has been found concerning the thermal reactions of any acyclic sesquiterpenes and the work that has been done on the other types of compounds is quite meager. The studies have resulted chiefly in rearrangements, hydrogenation, and dehydrogenation rather than in more deep-seated changes.

Ruzicka and his coworkers have dehydrogenated sesquiterpenes by refluxing them with sulfur. If the compound contains a hydrobenzene ring, the product is a benzene derivative having the same side chains as the original. The same relationship holds for hydronaphthalene derivatives provided there are no substituents on those carbon atoms which are common to both rings. In the latter case such substituents are removed as mercaptans.

It is worthy of note that of all the sesquiterpenes which yield naphthalene compounds on dehydrogenation with sulfur, not one is thought to contain a tri-, tetra- or penta-methylene ring. On the other hand caryophyllene, cedrene, santalene, and clovene, all of which contain one or more rings smaller than the hexamethylene ring, have been studied, but none has been found to yield naphthalene hydrocarbons.



Santalene (130b)

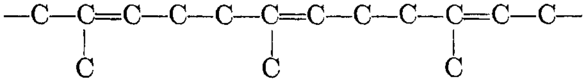


Clovene (74)

In fact, cedrene remains unchanged and the other three yield dehydrogenation products which were not identified further than to prove that they were not naphthalene derivatives. Furthermore, Nakatsuchi (110) has found that pinene, which contains a tetramethylene ring, yields a polymerized product and $C_{10}H_{16}S$, but no *p*-cymene.

At first glance it may seem that rubber is not a terpenic substance, for its most salient characteristics are not typical, but fundamentally it is a polyterpene, for its empirical formula is $(C_5H_8)_n$. Furthermore, the fact that it, along with terpenes and sesquiterpenes, is a product of polymerization of isoprene, and that it decomposes yielding terpenes and isoprene, definitely links it with terpenic substances.

There is a great amount of literature on the subject of the structure of rubber and no structure can be said to have been proven. The preponderance of evidence (163), however, is in favor of the long chain molecule



$$-\mathrm{C}-\underset{\mathrm{C}}{\underset{|}{\mathrm{C}}}=\mathrm{C}-\mathrm{C}-\mathrm{C}-\underset{\mathrm{C}}{\underset{|}{\mathrm{C}}}=\mathrm{C}-\mathrm{C}-\mathrm{C}-\underset{\mathrm{C}}{\underset{|}{\mathrm{C}}}=\mathrm{C}-\mathrm{C}-$$

which Pickles (117) first suggested. A compound of this structure should be expected to behave as other polyolefinic compounds, and that has been found to be true in the case of rubber. The linkage which seems to be most easily broken is that farthest removed from the double bonds, so that of the acyclic compounds formed on pyrolysis, those containing five carbon atoms to the molecule predominate. However, compounds containing six or seven atoms of carbon to the molecule have also been identified. All of these acyclic compounds are unsaturated and may condense to form cyclic substances which, in turn, may remain as terpenic hydrocarbons or undergo further change to completely saturated or to aromatic compounds. All of these possibilities have been realized.

III. HEMITERPENE

A. ISOPRENE

Only a little work has been done on the thermal decomposition of isoprene. On the other hand, polymerization of isoprene, to which brief reference was made in a paper on olefins by Egloff, Schaad, and Lowry (44), has been the subject of quite extensive research. Indeed, since 1860 when Williams (192) established the fact that isoprene is not only a product of pyrolytic decomposition of rubber, but has the same empirical composition as rubber, a great amount of interest has been shown in the polymerization of isoprene to produce a commercially valuable synthetic rubber.

Catalytic decomposition

Staudinger, Endle, and Herold (158) studied the pyrolysis of isoprene at temperatures from 400°C. to over 800°C. In a typical run, isoprene vapors (349 g.) were passed through a quartz tube filled with coke and heated to about 750°C. The resulting gas contained 13.6 per cent unsaturated hydrocarbons, chiefly ethylene, 58–66.3 per cent methane, and 23.5–19.9 per cent hydrogen. From the tar were obtained 10 g. of benzene, 53 g. of toluene (boiling at 80–130°C.), 21 g. of naphthalene, 19 g. of α-methylnaphthalene, 15 g. of anthracene and phenanthrene, 18 g. of chrysene, 5 g. of a fraction boiling at 400–420°C., and 38 g. of tar and carbon.

At 400–500°C., isoprene was partially polymerized to higher unsaturated hydrocarbons, terpenic in nature, similar to those obtained as by-products in its polymerization to rubber. Some amylene and a small amount of gas, as well as unchanged isoprene, were recovered.

At 600–700°C. the transformation was almost complete. The mixture of unsaturated hydrocarbons formed, however, was no longer terpene-like, but rather resembled a crude petroleum. Gaseous products were also obtained in considerable amount, ethylene, propylene, and butadiene being identified.

Above 700°C., aromatic compounds begin to appear, and above 800°C. they are formed exclusively.

At 700°C., under 20 to 25 mm. pressure, almost half of the isoprene was unchanged. Highly unsaturated compounds were formed, but no tar. It was also found that under 15 mm. pressure isoprene could be distilled several times over a platinum spiral heated to bright redness without marked change.

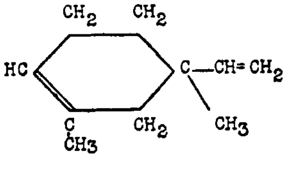
Polymerization under elevated temperatures

By heating isoprene in a sealed tube in an atmosphere of carbon dioxide for ten hours at 280–290°C., Bouchardat (22) obtained partial conversion to a product boiling at 167–171°C., which he called diisoprene (now called dipentene). In 1884 Tilden (171) confirmed this by heating isoprene to 250–280°C. in sealed tubes for twelve hours and obtained a yield of about 50 per cent dipentene.

Wallach (184) observed, as had Bouchardat and Tilden, that isoprene can be polymerized by the action of heat. He heated isoprene for several hours at 250–270°C., and obtained a product boiling at 180°C., which undoubtedly contained dipentene, for it yielded the characteristic dibromide.

Similarly, Harries (63) heated pure isoprene in a sealed tube at 300°C. A small portion polymerized to dipentene, but the chief product, besides the customary high-boiling oil, was an isomeric hydrocarbon, $C_{10}H_{16}$, which Wagner-Jauregg (182) later showed to be diprene.

Lebedev (94) reported that isoprene polymerized even below 0°C. The most suitable temperature, however, was 100–150°C., for at higher temperatures the reactions became complex. He heated the hydrocarbon in sealed tubes in this temperature range and distilled the product in a stream of hydrogen. The unaltered isoprene was taken off under ordinary pressure and a dimeride under 8 to 15 mm. pressure, while the polymeride remained behind. From experiments of different duration at 150°C., Lebedev (94) obtained the following amounts of polymer: 53 per cent in five hours, 79 per cent in fifteen hours, 90 per cent in thirty-eight hours. The dimeride fraction (95) consisted of two compounds, one of which was dipentene, b.p. 174–175°C., d_4^{20} 0.8454, and the other 1,3-dimethyl-3-vinyl-6-cyclohexene, b.p. 160–161°C., d_0^{20} 0.8331.



The higher the temperature, according to Lebedev (94), the greater is the ratio of dimeric to polymeric products, while at constant temperature this ratio remains the same regardless of the extent of transformation. The ratio is also affected by catalysts.

Gapon (52) studied the rate of polymerization of isoprene over the same temperature range in the absence of light. From experiments at 100°, 110°, 130°, and 150°C. he obtained, in all cases, four "primary" products:

dipentene, 1,3-dimethyl-3-vinyl-6-cyclohexene, and two polymers. His ideas of the mechanism of these changes have already been stated.

Ostromisslensky and Koshelev (114) reported that the polymerization of isoprene at a "higher temperature" gives normal isoprene caoutchouc. When, however, isoprene is heated to only 80 or 90°C. in a sealed vessel for three to five days, and its unchanged part removed by vaporization at 100°C., the residue after being steam-distilled yields a hydrocarbon, $C_{10}H_{16}$, which, on account of its resemblance to natural myrcene, Ostromisslensky called β-myrcene. It is a colorless mobile liquid, soluble in most organic solvents, boiling at 63.5°C. under 20 mm. pressure and, like natural caoutchouc, when treated with concentrated sulfur dioxide, gives a precipitate "with double unions." Recently Wagner-Jauregg (182) has shown that β-myrcene is identical with diprene.

TABLE 2

Polymerization of isoprene

TEMPERATURE	TIME	OIL	RUBBER	MOLECULAR WEIGHT	RELATIVE VISCOSITY*
degrees C.		*per cent*	*per cent*		
85	97.5 hours	9.07	17.05	4589	4.62
	101 hours	7.9	16.25		
	900 hours		35.3	5715	8.20
145	5.25 hours	38.2	10.03	3291	3.14
	12.5 hours	54.7	15.56	3936	4.69
10	1 year	0.005	0.01		6.13†
Room temperature	4½ years	1.0	16.6	2312	13.4

* At 30°C. 1 cc. of solution containing approximately 0.68 g. per 20 cc. of benzene.

† At 30°C. 1 cc. of solution containing approximately 0.492 g. per 20 cc. of benzene.

Whitby and Crozier (191), on the other hand, were unable to obtain β-myrcene from isoprene, even though Ostromisslensky's procedure was carefully followed. The only oily products isolated were cyclic dimers such as have been described by previous workers. They studied the effects of time and temperature on the polymerization of carefully purified isoprene, prepared from dipentene by use of the "isoprene lamp."

Their results were summarized in table 2.

Neither was there encountered any of the 1,3-dimethyl-3-vinyl-6-cyclohexane reported by Lebedev (94, 95). Except for the dimeric products mentioned by Harries (61), all of the dimers obtained from isoprene were clearly cyclic compounds. The sample which stood for four and one-half years was found to contain dipentene, and it was believed by the experimenters that the material obtained in all of their studies was "preponderantly dipentene," though only oily bromine addition products could be obtained.

Polymerization by action of light

Wallach (186) observed that isoprene, exposed to light in a sealed tube for a long time, polymerized to a rubber-like mass. Some authors have claimed, however, that his isoprene, which was obtained from the dry distillation of rubber, may have contained an impurity, such as a small particle of rubber from the original material. This might have caused the re-formation of rubber, since evidence from other investigators (95) indicates that rubber itself catalyzes the polymerization of isoprene to caoutchouc. On the other hand, Harries (62) has shown that pure isoprene can be polymerized, by means of ultra-violet light, to a solid white substance which contains a small proportion of rubber-like material.

Spontaneous polymerization

The spontaneous polymerization of isoprene to rubber was observed by Tilden (170) in 1892. His isoprene, prepared by the thermal decomposition of turpentine, spontaneously became a dense syrup after standing for some time in bottles. There were several large masses of solid floating in this syrup, which proved to be "india rubber." Tilden accounted for the change by the hypothesis that "a small quantity of acetic or formic acid had been produced by the oxidizing action of the air and that the presence of these compounds had been the means of transforming the rest."

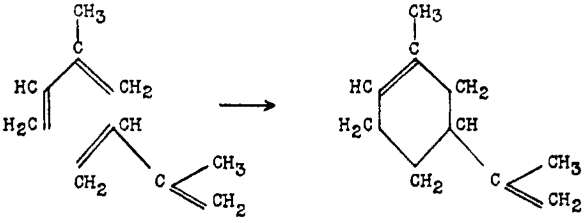
Two years after Tilden's paper was published, Weber (188) reported that 300 g. of isoprene, obtained from the dry distillation of rubber, were found after six months standing to be converted into a very viscous, treacly mass from which, by treatment with methyl alcohol, a solid, almost white, spongy substance could be separated. This substance, when dry, was identical with "india rubber." The by-products of the polymerization consisted of dipentene and polyterpenes.

More recently Pickles (117) confirmed the observations of both Tilden and Weber. He found that isoprene acquired the consistency of a thick syrup after standing in closed bottles for two and a half years, mostly in the dark. However, he stated that the rubber, which was precipitated by alcohol, was not equal to para rubber in tenacity, but resembled the product of young rubber trees. "It undoubtedly contained rubber, as it yielded the characteristic nitroside and tetrabromide." These results and those of Weber would seem to indicate that Tilden's hypothesis involving the formation of acetic and formic acid was unnecessary and possibly incorrect.

Harries (61) has gone even farther than Pickles, stating that comparative vulcanizing experiments indicated that the best specimens of isoprene caoutchouc are probably produced when polymerization takes place at the lowest possible temperature and without the addition of any foreign substance. "There were indications that isoprene caoutchouc contains an isomeric caoutchouc."

Aschan (5) has found that isoprene, kept in a sealed tube in an atmosphere of carbon dioxide in the dark for ten years, was only partially polymerized, 76 per cent of the unchanged isoprene remaining. From the dimeric compounds he obtained a small amount of diprene, b.p. 171–171.5°C., to which he assigned a formula based on a *p*-cymene structure. Later (6), he found that diprene and carvestrene yield identical dihydrochloride and dihydrobromide derivatives, but the hydrocarbons are not identical. Diprene, therefore, must have a *m*-cymene ring, but the double bonds are not located as in carvestrene.

Recently Wagner-Jauregg (182) has found (1) that the hydrocarbon ($C_{10}H_{16}$) obtained, together with caoutchouc and dipentene, by heating isoprene alone or with acetic acid, and regarded by Harries (61) as 2,6-dimethyl-1,5,7-octatriene, contains only two double linkages and when hydrogenated in the presence of platinum oxide, produces *m*-menthane; (2) that a *m*-menthadiene, obtained by autopolymerization of isoprene and described by Aschan (6) as diprene, is identical with Harries' hydrocarbon; and (3) that β-myrcene, obtained by Ostromisslensky (114) by heating isoprene at 80–90°C. for several days, is identical with diprene and is the sole dimeride of isoprene formed under these conditions. Diprene is not considered to be a pure compound, but a mixture of similar compounds which boil within a temperature interval of 4°C. The position of the double bonds in diprene has not yet been proven, but the reaction may be represented as follows:



Polymerization under high pressure

Isoprene is partially polymerized when subjected to a pressure of 9000 atmospheres for twenty-four hours. Bridgeman and Conant (27) have

TABLE 3

Polymerization of isoprene under high pressures

PRESSURE	TIME	EXTENT OF POLYMERIZATION
atmospheres	*hours*	*per cent*
12,000	50	Practically complete
9,000	24	40–45
6,000	48	10
3,000	68	Only a trace

TABLE 4

Polymerization of isoprene after standing

NO.	DAYS STANDING BEFORE POLYMERIZATION	PER CENT POLYMERIZATION
1	1	34
2	3	64
3	7	86
4	11	Apparently same as No. 3
5	9	88
6	9 (sample redistilled)	25

TABLE 5

Polymerization of two lots of isoprene after standing for eight days

Pressure, 12,000 atmospheres; temperature, 23–25°C.

TIME	PER CENT POLYMERIZED	REACTION CONSTANT $K \times 10^2$
	Lot No. 1	
hours		
5	27	6.3
5	33	8.0
5	35	8.6
16	83	11.2
20	87	10.2
Average		8.9
	Lot No. 2	
5	11	2.3
20	61	4.7
23	66	4.7
23	65	4.6
Average		4.1

found that the product formed on such treatment is a soft jelly-like solid which, on standing for twenty-four hours in the open, lost 60 per cent of its weight by evaporation and shrank to a denser rubber-like solid which was yellow but transparent.

On the assumption that the loss in weight by evaporation on standing represents the unpolymerized isoprene, the results of Bridgeman and Conant's work at various pressures may be expressed as in table 3.

Since the publication of the above preliminary paper, Conant and Tongberg (34) have attempted to measure the effect of pressure and temperature on the rate of polymerization of isoprene, but were severely handicapped by the difficulty of preparing uniform samples of isoprene. The use of freshly distilled material did not solve the difficulty, as varying amounts of peroxides were formed in irregular fashion and these were found to play an important part in the acceleration of the polymerization. The most consistent results were obtained with samples of isoprene which had been allowed to stand at least seven days at 2°C. in nitrogen or air, while standing for a longer time only slightly altered the tendency to polymerize. The data in table 4 serve to illustrate the above variations for tests of twenty hours duration.

The most significant data were obtained with two different lots of isoprene which had stood for at least eight days; they are shown in table 5.

The reaction velocity constants were calculated according to the first-order equation in order to have a means of comparing the extent of the reaction at different times, although it is presumably of high order.

The product obtained from these experiments was a transparent, colorless rubbery solid.[2]

In a study of the effect of pressure on the rate of polymerization, Tammann and Pape (168) state that the polymerization of isoprene follows the unimolecular law and suggest that the molecules undergo some change before union, the rate of this reaction determining the speed of the process as a whole. The velocity increases with increase in pressure much more rapidly than in other reactions occurring in liquids.

Polymerization catalyzed by various reagents

(1) Peroxides. Many patents for the use of peroxides as catalysts in the polymerization of isoprene have been issued, but the effect of such catalysts seems not to have been studied until recently.

Conant and Tongberg (34) stated that peroxide catalysts play a very important part in the acceleration of polymerization, but are not essential to the process. They found that the catalyst which gave the most con-

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[2] Conant and Tongberg give a detailed discussion of the nature of the products obtained under different conditions.

sistent results was a sample of pinene which had been shaken with oxygen for four or five hours and which was used from time to time without further treatment. The results are summarized in table 6, the first-order reaction constants being given as a rough measure of the rate of polymerization.

TABLE 6

Polymerization of isoprene catalyzed by pinene

Pressure, 12,000 atmospheres; temperature, 23–25°C.

AMOUNT OF CATALYST	TIME	PER CENT POLYMERIZED	REACTION CONSTANT $K \times 10^2$
per cent	*hours*		
0.1	4.5	83	39.3
0.1	4.5	63	22.1
Average			30.7
0.04	4.5	28	7.3
0.04	4.5	41	11.7
0.04	4.5	63	22.1
Average			13.7
0.01	4.5	38	10.6
0.01	4.5	12	2.8
0.01	16.0	54	4.8
Average			6.1
0.002	15.75	55	5.1
0.002	15.75	55	5.1
Average			5.1
0.001	4.5	7	1.6
0.001	4.5	12	2.8
0.001	15.0	24	1.8
Average			2.1

Many experiments were carried out in an attempt to obtain sufficient information for the determination of the pressure and temperature coefficients of the rate of polymerization. "A comparison of these coefficients shows that, at higher pressures and room temperature, a change of 15°C. is about equivalent to 3000 atmospheres pressure, with regard to the effect on the reaction rate. Over a wider range it is estimated that raising the pressure from 2000 atmospheres to 12,000 atmospheres increases the rate about one hundred-fold; this increase could also be obtained by raising the temperature from about 20 to 60°C. If the temperature and pressure coefficients of the polymerization of isoprene are typical, it is clear that the mere acceleration of the reaction is more readily accomplished by raising the temperature than by increasing the pressure. However, there must be many cases (and the polymerization of isoprene is probably one) where the nature of the products differs according to whether they are formed at high pressures or elevated temperatures."

More recently Conant and Peterson (33) have come to the conclusion that peroxide catalysis is essential to the pressure polymerization of isoprene, and present the following evidence. "Peroxides and ozonides have a strong positive catalytic action. Freshly distilled isoprene polymerizes at a rate only one-fifth to one-tenth of that of isoprene which has stood in the air for some days. This increased tendency to polymerize on standing is almost certainly due to the formation of peroxides from the dissolved oxygen. If peroxides (or dissolved oxygen which will form a peroxide) are essential to the polymerization, we must assume that when the isoprene was distilled in nitrogen some trace of oxygen or volatile peroxides was in the distillate. We have now strong evidence for this assumption, since we have found that by adding hexaphenylethane (which reacts rapidly with oxygen) to isoprene in nitrogen and distilling, the rate of polymerization of the distillate is reduced tenfold. The material thus prepared still polymerizes under pressure (14 per cent at 12,000 atmospheres in forty-eight hours); it can be argued that this represents the uncatalyzed reaction, but it seems equally probable that traces of oxygen or peroxide are still present adsorbed to the glass."

In view of these facts, they suggest "that the mechanism is a series of chain reactions in the liquid initiated by the spontaneous decomposition from time to time of the peroxide. The accelerating effect of great pressures is due, according to our theory, to the orientation of the molecules of the isoprene into a more compact bundle in which longer reaction chains would be propagated by the spontaneous decomposition of a single peroxide molecule. It seems quite certain that as the volume of a liquid is diminished by the application of pressure, a definite orientation of the molecules is approached and we assume that this orientation is very similar to that existing in the polymer itself. It seems reasonable to suppose that the spontaneous decomposition of a peroxide molecule would be more effective in producing long reaction chains, the less the random motion of the molecules and the more compact and oriented they were assembled. We imagine that as each molecule becomes in turn activated by the energy originally coming from the peroxide, it unites with its neighbor, which in turn becomes active by virtue of the exothermic nature of the polymerization process. The pressure polymerization is thus to be thought of as a chain reaction in which the energy is passed on in a chain and all the reacting molecules actually unite. The accelerating effect of temperature is easily explained as being due to the more frequent initiation of peroxide decompositions and hence of reaction chains."

Staudinger and Lautenschlager (161) have determined the rate of polymerization of isoprene by heating 10 g. at 80°C. in the presence of carbon dioxide or oxygen for four days and removing all of the material volatile below 80°C. under vacuum. The per cent of polymerization and of oxidation is shown in table 7.

Addition of peroxides causes polymerization to occur more rapidly than in carbon dioxide, but not so quickly as in oxygen. Therefore, it is concluded that the peroxides are not the actual catalysts and that primary peroxides with more pronounced accelerating action are formed during autoxidation.

TABLE 7

Polymerization of isoprene

TIME	AUTOXIDATION*	POLYMERIZATION IN OXYGEN	POLYMERIZATION IN CARBON DIOXIDE
days	*per cent*	*per cent*	*per cent*
1	0	10	5
2	0	13	6
3	0	18	7
4	3	23	9

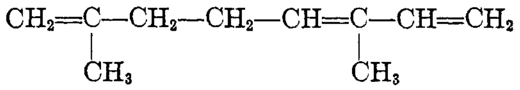
* This calculation is based on the assumption that one molecule of hydrocarbon absorbs only one molecule of oxygen.

(*2*) *Caoutchouc.* As mentioned above, the polymerization of isoprene is aided by the presence of caoutchouc or caoutchouc-like material. Lebedev and Skavronsky (95) report that when a small piece of caoutchouc is sealed with 35 g. of isoprene, it gradually grows and in three years the polymerization is complete. If no polymer is originally introduced, the liquid becomes very viscous, the first insoluble polymer is noticed only toward the end of the second year, and at the end of three years much liquid is still left.

(*3*) *Acids.* In 1879 Bouchardat (24) found that the distillation of the hydrochlorides of isoprene (formed by allowing isoprene to stand in hydrochloric acid for twenty-five days) yielded a solid residue with the elasticity and other properties of rubber. It contained little more than 1 per cent of chlorine. This work was confirmed by Tilden (171) in 1884. However, there has been controversy over the question of the formation of rubber from isoprene in the presence of hydrochloric acid. Pond (118) has reviewed this controversy and attempted to repeat the work of Bouchardat and Tilden but without success.

In 1910 Harries (64) reported the discovery that isoprene can be converted to rubber by heating it with glacial acetic acid to about 100°C. in a sealed tube. This rubber was identical with "india rubber" in physical as well as chemical properties. He stated that unless the various conditions are maintained constant, all sorts of viscous oils, resins, etc., are obtained, but he did not report the optimum conditions. A year later (61) he stated that when isoprene is converted to isoprene caoutchouc by heating (on a water bath) under pressure with an equal volume of glacial acetic acid for eight days the yield varied widely, but was little if at all affected by marked variation in the proportion of acetic acid or by changes in the temperature between 95 and 120°C.

As a by-product of this process Harries obtained a hydrocarbon, $C_{10}H_{16}$, which he considered to have the following formula.



$$\mathrm{CH_2{=}\underset{\substack{|\\ CH_3}}{C}{-}CH_2{-}CH_2{-}CH{=}\underset{\substack{|\\ CH_3}}{C}{-}CH{=}CH_2}$$

As has already been shown, Wagner-Jauregg (182) has repeated Harries' work and found that this terpene is identical with diprene.

More recently he (183) obtained a hydrocarbon, to which he gave the formula $C_{15}H_{24}$, by treating isoprene with an excess of glacial acetic acid, containing a little concentrated sulfuric acid, for three days at room temperature. Various terpene alcohols were produced together with the hydrocarbon, when the reaction mixture was hydrolyzed. Similar treatment with a mixture of glacial acetic acid and a little dilute sulfuric acid yielded the same hydrocarbon, together with a mixture of terpene alcohols and ethers, without subsequent hydrolysis.

Hydration of ethylenic bonds in the molecules produced by the polymerization of isoprene, either simultaneously with or subsequently to the polymerization, was thought to be the source of the alcohols and ethers which were found.

The hydrocarbon appeared to be a monocyclic compound with three double bonds, isomeric with bisabolene and zingiberene, but gave no crystalline hydrogen chloride addition product. It added three moles of hydrogen, catalytically.

Refluxed with 98 per cent formic acid, there resulted a product thought to be a bicyclic hydrocarbon of the caryophyllene group, containing two double bonds. Similar treatment of bisabolene and zingiberene yields bicyclic hydrocarbons of the cadinene group.

(*4*) *Alkali metals.* Harries (61) prepared a so-called sodium-caoutchouc from the polymerization of isoprene with 0.4 per cent sodium at 60°C. Fifty hours heating produced an almost quantitative yield of caoutchouc.

It is interesting to note that Harries claimed that his caoutchouc had properties "identical" with those of natural rubber save that it yielded different ozonization products.

Aschan (8) claims to have discovered the condensing action of sodium on isoprene independently of, and simultaneously with, Harries. He obtained, from crude isoprene and sodium, a product insoluble in alcohol but soluble in ether, which he termed "semi-caoutchouc," and which could be vulcanized. Pure isoprene, heated alone for thirteen days, was less completely polymerized than in three days in the presence of sodium.

Midgley and Henne (104) have found that isoprene is dimerized when placed in contact with metallic potassium chips and ethyl alcohol added at a rate just sufficient to give a moderate evolution of hydrogen at the surface of the metal. The light yellow oil which resulted, proved to be a mixture of 2,6-, 2,7-, and 3,6-dimethyl-2,6-octadienes. These isomers are the dihydro dimers of isoprene resulting from a junction at the 1,4-, the 4,4- and the 1,1-carbon atoms, respectively, and the addition of hydrogen at the 1,8-positions of the dimer. No trace of a cyclic compound could be detected.

(5) *Metallic chlorides.* High molecular weight polymers, said to be isomeric with rubber, have been produced by catalytic action at room temperature. Whitby and Crozier (191) treated 0.5 cc. portions of pure isoprene with inorganic halides with the following results:

(a) Stannic chloride.—Polymerization was complete in three hours, yielding a clear, soft, amber colored, non-elastic mass, which when warmed showed elastic properties if squeezed, and which swelled but did not dissolve in benzene. The addition of alcohol converted this substance to a white powder.

(b) Antimony pentachloride.—If the catalyst was added undiluted, there resulted a violent reaction, producing a pitch. If diluted with an organic solvent, or used at the temperature of solid carbon dioxide, the product resembled that produced by stannic chloride at room temperature.

(c) Antimony trichloride.—At room temperature, violent reaction, with charring, resulted. At the temperature of solid carbon dioxide the product was similar to that from stannic chloride.

(d) Ferric chloride.—Only a slight effect after two days.

(e) Ferric bromide.—A brown, weak gel after twelve hours.

(f) Aluminum chloride.—Complete polymerization after twenty-four hours to a yellow flaky mass, only slightly soluble in benzene.

(g) Thorium bromide and thorium chloride.—Little or no action in dilute solution after twenty-four hours. The addition of alcohol precipitated small amounts of the powdery polymer.

Similar products were obtained by treating 3 per cent solutions of rubber in benzene with the same catalysts, and then with alcohol.

More recently Wagner-Jauregg (183) treated isoprene with titanium tetrachloride at room temperature and obtained a similar polymer. It was a slightly yellow, amorphous substance which first softened and then melted with decomposition when heated. It was soluble in benzene, partially so in ether and pyridine, and was precipitated from these solvents by alcohol. Its molecular weight in benzene was about 2800.

This polymer resembled that obtained from Dammar resin $(C_5H_8)_x$, the molecular weight of which averages 2800 to 3000, and which possesses similar solubilities. It was supposed that they belong to the same class of substances.

On being heated with selenium, dehydrogenation occurred, yielding 1,2,5-trimethylnaphthalene, obtained by Ruzicka (133) by the selenium dehydrogenation of certain triterpenes and sapogenins.

At a temperature of 110°C., antimony trichloride was found by Euler and Ahlström (46) to give with isoprene an amorphous product which did not melt at 300°C. The authors supposed it to be a very high condensation product of isoprene, although the carbon content analyzed about 3 per cent low. At room temperature an amorphous product having the formula $C_{10}H_{16} \cdot 2SbCl_3$ resulted.

The same authors found that when isoprene was heated with azobenzene at 100–120°C. some dipentene appeared among the reaction products.

Heating with amyl nitrite at 130–140°C. produced a dark rubbery mass containing no nitrogen.

Aschan (9) has shown that in the presence of aluminum chloride isoprene condenses with itself and also with other hydrocarbons containing an ethylenic linkage, such as amylene, trimethylethylene, pinene, camphene, isopinene, dipentene, and sylvestrene, yielding amorphous compounds of high molecular weight which do not possess the physical properties of caoutchouc. The time necessary for the completion of the condensation, when "commercial" isoprene (4) is used, is only a few minutes. The product can always be separated into two components, both unsaturated solids, one of which is completely insoluble in all solvents, while the other dissolves in most organic media with the exception of alcohol. Experiments with mixtures of isoprene and amylene showed that, practically, only the isoprene was acted on if the proportion of amylene was small and the test cautiously performed. Oily substances, which are possibly synthetic hydrocarbons of the sesqui-, di-, and poly-terpene series, are obtained as by-products of these condensations.

Recently Thomas and Carmody (169) have published the results of a similar study of isoprene and pentene-2. These authors found that the insoluble substance, $(C_5H_8)_x$, was converted at 300°C. to a dark oil which solidified on cooling to a dark transparent resin, soluble in hydrocarbon and chlorinated hydrocarbon solvents. The quantity of this polymer produced was an inverse function of the amount of pentene-2 present.

The soluble polymer varied in physical state from a viscous oil to a hard resin, depending on the amount of pentene-2 present and the subsequent treatment. It consisted of a mixture of higher oils and a hydrocarbon resin. The hardness and molecular weight were inverse functions of the amount of pentene-2 added, the latter varying from 845 to 1240. As the lower oils were removed, the formula approached $(C_5H_8)_x$.

It was found that any solvent in which isoprene and aluminum chloride were mutually soluble caused formation of the soluble polymer. Thus nitrobenzene and ethyl acetate could be used. With the former, in which aluminum chloride is completely soluble, only the soluble polymer was formed, while with the latter, in which the chloride is less soluble, some of the insoluble polymer was produced, the quantity being less with increasing quantities of the ester.

Dry hydrogen chloride, bubbled through isoprene containing aluminum chloride, caused a violent reaction, producing both polymers because the hydrochloride of isoprene formed a complex with aluminum chloride in which both isoprene and the salt were soluble to some extent.

There was only a slow polymerization to the insoluble form, when pure isoprene and aluminum chloride were allowed to stand at room temperature. Thomas and Carmody supposed that this polymer had a high molecular weight, while the soluble form had a much lower molecular weight, the actual value of which depended on the amount of mutual solvent present.

The formation of the two polymers was explained by assuming that in the absence of a mutual solvent only a small catalytic surface was exposed, and that the isoprene molecules could only continue to build up on the comparatively few nuclei started at that surface. In the presence of a mutual solvent, however, the dissolved catalyst presented a very much larger surface, many more polymeric molecules formed, and therefore the formation of large, insoluble molecules or aggregates was prevented because of the relatively fewer isoprene molecules available for polymerization at a given point.

Böeseken and Adler (20) have found that isoprene, if brought into contact with aluminum chloride in benzene solution, is converted to a mixture of polyisoprenes which have no resemblance to caoutchouc.

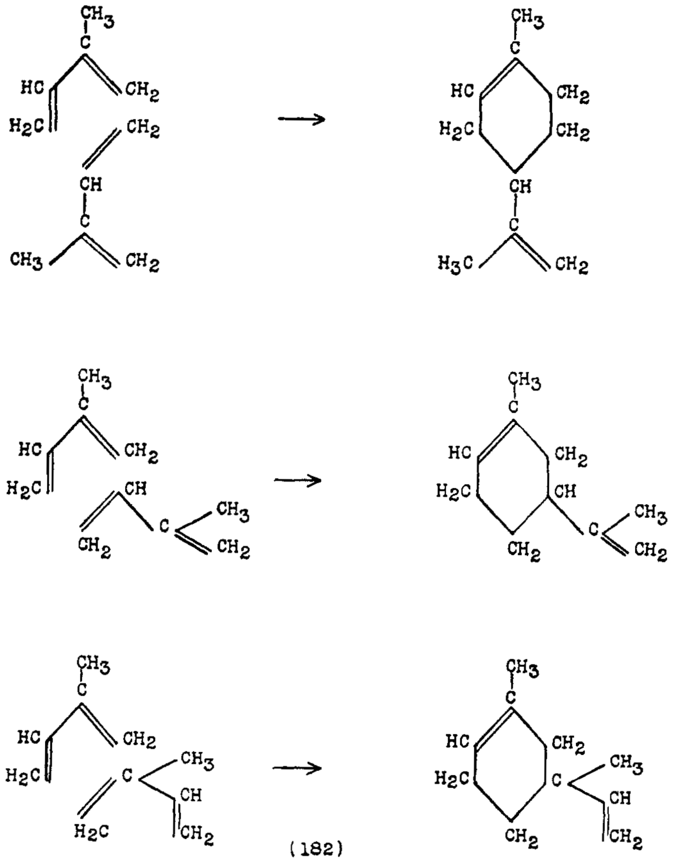
(6) Aluminum–mercury couple. At about the same time that Aschan's work on the catalytic effect of aluminum chloride appeared, Böeseken and Nooduijn (21) reported the polymerization of isoprene in benzene solution under the influence of an aluminum–mercury couple. This catalyst was prepared by pouring 0.2 g. of powdered aluminum into a dry benzene

solution of 3 g. of mercuric chloride and warming gently. After cooling, 10 g. of isoprene in 40 cc. of benzene was added, the mixture warmed half an hour on the water bath, and allowed to stand twenty-four hours.

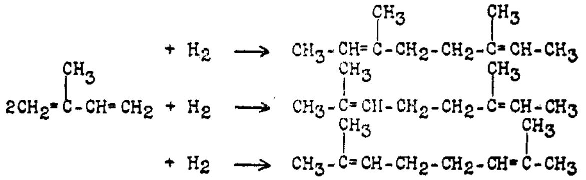
Like Aschan, they obtained two kinds of products, both unsaturated polymers of high molecular weight, which were only slightly viscous and could not be vulcanized. One of the products was soluble in benzene, ether, chloroform, etc., while the other was nearly insoluble.

(*7*) *Radon.* Heisig (73) studied the action of radon on isoprene, and pointed out that a rubber-like product might have been expected, but that the material obtained was a very viscous light-colored liquid which had the same general appearance as the rubber left after the evaporation of the "solvent" from rubber cement. The indications were that hydrogen and methane were formed.

The present state of our knowledge of the manner in which isoprene may be dimerized is summarized by the following equations.



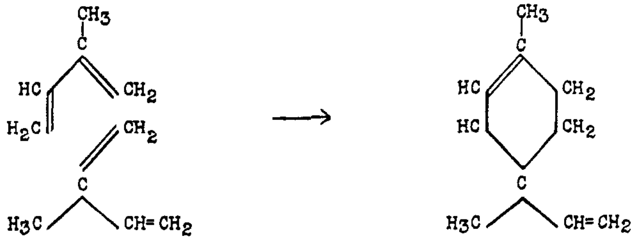
(182)



$$\begin{aligned} & && \xrightarrow{} CH_3\text{-}CH{=}\overset{CH_3}{\overset{|}{C}}\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{C}}{=}CH\text{-}CH_3 \\ 2CH_2{=}\overset{CH_3}{\overset{|}{C}}\text{-}CH{=}CH_2 & + H_2 && \xrightarrow{} CH_3\text{-}\overset{CH_3}{\overset{|}{C}}{=}CH\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{C}}{=}CH\text{-}CH_3 \\ & + H_2 && \xrightarrow{} CH_3\text{-}\overset{CH_3}{\overset{|}{C}}{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH{=}\overset{CH_3}{\overset{|}{C}}\text{-}CH_3 \end{aligned}$$

(104)

The reaction represented below seems reasonable, although it has not been realized as yet.



The patent literature on the polymerization of isoprene is too voluminous to include in this paper. However, it reports that polymerization of isoprene may be hastened by heat, light, radon, silent electric discharge, and many chemical reagents. The products obtained are terpenes and rubber or rubber-like materials.

TABLE 8

Pyrolysis of isoprene

(Quartz tube with coke as catalyst (158))

TEMPERATURE	PRODUCTS
degrees C.	
400–450	Isoprene, terpenes, amylene, a little gas
600–700	Unsaturated mixture resembling crude petroleum, ethylene, propylene, butadiene
700	Aromatics begin to appear
750	Gaseous unsaturated hydrocarbons, ethylene, methane, hydrogen, benzene, toluene, naphthalene, α-methylnaphthalene, anthracene, phenanthrene, chrysene, tar, carbon
800	100 per cent aromatics
700 (under 20 mm. pressure)	50 per cent isoprene, gases, unsaturated compounds (no tar)

The results of investigations on isoprene reported in this paper, are summarized in tables 8 and 9.

TABLE 9

Polymerization of isoprene

REFERENCE NO.	TIME	TEMPERATURE	PRODUCTS	REMARKS
		degrees C.		
(22)	10 hours	280–290	Diisoprene	Sealed tube with atmosphere of CO_2
(171)	12 hours	250–280	Dipentene	Sealed tube
(184)	"Several hours"	250–270	Dipentene	Sealed tube
(63)	—	300	Dipentene, and an isomeric substance	
(94)	—	100–150	Dipentene, 1,3-dimethyl-3-ethylenyl-6-cyclohexene	Heated in sealed tube and then distilled in stream of hydrogen
(114)	3–5 days	80–90	(β-Myrcene)	Sealed tube
(53)	—	100–150	Dipentene, 1,3-dimethyl-3-vinyl-6-cyclohexene, two polymers	Absence of light
(186)	—	Room temperature	Caoutchouc-like mass	Presence of light
(62)	—	Room temperature	Rubber-like material, and solid white substance	Ultra-violet light
(170)	—	Room temperature	Dense syrup, rubber-like solid	
(188)	6 months	Room temperature	Viscous mass	
(117)	2½ years	Room temperature	Rubber-like product	Absence of light
(5)	10 years	Room temperature	Diprene	Absence of light
(27)	20 hours	Room temperature	Rubber-like product	High pressure
(95)	3 years	Room temperature	Complete polymerization	Small piece of rubber added
(95)	3 years	Room temperature	Liquid polymer	
(24)	25 days	Room temperature	Elastic solid residue, and hydrochlorides of isoprene	Products obtained on distillation after standing with HCl
(171)			—	Confirmation of HCl action above
(64)	8 days	100	Rubber, viscous oils, resins, $C_{10}H_{16}$ oil	Heated in sealed tube with glacial acetic acid

TABLE 9—*Continued*

REFERENCE NO.	TIME	TEMPERATURE	PRODUCTS	REMARKS
		degrees C.		
(61)	50 hours	60	Caoutchouc	Almost quantitative yield. Sodium used as catalyst
(8)	3 days	"Heat"	Caoutchouc	Crude isoprene catalyzed by sodium
(104)	—	—	2,6-, 2,7-, and 3,6-dimethyl-2,6-octadiene	Sodium and ethyl alcohol
(4)	Few minutes	—	Two unsaturated solids, oily by-products	"Commercial" isoprene catalyzed by $AlCl_3$
(20)	—	—	Polyisoprenes	$AlCl_3$ in benzene solution
(21)	24 hours	100 for ½ hour then room temperature	Products same as above	Benzene solution with or without H_2 atmosphere in presence of Al–Hg couple
(73)	—	—	Viscous liquid, hydrogen (?), methane (?)	Radon
(191)	5 hours to 4½ years	Room temperature to 145	Oil and rubber, dipentene	No β-myrcene or 1,3-dimethyl-3-vinyl-6-cyclohexane
(182)	3 days	Room temperature	$C_{15}H_{24}$ hydrocarbon	Acetic–sulfuric acid added
(191)	3 hours	Room temperature	High molecular weight polymer	$SnCl_4$ added
	—	−80 or room temperature, if diluted	High molecular weight polymer	$SbCl_5$ added
	—	−80 or room temperature, if diluted	High molecular weight polymer	$SbCl_3$ added
	2 days	Room temperature	Slight effect	$FeCl_3$ added
	12 hours	Room temperature	Weak gel	$FeBr_3$ added
	24 hours	Room temperature	Flaky polymer	$AlCl_3$ added
		Room temperature	Little or no action	$ThBr_4$ and $ThCl_4$ added

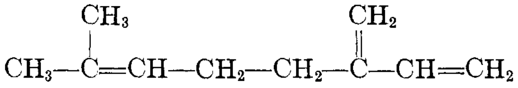
TABLE 9—*Concluded*

REFERENCE NO.	TIME	TEMPERATURE	PRODUCTS	REMARKS
		degrees C.		
(182)	—	Room temperature	High amorphous polymer	$TlCl_4$ added
(46)	—	110	Amorphous polymer	$SbCl_3$ added
		100–120	Dipentene and other products	Azobenzene added
		130–140	Rubbery polymer	Amyl nitrite added
(169)	—	Room temperature	High molecular weight insoluble polymer, low molecular weight soluble polymer	$AlCl_3$ and pentene-2 added

IV. MONOTERPENES

A. ACYCLIC

1. Myrcene



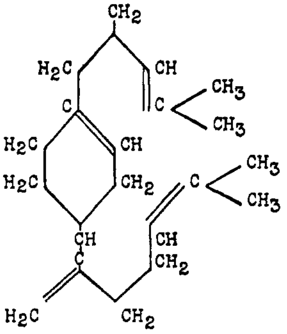
$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_2}{\overset{\|}{C}}-CH=CH_2$$

Thermal decomposition. As has already been stated, the formula of myrcene indicates that its reactions under the influence of heat should be similar to those of isoprene. However, the decomposition products of myrcene have not been studied to as great an extent.

When myrcene was subjected to pyrolytic decomposition using a glowing platinum wire and brass jacket, Prodrom (120) found that the product contained 3.6 per cent gases, 15.9 per cent of material boiling between −80° and 25°C., 39 per cent crude isoprene, 26.8 per cent of liquids boiling above 45°C., and 14.6 per cent of residue. A 60 to 70 per cent yield of isoprene from the decomposition of myrcene in the presence of benzene vapors has been reported by Ostromisslensky (113).

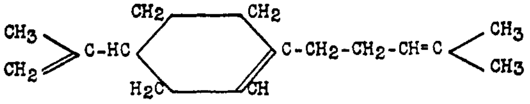
Polymerization. Like the thermal decomposition, the polymerization of myrcene has not been studied in great detail. Harries (63) reported that myrcene is polymerized to a thick greenish yellow oil when heated for four hours in a sealed tube at 300°C. On fractionation of the product under 13 mm. pressure, three fractions were obtained: (1) unchanged or "cyclomyrcene" boiling at 50–100°C., (2) dimyrcene ($C_{20}H_{32}$), boiling at 160–200°C., and (3) a residue of polymyrcene ($C_{40}H_{64}$).

Similar to the work of Harries was that of Semmler and Jonas (152), who heated myrcene for four hours in a sealed tube at 250–260°C. and fractionated the product. The fraction which corresponded to Harries dimyrcene contained 50 per cent α-camphorene, and other diterpenes some of which were probably bicyclic. The formula of α-camphorene as suggested by Ruzicka and Stoll (132) is as follows:



Prodrom (120) found that purified myrcene heated for three weeks at 100°C. under pressure was converted to a transparent viscous oil, which on fractionation under 1 mm. pressure gave products with boiling ranges of 50–53°, 170–176°, and above 269°C., respectively.

When heated at 225°C. for three and one-half hours, a mixture of 20 g. of myrcene and 10 g. of isoprene (152) yielded the following fractions upon distillation under 8 mm. pressure: (1) dipentene, boiling range 52–65°C.; (2) cycloisoprene-myrcene, boiling range 120–150°C.; (3) oil of boiling range 175–195°C.; and (4) residue. The following formula for cycloisoprene-myrcene has been suggested by Ruzicka and Bosch (126).



Concerning the rate of polymerization of myrcene, Lebedev (94) has found that at 150°C. myrcene is polymerized to the extent of 53 per cent in four and one-half hours, 68 per cent in thirteen and one-half hours, 78 per cent in one hundred and fifteen hours, and 82.5 per cent in two hundred and eighty-eight hours.

Staudinger and Lautenschlager (161) reported that at 80°C. myrcene undergoes oxidation and polymerization to the extent shown in table 10.

Gapon (54) considers that myrcene is most likely a mixture of two isomers, and that on activation three active forms will be produced, thus giving rise to two dimers and two polymers. The kinetics of the reaction were studied and it was found that two processes occurred, a polymerization and an isomerization. Gapon determined the rates of the two reactions at 150°C.

TABLE 10

Myrcene

TIME	AUTOXIDATION	POLYMERIZATION IN OXYGEN	POLYMERIZATION IN CARBON DIOXIDE
days	*per cent*	*per cent*	*per cent*
1	62	20	10
2	78	32	14
3	82	42	17
4	90	50	22

TABLE 11

Myrcene

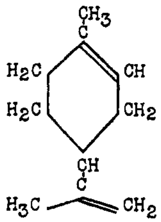
REFERENCE NO.	TIME	TEMPERATURE	PRODUCTS	REMARKS
	hours	*degrees C.*		
(120)	—	Glowing platinum wire	Gases, crude isoprene, liquid boiling above 45°, residue	Brass jacket
(113)	—	—	Isoprene	Benzene vapor used as diluent
(63)	4	300	Unchanged or cyclomyrcene, dimyrcene ($C_{20}H_{32}$), residue ($C_{40}H_{64}$)	
(152)	4	250–260	Same as above with addition of α-camphorene	Sealed tube
	3.5	225	Dipentene, cycloisoprene-myrcene, unknown boiling at 175–195°, residue	Myrcene and isoprene heated in sealed tube
(120)	3 weeks	100	Unknowns of following boiling point: 50–53° at 1 mm. pressure, 170–176° at 1 mm. pressure, above 269°	Purified myrcene heated under pressure
(94)	4.5 13.5 115 288	150	53 per cent polymer, 68 per cent polymer, 78 per cent polymer, 82.5 per cent polymer	

Since β-myrcene has been found to be identical with diprene, its behavior is discussed under the latter heading.

Table 11 summarizes the results of investigations of the polymerization and depolymerization of myrcene.

B. MONOCYCLIC TERPENES

1. *Limonene (dl-limonene = dipentene)*



Non-catalytic decomposition. In spite of the wide distribution of *d*- and *l*-limonene and the *dl* (racemic) form, dipentene, there are comparatively few detailed accounts of their pyrolysis.

In 1902 Harries (63) reported that both limonene and dipentene remain for the most part unchanged on being heated for four hours in a sealed tube at 300°C.

Several years later Harries and Gottlöb (65) developed the "isoprene lamp" for the decomposition of terpenes to isoprene. This consisted of an electrically heated platinum filament suspended in the upper portion of a flask equipped with a reflux condenser maintained at 50°C. Thus the isoprene and low-boiling products were continuously removed, and the higher boiling terpenes remained in the flask. Using the isoprene lamp Harries and Gottlöb obtained 30 to 50 per cent of isoprene from commercial carvene (largely dipentene), depending upon the dipentene content.

Some doubt was cast on Harries' work when Herty and Graham (77) obtained, with the isoprene lamp, only a 12 per cent yield of isoprene from the volatile oil of *Pinus Serotina,* an oil which had been found by Herty and Dickson (76) to be particularly rich in limonene. Furthermore, Mahood (99) has pointed out that wood turpentine, which contains a considerable amount of limonene, might be expected to give a larger yield of isoprene than gum turpentine, which is largely pinene. His results, however, did not confirm this supposition.

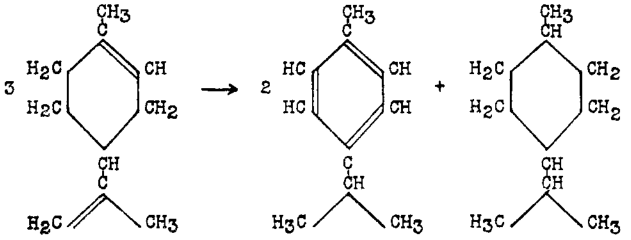
In order to get a little more direct evidence of the yields of isoprene available from pinene and limonene, Mahood (99) carried out experiments in which turpentine was treated so as to convert the pinene into limonene before cracking. Wallach (184) had observed previously that pinene is converted to limonene by prolonged heating at 250–270°C. Mahood ran several experiments in which the vapors of gum turpentine were passed through an iron tube heated to 250–270°C. for two to twenty hours. The original turpentine, which consisted largely of pinene, was converted to a more complex and higher boiling mixture of which limonene was one of the chief constituents. There was, however, no appreciable increase in the yield of isoprene upon cracking this product by passing it through a Pyrex glass tube at 450°C.

On the other hand, Supniewsky (167), in a more recent paper reported that he obtained 100 g. of pure isoprene and 80 g. of a mixture containing some isoprene from 300 g. of limonene, the isoprene lamp being the means of conversion.

Staudinger and Klever (160) obtained a 60 per cent yield of isoprene by passing the vapors of dipentene in high dilution with nitrogen over a hot platinum coil at a pressure of 20–30 mm. When the pressure was reduced to 2–3 mm., even larger yields of isoprene were obtained. In both cases they obtained a small quantity of gaseous hydrocarbons of the olefin and acetylene series and of liquid hydrocarbons boiling from 100–150°C. Hardly any higher boiling compounds were produced.

Ostromisslensky (113) has stated that Staudinger and Klever's results were not due to the dilution of the limonene vapor but to the high temperature at which this vapor is formed. He states also that "good results" are obtained when limonene is mixed with benzene, toluene, xylene or light petroleum.

Catalytic decomposition. In the work in which the isoprene lamp was used, the glowing platinum wire was considered simply as a source of heat, and no mention was made of any catalytic action. Palladinized asbestos at 180–185°C., however, was found by Zelinsky (196) to exercise a non-reversible catalytic effect on limonene. The limonene, b.p. 166.5–177.5°C., was converted after a single passage over the catalyst into about 66 per cent *p*-cymene and 33 per cent menthane. The same transformation was effected at 130°C. under 120 mm. pressure.



Limonene Cymene Menthane

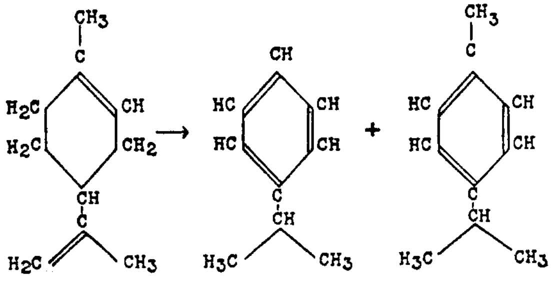
Komatsu and Kurata (90) have found that *d*-limonene passed over a reduced copper catalyst at 280–300°C. yielded cymene quantitatively. However, if the temperature was lowered to 200°C. and the limonene passed over the copper at the same rate, both cymene and menthane were found in the products.

The action of nickel and copper catalysts on limonene was found by Treibs and Schmidt (172) to be analogous to that of Zelinsky's palladium-asbestos catalyst, yielding cymene and menthane as products.

Decomposition in glow discharge. The decomposition of limonene and dipentene in a glow discharge has been studied by Linder and Davis (96). As might be expected, the rate of decomposition, measured by gas production, is about the same in both cases. The products obtained from dipentene were hydrogen, gaseous acetylenes, olefins and paraffins, and hexaethylbenzene. The gases from limonene were similar to those from dipentene but the solid which was reported was *o*-diphenylbenzene.

Catalytic hydrogenation. Some very interesting work has been done on the hydrogenation of limonene and dipentene at elevated temperatures. Sabatier and Senderens (138) have found that limonene and hydrogen passed over a nickel catalyst at 180°C. yield hydrocymene (*p*-menthane) and a small quantity of decomposition products. The same authors (139) reported that the hydrogenation of limonene over copper at 190°C. changes limonene to *p*-1-menthene. Somewhat later, Vavon (180) studied the stepwise hydrogenation of limonene using platinum black as catalyst and found that *p*-1-menthene can be obtained by stopping the hydrogenation after one mole of hydrogen has been absorbed, while *p*-menthane is obtained if the reaction is allowed to go to completion.

At somewhat higher temperatures, 350–360°C., Sabatier and Gaudion (136) found that the vapors of limonene carried along by hydrogen and directed on a column of nickel yielded for the most part cymene mixed with cumene:



Limonene Cumene Cymene

Only a small amount of saturated hydrocarbons is obtained.

Recently a patent has been issued to Schering-Kahlbaum A.-G. (140) for the preparation of menthenes by hydrogenation of terpenes at 40–80°C. in the presence of nickel. Dipentene, one of the terpenes mentioned, is claimed to yield carvomenthene, i.e., menthene in which the double bond outside of the ring has been reduced.

In another patent to the same people (141) carvomenthene (1-menthene) is claimed to be converted into 2-menthane by passing its vapor over a surface catalyst, such as bleaching earth, pumice, silica gel, or "tonsil," or a metal salt such as magnesium sulfate or copper phosphate at 300–450°C.

Polymerization. Table 12, taken from the work of Staudinger and Lautenschlager (161), shows that limonene is not readily polymerized at 80°C.

On the other hand, Humphrey's patent (80) for the polymerization of dipentene in the vapor phase at temperatures ranging from 175 to 550°C. claims a yield of about 30 per cent of "dipolymer." The following example is given:

"Through an iron tube heated to about 400°, containing 8–10 mesh Fuller's earth, is passed 200 cc. of dipentene at a rate of 50 cc. per hour. There were recovered 164 cc. of a product containing 62 cc. of 'dipolymer.' The reaction may be represented as

$$xC_{10}H_{16} \rightarrow \underset{\text{Dipolymer}}{(C_{10}H_{16})_2} + (C_{10}H_{16})_x\text{''}$$

TABLE 12

Limonene

TIME	AUTOXIDATION	POLYMERIZATION IN OXYGEN	POLYMERIZATION IN CARBON DIOXIDE
days	*per cent*	*per cent*	*per cent*
1	45	4	2
2	60	6	3
3	70	7	4
4	80	9	5

d-Limonene was found by Carter, Smith, and Read (36) to be readily polymerized to a diterpene or diterpenes ($C_{20}H_{32}$), to the extent of about 75 per cent by prolonged shaking at room temperature with syrupy phosphoric acid. α- and γ-terpinene were produced at the same time. The mechanism of this reaction will be discussed in the section on phellandrene, which exhibits the same phenomenon.

Dehydrogenation by sulfur. In Ruzicka's (128) studies of the dehydrogenation of terpenes by means of sulfur, limonene was used to determine whether the position of the side chains was altered. No rearrangement took place, for limonene was converted to *p*-cymene. The reaction may be represented as follows:

$$C_{10}H_{16} + 2S \rightarrow C_{10}H_{14} + 4H_2S$$

TABLE 13

Limonene and dipentene

REFERENCE NO.	HYDROCARBON	TEMPERATURE	CATALYST	PRODUCTS	REMARKS
		degrees C.			
(63)	Limonene	300	—	No change	Heated in sealed tube for 4 hours
(63)	Dipentene	300	—	No change	
(65)	Carvene	Isoprene lamp	—	Isoprene	Other products not enumerated
(77)	Limonene	Isoprene lamp	—	Isoprene	Oil of *Pinus Serotina*
(99)	Limonene	450	—	Isoprene	Wood turpentine
(99)	Limonene	450	—	Isoprene	Limonene from heating of pinene
(167)	Limonene	Isoprene lamp	—	Isoprene	
(160)	Dipentene	Hot platinum coil	—	Isoprene	Vapors in high dilution with nitrogen at 2–3 mm. pressure
(196)	Limonene	180–185	Pd–Asbestos	*p*-Cymene, *p*-menthane	Atmospheric pressure
(196)	Limonene	130	Pd–Asbestos	*p*-Cymene, *p*-menthane	120 mm. pressure
(90)	*d*-Limonene	280–300	Cu	100 per cent cymene	Rate of flow 4.5 g. per hour
(90)	*d*-Limonene	200	Cu	Cymene, menthane	Rate of flow 4.5 g. per hour
(96)	Limonene	—	—	Hydrogen, gaseous hydrocarbons, hexaethylbenzene	Glow discharge
(138)	Limonene	180	Ni	*p*-Menthane	H_2 added
(139)	Limonene	190	Cu	*p*-1-Menthene	H_2 added and reaction allowed to go to completion
(180)	Limonene	190	Platinum black	*p*-1-Menthene, *p*-menthane	H_2 added and reaction stopped before completion

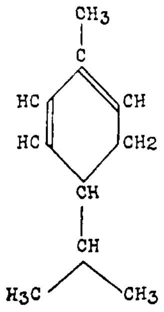
TABLE 13—*Concluded*

REFERENCE NO.	HYDROCARBON	TEMPERATURE	CATALYST	PRODUCTS	REMARKS
		degrees C.			
(136)	Limonene	350–360	Ni	*p*-Cymene, cumene, saturated hydrocarbons	H_2 added
(80)	Limonene	400	Fuller's earth	Dimer, polymer	50 cc. per hour through iron tube
(128)	Limonene	ca. 180	S	*p*-Cymene	Terpene refluxed with sulfur
(172)	Limonene	—	Ni	Cymene and menthane	
	Limonene	—	Cu	Cymene and menthane	
(141)	Carvomenthene (Δ^1-menthene)	300–450	Bleaching earth, pumice, silica gel, tonsil, $MgSO_4$, $CuSO_4$, etc.	Δ^3- Menthene	
(36)	*d*-Limonene	Room temperature	H_3PO_4	A dipentene, α- and γ-terpinene	

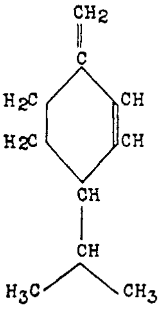
The details of the procedure are given in the section on sesquiterpenes, since the method has been used as a tool in determining the structure of some of the sesquiterpenes.

Table 13 summarizes the results obtained from the thermal treatment of limonene and dipentene with and without catalysts.

2. Phellandrene



α-Phellandrene



β-Phellandrene

Although the phellandrenes have been known for some time, it was not until the work of Wallach that their structures were clearly established. They are so unstable that they decompose to some extent when distilled at ordinary pressure (155), and readily resinify and lose rotatory power on exposure to air so that it is difficult to obtain them in pure condition. This marked instability is due, in part at least, to conjugated double bonds.

Polymerization. Pesci (116) has reported that these hydrocarbons polymerize by repeated distillation and if heated for twenty hours in a sealed tube are converted to a glassy mass, $(C_{10}H_{16})_x$.

Semmler and Jonas (152 and 153) found that both α- and β-phellandrene polymerize when heated to about 300°C. The product in the case of the α-compound is a diterpene, b.p. 175–185°C., $n_d - 6°$. From the β-compound the product is also a diterpene, b.p. 175–185°C., but it has a rotation of +9.5°.

TABLE 14

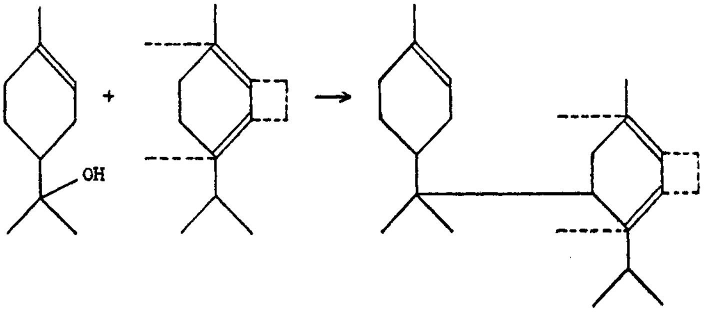
Formation of diterpenes by action of H_3PO_4 *on monoterpenes*

SOURCE	APPROXIMATE YIELD OF CRUDE DITERPENE	BOILING POINT	$[\alpha]_D^{20}$
	per cent	*degrees C.*	
l-α-Phellandrene	40	182–184 at 16 mm.	+14.96
E. dives oil	50	193–195 at 24 mm.	+13.20
E. phellandra oil	40	194–196 at 24 mm.	+3.28
M. acuminata oil	45	191–193 at 22 mm.	+1.00
d-Limonene	75	192–194 at 23 mm.	+0.16
d-Pinene	75	179–181 at 13 mm.	−0.10
l-Pinene	75	197–200 at 29 mm.	+0.07

Carter, Smith, and Read (36) found that after prolonged shaking with syrupy phosphoric acid *l*-α-phellandrene yielded 40 per cent of a diterpene $(C_{20}H_{32})$ along with α- and γ-terpinene. Parallel experiments with other terpenes led to similar results; the chief products in all instances appearing to be α-terpinene and a diterpene, or a mixture of diterpenes, both of which strongly resisted the further action of phosphoric acid at ordinary temperatures.

The results obtained are shown in table 14.

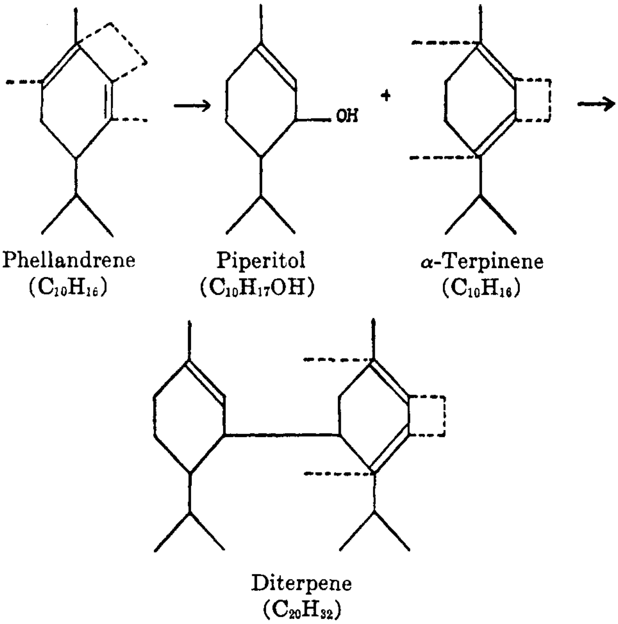
The following points are worthy of interest: absence from the products of limonene (except in the case where that substance was used), dipentene, or terpinolene; practical identity of physical constants of the diterpenes, except for optical activity; failure to obtain crystalline derivatives of any diterpene; stability of the diterpenes to distillation at ordinary pressure, in contrast to colophene ($C_{20}H_{32}$) which breaks down; and the corresponding formation of a similar diterpene from cineole, the reaction mixture of which yielded terpin hydrate. These facts "point to the formation in all of these instances of an optically active intermediate product, such as the symmetrical substance, terpin. By dehydration and isomerization this substance could give rise to α-terpineol, α-terpinene, etc.; moreover it appears likely that the diterpene is formed as the intermediate result of condensation between the hydroxyl group of a molecule of the first type and an activated hydrogen atom of a terpene molecule, rather than by polymerization of two terpene molecules. In the appended possible scheme, it is seen that the hydrogen atoms attached to carbon atoms 5, 6, 7, or 8 of the α-terpinene molecule may be regarded as activated owing to their relationship to the conjugated system formed by the remaining carbon atoms of the ring:



α-Terpineol ($C_{10}H_{17}OH$) α-Terpinene ($C_{10}H_{16}$) Diterpene ($C_{20}H_{32}$)

"Even for the specific scheme here postulated, condensation might conceivably occur either at position 5, 6, 7, or 8 in the α-terpinene molecule. Altogether, therefore, it would seem that all specimens of diterpenes produced in such ways are likely to consist of complex mixtures of isomerides, which may possibly afford some explanation of their reluctance to crystallize or yield crystalline derivatives.

"The optical activity of the diterpene from *l*-α-phellandrene calls for a mechanism which does not involve intermediate conversion to an optically inactive substance, and the following scheme may be brought forward in illustration of the various possibilities:"



Catalytic hydrogenation. Like limonene, β-phellandrene has been found (140) to yield a menthene when hydrogenated at 40–80°C. in the presence of a nickel catalyst.

TABLE 15

Phellandrene

REFERENCE NO.	HYDROCARBON	TEMPERATURE	PRODUCTS	REMARKS
		degrees C.		
(116)	Phellandrene	Not given	$(C_{10}H_{16})_x$	Heated in sealed tube
(152) (153)	Phellandrene α- or β-	300	Diterpene	
(152) (153)	α- or β-Phellandrene + isoprene	300	Sesquiterpene	
(90)	Phellandrene	300	*p*-Cymene, menthane	Cu catalyst
(140)	β-Phellandrene	40–80	*p*-2-Menthene	Ni catalyst
(36)	*l*-α-Phellandrene	Room temperature	A diterpene, α- and *γ-terpinene*	H_3PO_4 catalyst
(172)	Phellandrene	—	*p*-Cymene, menthane	Ni or Cu catalysts

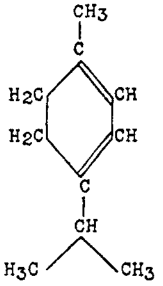
When either α- or β-phellandrene is heated with isoprene to about 300°C., a sesquiterpene is formed. In the case of the α-compound the product boils at 129–132°C. under 15 mm. pressure and has a rotation of −15°, while the β-compound yields a sesquiterpene boiling at 137–140°C. under 15 mm. pressure and having a rotation of +4°.

Komatsu and Kurata (90) have shown that phellandrene is converted to cymene and menthane when passed over finely divided copper at 300°C.

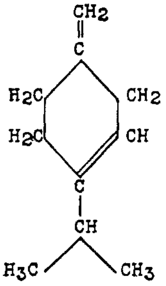
Treibs and Schmidt (172) obtained the same result by using nickel and copper catalysts.

A summary of the results obtained from treating phellandrene is given in table 15.

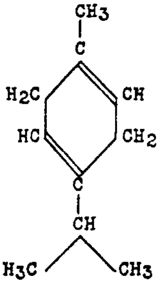
3. Terpinene



α-Terpinene



β-Terpinene



γ-Terpinene

Non-catalytic decomposition. According to Staudinger and Klever (160) terpinene gives little or no isoprene when refluxed in an isoprene lamp.

Catalytic decomposition. Zelinsky and Lewina (200) have extended the former's studies of non-reversible catalysis to include α-terpinene. This compound, like other terpenes, yields *p*-cymene and *p*-menthane when passed slowly in a stream of carbon dioxide over palladinized asbestos at 190°C.

TABLE 16

Terpinene

TIME	AUTOXIDATION	POLYMERIZATION IN OXYGEN	POLYMERIZATION IN CARBON DIOXIDE
days	*per cent*	*per cent*	*per cent*
1	57	6	3
2	73	8	5
3	78	9	7
4	83	12	8

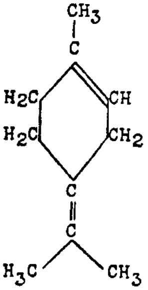
Hydrogenation. Like sylvestrene, terpinene has been found by Sabatier and Senderens (138) to yield *p*-menthane on hydrogenation with a nickel catalyst at 180°C.

Incomplete hydrogenation of β-terpinene (140) at 40–80°C. in the presence of nickel yields *p*-3-menthene.

Polymerization. Terpinene is very much like limonene in its behavior on being heated at 80°C. for four days. Staudinger and Lautenschlager's (161) data on the per cent polymerized and oxidized at given time intervals are presented in table 16.

Dehydrogenation with sulfur. Terpinene, like limonene, was used by Ruzicka (128) to test his dehydrogenation method using sulfur. In this case he obtained an even better yield of *p*-cymene than from limonene.

4. Terpinolene



Terpinolene is a comparatively unstable terpene which, as Wallach (184) observed, is easily converted to its isomer, terpinene, by the action of halogen acids or acetic acid solutions in the cold. Wallach does not indicate, however, which isomer is formed.

Non-catalytic decomposition. Staudinger and Klever (160) found that this hydrocarbon yields only a little isoprene when its vapors are passed over a hot platinum filament.

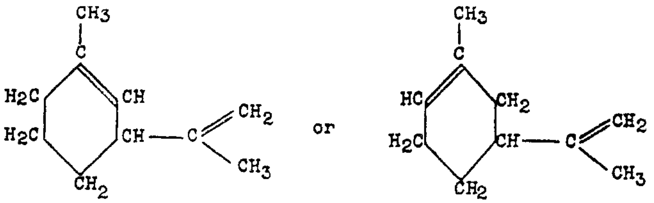
Catalytic decomposition. Mailhe (100) has reported a rather detailed study of the pyrolysis of terpinolene using reduced copper as a catalyst. At 500–550°C. the following products were obtained: (1) gaseous olefinic and paraffinic hydrocarbons and hydrogen, (2) benzene, (3) toluene, (4) methylcyclohexane, (5) *m*-xylene, and (6) *m*-cymene.

The absence of isoprene is a little conspicuous, but Mailhe pointed out that any isoprene formed might well have been hydrogenated at such a high temperature in the presence of the large amount of hydrogen produced in the process.

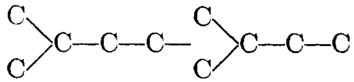
When passed over palladinized asbestos at 160–170°C., terpinolene (200) yielded *p*-cymene and *p*-menthane.

5. Sylvestrene

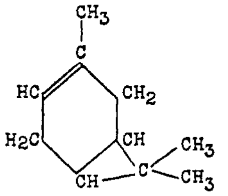
(dl-Sylvestrene = carvestrene)



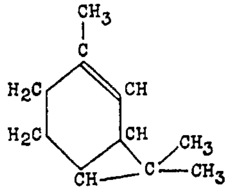
Until recently sylvestrene was considered a natural product and, as such, was an enigma, for it did not fit in with Ingold's (83) suggestion that terpenes were built up by the union of two isoprene molecules forming the geranial chain



with subsequent condensation to the *p*-cymene type of ring. The absence of sylvestrene in naturally occurring oils was established by Rao and Simonsen (121), who showed that it resulted from the action of hydrochloric acid on *d*-3-carene or *d*-4-carene.



d-3-Carene



d-4-Carene

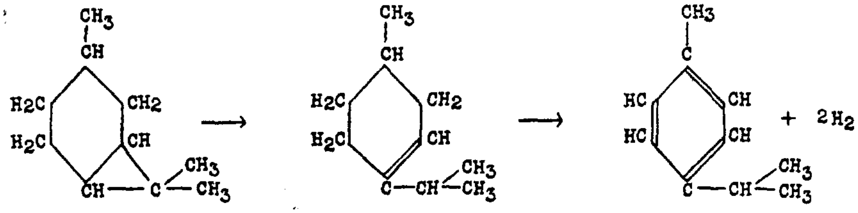
Pyrolysis. The fact that sylvestrene and its *dl*-form, carvestrene, were such a puzzle may have been a determining factor in the study of their pyrolysis, in spite of the fact that their relation to *m*-cymene was made known by Baeyer and Villiger (12) in 1898. Whatever the cause may be, the fact remains that the only reference found concerning sylvestrene's reaction toward heat is a brief one made by Wallach (187), in which he states that sylvestrene is a very stable hydrocarbon and shows no tendency to isomerize when heated in a sealed tube at 250°C.

Catalytic hydrogenation. Sabatier and Senderens (138) have found that sylvestrene yields *p*-menthane or hydrocymene when passed over nickel at 180°C. in the presence of hydrogen. In order to obtain these products a rearrangement must have taken place, for sylvestrene is a meta compound.

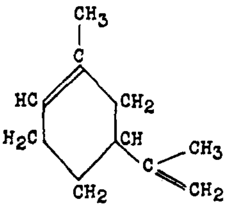
On the other hand, the patent to Schering-Kahlbaum A.-G. (140), referred to previously, indicates that *m*-1-menthene is the product of partial hydrogenation of sylvestrene at 40–80°C. in the presence of nickel.

Since carene is the precursor of sylvestrene, it is of interest to note Zelinsky's (199) work on carane, $C_{10}H_{18}$. When carane is passed over platinized charcoal at 160°C. in a stream of hydrogen, *p*-menthane is formed. Zelinsky compares his results with those of Semmler, who had found that carane was not reduced by hydrogen and platinum black at ordinary temperatures.

Irreversible catalysis. In the study of dehydrogenation by means of platinized charcoal at 300°C. in the presence of carbon dioxide, Zelinsky (199) found that carane underwent the following changes:



6. *Diprene*

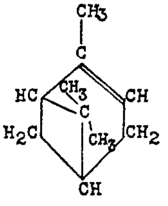


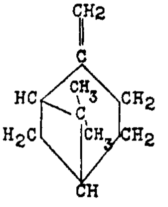
Diprene, a synthetic terpene, has been isolated from the polymerization products of isoprene. Earlier in this paper (182) it has been pointed out that the 2,6-dimethyloctatriene of Harries (61), the diprene of Aschan (6), and the β-myrcene of Ostromisslensky (114) are identical. Furthermore, as the above formula indicates, they are shown to be cyclic compounds rather than acyclic as Harries and Ostromisslensky had thought.

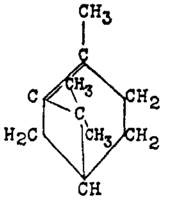
Polymerization. Ostromisslensky (114) polymerized diprene (β-myrcene) by shaking it with sodium and barium peroxide at 60–70°C. for five days, and found that it gave a quantitative yield of the same "normal isoprene caoutchouc" as that obtained from the polymerization of isoprene at "high temperatures." Under these conditions natural myrcene remained unchanged, while isoprene yielded an "isomeric abnormal caoutchouc."

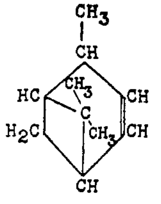
C. DICYCLIC TERPENES

1. Pinene


α-Pinene


β-Pinene


γ-Pinene


δ-Pinene

Pinene occupies a rather enviable position in the field of terpene pyrolysis for, in spite of the fact that it is a bicyclic terpene, it has been the most extensively studied. The term pinene, which should be replaced by the plural "pinenes," is used rather indiscriminately throughout the literature, so that there is no way of determining which of the four isomers some investigators used. In the few cases where the particular isomer was designated, that information has been carried into this paper. In the majority of cases where the term "pinene" occurs, the assumption may be made that the material was a mixture of α- and β-pinenes obtained by fractionation of some naturally occurring product, for the other two

TABLE 17

Turpentine components

TURPENTINE	COMPONENTS							
	α-Pinene	β-Pinene	Limonene + dipentene	Carene	Other terpenes	Sesquiterpenes	Heptane	Residue
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Bordeaux (*Pinus Maritima*)	62.6	26.8	—	—	—	—	—	10.6
American (longleaf and spruce pine)	71	29	—	—	—	—	—	—
Longleaf pine (Dupont 80)	64.3	31.8	—	—	—	—	—	—
Cuban	75.6	21.2	—	—	—	—	—	—
Russian (Dupont)	72	28	—	—	—	—	—	—
Russian (Krestinsky (56))	42.5	—	—	32.5	4	3	—	18
Indian (*Pinus Longifolia*)	24.8	9.7	—	37.6	1.7	20.3	—	5.9
Chinese	85	—	—	—	—	11	—	—
Alpine (*Pinus Halepenis*)	95	—	—	—	—	3.8	—	1.14
Italian (*Pinus Pinea*)	—	—	90	—	—	10	—	—
French (*Pinus Serotina*)	—	—	90	—	—	10	—	—
Western U. S. (*Pinus Sabiniana*)	—	—	—	—	—	—	90	—

isomers, γ- and δ-, have been prepared from natural oils but do not occur in them.

The most obvious reasons for the extensive study of pinenes are (1) the value of the isoprene obtained and (2) the abundance of the pinenes in turpentine and other relatively inexpensive naturally occurring oils. Quoting from Dupont (41), "The majority of the oils of turpentine have pinenes as their principal constituents; among these α-pinene always dominates and is sometimes the exclusive constituent. These terpenes always appear to be accompanied by a certain proportion of sesquiterpenes. However, in some turpentines other terpene constituents appear and even dominate, for example, limonene, carene and others and even hydrocarbons of nonterpenic nature as heptane."

Since pinene is the chief constituent of most turpentines, the pyrolysis of turpentine has been included in this section. Wherever given by the investigator, the source of the turpentine used is stated. Table 17 compiled from Dupont's (41) survey and other recent publications gives what is known of the composition of the turpentines included.

With respect to carene and the terpenes other than the pinenes found in Russian turpentine (2), it has been claimed by Lyubarskii (98) that their presence is due to the fact that *d*-1-pinene can isomerize in the following manner:

$$\begin{tikzcd} & & m\text{-terpinolene} \arrow[r] & \text{sylvestrene} \\ d\text{-1-Pinene} \arrow[r] & \Delta^3\text{-carene} \arrow[ur] \arrow[dr] & & \\ & & p\text{-terpinolene} \arrow[r] & \text{dipentene} \end{tikzcd}$$

Early work. The earliest reference to the pyrolysis of turpentine seems to be in the work of Gay-Lussac and Lariviere in 1841 (55), who found that turpentine yielded some oils that were more volatile than turpentine and others less volatile.

Some twenty years later Berthelot (14) found that French turpentine could be refluxed for sixty hours in an atmosphere of carbon dioxide with little change in rotatory power or other properties. However, when French, English, or Swiss turpentine was heated in closed tubes at 250°C. for ten hours, polymerization took place, accompanied by change in rotation but without gas formation. From the polymeric substances he isolated the two chief constituents and designated them as iso- and metaturpentine. English turpentine heated for two hours at 300°C. also yielded "isoturpentine," b.p. 176–178°C. This substance differed from "metaturpentine" in that it added two molecules of hydrogen chloride for every three molecules of $C_{10}H_{16}$, while "metaturpentine" added an equimolar quantity of hydrogen chloride based on the molecular weight of $C_{10}H_{16}$.

In 1860 Schiel (144) reported that the dry distillation of "colophonium" (turpentine) yielded "colophonon," an oxidation product, and "tereben" a $C_{10}H_{16}$ hydrocarbon.

Hlasiwetz and Hinterberger (79) passed turpentine through a red-hot iron tube filled with porcelain sticks. They obtained a gas, carbon, and a dark brown oily liquid condensation product. They isolated a hydrocarbon C_5H_8, b.p. 60–70°C., and an isomer of "terpintinol."

A year after this preliminary note by Hlasiwetz, Berthelot (16) observed that turpentine, passed through a porcelain tube at a moderate red heat, underwent radical change. In the fraction boiling below 250°C. the following products were identified: benzene, in small quantity; toluene, principal product; xylene, notable quantity but less abundant than toluene; cumolene, still less abundant; cymene, a very small amount; and naphthalene, notable quantity. No mention was made of any products more volatile than benzene, although such were probably formed.

Schultz (148) dropped turpentine into an iron tube which was maintained at dull red heat. There was a large amount of gas liberated, which was assumed to be a mixture of hydrogen and hydrocarbons and was allowed to escape. From the fraction of the liquid products boiling below 200°C., he isolated benzene, toluene, *m*-xylene, naphthalene, anthracene, methylanthracene, and phenanthrene, but again no substances of lower boiling point than benzene were identified.

In Tilden's (171) study of the pyrolysis of American turpentine, the commercial oil was fractionated and only that portion boiling between 156 and 160°C. was used.[3] This fraction was boiled in a copper flask and the vapors passed through an iron tube heated to the first visible redness. From 4 liters of turpentine there were collected 1275 cc. of liquid boiling below 140°C., 850 cc. boiling between 140 and 200°C., and 650 cc. of material boiling above 200°C. The remainder was accounted for in the gas produced, slight loss by evaporation, and deposition of sooty carbon.

The fraction up to 30°C. was reported to contain some acetylene by reason of the formation of a small quantity of a greenish-yellow precipitate on the addition of ammoniacal cuprous chloride.

From the fractions up to 150°C. benzene, toluene, *m*-xylene, and a "hydrocarbon which is probably identical with the heptine[4] of rosin spirit" were obtained, but "the chief volatile ingredient here is a pentine,

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[3] Since Vavon (180) has concluded that α- and β-pinene are the only constituents of that fraction of turpentine boiling between 135 and 165°C., it is reasonable to consider that Tilden's investigation was made on a mixture of these two isomers.

[4] This "heptine" (C_7H_{12}) is not an acetylene hydrocarbon but a homolog of isoprene, i.e., a diolefin.

b.p. 33–35°C., C_5H_8 (isoprene), and it would seem, therefore, that the original terpene is more readily depolymerized than is the optically inactive isomeride 'terpilene' (dipentene) which also results from the action of heat upon it." (See Wallach, Mahood, and others on rearrangement of pinene to dipentene.)

With regard to the yield of isoprene obtained, Mokiewski (107) has pointed out that Tilden's isoprene fraction was probably 50 per cent trimethylethylene, for trimethylethylene is formed in the pyrolysis of turpentine and cannot be separated from isoprene by distillation.

In the fraction boiling at 150–180°C. "terpilene (dipentene) is present, but on treating the portion which came over between 170 and 180° with small quantities of sulfuric acid and then steam-distilling, it yielded more than half its volume of cymene, the presence of which effectually prevented the isolation of the dihydrochloride of terpilene (dipentene) in a crystalline state."

When the vapors of the above fraction of turpentine were passed through the iron tube heated to bright redness, a large quantity of gas was evolved, with some liquid of which the most volatile constituent was benzene. It was only at the lower temperatures that an appreciable quantity of low-boiling liquid products was obtained. As a consequence of these results, Tilden pointed out that the difference in the results obtained by Schultz (148) and Hlasiwetz (79) was probably due to a difference in temperature, the temperature of the tube in the Schultz experiments being much higher than in those of Hlasiwetz.

Non-catalytic decomposition. In 1904, Mokiewski (108) pyrolyzed 40 kg. of turpentine oil (b.p. 155–156°C.) by passing it through a glass tube at dull red heat. He obtained gases containing ethylene and propylene, 300 g. of material (b.p. 20–30°C.) containing divinyl and butylene, 2500 g. of material (b.p. 30–40°C.) consisting for the most part of isoprene and trimethylethylene, 700 g. of material (b.p. 70–80°C.) consisting of 10 per cent of benzene and also containing olefins and diolefins, 400 g. of material (b.p. 95–110°C.) consisting of 60 per cent of toluene, and also olefins and diolefins, and finally 400 g. of material (b.p. 95–100°C.) consisting of more than 75 per cent of xylene.

Except for the work of Mokiewski there seems to have been little interest in the pyrolysis of pinene or turpentine from about 1884 to 1909. In 1909 this subject came to the fore because of the developments in research on synthetic rubber and the consequent need of a cheap source of isoprene.

Harries and Gottlöb (65) obtained a 1 per cent yield of isoprene from commercial *d*- and *l*-pinene by means of the isoprene lamp. However, they attributed the formation of isoprene to limonene present as impurity in pinene. In addition to the isoprene, gaseous compounds were liberated, while thick saturated oils of high boiling point remained in the flask.

Contrary to the assumption of Harries and Gottlöb, Herty and Graham (77) have shown that isoprene is formed from pinene. They separated turpentine into fractions boiling at 155–156°C., 169–175°C., and above 175°C. The first fraction should be primarily pinene, and the second and third should include all of the dipentene or limonene. They used a modified isoprene lamp and obtained an 8 per cent yield of isoprene from the pinene fraction, a 0.5 per cent yield from the middle fraction, and no isoprene from the highest boiling fraction. Turpentine without fractionation yielded 5.5 per cent of isoprene, but no information was given concerning the nature of the other products obtained.

TABLE 18

Pyrolysis of turpentine

MATERIAL USED	TUBE AND CONTENTS	TEMPERATURE	ISOPRENE
		degrees C.	*per cent*
Fraction of wood turpentine boiling 150–180°	Pyrex tube (empty)	450	0.0
		500	0.75
		550	3.0
		600	4.5
		650	2.7
		700	2.5
Fraction of wood turpentine boiling 150–180°	Pyrex filled with porcelain chips	350	0.0
		400	0.5
		450	2.5
		500	4.4
		550	4.0
		600	Av. = 4.5
Wood turpentine (not fractionated)	Pyrex tube with CuO and $CuCl_2$	450	1.5
		500	2.0
		550	2.5
		600	2.5
		650	Tube plugged by carbon deposition
Gum turpentine (not fractionated)	Iron tube (empty)	450	Av. = 4.98
		500	0.5 ?

Schorger and Sayre (146) are in agreement with Herty and Graham's opinion that the formation of isoprene from turpentine is not due to the dipentene or limonene present. They have shown that under the same conditions turpentine and α- and β-pinene yield about the same amount of isoprene, approximately 10 per cent.

The thermal decomposition of turpentine has also been studied by Mahood (99), who found that when the vapors were passed through an empty Pyrex tube the maximum yield of isoprene was obtained at 600°C., while when the same tube was filled with porcelain 500°C. appeared to be the optimum temperature. When this tube was filled with a mixture of copper oxide and cupric chloride, prepared according to the patent issued to Gross (58), there was no increase in yield, although Gross claimed a 40 per cent yield of isoprene from turpentine. With an iron tube and no contact material the most suitable temperature for the production of isoprene appeared to be 450°C.

Wood turpentine, which contains a considerable amount of limonene, might be expected to give a larger yield of isoprene than gum turpentine according to Harries, but Mahood's results do not confirm this. Table 18 compiled from Mahood's data serves to illustrate this.

"Complete analyses of the various fractions were not made, but qualitative tests showed considerable quantities of terpenes in the higher boiling fractions obtained in cracking at lower temperatures, while hydrocarbons of the benzene series and olefinic hydrocarbons are the chief constituents of all fractions formed at cracking temperatures above 400°."

Toluene was found to be a chief constituent of the fraction boiling between 100–125°C. Cymene was identified in the fraction boiling between 165 and 180°C. and *m*-xylene in the fraction boiling at 150 to 165°C. "The gas formed had an odor somewhat similar to coal gas and burned with a luminous flame. Of this material 10 to 22.5 per cent by volume dissolved in fuming sulfuric acid, showing that olefins were present to that extent."

Non-catalytic decomposition in the presence of diluents or under reduced pressure. Staudinger and Klever (160) have found that turpentine yields a very small amount of isoprene when the vapors in high dilution with nitrogen or under 2–3 mm. pressure are passed over a hot platinum coil. However, they point out the fact that contrary to the results obtained by earlier investigators (107), the isoprene fraction contains very little trimethylethylene. On the other hand, Prodrom (120) has reported that the decomposition of pinene in vacuo at "high" temperatures gives the following components: crude distillate, 42 per cent (crude isoprene, 25 per cent); residue, 44 per cent; and losses due to gas, 14 per cent.

A patent to Silberrad (154) for the production of isoprene by heating turpentine under reduced pressure gives the following results: "Eight liters of turpentine were passed through a metallic tube heated to 550°, and the pressure was reduced to 5–16 mm. The products obtained were 24 cc. of a liquid, b.p. 5–16°, 723 cc. crude isoprene, 537 cc. benzene, toluene, xylene, etc., and 6686 cc. unchanged turpentine but no sesquiterpene or resin. Calculating the yield of isoprene on the basis of turpentine converted, the yield of crude isoprene is 55 per cent and pure isoprene

35 per cent. At the same temperature but about 200 mm. pressure the yield of crude isoprene is only 33 per cent and that of sesquiterpene and resin 9.2 per cent."

In 1909 Woltereck (193) obtained a patent covering the production of isoprene by passing turpentine mixed with nitrogen through an iron tube filled with inert material, such as wire gauze or perforated disks, the purpose of the inert material being to augment the contact surface. He stated that the yield of isoprene was proportional to the dilution and claimed a better yield than Tilden. However this means little, for Tilden's yield, based on his own figures, was less than 5 per cent and according to Mokiewski's statement, was less than 2.5 per cent.

Heinemann (71) patented the use of steam as a diluent for turpentine vapors. The mixed vapors were passed through a tube of suitable metal or refractory material at a temperature of about 750°C. The temperature range specified is from 650–950°C., as temperatures above 950°C. are not suitable because of the decomposition of the water. At 750°C. Heinemann claims a 40 to 50 per cent conversion of the turpentine into hydrocarbons boiling below 100°C., 60 per cent of which is isoprene.

Some years after these patents were issued, Ostromisslensky (113) stated that the gases and liquid hydrocarbons boiling between 60 and 150°C., obtained from the pyrolysis of turpentine, might be used as diluents for the pyrolysis of additional quantities of turpentine.

Catalytic decomposition. Undoubtedly some of the early work on the pyrolysis of turpentine might be classed as catalytic. For example, it will be shown in the following paragraphs that iron has a definite catalytic effect in this reaction, and Hlasiwetz, Schultz, and Tilden used iron tubes for their experiments. Since this is the case, the work of Sabatier, Mailhe, and Gaudion (137) may be considered as a continuation of some of the early work, for they have included iron in their study of the effect of different metals at different temperatures.

Using finely divided copper maintained at 500°C., the products from the pyrolysis of pinene were (1) a large quantity of gas which contained hydrogen and ethylenic hydrocarbons, (2) an 8 per cent yield of a greenish liquid boiling below 120°C., (3) a 5.9 per cent yield of a liquid boiling between 120 and 150°C., (4) a 76.1 per cent yield of liquid boiling between 150 and 185°C., and (5) a 10 per cent yield of products boiling above 185°C.

With copper at 600–630°C. more gas was formed, the low-boiling fraction was amber colored, and a tarry residue was deposited on the catalyst. A liquid fraction amounting to 13.3 per cent, which boiled below 95°C., contained a small amount of benzene and toluene with isoprene, 1,3-

pentadiene, amylene, and hexene. The next fraction, boiling range 95–150°C., of which there was 27 per cent, was made up of 63 per cent ethylenic compounds and the remainder aromatics. The third fraction, comprising 31.4 per cent and boiling at 150–185°C., contained cumene, cymene, methylbenzene, and terpenes isomeric with pinene. The last fraction, of which there was 9 per cent, was made up of condensed terpenes, olefins, and diolefins and boiled above 185°C. The total amount of aromatics formed at 600–630°C. was about 31 per cent, much more than the amount produced at the lower temperature.

Nickel at 600°C. caused a very energetic decomposition of pinene, and the reaction differed from that with copper in that there was an abundant deposition of carbonaceous material. The gas liberated was rich in hydrogen and little liquid condensed. The activity of the metal soon diminished, as carbonaceous material deposited on it, and with this diminution the gas became less abundant, and the reaction products resembled those formed in the presence of copper. This may be due to carbon acting as a catalyst in both cases.

Cobalt at 600°C. gave results intermediate between those of copper and nickel. Iron acted more like nickel, causing intense charring.

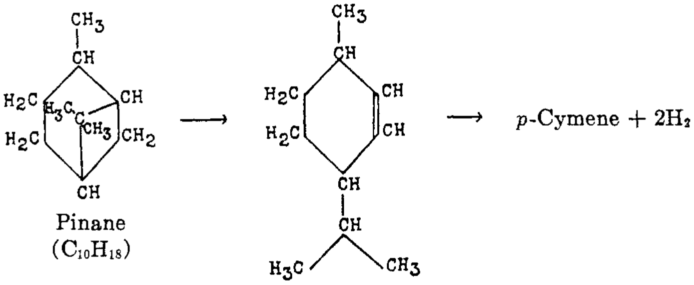
Heinemann (72) was granted patents for the production of isoprene by passing turpentine through copper or silver tubes or over finely divided copper or silver at temperatures of 480° and 450°C., respectively. He claimed good results with a copper tube of 6 mm. diameter and 4 meters in length closely wound into a coil. With a rate of flow of vapors of 2000 cc. per hour, a yield of 25 per cent of isoprene is claimed. Heinemann warns that the higher the temperature the more polymerization there is of isoprene to dipentene.

A few years after this patent was issued, Stephan (166) obtained a patent for the production of isoprene by passing nopinene (β-pinene) over iron or other metal so that the nopinene was heated above 600°C.

In the course of his investigations of irreversible catalysis, Zelinsky (197) found that either *d*- or *l*-pinene yields a mixture of cymene and dihydropinene when the vapors are mixed with carbon dioxide and passed over palladinized asbestos at 190–200°C. The mixture of cymene and dihydropinene was passed through the same tube containing palladinized asbestos at 200°C. and again at 150°C. The final product was a mixture of menthane and dihydropinene, and the reaction was outlined as follows:

$$\text{Menthane} \leftarrow \text{cymene} \leftarrow \text{pinene} \rightarrow \text{dihydropinene}$$

The dihydropinene (pinane) resulting from the above reaction was dehydrogenated by Zelinsky and Lewina (199) to *p*-cymene. The equation for the reaction in the presence of carbon dioxide and platinized charcoal at 300°C. is as follows:



Pinane ($C_{10}H_{18}$)

Tetrahydrocymene ($C_{10}H_{18}$)

Zelinsky and Lewina (200) later extended their study of irreversible catalysis to nopinene (β-pinene). When this hydrocarbon is passed over palladinized asbestos at 190°C. at the rate of six to eight drops per minute, a mixture of *p*-cymene and dihydropinene is obtained. Like α-pinene, then, the beta compound, in contact with palladinized asbestos, undergoes simultaneous hydrogenation and dehydrogenation. The suggestion is offered that β-pinene is first converted to the α-form.

Treibs and Schmidt (172) found that nickel and copper catalysts exhibited a somewhat similar behavior, transforming β-pinene into cymene and pinane.

Freund (48) treated French turpentine, containing *l*-pinene as its chief constituent, with anhydrous aluminum chloride under varying conditions, until solid or semisolid polymers were obtained. These polymers were then pyrolyzed at temperatures up to about 360°C. It was found that the resulting hydrocarbon fractions closely resembled those obtained from Java petroleum, particularly with respect to their optical rotations. Freund therefore concluded that terpenes were present among the mother substances of petroleum.

Previously Steinkopf and Freund (165) allowed aluminum chloride to react with turpentine oil, first at ice bath temperatures and then for various periods at room temperature, and obtained liquid and solid products along with considerable unchanged turpentine. The solid was a brittle substance (m.p. 77–78°C.) having the formula $(C_{10}H_{16})_x$.

Similar treatment of pure *l*-pinene gave the same result.

When the aluminum chloride was added with vigorous stirring a "tough mass" resulted, and if this was then heated, liquid and gaseous products were formed. From 200 g. of turpentine there was obtained 3.5 l. of gas, 126 g. of liquid, and about 100 g. of residue, including the aluminum chloride.

The gas consisted chiefly of paraffin hydrocarbons, with some cycloparaffins, and traces of unsaturates.

The following substances from the liquid product were identified by means of physical constants: pentane, isopentane, trimethylethylmethane (?), octanaphthene, various polynaphthenes not absolutely identified, fractions containing mixtures of C_nH_{2n-2} and C_nH_{2n-4} hydrocarbons, and possibly dihydropinene. Decanaphthene and benzene were identified by nitration. There was also obtained a high-boiling fraction resembling natural lubricating oil.

Routala (124) treated Finnish turpentine oil with condensation agents such as zinc chloride, alumina and chlorine, aluminum bromide, and aluminum chloride. The latter was the most effective. A turpentine fraction (b.p. 160–167°C.) yielded a mixture of paraffin, olefin, polyolefin, and naphthene hydrocarbons, similar in composition to ordinary petroleum. Ethyl and methyl chlorides were also produced.

Crude or partially purified turpentine oil gave, on treatment with aluminum chloride, principally semisolid pitchy substances.

Electrical decomposition. Berthelot (17) observed that no gas was liberated by the action of the electrical discharge on pinene, but that a slight rise in temperature resulted. The liquid was not discolored, and most of the pinene was recovered unchanged. There was isolated, however, a small amount of a diterpene formed by the polymerization of pinene. This polymerization, though slow, was especially clean cut in an atmosphere of nitrogen or hydrogen.

Urbain (176) reported that ethylene, acetylene, isoprene, and other substances were produced by the action of the electric arc on pinene.

The decomposition of pinene in a glow discharge has been carried out by Linder and Davis (96). The gases produced are hydrogen, acetylenes, olefins, and paraffins, but it is worthy of note that these gases are produced at a very much slower rate than in the case of limonene and dipentene. The solid product identified was *p*-diphenylbenzene.

Catalytic hydrogenation and dehydrogenation. Sabatier and Gaudion (136) have done some interesting work on the hydrogenation of pinene, using various metals as catalysts. They point out that it is well-known that the hydrogenation of benzene hydrocarbons, cyclohexenes, and terpenes, under the action of nickel at temperatures in the neighborhood of 180°C., yields the corresponding cyclic hydrocarbons or cycloalkanes. In particular, pinene (138) forms the dihydride without any secondary reaction, but the phenomenon changes its aspect when the temperature is raised.

If the vapors of pinene, carried along by hydrogen, are directed onto a column of nickel maintained at 350–360°C., a liquid is obtained which distills at 160–175°C. and is composed of hydrocarbons—cumene, probably menthane (rather than pinane) and, above all, cymene—resulting from simultaneous hydrogenation and dehydrogenation. The presence of hydrogen is indispensable for the reaction, for if the current of hydrogen is stopped, pinene gives only a mixture of terpenes, the principal constituent of which is dipentene. The main reaction in this case, then, is a simple isomerization by heat.

Turpentine has also been treated in the above manner and, as would be expected, was converted into a complex mixture which contained little benzene but an abundance of cyclic and diethylenic hydrocarbons.

Zelinsky and Lewina (199) found that when *l*-pinene was mixed with hydrogen and the vapors passed over palladinized asbestos at 195–200°C., a dihydro product was obtained which was identical with dihydropinene.

TABLE 19

Pinene

TIME	AUTOXIDATION	POLYMERIZATION IN OXYGEN	POLYMERIZATION IN CARBON DIOXIDE
days	*per cent*	*per cent*	*per cent*
1	44	2	1
2	55	3	2
3	70	4	3
4	86	5	4

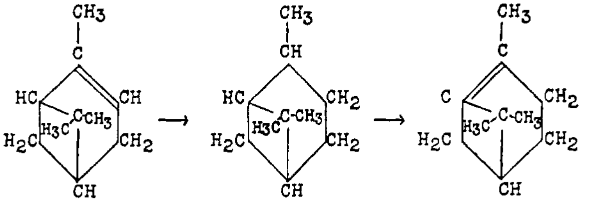
However, when *d*-α-pinene was used and the temperature changed to 157–158°C., the dihydro product boiled at 169–169.5°C. instead of 166.5–167.5°, the boiling point of dihydropinene. This fact, as indicated by Zelinsky, shows that catalytic reduction of pinene varies according to the temperature.

Rearrangement and polymerization. (*1*) *Elevated temperatures.* As has been stated previously, Wallach (184) discovered the conversion of pinene to limonene by heat, and Mahood used this procedure to prepare dipentene. Recently Conant and Carlson (32), from their study of the rate of isomerization, have indicated that fifty hours heating at 200°C. is necessary for the complete conversion of pinene to dipentene.

As Kassel (86) points out, this reaction is of particular interest, for it is the only known example of a presumably unimolecular rearrangement, while all other first-order gas reactions are decompositions. Smith (156) had determined the order of the reaction but considered it a racemization rather than a rearrangement.

(*2*) *Elevated temperatures in the presence of oxygen.* The relative rate of autoxidation and polymerization of pinene at 80°C. was studied by Staudinger and Lautenschlager (161), and the relationships shown in table 19 were determined.

(*3*) *Catalyzed by hydrogen and palladium black.* In some earlier work Zelinsky (195) found that α-pinene obtained from French turpentine oil (levo) was isomerized at room temperature by the action of palladium black covered with anhydrous ether and saturated with hydrogen. The isopinene so formed was supposed to be produced from a hypothetical intermediate, hydropinene, as follows:



α-Pinene Hydropinene Isopinene (γ-pinene)

It is of interest to note that the structure which Zelinsky gives for isopinene is contrary to Bredt's rule (82).

It was observed by Richter and Wolff (122) that an almost quantitative conversion of β-pinene into α-pinene resulted when the former was shaken with palladium and hydrogen at room temperature. If the reaction was allowed to continue indefinitely, hydrogenation to pinane resulted.

(*4*) *Catalyzed by salts and weak acids.* Berthelot (15) in 1853 observed that boron trifluoride readily transformed pinene into a polymer (boiling at 300°C. or above) with the evolution of heat, but without decomposition or gaseous evolution. The optical activity disappeared during the reaction.

Weak acids, as oxalic, tartaric, and acetic, as well as zinc chloride and silicon tetrafluoride, were without action in the cold, although polymerization occurred to a greater or less extent at 100°C. in the presence of all but acetic acid and silicon tetrafluoride. The action of zinc chloride, slight at 100°C., was much more intense at 270°C., where pinene begins to be affected by heat alone. The course of the reaction was followed by the changes in density and optical rotation.

Heating at 100°C. in the presence of calcium, barium, and strontium chlorides, potassium cyanide, calcium fluoride, magnesia, sodium chloride, and mossy platinum caused no change, although at 200–240°C., where heat alone begins to have an effect, most of these substances did appear to exhibit a catalytic influence. The chief product in each case was given the formula $C_{20}H_{32}$.

The product of the action of oxalic acid formed only a trace of artificial camphor on treatment with hydrochloric acid, and was not hydrated in the presence of nitric acid. The product of the action of zinc chloride at 100°C., on the other hand, was readily hydrated. The action of zinc chloride also resulted in the evolution of hydrogen.

Carter, Smith, and Read (36) have recently found that both *d*- and *l*-pinene were readily polymerized to diterpenes in the presence of syrupy phosphoric acid. α- and γ-terpinene were formed simultaneously.

A similar observation was reported by Dehn and Jackson (40), who found that pinene and other terpenes were polymerized, and pinene was isomerized to dipentene and terpinene.

Turpentine gave a variety of products, among them colophene.

The polymerization of pinene with phosphoric acid has been discussed in the section on phellandrene, which behaved similarly.

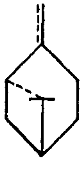
Dulou (38) made a careful study of polymerization of the pinenes to give dipinenes. He catalyzed the reaction by acetic–sulfuric acid mixtures. From carefully purified α-pinene, obtained from Aleppo turpentine, he obtained a dipinene ("α-dipinene," b.p. 194°C. at 27 mm., d_{15} 0.930, n_0^{20} 1.5107, $(\alpha)_J$ 0, slightly viscous). On using β-pinene, obtained from Bordeaux turpentine, there resulted another dipinene ("β-dipinene," b.p. 174°C. at 17 mm., d_{20} 0.938, n_0^{20} 1.5177, $(\alpha)_J$ 0).

Both the bromine number and the Raman spectra indicated these two dipinenes to be mixtures of mono- and di-ethylenic hydrocarbons, with the monoethylenic compound being present in α-dipinene in the larger amount. Carter, Smith, and Read (36), on the other hand, found that the molecular refractivity of the diterpenes which they obtained by the action of phosphoric acid pointed to the presence of three double bonds. These authors, as well as Dulou, believed them to be dicyclic. The latter found that his α- and β-dipinenes were hydrogenated only to the extent of about 1 per cent in the presence of palladium or platinum black.

On dehydrogenation with sulfur, Dulou obtained a small amount of what he believed to be a diisopropyldiphenyl.

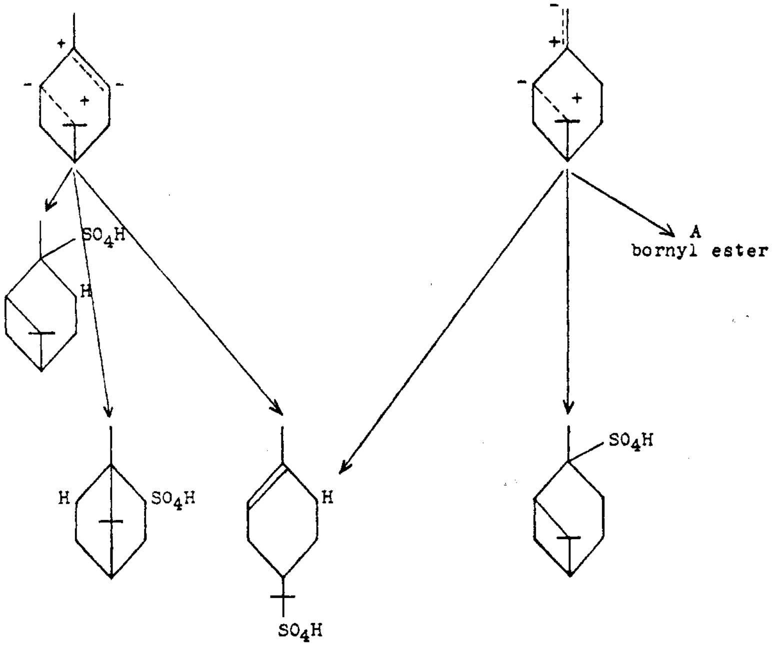
In devising a mechanism for the formation of dipinenes, Dulou applied the electronic theory of valence to the pinenes. He considered α- and β-pinenes to be conjugated systems, and formulated them thus:

α-Pinene

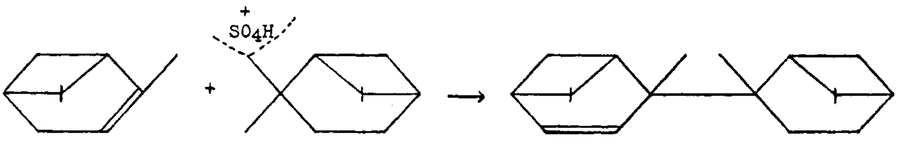


β-Pinene

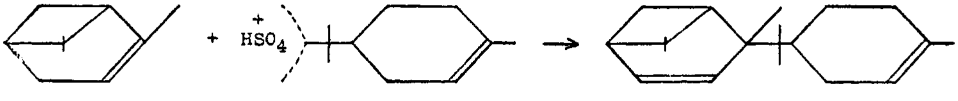
They were believed to be polarized, and to possess the possibility of adding sulfuric acid as shown in the following scheme:



On this basis Dulou proposed the following mechanisms for the formation of mono- and di-ethylenic diterpenes:



Monoethylenic diterpene



Diethylenic diterpene

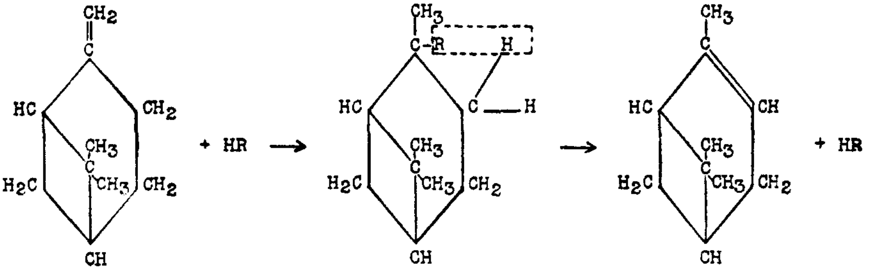
The mechanism of Carter, Smith, and Read, previously described, was similar to that of Dulou in that both were based on the conjugated system existing in α- and β-pinenes. At that point, however, the two differed somewhat, in that that of the former postulated the addition and subsequent splitting out of water with the formation of triethylenic diterpenes.

Delepine (37) heated β-pinene with an approximately equal weight of benzoic acid at 150°C. for twenty to fifty hours, and found some α-pinene among the resulting esters and alcohols. By heating *l*-β-pinene with an excess of trichloroacetic acid at 60°C. there resulted a rapid transformation of a part of the β-pinene into α-pinene. He suggested that an ester might be intermediate in this reaction.

Austerweil (10) heated β-pinene with organic acids, e.g., two moles of salicylic acid with one mole of β-pinene at about 160°C. Besides a 35 to 36 per cent transformation into bornyl esters, he obtained a 1 per cent conversion to a mixture of α-pinene, limonene, and terpinene.

By using a weaker acid, as benzoic or abietic acid, at a temperature not exceeding 145°C., α-pinene was the chief product. The weaker the acid, the less the quantity of bornyl esters produced. Thus when phenol was used, in the absence of water, only traces of bornyl and fenchyl esters were found, α-pinene being the only product.

The reaction was formulated as follows:



β-Pinene α-Pinene

Aschan (7) gave a similar mechanism for the analogous action of hydrochloric acid on β-pinene.

On heating α-pinene for ten to twenty hours with an equal weight of benzoic acid at 125–130°C., Austerweil (11) obtained a very small quantity of limonene and 3 to 5 per cent of bornyl benzoate. Most of the α-pinene remained unchanged.

The addition of antimony trichloride in small amounts to *l*-pinene was found by Riban (123) to cause polymerization with the evolution of heat. The chief product was a transparent solid corresponding to the formula $C_{40}H_{64}$, and called tetrapinene (tétratérébenthène) as it was supposed to be a tetramer of *l*-pinene. It formed a monohydrochloride, a dihydrochloride, and a dihydrobromide, all amorphous.

The existence of colophene ($C_{20}H_{32}$) among the reaction products was also indicated.

On being heated above 350°C. the tetramer decomposed to simpler hydrocarbons; colophene, a hydrocarbon with a citrus-like odor, corresponding to the formula $C_{10}H_{16}$, called "β-isopinene," and a viscous substance of high boiling point, probably the "metapinene" of Berthelot.

The reaction of depolymerization was represented by Riban thus:

$$\underset{\text{Tetrapinene}}{C_{40}H_{64}} \rightarrow \underset{\text{Colophene}}{C_{20}H_{32}} + \underset{\text{Isopinene}}{2\,C_{10}H_{16}}$$

Genveresse (57) found that heating 1 kg. of pinene with 250 g. of crystalline arsenic acid just below the boiling point for half an hour resulted in an energetic reaction. The chief product was terpinene, along with terpineol. The transformation was explained on the basis of the hydration of pinene, followed by a dehydration of a part of the hydrate.

A recent patent (142) describes the catalytic conversion of α- or β-pinene to camphene by the use of water-soluble neutral sulfates that retain one molecule of water of crystallization up to 220°C. Among the examples cited, pinene is refluxed with $MgSO_4 \cdot H_2O$ to yield camphene. This catalyst may be replaced by the corresponding sulfates of zinc, iron, cobalt, nickel, etc.

Another patent (143) claims that acid catalysts, e.g., for the transformation of nopinene to pinene, or nopinene and pinene to camphene, are made more regular and of high efficiency by converting them to salts by means of bases and liberating them afresh from the salts. The catalysts are inorganic acids as titanic, silicic, vanadic, arsenic, molybdic, antimonic, or tungstic acids, complex acids such as borotungstic, tungstosilicic, stannophosphoric, boroacetic, or aluminoöxalic acids, or acid salts such as acid phosphates of magnesium, manganese, or vanadium.

(*5*) *Catalyzed by sulfuric acid.* Like other olefins one would expect the terpenes to form addition products with sulfuric acid, and this possibility is not excluded, but some interesting rearrangements and polymerizations have also been noted.

The first dipinene was prepared by Deville (39) in 1840. He obtained colophene by treating turpentine oil with sulfuric acid. No camphene was found, but rather an isomeric substance was formed during the reaction.

Bouchardat and Lafont (26) treated levorotatory turpentine oil with one-tenth its weight of sulfuric acid. The reaction mixture was then heated at 150°C. in an autoclave with an excess of alcoholic potash, giving camphene, terpinene, terpinolene, and polymers of those substances.

In some experiments on the hydration of pinene, Flavitski (50) found that when *l*-pinene was warmed with alcoholic sulfuric acid, an isomeric hydrocarbon appeared to be formed.

Armstrong and Tilden (1) obtained camphene from turpentine by the action of concentrated sulfuric acid. Wallach (187) interpreted this change as an addition of the acid to one of the double bonds and its subsequent splitting off, taking a hydrogen atom from a different position. Wallach obtained α-terpinene by heating α-pinene with concentrated sulfuric acid.

The rearrangement of *dl*-α-pinene to terpinolene when the former is shaken with half its volume of 50 per cent alcoholic sulfuric acid was reported by Henry and Paget (75).

The composition of the monoterpene fraction obtained by the treatment of turpentine with 50 per cent sulfuric acid at 80°C. has recently been studied by means of Raman spectra. Dupont and Gachard (43) have thus identified cymene, camphene, limonene, α-terpinene, γ-terpinene, terpinolene, and 1,4-cineole. In addition it was determined that four other substances, of unknown nature, were present.

Contrary to the opinion of other investigators, terpinolene was found to be present only in small amounts.

(6) Catalyzed by adsorbents. It has been observed by Gurwitch (59) that when pinene was mixed with 5 per cent of freshly dehydrated Florida earth, vigorous boiling occurred. A larger proportion of the earth might occasion the ejection of the whole of the liquid from the containing flask. Fractionation of the product of this reaction yielded 6 to 7 per cent of camphene and 37 per cent of sesqui- and poly-terpenes boiling above 200°C. No dipentene was found. No other adsorbents were found to cause polymerization, although a small amount of heat was generated by the action of blood charcoal or alumina.

More recently Venable (181) has studied the same reaction and finds that pinene yields no camphene. He attributes the camphene in Gurwitch's product to its presence in Russian turpentine oil from which Gurwitch probably obtained his pinene. Other products similar to those of Gurwitch were obtained, including a large amount of monoterpenes other than pinene, boiling from 160–185°C., and a polymeric fraction which begins to boil at 320°C.

Venable states that the dipinene, present in his high-boiling products (b.p. 320°C.), is almost always formed when a terpene is treated with active fuller's earth. This is the case not only with α-pinene but also with dipentene, terpinene, camphene, β-pinene, active limonene, and sabinene. Aromatic compounds such as *p*-cymene, however, are nonreactive. The reaction is not promoted by iron gel, silica gel, or activated charcoal.

In a paper published at about the same time as that of Venable, Gurwitch (60) reaffirmed the formation of camphene from pinene in the presence of floridin, and proceeded to discuss the mechanism of the transformation.

According to him, the rearrangement has three possible explanations; (1) the pinene molecule rearranges directly, without the formation of any intermediate, as a result of the direct catalytic action of floridin; (2) pinene combines with the water of hydration of floridin to give an alcohol, which then splits off water to give the isomeric hydrocarbon; (3) floridin first brings about, as the result of strong adsorption, a polymerization of pinene, analogous to that of amylene, which then, as a result of the liberated heat, is broken down to the isomeric terpenes. Such decompositions, with the formation of camphene, terpinene, and other monoterpenes, have been observed by Tilden and Armstrong (173) as a result of the distillation of polyterpene mixtures obtained in the treatment of pinene with concentrated sulfuric acid.

The reaction, itself, was violent unless both pinene and floridin were cooled before being mixed. At −20°C. it proceeded smoothly and slowly, hence Gurwitch argued that the products of the rearrangement remained adsorbed on the surface of the catalyst. In confirmation, it was found that if the mixture was then allowed to come to room temperature, the action continued slow, being hindered by the adsorbed material. The slowing up of the reaction at low temperatures was not thought to be due to any lessened tendency for the reaction, itself, to occur, but rather to slower diffusion of the products of reaction from the surface of the catalyst. Conversely, without cooling, the reaction was violent because of the rapid diffusion from the surface of the catalyst, which became even more rapid with mounting temperature.

Besides isomeric monoterpenes, the action of floridin on pinene at low temperatures gave polymerization products. If one of the first two of the above explanations is correct, then these polymerization products are the result of secondary reactions, and the quantities of rearrangement products should be less than at higher temperatures. On the other hand, if the polyterpenes are intermediates in the rearrangement, in accordance with the third explanation, they must break down into isomeric monoterpenes as a result of thermal action. The reaction products should therefore be correspondingly richer in undecomposed polyterpenes at low temperatures. As shown in table 20, the latter was found to be the case.

All of these experiments were performed with catalysts selected from one lot of floridin with water content of 6.19 per cent. It is possible, however, to suppose that under the influence of various temperatures, the water content may have varied. The data in table 21 were collected by shaking the pinene and floridin, both at −20°C., for half an hour, and then at room temperature for two and one-half hours.

The water content of the floridin also affected the intensity of the reaction started at room temperature, as shown in table 22.

A comparison of tables 21 and 22 shows that the intensity of the reaction decreases and the polyterpene content increases with increasing water content. If the rearrangement proceeds by addition and splitting-out of water, it would be expected that at low temperatures, where the reaction proceeds slowly, a part of the pinene, by addition of water, would on depolymerization result in the presence of some terpene alcohols. None were found, however.

TABLE 20

Polymerization of pinene in the presence of floridin

TEMPERATURE	UNCHANGED PINENE	POLYTERPENES IN UNCHANGED PINENE
degrees C.	*per cent*	*per cent*
About −20	About 0.6	>35
About −12	About 5.0	22
About 0	About 27	10.5
About 20	About 99	4.9

TABLE 21

Effect of water content on the polymerization of pinene

WATER CONTENT OF FLORIDIN	UNCHANGED PINENE	POLYTERPENES IN UNCHANGED PINENE
per cent	*per cent*	*per cent*
6.19	99	4.9
8.1	67	7.1
10.0	11.2	20.1
11.83	1.2	30.0
18.2	0	—

TABLE 22

Effect of water content of floridin on intensity of reaction in polymerization of pinene

WATER CONTENT OF FLORIDIN	INITIAL TEMPERATURE OF PINENE AND FLORIDIN	MAXIMUM TEMPERATURE ATTAINED IN REACTION
per cent	*degrees C.*	*degrees C.*
6.19	18	184
8.1	18.5	161
10.0	19	38
11.83	18	22
18.2	18.3	18.5

Gurwitch drew the following conclusions regarding the mechanism of the rearrangement: (1) the primary products of the action of floridin on pinene are polyterpenes; (2) isomeric monoterpenes are formed by the splitting of these polyterpenes by the heat of polymerization; (3) the water of hydration of the floridin plays a part in the process; and (4) a source of the energy required for the polymerization of pinene is to be found in the physicochemical affinity between pinene and the strongly dehydrated floridin.

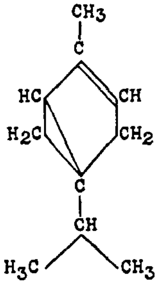
Further work in this field is that of Gallas and Montanes (51), who report that pinene gave no camphene on being heated to 150–200°C., with silex, active carbon, kieselguhr, or manganese oxide, but that dipentene was formed. Of course the formation of dipentene might be attributed to a simple conversion of pinene by heat. Mulcey (109) has obtained similar results from pinene using alumina.

While none of the above authors mentioned the formation of cymene or menthane by the action of fuller's earth, Humphrey (81) has been granted a patent for the production of *p*-cymene from pinene, dipentene, or other terpenes, using fuller's earth, kieselguhr, and related substances as catalysts. An example follows: "305 parts of terpene, boiling point 170–185°, are heated under reflux condenser with 75 parts of fuller's earth at a temperature of 170–200° for a period of 10 hours." About 125 parts of crude cymene are obtained from the residual oil by fractionation. The crude product contains *p*-menthane and a large proportion of polymerized terpenes as well as *p*-cymene. In fact, the patentee states that two-thirds of the terpene is converted to polymers, $(C_{10}H_{16})_x$, distilling above 300°C. Higher temperatures and pressures yield different proportions of cymene and menthane.

Carpmall (28) claimed that α-pinene "can be prepared by heating β-pinene or oils containing substantial quantities of β-pinene in the presence of catalysts comprising inert substances of porous structure, e.g., porous pot, "permutit," bleaching earths, fuller's earth, and similar porous substances which contain silicic acid in hydrated form."

The work on turpentine and pinene is summarized in tables 23 and 24.

2. Thujene



α-Thujene

TABLE 23

Turpentine

REFERENCE NO.	TIME	TEMPERATURE	PRODUCTS	REMARKS
	hours	*degrees C.*		
(55)	—	"Heat"	More volatile than original; less volatile than original	
(14)	60	—	Little change	Refluxed in atmosphere of CO_2
(14)	10	250	Polymerization products (iso- and meta-turpentine)	Closed tube
(14)	2	300	Isoturpentine	
(144)	—	—	"Colophonon," terpene	Dry distillation
(79)	—	Red hot tube	Gas, carbon, dark brown oil, C_5H_8	Porcelain sticks in tube
(16)	—	Porcelain tube at moderate red heat	Benzene, toluene, xylene, cumolene, cymene, naphthalene	
(148)	—	Iron tube at dull red heat	Gas, benzene, toluene, *m*-xylene, naphthalene, anthracene, methylanthracene, phenanthrene	
(107)	—	—	Trimethylethylene and other products	
(77)	—	—	5.5 per cent yield of isoprene	
(146)	—	—	10 per cent yield of isoprene	
(99)	—	600	4.5 per cent yield of isoprene	Empty pyrex tube
		500	4.4 per cent yield of isoprene	Pyrex tube with porcelain
		550	2.5 per cent yield of isoprene	Pyrex tube with CuO and $CuCl_2$
		450	5.0 per cent yield of isoprene	Iron tube—no contact material
(160)	—	Hot platinum coil	Small amount of isoprene	Vapors in high dilution with N_2 or under 2–3 mm. pressure
(154)	—	550	Isoprene, benzene, toluene, xylene, no sesquiterpene or resin	Heating under 5–16 mm. pressure
(193)	—	—	Isoprene	Vapors mixed with N_2 and passed through iron tube
(71)	—	750	27 per cent yield of isoprene	Steam used as diluent

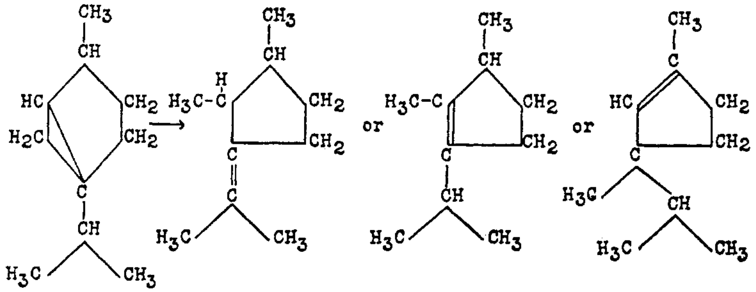
TABLE 23—*Concluded*

REFERENCE NO.	TIME	TEMPERATURE	PRODUCTS	REMARKS
	hours	*degrees C.*		
(72)	—	450–480	25 per cent yield of isoprene	Cu or Ag tubes or finely divided Cu or Ag in iron tube
(136)	—	350–360	A little benzene; abundance of cyclic and diethylenic hydrocarbons	Ni and stream of H_2
(1)	—	—	Camphene	Concentrated H_2SO_4
(108)	—	Dull red heat	Ethylene, propylene, butylene, divinyl, isoprene, trimethylethylene, benzene, toluene, xylene, olefins, and diolefins	Passed through a glass tube
(165)	—	0 and room temperature	Brittle polymer, $(C_{10}H_{16})_x$	$AlCl_3$ added
	—	0 and room temperature	"Tough mass"	$AlCl_3$ added with stirring
(165)			Paraffin and cycloparaffins, pentane, isopentane, trimethylethylmethane (?), octanaphthene, polynaphthenes, C_nH_{2n-2} and C_nH_{2n-4} hydrocarbons, dihydropinene (?), benzene, decanaphthene, high-boiling oil	Above "tough mass" heated
(124)	—	Room temperature	Paraffin, olefin, and naphthene hydrocarbons similar to petroleum	$ZnCl_2$, $Al_2O_3 + Cl_2$, $AlCl_3$ added
(40)	—	Room temperature	Variety of products, colophene	H_3PO_4 added
(26)	—	Room temperature and 150	Camphene, terpinene, terpinolene, polymers	H_2SO_4 added
(43)	—	80	Cymene, camphene, limonene, α-terpinene, γ-terpinene, terpinolene	50 per cent H_2SO_4; analysis by means of Raman spectra
(39)	—	—	Colophene, hydrocarbon isomeric with camphene	H_2SO_4 used

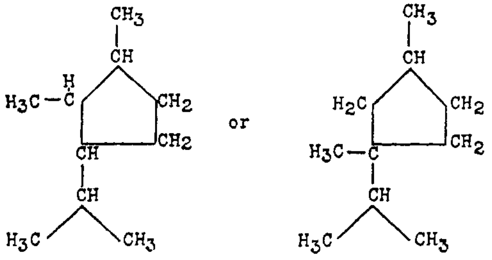
Catalytic decomposition. While no study of the non-catalytic pyrolysis of thujene has been found in the literature, Zelinsky and Kasansky (198) have reported that α-thujene, like pinene, undergoes irreversible catalysis in the presence of palladinized asbestos at 197–200°C. to form cymene, thujane ($C_{10}H_{18}$), and a hydrocarbon $C_{10}H_{20}$. The original hydrocarbon was passed over the catalyst in a quartz tube at the rate of four or five drops per minute. Zelinsky has written the reaction as follows:

$$\underset{\text{Cymene}}{3C_{10}H_{14}} \leftarrow \underset{\text{Thujene}}{5C_{10}H_{16}} \rightarrow \underset{\text{Thujane}}{C_{10}H_{18}} + C_{10}H_{20}$$

Thujane (199) in a strong stream of carbon dioxide was passed over platinized charcoal. Instead of the expected cymene and hexamethylene compound, the product proved to be a pentamethylene compound which could not be dehydrogenated further. The reaction is represented as follows:



Hydrogenation. In an earlier study of thujene, Zelinsky (194) reduced it, in the presence of nickel, to a hydrocarbon $C_{10}H_{20}$. On the basis of its physical constants he suggested the following formulas for this compound. Kasansky (87a) has shown the first formula to be correct.



Tschougaeff and Fomin (174) pointed out that thujene adds only one molecule of hydrogen when reduced under pressure in the presence of platinum at room temperature. The product is a bicyclic dihydrothujene or thujane.

TABLE 24

Pinenes

REFERENCE NO.	TEMPERATURE	CATALYST	PRODUCTS	REMARKS
	degrees C.			
(171)	Iron tube at dull red heat	—	Gas, acetylene, isoprene, benzene, *m*-xylene, cymene, carbon	Boiled in copper flask
(171)	Iron tube at bright red heat	—	Gas, benzene	
(65)	Glowing platinum wire	—	1 per cent yield of isoprene	
(77)	Glowing platinum wire	—	8 per cent yield of isoprene	
(146)	Glowing platinum wire	—	10 per cent yield of isoprene	
(120)	"High"	—	25 per cent isoprene, 17 per cent unidentified distillate, 44 per cent residue, 14 per cent gases	
(137)	500	Cu	Hydrogen, gaseous ethylenic hydrocarbons, 8 per cent liquid of b.p. <120°, 5.9 per cent liquid of b.p. 120–150°, 76.1 per cent liquid of b.p. 150–180°, 10 per cent liquid of b.p. >180°	
(137)	600–630	Cu	More gases than above, benzene, toluene, isoprene, 1,3-pentadiene, amylene, hexene, ethylenic compounds, aromatics, cumene, cymene, methylbenzene, isomeric terpenes, condensed terpenes, olefins, diolefins, tarry residue	

(137)	600	Ni	Large amount of carbon, gas rich in H_2, little liquid	
(137)	600	Co	Results intermediate between those from Cu and Ni at 600°	
	600	Fe	Like Ni causing intense charring	
(166)	500	—	Isoprene	β-Pinene used
(197)	190–200	Pd–asbestos	*p*-Cymene, dihydropinene, menthane	Vapors mixed with CO_2; α-pinene used
(199)	300	Pd–asbestos	*p*-Cymene	Vapors mixed with CO_2; dihydropinene used instead of pinene
(200)	190	Pd–asbestos	*p*-Cymene, dihydropinene	Vapors mixed with CO_2; β-pinene used
(136)	180	Ni	Dihydropinene	H_2
(136)	350–360	Ni	Cymene, menthane	Vapors mixed with H_2
(199)	195–200	Pd–asbestos	Dihydro derivative	H_2 and *l*-α-pinene
(199)	157–158	Pd–asbestos	Dihydropinene, but not same as above	H_2 and *d*-α-pinene
(184)	"Heat"	—	Limonene	
(32)	200	—	Dipentene	50 hours
(195)	Room temperature	Palladium black	Isopinene	H_2
(187)	100	—	α-Terpinene	α-Pinene used; concentrated H_2SO_4; 24 hours
(75)	Room temperature	—	Terpinolene	*dl*-α-Pinene shaken with 50 per cent alcoholic H_2SO_4
(59)	—	Florida earth	Camphene, sesquiterpenes, polyterpenes (no dipentene)	
(181)	—	Florida earth	No camphene, monoterpenes, polymers, dipinene	
(51)	150–200	—	No camphene, dipentene	Silex, active carbon, MnO_2, kieselguhr

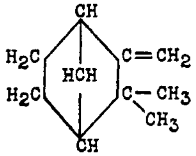
TABLE 24—*Concluded*

REFERENCE NO.	TEMPERATURE	CATALYST	PRODUCTS	REMARKS
	degrees C.			
(109)	—	Alumina	Similar to above	
(81)	170–200	—	*p*-Cymene, *p*-menthane, polymers	Fuller's earth, kieselguhr, etc.; 10 hours
(172)	—	Ni and Cu	Cymene, pinane	α-Pinene used
(17)	Room temperature	Electric discharge	Little change, slow polymerization to a diterpene	
(176)	Room temperature	Electric arc	Ethylene, acetylene, isoprene and other substances	
(122)	Room temperature	Pd + H_2	α-Pinene, pinane	β-Pinene used on continued action
(15)	Room temperature	BF_3	Dipinene	
	100	$(COOH)_2$	A dipinene	
		Tartaric acid	A dipinene	
		$ZnCl_2$	A dipinene	
	200–240	$CaCl_2$, $BaCl_2$	Slight effect	Heat alone begins to be effective at this temperature
		$SrCl_2$, KCN	Slight effect	
		CaF_2, MgO	Slight effect	
		NaCl, Pt	Slight effect	
(36)	Room temperature	H_3PO_4	A dipinene, α- and γ-terpinene	*d*- and *l*- pinene used
(40)	Room temperature	H_3PO_4	A dipinene, dipentene, terpinene	"Pinene and other terpenes" act thus
(38)	Room temperature	Acetic–sulfuric acid mixtures	α- and β-Dipinene	
(37)	150	Benzoic acid	α-Pinene	β-Pinene used
	60	Trichloroacetic acid	α-Pinene	*l*-β-Pinene used

(10)	160	Salicyclic acid, limonene, terpinene	α-Pinene	β-Pinene used
	145	Benzoic or abietic acid	α-Pinene	β-Pinene used
	—	Phenol	α-Pinene	β-Pinene used
(11)	125–130	Benzoic acid	Limonene	α-Pinene used
(123)	Room temperature	$SbCl_3$	$C_{40}H_{64}$ hydrocarbon, colophene	*l*-Pinene used
(57)	"Heated"	Crystalline arsenic acid	Terpinene	
(142)	220	$MgSO_4 \cdot H_2O$ or analogous salts of Zn, Fe, Co, Ni, etc.	Camphene	
(143)	—	Titanic, vanadic, silicic, arsenic, molybdic, antimonic, or tungstic acids; borotungstic, tungstosilicic, stannophosphoric, boroacetic, or aluminoöxalic acids; acid salts as acid phosphates of Mg, Mn, or U	α-Pinene	β-Pinene used
(50)	"Warmed"	Alcoholic H_2SO_4	Isomeric hydrocarbon	*l*-Pinene used
(60)	—	Floridin	Camphene	
(28)	"Heated"	Porous pot, "permutit," fuller's earth, etc.	α-Pinene	β-Pinene used

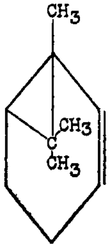
At a temperature of 155°C., Zelinsky and Kasansky (198) reduced thujene, in the presence of palladinized asbestos, to form a hydrocarbon $C_{10}H_{20}$, the properties of which are very nearly the same as those of the product of reduction over nickel. Similarly, thujane ($C_{10}H_{18}$), when treated in the same way, yields a product which appears to be 1,2-dimethyl -3-isopropylpentane, but its identity with this known compound was not fully established.

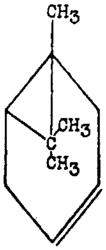
3. Camphene

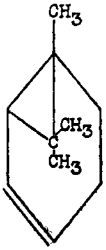


Camphene, which occurs in many natural oils (93), has been studied very little from the point of view of pyrolysis. Tilden (171) reported that its vapors when passed at atmospheric pressure through a glowing iron tube yielded "colophene." The term "colophene" has been used so differently by various investigators that it is safest to define it simply as a high-boiling polymerization product of terpenes.

By heating camphene with half its weight of phosphoric acid at 200°C. for ten to twenty hours, Fujita (49) obtained a terpene, isomeric with carene, and a diterpene, closely related to thujane. The structure of the terpene was said to be one of the following:







When heated with a mixture of sulfur and phosphorus pentoxide, camphene yielded *p*-cymene.

Kuwata (92) has recently obtained a dicamphene (b.p. 318–321°C.) by stirring a benzene solution of camphene with Japanese acid clay for five hours. The yield of the crude dimer was 66 per cent.

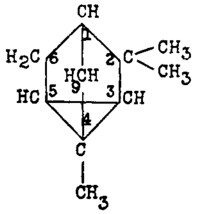
Staudinger and Klever (160) treated camphene, in high dilution with nitrogen under 2–3 mm. pressure, in a modified isoprene lamp and found that little or no isoprene was formed. What the products were, they did not state.

Simultaneous hydrogenation and dehydrogenation. In Sabatier and Gaudion's (136) work on simultaneous hydrogenation and dehydrogenation, which has been referred to previously, camphene was included in the group of terpenes studied. Camphene vapors mixed with hydrogen were directed onto a column of nickel at 350–360°C., with the result that the terpene was converted for the most part into cymene and cumene and only a small amount of a saturated hydrocarbon was obtained. These results are quite analogous to those obtained with limonene.

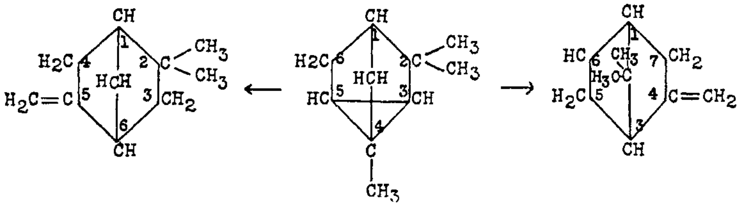
Hydrogenation. Some years previous to the above work, Sabatier and Senderens (138) had found that camphene yields a dihydro derivative, $C_{10}H_{18}$, when passed, with hydrogen, over nickel at 180°C.

D. TRICYCLIC TERPENES

1. *Cyclofenchene*



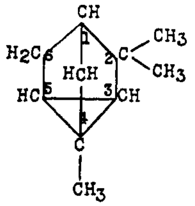
Catalytic decomposition. Zelinsky (199) has found that when cyclofenchene is passed over platinized charcoal at 300°C. it gives, in part, a mixture of α- and β-fenchene which arise from rupture of the trimethylene ring between carbon atoms 4 and 5 or 4 and 3.



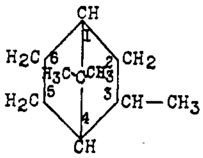
β-Fenchene (4-3 broken)   Cyclofenchene   α-Fenchene (5-4 broken)

But Zelinsky states: "Tricyclic systems are not so easily broken as bicyclic so part of the original material is recovered. The fenchene obtained, like fenchane and isobornylane, is not dehydrogenated at 300°."

Hydrogenation. Zelinsky (199) has studied the hydrogenation of cyclofenchene over platinized charcoal, forming isobornylane at a temperature of 155–160°C. The change, as shown below, involved the breaking of the trimethylene ring between carbon atoms 4 and 5.

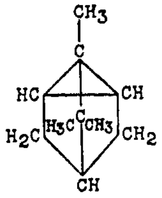


Cyclofenchene

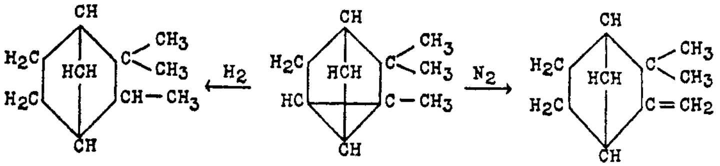


Isobornylane

2. *Tricyclene*

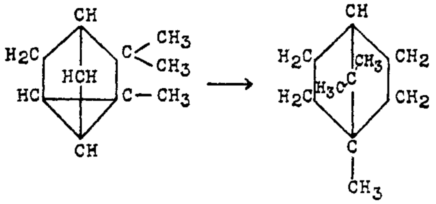


Meerwein and Emster (102) have reported that tricyclene is converted to camphene in quantitative yield if it is passed over nickel at 180–200°C., the vapors being carried along by a slow stream of nitrogen. If the nitrogen is replaced by hydrogen, isocamphene is obtained. The reactions may be represented by the following equation, in which a rearranged formula for tricyclene is used in order to make the actual relation between the compounds a little more clear.



Isocamphene ($C_{10}H_{18}$) Tricyclene ($C_{10}H_{16}$) Camphene ($C_{10}H_{16}$)

Platinized charcoal and hydrogen at 155–160°C., according to Zelinsky (199), cause the conversion of tricyclene to camphane. This is a result similar to those above, in that the trimethylene ring is broken, but in this case the break occurs between carbon atoms 4 and 5, while in Meerwein's work it was between carbon atoms 3 and 5.

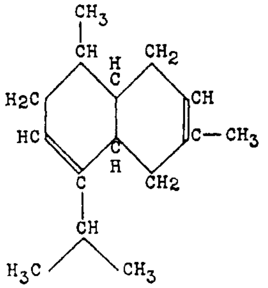


Tricyclene Camphane

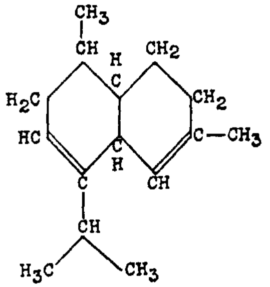
V. SESQUITERPENES

The pyrolysis of sesquiterpenes is almost an unexplored field. This may be due to the fact that the sesquiterpenes are of complex and, until recent years, largely unproven structures. But probably a greater deterring factor is the difficulty of obtaining them in pure condition.

1. CADINENE



β-Cadinene



α-Cadinene (131)

Cadinene appears to be quite stable, for Semmler and Jakubowitz (151) report that it is little changed even when heated for twelve hours at 330°C. in a bomb tube. The small amount of converted product appeared to be a monocyclic isomer of cadinene.

Lipishkin (97) has reported that when cadinene is heated in glacial acetic acid at 180–200°C., its rotation goes from −111.28° to −8°. The changes occurring were not investigated further.

Dehydrogenation

More recently Ruzicka and Stoll (131) have found that cadinene is dehydrogenated to cadalene, $C_{15}H_{18}$, when passed over platinum black and asbestos at 300–310°C. in a stream of inert gas such as nitrogen.

As stated previously, Ruzicka and his coworkers have dehydrogenated sesquiterpenes with sulfur. In this process the hydrocarbon is heated with three moles of powdered sulfur at temperatures ranging from 180–

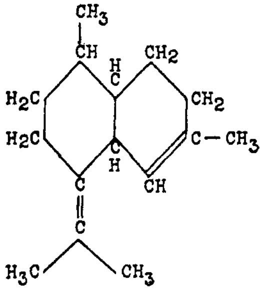
225°C. The reaction is complete within four or five hours and in some cases even less time is required. Ruzicka and Meyer (127) have written the equation

$$C_{15}H_{24} + 3S \rightarrow C_{15}H_{18} + 3H_2S$$

to represent the change that takes place in the case of compounds of the cadinene type.

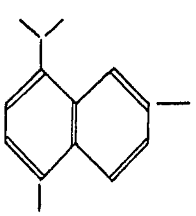
The first sesquiterpene (127) treated in this way was cadinene, from which cadalene, $C_{15}H_{18}$, was obtained. Shortly after this work was published, cadalene was proven (130) to be 1,6-dimethyl-4-isopropylnaphthalene. Calamene, zingiberene, and isozingiberene all behave like cadinene, yielding cadalene.

2. SESQUITERPENE FROM JAPANESE CEDAR OIL

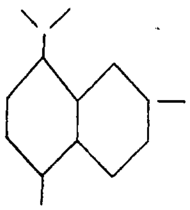


Catalytic decomposition

An unnamed sesquiterpene from Japanese cedar oil, according to Kimura (88), undergoes catalytic oxidation and reduction when heated to 280–300°C. for two hours in the presence of carbon dioxide and palladinized asbestos. The above structure has been proposed for this sesquiterpene, since this reaction yields decahydrocadalene and cadalene.



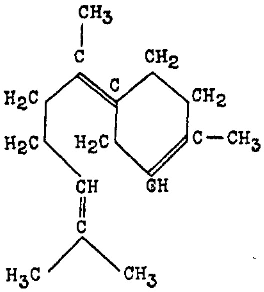
Cadalene



Decahydrocadalene

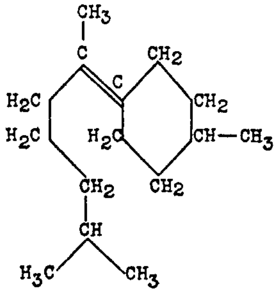
This work would indicate that the sesquiterpene is closely related to cadinene, but Kimura does not state that the two are isomeric.

3. BISABOLENE



Hydrogenation

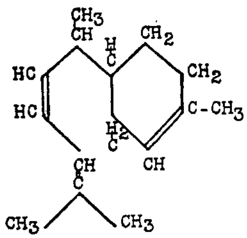
Bisabolene in cyclohexane solution may be hydrogenated to the tetrahydro derivative in the presence of platinum black at room temperature. Even at elevated temperatures Ruzicka and van Veen (135) have found that it does not add more than two molecules of hydrogen in this solvent. However, in glacial acetic acid the third molecule is absorbed quickly at room temperature. The suggested formula of the tetrahydro product is as follows:



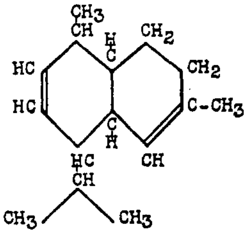
Dehydrogenation by sulfur

Ruzicka and van Veen (135) heated bisabolene with two moles of sulfur and obtained a compound with a benzene ring, as proven by oxidation to terephthalic acid.

4. ZINGIBERENE



Zingiberene
(135)

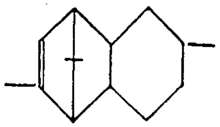


Isozingiberene
(155a)

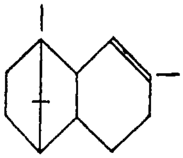
In Semmler and Becker's (149) work zingiberene was heated with isoprene for four hours in a bomb tube at 215°C. and yielded dipentene (probably from polymerization of isoprene); metazingiberene, boiling range 100–150°C. under 11 mm. pressure; a diterpene $C_{30}H_{32}$, boiling range 150–200°C. under 11 mm. pressure; and dizingiberene $C_{30}H_{48}$, boiling range 260–280°C. under 11 mm. pressure. By the addition and removal of hydrogen chloride and by heating with acetic–sulfuric acid at 60°C., isozingiberene, a dicyclic hydrocarbon, is obtained. The authors did not give a structure for metazingiberene. The proposed structures for zingiberene and isozingiberene are given above.

As already stated (127), zingiberene reacts with sulfur as does cadinene, yielding cadalene.

5. GURJUNENE



Ruzicka's cedrene type formula



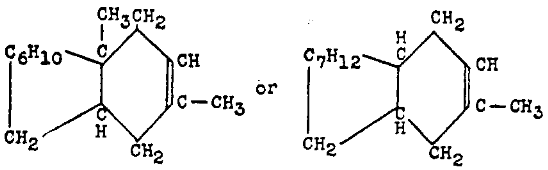
Semmler's cedrene type formula

Semmler and Jakubowitz (150) found that β-gurjunene (tricyclocedrene type) undergoes little change in properties when heated for four hours at 290°C. The only noteworthy change was that of rotation from +27° to +60°, so the authors concluded that there could have been no decomposition. On the other hand α-gurjunene is completely inverted when treated under the same conditions.

In a more recent paper, Semmler and Jakubowitz (151) report that when heated to 330°C., β-gurjunene was converted to a brown, somewhat fluorescent oil yielding 12 per cent of a fraction consisting chiefly of α-terpinene with possibly small amounts of β-terpinene. The products also included unchanged β-gurjunene and a diterpene.

The α-gurjunene yielded an inactive terpene, $C_{10}H_{16}$, which is not terpinene, along with unchanged α-gurjunene and a diterpene.

6. CEDRENE

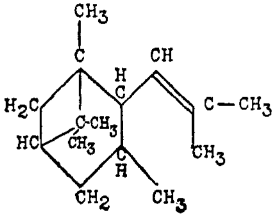


Ruzicka (134)

Cedrene has a great tendency to polymerize. Blumenn and Schulz (19) state that in the presence of acetic anhydride, or boiling under atmospheric pressure, it changes to a powdery, amorphous mass which regenerates the original cedrene when heated in vacuo.

When Semmler and Jakubowitz (151) treated cedrene as they did gurjunene, they obtained a terpene, $C_{10}H_{16}$, boiling range 65–70°C. under 10 mm. pressure; a fraction boiling between 90 and 130°C. under 10 mm. pressure (sesquiterpene); and a fraction boiling between 130 and 190°C. under 10 mm. pressure (diterpene).

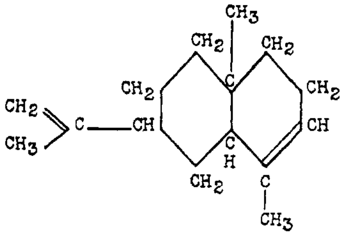
7. CARYOPHYLLENE



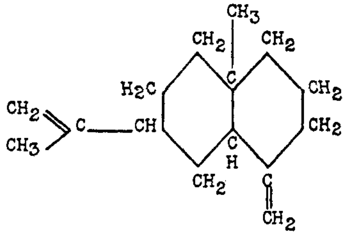
Ruzicka (128)

Caryophyllene (151), heated for twelve hours in a bomb tube at 330°C., yielded a terpene and a diterpene. The terpene was not pinene or limonene for it did not yield any crystalline derivative.

8. SELINENE



α-Selinene (130a)



β-Selinene (130a)

Ruzicka, Meyer, and Mingazzini (128) discovered that some sesquiterpenes lose a methyl group when dehydrogenated with sulfur. The reaction is represented as follows:

$$C_{15}H_{24} + 3S \rightarrow C_{14}H_{16} + CH_3SH + 2H_2S$$

When selinene is treated in this manner it yields eudalene (129), 3-isopropyl-5-methylnaphthalene.

Table 25 summarizes the conditions of treatment and products obtained from the polymerization and decomposition of the sesquiterpenes.

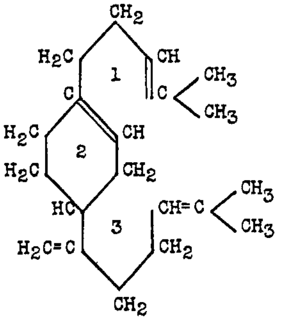
TABLE 25

Sesquiterpenes

REFERENCE NO.	HYDROCARBON	TIME	TEMPERATURE *degrees C.*	CATALYST	PRODUCTS	REMARKS
(151)	Cadinene	12 hours	330	—	Monocyclic isomer or cadinene	Heated in bomb tube
(97)	Cadinene		180–200	—	Change of rotation from −111.28° to −8°	Heated in presence of glacial acetic acid
(131)	Cadinene	—	300–310	Platinum black	Cadalene ($C_{15}H_{18}$)	Passed in stream of inert gas
(127)	Cadinene	4 or 5 hours	180–250	—	Cadalene ($C_{15}H_{18}$)	Heated with sulfur
(88)	Sesquiterpene from Japanese cedar oil	2 hours	280–300	Pd-asbestos	Decahydrocadalene, cadalene	CO_2 present
(135)	Bisabolene	—	Room temperature	Platinum black	Tetrahydrobisabolene	H_2 in cyclohexane
(135)	Bisabolene	—	Room temperature	Platinum black	Hexahydrobisabolene	H_2 in glacial acetic acid
(135)	Bisabolene	4 or 5 hours	180–250	—	Benzene derivative	Heated with sulfur
(149)	Zingiberene and isoprene	4 hours	215	—	Metazingiberene, diterpene, dizingiberene	Bomb tube
(149)	Zingiberene	—	60	HCl or acetic–sulfuric acid	Isozingiberene	—
(127)	Zingiberene	4 or 5 hours	180–250	—	Cadalene	Heated with sulfur
(150)	β-Gurjunene	4 hours	290	—	Change of rotation from +27° to +60°	—
(150)	α-Gurjunene	4 hours	290	—	Complete inversion	—
(151)	β-Gurjunene	—	330	—	12 per cent α-terpinene, β-terpinene, diterpene	—
(151)	α-Gurjunene	—	330	—	Inactive terpene, diterpene	—
(19)	Cedrene	—	Room temperature	—	Powdery amorphous mass	Acetic anhydride
(19)	Cedrene	—	At boiling point	—	Powdery amorphous mass	Atmospheric pressure
(151)	Cedrene	—	300	—	Terpene, sesquiterpene, diterpene	—
(151)	Caryophyllene	12 hours	330	—	Terpene, diterpene	Bomb tube
(128)	Selinene	—	—	—	Eudalene, CH_3SH	Boiled with sulfur

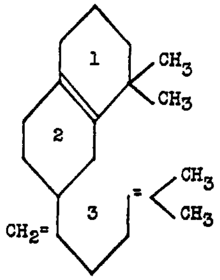
VI. DITERPENES

1. α-CAMPHORENE

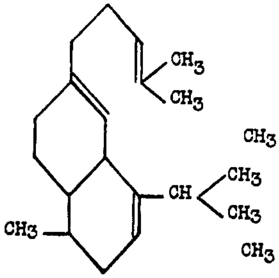


The above formula for α-camphorene has been suggested by Ruzicka and Stoll (132).

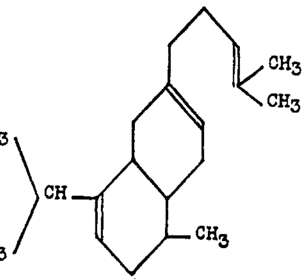
It was found by Semmler and Jonas (153) that heating with acetic–sulfuric acid mixtures caused the isomerization of α-camphorene to what they believed a bicyclic isomer which they called "iso-α-camphorene." Ruzicka and Stoll (132) obtained the same product by boiling α-camphorene for half an hour with two parts of 95 per cent formic acid. It boiled at 192–194°C. at 12 mm. The most probable formula for the bicyclic isomer was thought to be represented by I (below), although isomers represented by formulas II and III may also have been present.



I

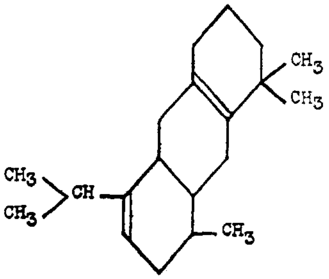


II

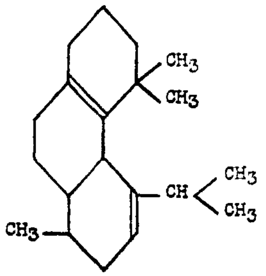


III

On three hours further boiling, either of α-camphorene or the bicyclic product, with formic acid, a tricyclic isomer (b.p. 180–181°C. at 12 mm.) was obtained, for which formula IV was thought most probable, though the isomer represented by formula V was probably also present.

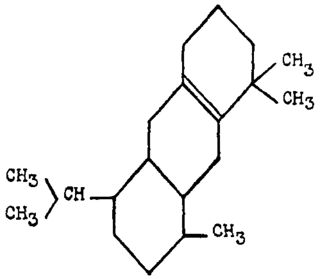


IV

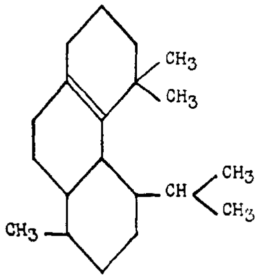


V

The tricyclic product was found to add only one mole of hydrogen in the presence of platinum black, forming a dihydro derivative of the formula VI or VII (b.p. 176°C. at 12 mm.).



VI



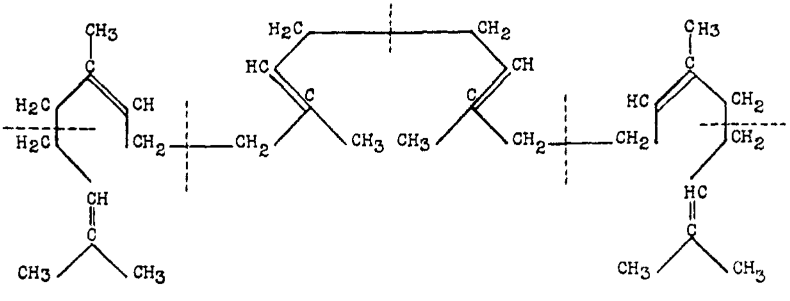
VII

2. DACRENE

Blackie (18) has subjected dacrene, a naturally occurring diterpene of unknown structure, to cracking conditions with the hope that the results might aid in determining its structure. Eight grams of dacrene were gently distilled under 1 mm. pressure through a silica tube heated to 800–900°C. Decomposition occurred with the evolution of gas in such quantity that distillation was prevented until the "hyvac" pump could cope with the gases.

VII. TRITERPENES

SQUALENE



Squalene
Karrer and Helfenstein (85)

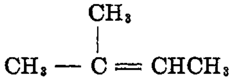
Considerable chemical and biological interest is attached to squalene, the dihydroterpene obtained from the unsaponifiable matter in the livers of elasmobranch fish, since metabolic processes in animals do not usually give rise to hydrocarbons. Though its biological significance is not well understood, it is suspected of having some connection with the origin of cholesterol.

Discovered in 1906 by Tsujimoto (175) and by him assigned the formula $C_{30}H_{50}$, its recent synthesis by Karrer and Helfenstein (85) indicates the above structure, which shows its relationship to the terpenes. It is seen to consist of six isoprene units.

The "spinacene" of Chapman (29) has been shown to be identical with squalene.

TABLE 26

Decomposition of squalene

BOILING POINT	PRESSURE	CONTENT	REMARKS
degrees C.	*mm.*		
30–45	760	 $CH_3-\overset{\overset{CH_3}{\vert}}{C}=CHCH_3$	No isoprene, as reported by Majima and Kubota (101)
60–100	20	Mono- and di-hydromonoterpenes	Under investigation
120–170	20	Mixture of monocyclic sesquiterpenes. Bisabolene identified	Cyclized by formic acid to dicyclic isomer
170–210	15	$C_{20}H_{32}$. Mixture of open chain and cyclic compounds	Oils, thought to be identical with compound obtained by Staudinger (164) on heating rubber ($C_{25}H_{40}$), were also present
210–240	15		Not investigated

Non-catalytic decomposition and polymerization

Heilbron, Kamm, and Owens (66) decomposed squalene by distillation at ordinary pressures. On fractionation of the product, the results shown in table 26 were obtained.

Abe and Shobayashi (3) found that when squalene was heated, it exhibited an exothermic reaction at about 185°C. This exothermic reaction increased suddenly at about 300°C. The data collected at 280–300°C. are given in table 27. Above about 355°C. the reaction became endothermic. These data were interpreted as meaning that in the cracking of squalene there is first a polymerization, followed by a decomposition of the unstable polymer to more volatile substances.

Oda (111) arrived at the same conclusion by heating squalene under 100 atmospheres of hydrogen. Heating for one hour at temperatures of 300–410°C. caused no change of pressure. At 450°C., however, the pressure increased rapidly to 260 atmospheres, and then fell off to 236 atmospheres at the end of one hour. The product had a boiling range of 39–260°C. (original b.p. 250–253°C.) and contained aliphatic hydrocarbons and terpenes.

Although heating at 300°C., with and without hydrogen pressure, caused the decomposition of squalene, it permitted polymerization to occur as a side reaction. The presence of hydrogen pressure appeared to cause depolymerization of a part of the polymer, with the result that in such experiments more of the unpolymerized hydrocarbon was present. Furthermore, the higher the temperature, the greater the quantity of low-boiling material, although no constant-boiling fractions appeared.

TABLE 27

Decomposition of squalene at 280–300°C.

TIME OF HEATING	IODINE NO. (Wijs)	MOLECULAR WEIGHT
minutes		
0	396.7	408.8
400	314.6	418.8
600	280.1	526.0
1045	247.1	555.4
1360	242.2	600.9
1700	227.5	747.7

Catalytic decomposition and isomerization

Chapman (30) decomposed squalene by distilling it at 45 mm. from a Wurtz flask, in the neck of which was suspended a platinum grid maintained at dull red heat. The gas which was produced consisted of 75 per cent of olefinic, and 25 per cent of paraffinic hydrocarbons. The liquid product was fractionated and contained considerable unchanged squalene. A small fraction (b.p. 40–50°C.) was thought to consist largely of isoprene and possibly some amylene. The chief product was a fraction boiling at 79–83°C. at 33 mm., or 160–167°C. at 750 mm., which corresponded closely to the formula $C_{10}H_{18}$. The bromine estimation indicated a mixture of mono- and di-ethylenic hydrocarbons, and a crystalline compound was isolated which corresponded closely to the formula $C_{10}H_{18}Br_4$. On being heated at its boiling point under atmospheric pressure, the hydrocarbon partially polymerized.

Heilbron, Owens, and Simpson (67) repeated the hot-wire decomposition of squalene, but failed to confirm the existence of any individual substance. They obtained the same indefinite fractions as were found on direct pyrolytic decomposition. On boiling the monoterpene fraction from the hot-wire decomposition, there was produced a high-boiling hydrocarbon which closely resembled dimyrcene in its physical properties. They regarded this as evidence for the presence of an open chain hydrocarbon, perhaps myrcene, in that fraction.

Chapman (30, 31) found that squalene was also decomposed by distillation at 40–45 mm. over metallic sodium. The chief product was claimed to be a cyclodihydroterpene, $C_{10}H_{18}$, which added one mole of bromine, and was similar to cyclodihydromyrcene in its properties. It boiled at 170–175°C. at atmospheric pressure. This work was also repeated by Heilbron, Owens, and Simpson (67). Taking the fraction which Chapman found to be similar to cyclodihydromyrcene, they distilled it from a Willstätter flask and found it to boil at 162–177°C. On this basis, and after demonstrating that the evidence of bromine and iodine numbers could not be used, they concluded it to be a mixture of substances, rather than an individual compound.

TABLE 28

Cyclization of squalene

TIME	NO. OF DOUBLE BONDS	IODINE VALUE		$(R_L)_D$	NO. OF RINGS
		Calculated	Found		
hours					
½	—	—	—	136.9	2
3	3	185.8	179.9	134.3	3
9	3	—	—	134.1	3
24 (or more)	2	124.6	117.4	130.9	4

Abe and Shobayashi (3) found that aluminum chloride favored the cracking of squalene, probably because it catalyzed the initial polymerization which was thought to occur.

When heated at ordinary pressure with Japanese acid clay, squalene was found by Kawai and Kobayashi (89) to give good yields of a mixture of hydrocarbons closely resembling natural petroleum. The mixture consisted chiefly of naphthenes, together with aromatic and unsaturated hydrocarbons.

The isomerization, or cyclization of squalene by certain catalysts was first discovered by Majima and Kubota (101), but they did not obtain a pure product. The best catalyst for this purpose is 98 per cent formic acid, and Heilbron, Kamm, and Owens (66) found that boiling with that acid resulted in cyclization, the extent of which depended upon the time of boiling. Their results are shown in table 28. The viscosity increased with the number of rings produced, the final product being a treacle-like mass.

Distillation of the tetracyclosqualene caused decomposition and gave products similar to those obtained by the distillation of squalene itself. In addition, there was obtained a portion which resembled pinene in odor.

Harvey, Heilbron, and Kamm (70) noted that when squalene was cyclized with formic acid which had been previously used for that purpose, there was obtained a tetracyclosqualene whose physical properties differed slightly from that produced by fresh acid.

Catalytic hydrogenation and dehydrogenation

Chapman (29) found that squalene was completely hydrogenated at 200°C. by passing hydrogen through the liquid in which was suspended a platinum black catalyst. The product was a saturated paraffin hydrocarbon, $C_{30}H_{62}$, colorless, odorless, and slightly viscous, boiling at 280–281°C. at 24 mm.

At 150°C. in the presence of a nickel catalyst deposited on kieselguhr or cocoanut charcoal, Heilbron, Hilditch, and Kamm (68) found that the double bonds of squalene underwent selective hydrogenation, the six such bonds being hydrogenated consecutively until the saturated hydrocarbon was produced. Boiling with 98 per cent formic acid resulted in cyclization of the product of the absorption of one mole of hydrogen, and partial cyclization of the product of the absorption of two moles. The other products did not undergo this isomerization.

Harvey, Heilbron, and Kamm (70) found that squalene reacted explosively with sulfur, but that tetracyclosqualene reacted smoothly with a vigorous evolution of gas, and gave small quantities of an oil resembling *p*-cymene, and another substance later identified by Heilbron and Wilkinson (69) as 1,2,5-trimethylnaphthalene.

The berginization of squalene by Ormandy, Craven, Heilbron, and Channon (112) gave a product resembling petroleum. It yielded 59.3 per cent of spirit boiling to 180°C., and 28.2 per cent of kerosene boiling to 300°C. The residue gave heavier oils and a benzene-soluble resin. Examination of the petroleum spirit fraction showed the following composition:

	per cent
Unsaturated hydrocarbons	6.8
Benzene	1.0
Toluene	5.1
Xylenes, etc	11.8
Open chain paraffins	49.7
Closed chain paraffins	25.6

TABLE 29

Squalene

REFERENCE NO.	TEMPERATURE	CATALYST	PRODUCTS	REMARKS
	degrees C.			
(66)	—	—	2-Methylpentene-2, bisabolene, mono- and dihydromonoterpenes, monocyclic sesquiterpenes, open and closed chain compounds, $C_{20}H_{32}$ hydrocarbon, oils	Distilled at ordinary pressure
(3)	150–400	—	Not isolated	Exothermic reaction to about 355°. Endothermic above 355°
(111)	300–450	—	Aliphatic hydrocarbons, terpenes, polymers	
(30)	Platinum grid at red heat	Pt	Olefinic and paraffinic gases, isoprene, amylene (?), $C_{10}H_{18}$ hydrocarbon, open chain	Distilled at 45 mm. through platinum grid
(31)	—	Na	Cyclic $C_{10}H_{18}$ hydrocarbon	Distilled at 40–45 mm. over sodium
(67)	Platinum grid at red heat	Pt	No definite product. An open chain hydrocarbon, perhaps myrcene (?)	Distilled at 45 mm. through platinum grid
	—	Na	No definite products identified	Distilled at 40–45 mm. over sodium
(3)	—	$AlCl_3$	Not isolated	Favored the cracking of squalene
(101)	—	Formic acid	Cyclic products	Boiled with formic acid
(66)	—	98 per cent formic acid	Di-, tri- and tetra-cyclosqualene	
(89)	—	Japanese acid clay	Mixture of hydrocarbons resembling petroleum	
(29)	200	Pt	Saturated $C_{30}H_{62}$ hydrocarbon	Hydrogen present
(68)	150	Ni	Di-, tetra-, hexa-, octa-, deca-, and dodeca-hydrosqualene	Hydrogen present
(69, 70)	—	S	1,2,5-Trimethylnaphthalene	Tetracyclosqualene used
(112)	—	—	Petroleum containing unsaturated hydrocarbons, paraffins, benzene, toluene, xylenes, cycloparaffins. Isopentane, cyclohexane (?)	

Isopentane was identified, and there was evidence for the presence of cyclohexane.

The work on squalene is summarized in table 29.

VIII. RUBBER

Rubber, one of the most complex terpenes, has been the subject of pyrolytic investigation for almost a century. Bouchardat and Himley (25), in 1838, subjected rubber to dry distillation and obtained a hydrocarbon which boiled at 36°C., a "double hydrocarbon," and a mixture of less volatile hydrocarbons (b.p. about 315°C.) which they named heveene.

About ten years later Himley (78) was able to isolate from the products of pyrolytic decomposition of caoutchouc, two liquids, one of which boiled at 33–34°C., and the other at 168–171°C. The latter had the composition $C_{10}H_{16}$.

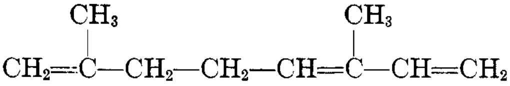
In 1860, Williams (192) found that the destructive distillation of rubber yielded a hydrocarbon boiling between 37 and 38°C. He found its formula to be C_5H_8. That this compound, which he named isoprene, was not only a product of pyrolytic action but had the same empirical composition as rubber, was first established by Williams. He seems further to have regarded rubber as a polymeride of isoprene, for he states that the action of heat on caoutchouc is merely the disruption of a polymeric body into substances having a simple relationship to the parent hydrocarbon. Like Bouchardat, he also obtained heveene.

Bouchardat (23) carried out quantitative experiments on the pyrolytic decomposition of caoutchouc. By distilling 5 kg. of fresh para rubber, he obtained the following fractions: (1) about 40 liters of gas, chiefly carbon monoxide, some methane and about 10 g. of olefins; (2) 250 g. of isoprene; (3) 2000 g. of a hydrocarbon $C_{10}H_{16}$ boiling from 176–180°C.; and (4) 600 g. of a hydrocarbon boiling between 255 and 260°C., to which he gave the formula $C_{15}H_{24}$, and the name heveene, although the substance that he had previously called heveene boiled at about 315°C. The third fraction was inactive to polarized light and was called the dipentene fraction.

Bouchardat, like Williams, regarded caoutchouc as a hydrocarbon $(C_5H_8)_n$ which is decomposed by heat into a series of lower polymerides of the single hydrocarbon C_5H_8. He considered that all the other distillation products were due in part to impurities and in part to the breaking-down of the products of oxidation of caoutchouc.

In addition to the products previously identified, Ipatieff and Wittorf (84) found trimethylethylene among the lower boiling products of destructive distillation of rubber.

In the so-called dipentene fraction, 2 kg. of which Bouchardat obtained from 5 kg. of rubber, Harries (63) found that only one-third of the material was dipentene. From the mixture that remained after the removal of dipentene, he was able to isolate two other compounds, one of which he thought was possibly diisoprene.



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH_2{-}CH_2{-}CH{=}\overset{\overset{CH_3}{|}}{C}{-}CH{=}CH_2$$

In contrast to the results obtained by Bouchardat under atmospheric pressure are those of Fischer and Harries (47), who dry-distilled "para caoutchouc" under a pressure of 25 mm. They obtained very little isoprene and dipentene, the chief product being a mixture which boiled from 180 to 300°C.

Staudinger and Fritschi (158a) also studied the pyrolytic decomposition of rubber under reduced pressure. They used 340 g. of rubber, from which 4 to 5 per cent of resins had been extracted by means of a mixture of chloroform and methyl acetate. The distillation was carried out at 0.1–0.3 mm. pressure. From 216 g. of distillate they obtained 3.1 per cent isoprene; 8.8 per cent dipentene; 4.4 per cent $C_{15}H_{24}$, boiling from 88–91°C. under 0.05 mm. pressure; and about 4 per cent $C_{20}H_{32}$, boiling at 118–122°C. under 0.02 mm. pressure. No open chain terpene was detected. The sesquiterpene fraction contained a dicyclic compound with two double bonds.

In continuation of this work Staudinger and Geiger (159) found that when caoutchouc is heated to 300°C. under ordinary pressure, pyrolytic decomposition takes place; they obtained about 30 per cent of distillate, from which isoprene (about 40 per cent), pure dipentene, other sesquiterpenes, and higher terpenes were obtained. The residue formed a thick mass on cooling. About 20 per cent of high-boiling hydrocarbons were obtained from this residue by heating it under high vacuum. From this distillation there remained a dark brittle resin from which polycyclocaoutchouc was obtained almost quantitatively by solution in ether and precipitation with alcohol.

Geiger (56) states that the pyrolytic decomposition of rubber takes place in two steps. The first step begins at 290–300°C. in vacuo or 300–310°C. at ordinary pressures. The distillate from this step consists of isoprene, dipentene, and about 20 per cent of high-boiling oil. At the same time that this splitting occurs, there is an isomerization of part of the caoutchouc into the stable polycyclocaoutchouc, which forms in 80 to 90 per cent yield if the process is stopped after the first step. The second step begins at 335–345°C. and the distillate from this phase contains a little isoprene, no dipentene, and about 60 per cent of high-boiling oil.

Staudinger and Bondy (157) have found that the degradation of raw rubber appears to be inhibited somewhat, up to 142°C., by the presence of protein. At higher temperatures it follows a course similar to that observed with pure rubber.

The dry distillation of polycyclic caoutchouc was studied by Staudinger and Widmer (162). Under atmospheric pressure of carbon dioxide they found that decomposition begins at 350°C. and as the distillation proceeds, the temperature must be raised to about 450°C. In this way they were able to obtain a 92 per cent yield of volatile liquid decomposition products; about 3 per cent of a gas which was a mixture of methane and a small amount of unsaturated hydrocarbons; and about 5 per cent of a dark resin. From a fractionation of the distillate, at 13 mm. pressure, they obtained a minute amount of what may have been impure isoprene, a small amount of a fraction boiling at 111–113°C. which was a very unsaturated hydrocarbon having the composition of caoutchouc, and a fraction which had approximately the same boiling point as dipentene (174–176°C.) but different density and refractive index. The results obtained from the distillation of polycyclocaoutchouc under 1 mm. pressure were about the same as these, with the addition of a hydrocarbon the analysis and molecular weight of which indicated that it contained about seven isoprene units.

Another study of the destructive distillation of rubber is that made by Midgley and Henne (103). Two hundred pounds of light pale crepe rubber in 16-pound batches were destructively distilled at atmospheric pressure in an iron vessel connected to a suitable condensing system. No attention was paid to temperature control, because of the large size of the batches, but the temperature was always raised as quickly as possible to about 700°C. After removal of isoprene from the distillate by fractionation, the residual oil was subjected to thorough fractional distillation in a carborundum-coated spiral column.

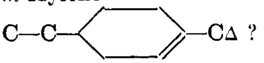
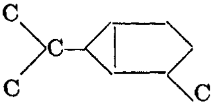
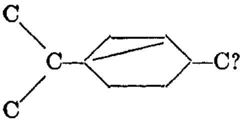
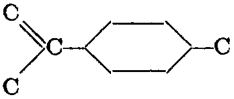
Briefly stated, the materials found in the distillate were olefinic, dienic, aromatic and hydroaromatic compounds, and a single dicyclic olefin. No fully saturated compound was detected. Table 30, taken from Midgley's paper, lists the compounds, the degree of accuracy of their identification, and the relative quantities present in the two types of distillates.

"In addition to the components which could be separated by fractional distillation, a substantial proportion of the original product polymerized, remaining as a jelly in the distilling flask. It may be safely assumed that the materials lost in this way consisted very largely of dienes which were too unstable to distill."

As the table indicates, the addition of magnesium to the rubber greatly increased the yield of materials other than isoprene and dipentene. The product is richer in compounds of the aromatic series and poorer in chain compounds. Zinc, iron, brass, and aluminum have a similar effect, but to a very much smaller extent, while copper is without effect. Later they (105) found that zinc oxide and magnesium oxide have an effect similar to zinc and magnesium, that of zinc oxide being by far the stronger.

TABLE 30

Compounds, identification and quantities

COMPOUNDS	DEGREE OF IDENTIFICATION	PER CENT IN DISTILLATE	
			With Mg
C—C(C)—C═C	Positive	0.04	0.2
C═C(C)—C—C	Positive	0.04	0.2
C═C(C)—C═C	Positive	10.0	10.0
C—C(C)═C—C	Positive	0.04	0.2
C—C(C)═C—C—C ?	Chain structure positive	0.06	0.30
C—C—C(C)—C—C	Positive	0.03	0.15
C═C—C (C)═C—C	Positive except for position of double bonds	0.03	0.15
Benzene	Positive	0.005	0.1
C—C—C(C)═C—C—C	Chain structure positive	0.03	0.15
Δ^3—C—C_6H_9	Not positive	0.01	0.1
Δ^2—C—C_6H_9	Suspected	....	....
C—C═C—C—C—C(C)—CΔ ?	Chain structure positive	0.02	0.1
Δ^1—C—C_6H_9	Positive	0.1	1.0
Toluene	Positive	0.05	1.0
C—C—C—C—C—C(C)═CΔ ?	Chain structure positive	0.04	0.2
Dihydro-*m*-xylene	Positive	0.1	1.0
m-Xylene	Positive	0.05	1.0
	Positive	0.08	0.8
	Hydrogenation product 	0.04	0.8
p-Methylethylbenzene	Positive	0.04	0.8
$C_{10}H_{18}$ (1 double bond)...............		0.04	0.8
C—C(C)═C—C—C—C(C)═C—CΔ?	Not positive	0.015	0.0
	Positive	20.0	20.0
Total..		30.87	39.05

"Because of the preponderance of isoprene (C_5), dipentene (C_{10}), and heveene (C_{15}) in the products of destructive distillation, it is held certain that the single bond farthest removed from the double bonds is the most easily broken by pyrolysis. The same conclusion is arrived at by Hurd (82) from purely theoretical considerations and is found to hold when the other pyrolysis products are examined.

"It can scarcely be doubted that, with the exception of benzene, the compounds of the aromatic series were all derived by dehydrogenation of the corresponding hydroaromatic forms, since only those aromatic compounds are formed whose hydro derivatives are also present. Dihydro-*m*-xylene is the only predictable ring compound in C_8, hence, if dehydrogenation occurs, only *m*-xylene should result. If, on the other hand, *m*-xylene is a primary pyrolysis product, small amounts of the ortho and para derivatives, at least, should be present. Particular care was taken to ascertain that no other xylene was present than the meta derivative.

TABLE 31

Compounds, identification and quantities

COMPOUNDS	DEGREE OF IDENTIFICATION	PER CENT IN DISTILLATE
Propylenes and butenes	Positive	0.3
$CH_3CH(CH_3)CH=CH_2$	Positive	0.2
$CH_2=C(CH_3)CH_2CH_3$	Positive	2.0
$CH_2=C(CH_3)CH=CH_2$	Positive	1.1
$CH_3C(CH_3)=CHCH_3$	Positive	4.2
Component boiling at 58°	Abridged	0.05
3-Methylpentenes	Positive	0.4
Component boiling at 68°	Abridged	0.1
Benzene	Positive	0.1
Isomeric heptane	Positive	0.03
Component boiling at 93–95°	Abridged	0.1
Tetrahydrotoluene	Positive	0.4
Toluene	Positive	0.1
Component boiling at 121–122°	Abridged	0.2
Hexahydroxylene	Possibly present	0.1
o-Xylene	Uncertain	0.006
m-Xylene	Positive	0.1
p-Xylene	Positive	0.02
Compounds with 9 carbon atoms	Similar to those from natural rubber but not investigated	0.5
Compounds with 10 carbon atoms	Similar to those from natural rubber but in too small amount to separate properly	6.4
Dipentene	Uncertain	0.1
Normal pentane, isopentane and dihydroxylene were absent		

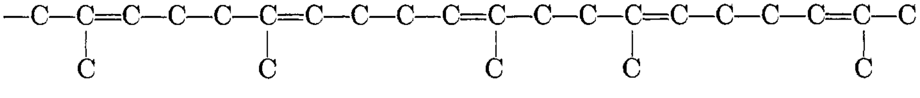
"The origin of benzene is obscure. It is not due to accidental contamination in the laboratory, since the presence of a metal in the rubber always increases the amount of benzene in the distillate. Extreme pyrolysis in locally overheated spots might account for its formation."

TABLE 32

Pyrolysis of rubber

REFERENCE NO.	TEMPERATURE	PRESSURE	PRODUCTS	REMARKS
	degrees C.			
(25)	—	Atmospheric	Hydrocarbon of b.p. 36°, "double hydrocarbon," heveene	
(78)	—	Atmospheric	Liquid, b.p. 33–34°, $C_{10}H_{16}$, b.p. 168–171°	
(192)	—	Atmospheric	Isoprene, b.p. 37–38°	
(23)	—	Atmospheric	Carbon monoxide, methane, olefins, isoprene, $C_{10}H_{16}$ (b.p. 176–180°), $C_{15}H_{24}$	
(84)	—	—	Above products, trimethylethylene	
(63)	—	—	Diisoprene	
(47)	—	25 mm.	Isoprene, dipentene, mixture b.p. 180–300°	
(158a)	—	0.01–0.3 mm.	Isoprene, dipentene, $C_{15}H_{24}$, $C_{20}H_{32}$	
(159)	300	Atmospheric	Isoprene, dipentene, sesquiterpenes, higher terpenes, residue	
(159)	—	High vacuum	High-boiling hydrocarbons, resin containing polycyclocaoutchouc	Initial material was residue from above
(56)	290–300	"In vacuo"	Isoprene, dipentene, high-boiling oil, polycyclocaoutchouc	
(56)	300–310	Atmospheric	Same as above	
(56)	335–345	—	Isoprene, no dipentene, high-boiling oil	Initial material was residue from above
(162)	350–450	Atmospheric pressure of CO_2	Methane, gaseous unsaturated hydrocarbons, isoprene?, $(C_5H_8)_x$ of b.p. 111–113° under 13 mm. pressure, terpene b.p. 174–176°	Initial material was polycyclocaoutchouc

In a more recent paper, Midgley, Henne, and Shepard (106) have studied the products of destructive distillation of sodium rubber. The results are summarized in table 31. The components marked "abridged" were noted during the course of the fractionation, but were not investigated more fully because of the limited amount of available material. The sodium rubber used was benzene-free. Hence the presence of benzene among the distillation products confirms the theory of its origin as expressed above. "*m*-Xylene is not the only xylene formed. This agrees with the expectation based on the structure of sodium rubber indicated in a previous paper (104)."



$$-C-\underset{\overset{|}{C}}{C}=C-C-C-\underset{\overset{|}{C}}{C}=C-C-C-C=\underset{\overset{|}{C}}{C}-C-C-\underset{\overset{|}{C}}{C}=C-C-C-C=\underset{\overset{|}{C}}{C}-C$$

The significant similarities and differences in the pyrolysis products of natural and synthetic rubber, as shown in the foregoing tables, were summarized as follows: "The arrangements of the carbon atoms in the compounds obtained from natural and sodium rubber are the same, except for the position of some methyl groups. Compounds with five and ten carbon atoms predominate in both cases."... . "The products obtained from sodium rubber are more saturated. This is shown by the decrease of the quantities of isoprene and dipentene, the increase of the amount of pentenes, and the appearance of small amounts of saturated hydrocarbons. The last were entirely absent in the natural rubber distillate."

Midgley and his coworkers conclude that their experiments indicate that sodium rubber is isomeric with natural rubber in the positioning of its methyl groups, but that the double bond of sodium rubber differs from the true ethylenic bond of natural rubber.

Bassett and Williams (13) have improved the yield of isoprene obtainable by the pyrolysis of rubber. Using a specially designed apparatus which permitted rapid removal and cooling of the products of pyrolysis, and reheating the higher liquid fractions containing dipentene and other terpenes, they obtain a total yield of 23 per cent of pure isoprene based upon the amount of rubber used.

Table 32 summarizes the work on the pyrolysis of rubber other than that of Midgley et al.

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