Examination of the mother liquid provided the second anomer, m.p. 158°[10] (after recrystallization from chloroform–light petroleum ether), $[\alpha]^{23}\mathrm{D}$ −12° in chloroform (*c* 0.3).

The *N*-phenyl-2,3-di-*O*-methyl-D-arabinosylamine prepared in the usual way by treatment with ethanolic aniline had m.p. 138°, $[\alpha]^{24}\mathrm{D}$ −143° after 10 min. in chloroform (*c* 0.4) changing in 4 hr. to −44° (constant value) (after recrystallization from chloroform–petroleum ether); lit.[11] m.p. 139° for L-isomer.

Prolonged Treatment of 3,4-Di-*O*-methyl-D-mannitol with Sodium Periodate.—When the periodate oxidation of 3,4-di-*O*-methyl-D-mannitol was allowed to proceed longer than 0.5 hr., the molar periodate consumption was: 1.0 mole (after 0.5 hr.), 1.06 (1.5 hr.), 1.35 (12 hr.), 1.47 (24 hr.), 1.52 (37 hr.), 1.60 (49 hr.), 1.66 (61 hr.), 1.71 (88 hr.), oxidation incomplete.

Oxidation of 2,3-Di-*o*-methyl-D-arabinose with Sodium Periodate.—When 2,3-di-*O*-methyl-D-arabinose (50 mg.) was allowed to react with 0.03 *N* sodium periodate (25 ml.) these reading changes in specific optical rotation and periodate consumption per mole of 2,3-di-*O*-methyl-D-arabinose, respectively, were observed: $[\alpha]\mathrm{D}$ −110° (after 3 min.); −110°, 0.03 mole (1 hr.); −110°, 0.103 mole (4 hr.); −105° 0.25 mole (18 hr.); −105°, 0.35 mole (30 hr.); −100°, 0.43 mole (42 hr.); −85°, 0.54 mole (56 hr.); −80°, 0.68 mole (5 days); −75°, 0.83 mole (9 days); −70°, 0.91 mole (17 days).

Reduction of 2,3-Di-*O*-methyl-D-arabinose with Sodium Borohydride.—To a solution of sodium borohydride (65 mg.) in methanol (2 ml.) was added a solution of 2,3-di-*O*-methyl-D-arabinose (298 mg.) in methanol (10 ml.). After 3 hr. the reaction mixture was treated with an additional portion (25 mg.) of sodium borohydride. Since this addition produced no change in rotation (observed for 2 hr.), the reaction mixture was neutralized with dilute acetic acid (tested with universal *p*H indicator paper) and evaporated to dryness.

The residue was boiled for 4 hr. with acetic anhydride (10 ml.) in the presence of anhydrous sodium acetate (0.5 g.) to facilitate[12] the isolation of the product. The reaction mixture was poured with stirring into water and the product extracted with chloroform. After washing with dilute sodium bicarbonate and with water, the chloroform extract was dried ($MgSO_4$) and evaporated. The 2,3-di-*O*-methyl-D-arabitol triacetate (400 mg.) thus obtained showed $[\alpha]^{23}\mathrm{D}$ +21° in ethanol (*c*, 4).

The sirupy 2,3-di-*O*-methyl-D-arabitol triacetate was heated for 0.5 hr. with *N* ethanolic potassium hydroxide (6 ml.). After standing overnight the solution was treated with water (10 ml.), deionized by passing successively through a cation (Amberlite IR-120) and an anion (Duolite A4) exchange resin. Evaporation of the solution yielded 2,3-di-*O*-methyl-D-arabitol as a clear, light-yellow liquid (208 mg.), $[\alpha]^{19}\mathrm{D}$ +5° in ethanol (*c*, 4), *R* 0.31 (solvent, butanone-water azeotrope; spray reagent, ammoniacal silver nitrate).

Treatment of 2,3-di-*O*-methyl-D-arabitol (25 mg.) with *p*-nitrobenzoyl chloride (67 mg.) in pyridine (1 ml.) in the usual way, gave the corresponding 1,4,5-tri-*p*-nitrobenzoate, m.p. 131.5°, $[\alpha]^{21}\mathrm{D}$ +43° in chloroform (*c* 0.8) (after recrystallization from acetone–ethanol). *Anal.* Calcd. for $C_{23}H_{25}O_{14}N_3$: C, 53.59; H, 4.02; N, 6.70; OCH_3, 9.88. Found: C, 53.99; H, 4.09; N, 6.61; OCH_3, 9.4.

Oxidation of 2,3-Di-*O*-methyl-D-arabitol with Sodium Periodate.—A solution of 2,3-di-*O*-methyl-D-arabitol in 0.044 *M* sodium periodate was allowed to stand at room temperature. After keeping overnight, 0.91 mole of periodate was consumed per mole of 2,3-di-*O*-methyl-D-arabitol. Addition of barium chloride to remove iodate and periodate, filtration and evaporation gave a distillate which was shown to contain formaldehyde since it yielded the crystalline dimedone derivative, m.p. and mixed m.p. 190°. The other product of this reaction, namely, 2,3-di-*O*-methyl-D-threose, is being examined and will form the subject of a later communication.

ST. PAUL, MINN.

---

[10] *Cf.* H. C. Srivastava and F. Smith, THIS JOURNAL, **79**, 982 (1957).

[11] F. Smith, *J. Chem. Soc.*, 753 (1939).

[12] H. Klosterman and F. Smith, THIS JOURNAL, **74**, 5336 (1952).

[CONTRIBUTION FROM THE NAVAL STORES STATION[1]]

The Decomposition of Pinane Hydroperoxide. II[2]

BY GUSTAV A. SCHMIDT[3] AND GORDON S. FISHER

RECEIVED AUGUST 11, 1958

Further studies of the decomposition of pinane hydroperoxide have revealed that the yield of pinan-2-ols can be increased to nearly 50% by carrying out the reduction in the presence of both pinane and a base. Evidence also was obtained for attack at the secondary carbon atoms of pinane during the oxidation and for isomerization of pinane to monocyclic hydrocarbons during the decomposition.

The previous paper of this series[4] reported the identification of 2,2-dimethyl-3-ethylacetylcyclobutane as one of the major decomposition products of pinane hydroperoxide. It was observed that in the absence of pinane up to half of the pinane hydroperoxide decomposed was converted to high boiling tars during decomposition and distillation. Little or no monomeric bicyclic products were obtained under these conditions. However, when pinane was used as a diluent, the yield of tars was reduced to about 28%, the yield of the ketone was increased to about 20% and some isopinan-2-ol[5] was isolated.

In view of the well known instability of the bicyclic terpenes toward acids it seemed reasonable that acids formed during the preparation and decomposition of the pinane hydroperoxide contributed to the destruction of the expected bicyclic products and the formation of tars. This was supported by the fact that the use of a diluent which lowered the concentration of acids decreased the production of tars during decomposition and increased the yield of isopinan-2-ol.

In the present investigation, the formation of acids during the peroxidation was minimized by operating at a relatively low temperature and terminating the oxidation before peroxide decomposition became excessive. Decomposition was

---

[1] One of the laboratories of the Southern Utilization Research & Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] Presented before the 6th Southeastern Regional American Chemical Society Meeting, Birmingham, Ala., October 21–23, 1954.

[3] General Electric Co., Waterford, N. Y.

[4] G. A. Schmidt and G. S. Fisher, THIS JOURNAL, **76**, 5426 (1954).

[5] The term "iso" has been widely used to designate *p*-menthane derivatives, such as isomenthol, in which the methyl and isopropyl groups are *cis*, as well as to denote a *cis* relation of the methyl group to the isopropylidene bridge in the 3- and 4-hydroxypinanes. The authors feel that use of the same convention in naming the two pinan-2-ols is preferable to the use of trivial names such as methyl nopinol or the prefixes *cis* and *trans*.

carried out in the presence of sodium methylate to remove acids as they were formed, and the decomposition mixture was washed before distillation. As shown in Tables I and II, peroxide retention during oxidation was high and recovery of unreacted pinane and products was good.

Table I

Materials Balance for Preparation of Pinane Hydroperoxide

	Wt., g.	Moles
Pinane charged	2078	15.06
Oxidate	2175	14.65
Oxidation products	834	4.94[a]
Pinane unreacted	1341	9.71
Pinane lost	57	0.41

[a] 4.63 moles peroxide, 0.31 mole of other oxidation products.

Table II

Materials Balance for Separation of Pinane Oxidates after Decomposition

	Wt., g.	Moles
Pinane recovered	1260	9.13
Volatile products[a]	710	4.67
Residue	85	0.54
Acids	55	0.30
Total recovery	2110	14.64
Loss[b]	65	0.01

[a] See Table III. [b] By difference.

The mixture of decomposition products was complex; but careful distillation gave adequate separation for the identification of the major products, and for semi-quantitative analysis on the basis of the infrared spectra (Table III).

Table III

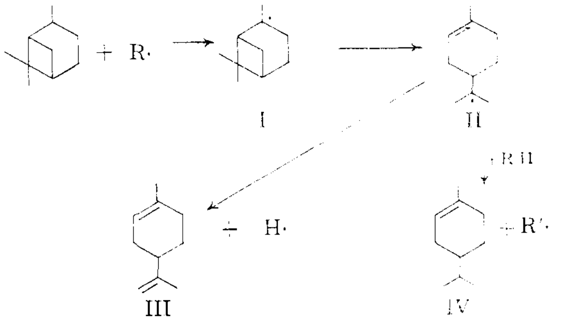
Decomposition Products

Product	Found in fractions[a]	B.p.,[b] °C.	Moles	Mole per cent. A[c]	Mole per cent. B[d]
l-Carvomenthene	11–13	69	0.49	..	8
l-Limonene	11–12	69	0.06	..	1
2,2-Dimethyl-3-ethylacetylcyclobutane	13–30	84	1.00	20	17
Pinan-2-ol	29–36	96	0.55	11	9
Isopinan-2-ol	36–43	102	1.86	38	31
β-Terpineol	41–43	108	0.12	2	2
α-Terpineol	44–54	111	.23	5	4
Isoverbanone	44–54	111	.10	2	2
Pinocampheols	55–58	115	.06	1	1
Unidentified alc. and ketones	13–20, 31–35, 55–58	..	.20	4	3
Residues	....	..	.54[e]	11	9
Acids	....	..	.30[f]	6	5
Total			5.51	100	92

[a] Fractions 1–10 were *cis*-pinane.[14] [b] B.p. of purest fraction at 20 mm. [c] Based on moles of oxidation products in oxidate. [d] Based on moles of pinane charged—moles of pinane recovered. [e] Molecular weight of 158 assumed on basis of elementary analysis. [f] Includes lactones and water-soluble products, average molecular weight of 184 assumed.

The low weight recovery after decomposition, accompanied by a good molar recovery suggests that a volatile or water-soluble product was lost. In view of the fact that most of the products were mono-oxygenated while the hydroperoxide is di-oxygenated, it was of interest to check the oxygen balance for the decomposition step. Assuming that the non-peroxidic products are mono-oxygenated, the oxidate contained 4.78 moles of oxygen. The products recovered after decomposition (see Table III) contained only 2.97 moles of oxygen. Therefore, the loss of oxygen was 1.81 moles or 58 g. calculated as molecular oxygen. There is also a net loss of hydrogen in the formation of the limonene, isoverbanone, residue, and acids amounting to about 1.5 moles. Hence, the total deficiency of oxygen and hydrogen in the decomposition products is 61 g., compared to the observed loss in weight of 65 g. Oxygen as well as water has been reported as a decomposition product of other tertiary hydroperoxides.[6]

Another noteworthy feature of the decomposition is the fact that only 9.13 moles of the unreacted pinane (9.71 moles) present in the oxidate was recovered after decomposition, while the recovery of oxygenated products was quantitative. This loss of pinane is almost exactly balanced by the 0.55 mole of carvomenthene (IV) plus limonene (III) formed, which indicates that these monocyclic compounds are formed from pinane during the decomposition step. Both are reasonable products from the pinan-2-yl free radical in the absence of oxygen.



The most marked effect of the use of sodium methylate during the decomposition was the increase in yield of the pinan-2-ols to nearly 50%. In addition, the amount of non-volatile products was reduced to about 16%. On the other hand, the yield of 2,2-dimethyl-3-ethylacetylcyclobutane was not changed.

The isolation of pinan-2-ol as well as isopinan-2-ol was unexpected since the former was not detected in the reduction products of the hydroperoxide.[7] Hence, the catalytic reduction of the hydroperoxide was repeated. When the infrared spectrum of the product was obtained using a double beam spectrophotometer and a suitable concentration of authentic isopinan-2-ol in the reference cell, the presence of pinan-2-ol readily was apparent. The previous failure to detect it undoubtedly was due to the use of a less precise spectrophotometer without compensation for the isopinan-2-ol. In addition, the infrared spectra indicated that there was 3 to 4 times as much isopinan-2-ol as pinan-2-ol in the

---

(6) F. H. Seubold, Jr., F. B. Rust and W. E. Vaughan, This Journal, **73**, 18 (1951); M. S. Kharasch, A. Fono, W. Nudenberg and B. Bischof, *J. Org. Chem.*, **17**, 207 (1952).

(7) G. S. Fisher, J. S. Stinson and L. A. Goldblatt, This Journal, **75**, 3675 (1953).

reduction product. This is in good agreement with the decomposition data. Hence, the isopropylidene bridge must exert a strong directive influence on the addition of oxygen to the pinan-2-yl radical but does not entirely prevent addition in the position *cis* to it.

The isolation of isopinocampheol and isoverbanone from the decomposition mixture indicates that under the oxidation conditions used the secondary positions also were oxidized. Presumably isopinocamphone and isoverbanols also were present and account for part of the alcohols and ketones which could not be separated well enough for characterization. Although only isopinocampheol was isolated in sufficient purity for identification, the levorotary liquid alcohol obtained along with the solid probably contains neoisopinocampheol.[8]

In spite of the precautions taken to remove acids as fast as they formed, the aqueous layer in the traps was acidic. Hence it is assumed that the α- and β-terpineol were formed by acid isomerization of the pinan-2-ols.[9] In a separate experiment it was found that even acetic acid is strong enough to isomerize these alcohols at the temperatures used for the decomposition.

Experimental[10]

***l*-Pinane Hydroperoxide.**—The *l*-pinane hydroperoxide was prepared by oxidation of *cis*-*l*-pinane (15.06 moles, α^{20}D $-19.5°$, d^{20}_4 0.8570, n^{20}D 1.4624)[11] at 100–105°, essentially as described previously.[7] The reactor consisted of a 5-liter 3-neck flask equipped with two oxygen dispersers, Dean–Stark trap, condenser and stirrer. After 7 hours oxidation, the oxidate (2,175 g.) contained 4.63 moles of pinane hydroperoxide. Removal of unoxidized pinane from a small aliquot at low temperature left the crude oxidation products as a residue which contained 94% (wt.) of pinane hydroperoxide. Hence the total weight of oxidation products would be 834 g. (787 g. of pinane hydroperoxide and 47 g. of by-products). Assuming that the by-products are monoxygenated, this corresponds to a total yield of 4.94 moles of oxidation products. On the basis of their infrared spectra, the recovered pinane was pure and the hydroperoxide[12] contained a small amount of carbonyl compound. Small amounts of alcohols in the hydroperoxide would be difficult to detect.

Decomposition of *l*-Pinane Hydroperoxide.—This oxidate (2,175 g.) was cooled to 70° in the reactor and 82 g. (1.5 moles) of sodium methylate was added with stirring. When the mixture was warmed to 80°, vigorous decomposition occurred. It was controlled by external cooling with ice-water. The maximum temperature was 140°. The vigorous reaction subsided after 20 minutes and the reaction mixture was allowed to cool slowly to 100°. One-fourth of the original peroxide remained undecomposed. The solution was neutral, but despite the added base the aqueous layer in the trap was slightly acidic. Decomposition was completed by heating the mixture for an additional hour at 100° in the presence of an additional 20 g. of sodium methylate and 0.5 g. of cobalt carbonate.

After cooling, the product was washed with water to remove the excess sodium methylate, sodium salts of the acids formed and any base-soluble neutrals.

Acids and Base-Soluble Neutrals.—The organic materials present in the alkaline washes were recovered by acidification and extraction with ether in the usual manner. Removal of the ether gave 55 g. of a viscous brown liquid (0.3 mole, assuming an average molecular wt. of 184). The neutral equivalent was 262, which suggests the presence of lactones or water-soluble neutral oxidation products. Attempts to identify the acids by chromatography[13] were unsatisfactory. Peaks corresponding to pinonic and pinic acids were obtained, but the infrared spectra of the fractions indicated that they were mixtures.

Distillation of Neutral Products.—The washed product was subjected to a preliminary distillation *in vacuo* to remove the bulk of the high boiling components. This distillation left a residue consisting of 59 g. of brown viscous liquid [C, 75.75; H, 10.52, O 13.73 (difference)]. This corresponds to an average monomeric molecular weight of 158 g. ($C_{10}H_{16.7}O_{1.33}$); so the residue represents 0.37 mole of pinane.

The crude distillate was then fractionally distilled through a Podbielniak column rated at 100 theoretical plates, using a high reflux ratio giving the 58 fractions described below. An additional 26 g. (0.16 mole) of residue was obtained from this distillation. The results of this distillation are summarized in Table III.

Identification of Volatile Products.—Fractions 1–10 were substantially pure *cis*-*l*-pinane.[14] The infrared spectra and physical constants checked with those of the starting material. Pinane recovered in the various cold traps used during decomposition and distillation was included in calculating recovery.

The physical properties of fractions 11 and 12 (n^{20}D 1.4595, d^{20}_4 0.8392, $[\alpha]$D $-104.3°$) indicated that the major component was *l*-carvomenthene and this was confirmed by the infrared spectra. However, there was an absorption band at 11.25 μ which is not present in the spectrum of carvomenthene. The position and magnitude of this band was correct for about 10% of limonene.

The infrared spectra of fractions 21–28 indicated that they were pure *cis*-*l*-2,2-dimethyl-3-ethylacetylcyclobutane, but the optical rotations (αD, 1 dm. neat) were only $-38°$, to $-26°$ instead of $-59°$.[7] Inasmuch as other *cis*-3-substituted acetylcyclobutanes are known to epimerize in the presence of base to give 20–30% of the *trans* isomer rotating in the opposite sense,[15] it is assumed that the basic conditions used for decomposition resulted in partial inversion of the *cis*-*l*-2,2-dimethyl-3-ethylacetylcyclobutane to the *trans*-*d* isomer, which was not separated by the distillation conditions used. To confirm this a sample of the ketone (α^{26}D $-43°$) prepared from the *l*-hydroperoxide under less basic conditions was heated in 2 *N* methanolic potassium hydroxide until the rotation became constant. The recovered ketone had α^{23}D $-26°$ and its infrared spectrum was substantially unchanged. Attempts to separate the isomers by refractionation of fractions 21–28 were unsuccessful. The maximum rotation was only $-41°$.

Pinan-2-ol and isopinan-2-ol were isolated by recrystallization of the solids which crystallized from fractions 31–35 and 27–40, respectively. The pure pinan-2-ol, m.p. 58–60°, and isopinan-2-ol, m.p. 81–82°, did not depress the melting points of the corresponding authentic samples[16] and their infrared spectra were identical with the knowns.

β-Terpineol was not obtained pure but was present in high enough concentration in fraction 42 to permit identification by comparison of infrared spectra. Characteristic absorption bands were observed at 3.20, 6.05, 8.75, 10.95 and 11.25 mμ. The absorption bands not accounted for by β-terpineol were at the proper wave length for isopinan-2-ol and isoverbanone. The $C{=}CH_2$ stretching band at 6.05 μ was used for the semi-quantitative estimation of the β-terpineol concentration.

l-Isoverbanone was isolated from fractions 44–54 through the semicarbazone. After recrystallization from ethyl ace-

---

(8) H. Schmidt, *Ber.*, **77**, 544 (1944).

(9) O. Wallach, *Ann.*, **360**, 88 (1908).

(10) Infrared spectra were run on a double beam instrument with NaCl optics by Mrs. Mary N. Woodroof. Microanalyses were made by L. E. Brown, Southern Regional Research Laboratory, New Orleans, La. All optical rotations are 1 dm. neat unless otherwise specified.

(11) G. Chiurdoglu, J. Decot and Mme. van Lancker-Francotte, *Bull. soc. chim. Belges*, **63**, 70 (1954), report $[\alpha]^{20}$D 23.1°, d^{20}_4 0.8575 and n^{20}D 1.4628 for *cis*-*d*-pinane.

(12) By catalytic reduction and infrared spectrophotometric analysis, the *cis:trans* ratio of a similar sample of pinane hydroperoxide was found to be 3 or 4 to 1.

(13) D. E. Baldwin, V. M. Loeblich and R. V. Lawrence, *Anal. Chem.*, **26**, 760 (1954).

(14) A liquid-gas chromatographic analysis, for which we are indebted to Dr. Harry Hunt of The Glidden Co., indicated that the recovered *cis*-pinane was 98% pure with 2% of a slightly lower boiling material presumed to be the *trans* isomer.

(15) M. Delépine, *Bull. soc. chim. France*, [5] **3**, 1369 (1936); M. Delépine and M. Badoche, *Ann. chim.*, [12] **6**, 777 (1951).

(16) The known pinan-2-ol was kindly supplied by Dr. J. P. Bain, The Glidden Co.

tate, the semicarbazone (5.4 g.) obtained from a portion (21 g.) of these fractions melted at 225–227° dec.

Anal. Calcd. for $C_{11}H_{19}ON_3$: N, 20.07. Found: N, 19.99.

The ketone obtained from this semicarbazone by regeneration with sulfuric acid boiled at 222° without decomposition and had the physical constants: $n^{20}D$ 1.4760, d^{20}_4 0.9617, $[\alpha]^{20}D$ −56.07° (1 dm. neat). Its infrared spectrum was identical with that of dihydroverbenone produced by hydrogenating verbenone with Adams catalyst. Schulz and Doll[17] list the material as isoverbanone with the constants: b.p. 84° (20 mm.), d^{20}_4 0.9644, $n^{20}D$ 1.4779, $[\alpha]D$ −59°, semicarbazone, 227°.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.80; H, 10.47.

α-Terpineol.—The major component of fractions 44 to 54 was an alcohol. The residual infrared absorption spectra after correction for the isoverbanone were essentially identical with that of authentic α-terpineol.

The secondary alcohols present in fractions 55–58 were converted to the *p*-nitrobenzoates for purification. Exhaustive recrystallization from pentane yielded an ester, m.p. 84–85°, $[\alpha]D$ 29.5° (*c* 3.8, chloroform), 48° (*c* 3.34, benzene).

Anal. Calcd. for $C_{17}H_{20}O_4N$: C, 67.30; H, 6.97. Found: C, 67.65; H, 7.09.

The 3,5-dinitrobenzoate, m.p. 90–91.5°, was prepared in a similar manner.

Saponification of a sample of the *p*-nitrobenzoate (m.p. 80–81°) gave an alcohol in 90% yield, b.p. 220–221°, $n^{20}D$ 1.4843, d^{20}_4 0.9568, $[\alpha]D$ 2.8° (*c* 5.4, benzene). The alcohol on standing partially solidified in long needles. One recrystallization from pentane gave a solid which melted at 54–56°. The infrared spectrum of the solid alcohol was substantially equivalent to that of the mixture from which it was isolated. Attempts to prepare a solid phenylurethan were unsuccessful.

Anal. Calcd. for $C_{10}H_{18}O$; C, 77.87; H, 11.83. Found: C, 77.35; H, 11.66.

Samples of authentic isopinocampheol were prepared by reduction of hydroxypinocamphone by the procedure of Kuwata,[18] and by catalytic hydrogenation of *trans*-pinocarveol.[8] The starting materials available were not optically homogeneous; hence the products were semi-solid. Infrared spectra of the two reduction products and of the alcohol isolated from the decomposition mixture were all substantially identical.

OLUSTEE, FLA.

---

[17] L. Schulz and W. Doll, "Ber. Schimmel & Co. Akt.-Ges.," 1942–1943, p. 50.

[18] T. Kuwata, THIS JOURNAL, **59**, 2509 (1937).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Preparation and Aromatization of Poly-1,3-cyclohexadiene[1]

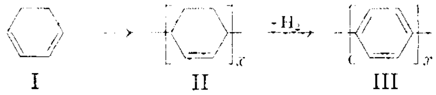
BY C. S. MARVEL AND GORDON E. HARTZELL[2]

RECEIVED JULY 31, 1958

The polymerization of 1,3-cyclohexadiene to a low molecular weight polymer utilizing a Ziegler catalyst composed of triisobutylaluminum and titanium tetrachloride is reported. Although attempted dehydrogenation of the poly-1,3-cyclohexadiene failed to give a completely aromatized *p*-polyphenyl which could be isolated, evidence obtained from infrared spectra, analyses and X-ray diffraction studies confirmed the presence of *p*-polyphenyl in the products of the dehydrogenation reactions.

The lower members of the *p*-polyphenyl series possess remarkably high melting points, with *p*-quinquiphenyl and *p*-sexiphenyl melting without decomposition at 380 and 460–465°, respectively.[3,4] Numerous attempts have been made to obtain high molecular weight *p*-polyphenyls. The Ullmann reaction has not been successful for the preparation of *p*-polyphenyls larger than *p*-sexiphenyl.[5] A polyphenyl having a molecular weight of 2700–2800 has been reported from the condensation of *p*-dichlorobenzene in the presence of a liquid potassium-sodium alloy.[6] However, the physical properties of the polymer indicate that it was probably not an all-*para* polyphenyl.

Research was undertaken to determine the feasibility of preparing a high molecular weight *p*-polyphenyl (III) by dehydrogenation of poly-1,3-cyclohexadiene (II).



I II III

Numerous preparations of 1,3-cyclohexadiene (I) have been reported, including dehydrobromination of 1,2-dibromocyclohexane either with quinoline[7] or with sodium ethoxide,[8] dehydrobromination of 3-bromocyclohexene with quinoline[9] and pyrolysis of 1,2-diacetoxycyclohexane.[10] The most convenient synthesis yielding the highest purity 1,3-cyclohexadiene was that involving dehydrobromination of 3-bromocyclohexene, which was obtained in 70–80% yield from the reaction of N-bromosuccinimide and cyclohexene. The bromocyclohexene was heated with quinoline at 190° to give 1,3-cyclohexadiene in 50–60% yield. Vapor phase chromatography analysis showed the product to contain a minimum of 99% 1,3-cyclohexadiene. The other preparations were judged less convenient and generally gave 1,3-cyclohexadiene contaminated with cyclohexene and benzene. Dehydrobromination of 1,2-dibromocyclohexane with quinoline gave a product containing only 45% 1,3-cyclohexadiene, with 40% cyclohexene and 15% benzene.

---

[1] The work discussed herein was supported in part by Contracts AF 33(616)-3772 and -5486 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. Reproduction of this paper in whole or in part is permitted for any purpose of the United States Government. The paper is abstracted from a portion of a thesis submitted in partial fulfillment of requirements for the Ph.D. degree by Gordon Ellsworth Hartzell to the Graduate College of the University of Illinois in 1958.

[2] National Science Foundation Fellow, 1956–1958.

[3] A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, 1170 (1939).

[4] R. Pummerer and L. Seligsberger, *Ber.*, **64**, 2477 (1931).

[5] P. E. Fanta, *Chem. Revs.*, **38**, 139 (1946).

[6] G. A. Edwards and G. Goldfinger, *J. Polymer Sci.*, **16**, 589 (1955).

[7] J. Pirsch, *Ber.*, **67**, 1303 (1926).

[8] M. Mousseron and F. Winternitz, *Bull. soc. chim.*, **13**, 332 (1946).

[9] A. T. Blomquist and J. Kwiatek, THIS JOURNAL, **73**, 2098 (1951).

[10] W. J. Bailey and W. B. Lawson, *ibid.*, **79**, 1444 (1957).