tively. These curves intersect at the enantiotropic transition point T. In the mestastable region, the solubility of the α'-form is represented by points on the curve CT′. This curve intersects the metastable solubility curve of the β-modification (shown by points on DT″T) at the metastable enantiotropic transition point T′.

The locations of the intersections of the solubility curves of dodecylammonium chloride with reference to temperature and concentration have been inserted in Table I. These data establish the transition temperature T quite definitely at 57.5 ± 0.1°, which is the value obtained by microscopic observations.[1,2] The change of slope in the metastable region at T′ occurs consistently at 54.7 ± 0.1°. Re-examination of the data[1] for the solubility in 95% ethanol shows a slight hint of a similar (unreported) intersection in the metastable region of this region of this system in the neighborhood of 54.5°, but too few experimental points have been recorded to demonstrate the point conclusively. The changes in slope of the solubility curves[4] of dodecylammonium bromide and iodide in benzene and 95% ethanol suggest that these substances may possess transitions similar to those of dodecylammonium chloride.

The data for the anhydrous ethanol show no "break" in the solubility curve above the transition temperature.[2]

The system of dodecylammonium chloride with carbon tetrabromide, with a eutectic at 69.8°, involves only the higher-temperature form, beta.

[4] C. W. Hoerr and A. W. Ralston, THIS JOURNAL, **64**, 2824 (1942).

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE GLIDDEN COMPANY—NAVAL STORES DIVISION]

Nopol. III. Thermal Isomerization in the Liquid Phase

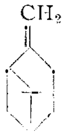
BY JOSEPH P. BAIN, ALBERT H. BEST AND ROBERT L. WEBB

RECEIVED JANUARY 31, 1952

Upon being heated in the liquid phase, nopol showly racemizes and undergoes loss of formaldehyde to form a partly racemic β-pinene through reversal of the β-pinene–formaldehyde condensation. Simultaneously, the isomeric alcohols, dipentene-7-carbinol and alloöcimenecarbinol are formed. Infrared and ultraviolet absorption spectral data are presented in support of the suggested course of the reaction.

β-Pinene (I) and formaldehyde condense to form nopol[1] (II) (6,6-dimethylbicyclo[3,1,1]hept-2-ene-2-ethanol), a structural derivative of α-pinene (III). Infrared spectra are shown in Fig. 1 for the two pinenes and for nopol.

The products of pyrolysis of α-pinene ordinarily[2] recovered are dipentene and the triene alloöcimene although it was recently shown[3] that ocimene can be recovered from the pyrolysis products when a suitable method is employed to avoid its isomerization. Ocimene is so readily isomerized to alloöcimene that the latter is usually the sole acyclic product isolated. Two geometric isomers of alloöcimene have been described.[4] Alloöcimene may be recyclized[5,6] in the vapor phase to a complex mixture consisting chiefly of alkyl cyclohexadienes in which α- and β-pyronene and 1,3-dimethyl-1-ethyl-3,5-cyclohexadiene predominate. At lower temperatures and in the liquid phase, alloöcimene may be converted[7] in high yields to a dimer or mixture of dimers.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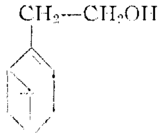
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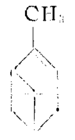
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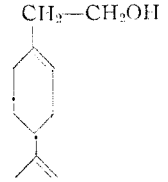
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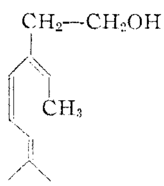
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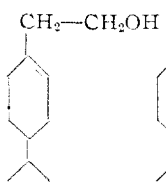
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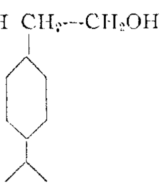
VII

Nopol behaves similarly in the vapor phase since there were isolated products described as menthadiene-7-carbinol[1] and alloöcimenecarbinol[8] from nopol pyrolysis mixtures, but structures were not proved nor were secondary products of pyrolysis described.

It is the purpose of this paper to report that thermal isomerization of nopol is analogous to that of α-pinene and to show that the products of pyrolysis are dipentene-7-carbinol (IV), the allo-ocimenecarbinol (V) and partly racemized nopol. Simultaneously, a partly racemic β-pinene is formed by loss of formaldehyde from the partly racemized nopol. Secondary products of pyrolysis will be referred to, but will be more fully described in a forthcoming paper.

Initial experiments showed that as nopol was heated at reflux at atmospheric pressure, the boiling point gradually rose, small amounts of paraformaldehyde appeared in the condenser and, as shown in Fig. 2, absorptions in the ultraviolet region of the spectrum developed at about λ_{max} 278 mμ. After about 2.5 hours of refluxing, the absorption maxi-

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[1] J. P. Bain, THIS JOURNAL, **68**, 638 (1946).

[2] B. Arbuzov, *J. Gen. Chem.* (*U.S.S.R.*), **3**, 21 (1933); *Ber.*, **67B**, 563 (1934).

[3] J. E. Hawkins and H. G. Hunt, THIS JOURNAL, **73**, 5379 (1951).

[4] J. J. Hopfield, S. A. Hall and L. A. Goldblatt, *ibid.*, **66**, 115 (1944).

[5] L. A. Goldblatt and S. Palkin, *ibid.*, **66**, 655 (1944).

[6] E. E. Parker and L. A. Goldblatt, *ibid.*, **72**, 2151 (1950).

[7] R. E. Fuguitt and J. E. Hawkins, *ibid.*, **67**, 242 (1945); **69**, 319 (1947).

[8] J. P. Bain and A. H. Best, U. S. Patent 2,453,110 (November 9, 1948).

mum began to decrease and shift toward shorter wave lengths. Finally, after 13 hours of heating, a new λ_{max} at about 240 mμ had appeared.

Alloöcimene has been found to possess λ_{max} about 275 mμ, maximum extinction coefficient ($\alpha = E^{g./l.}_{1\ cm.}$) about 320[9] whereas the alkyl cyclohexadienes[6] formed by cyclization of alloöcimene show λ_{max} 265 mμ, α about 40. Alloöcimene polymer[10] exhibits λ_{max} 242 mμ and α 95. Ultraviolet spectra for alloöcimene, alloöcimene polymer and alloöcimenecarbinol (V) are shown in Fig. 4. The series of ultraviolet spectra shown in Fig. 2 are interpreted as indicating the formation of alloöcimenecarbinol (V) then conversion of this product on continued heating to alloöcimenecarbinol polymer. That there is also present a mixture of alkyl cyclohexadiene carbinols in all heat treated samples of nopol is more evident from examination of the ultraviolet spectra of the fractionated pyrolysis products boiling close to nopol. These fractions of crude recovered nopol possess λ_{max} 265 mμ and are free of alloöcimene carbinol and its polymer which dominate the spectra of crude pyrolysis mixtures shown in Fig. 2. There is no evidence that the presence of a carbinol group appreciably affects λ_{max} of the particular chromophore groups present.

A sample of nopol heated at reflux (225 to 240°) for 2.5 hours was fractionated carefully to separate the pyrolysis products. The data are shown in Fig. 3. The lowest boiling product was β-pinene, α^{25}_{D} −15.9° (10-cm. tube), while natural β-pinene[11] is −18.61°. α-Pinene racemizes[1,7,12] at as low temperatures as 175–200°, but β-pinene does not racemize even at the somewhat higher temperature of refluxing nopol, about 225 to 240°. The next higher boiling fraction was nopol, α^{25}_{D} −26.3° (10-cm. tube), although the starting material was −35.86°. It is evident that, like α-pinene, nopol slowly racemizes and that the partly racemic β-pinene recovered was derived from the partly racemized nopol through a reversal of the β-pinene–formaldehyde condensation.

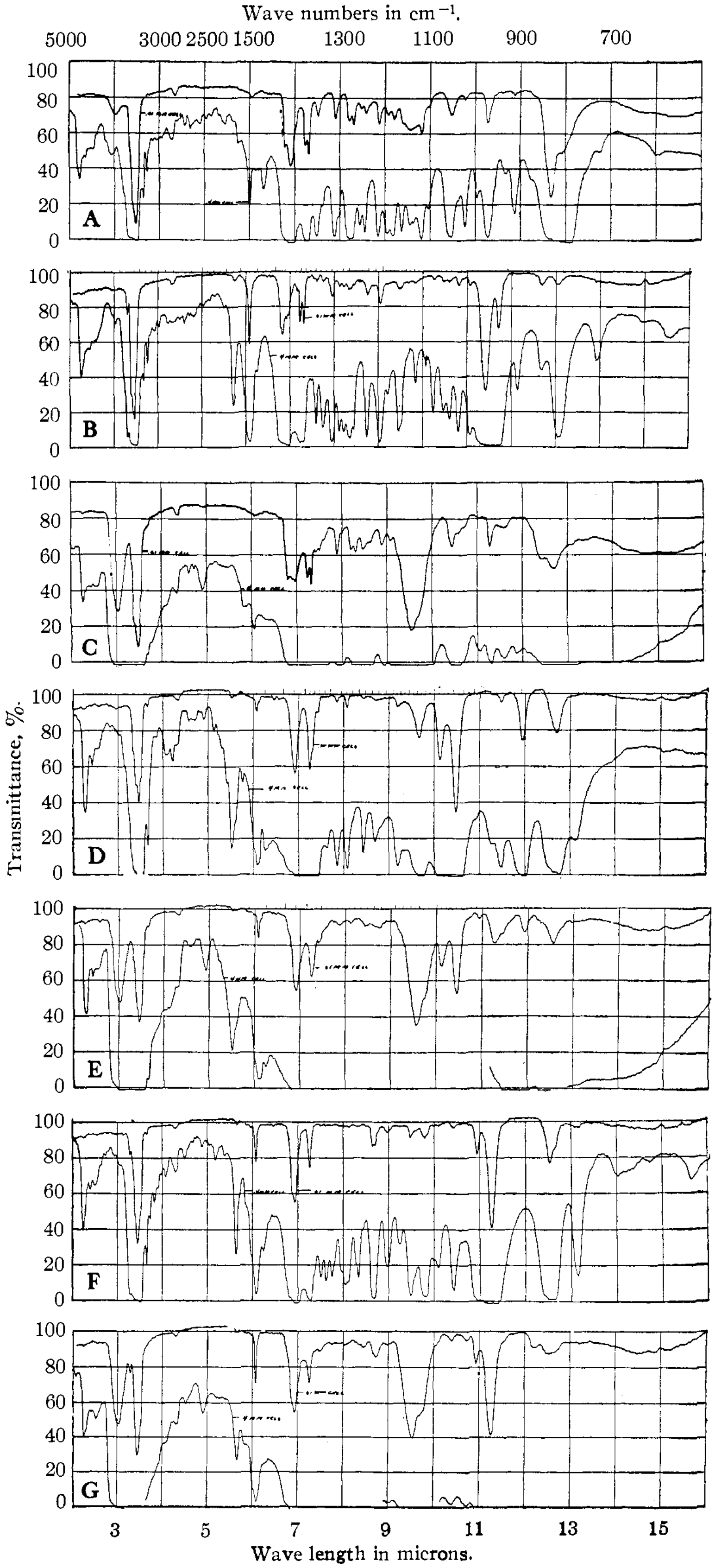

Fig. 1.—Absorption spectra of: A, α-pinene; B, β-pinene; C, nopol; D, alloöcimene; E, alloöcimenecarbinol; F, limonene; G, dipentene-7-carbinol.

Fractions on both sides of the purest recovered nopol fractions showed λ_{max} 265

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(9) Personal communication from Dr. L. A. Goldblatt.

(10) R. D. Walker, Jr., Thesis, University of Florida, Feb., 1951.

(11) R. E. Fuguitt, W. D. Stallcup and J. E. Hawkins, THIS JOURNAL, 64, 2978 (1942).

(12) T. R. Savich and L. A. Goldblatt, *ibid.*, 67, 2027 (1945).

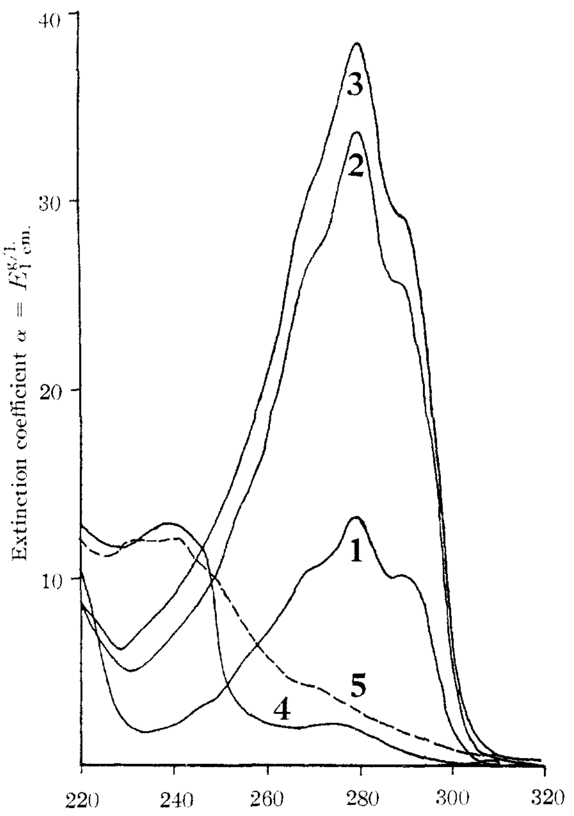

Fig. 2.—Nopol refluxed at 235–245° for: 1, 40 minutes; 2, two hours; 3, three hours; 4, 13 hours; 5, 20 hours.

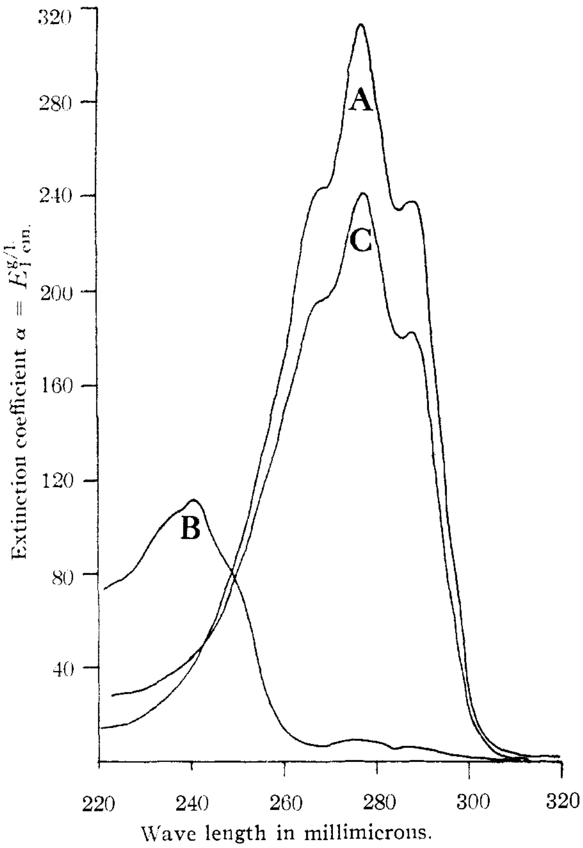

Fig. 4.—Ultraviolet absorption spectra of: A, *allo*öcimene; B, alloöcimene polymer; C, alloöcimenecarbinol.

mμ characteristic of alkyl cyclohexadienes having both double bonds in the ring. That the compounds responsible for these absorptions are alkyl cyclohexadienecarbinols is suggested by the fact that as the alloöcimenecarbinol (V) is formed and passes from a maximum to a minimum concentration, the total amount of materials possessing absorptions in the 260–270 mμ region of the crude nopol recovered by fractionation of the incompletely pyrolyzed material increases as would be expected if V cyclizes as does alloöcimene.

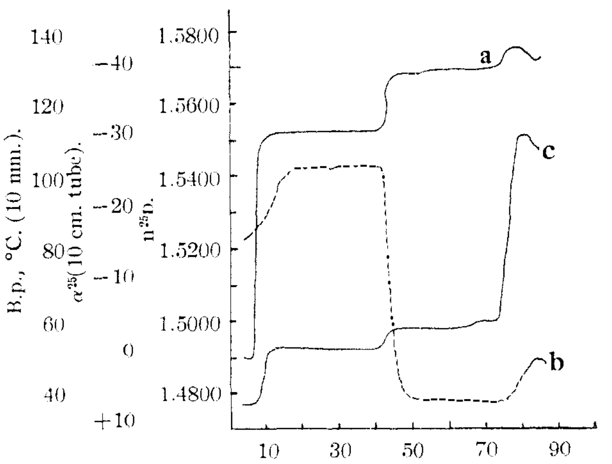

Fig. 3.—a, boiling point (10 mm.); b, optical rotation (10 cm. tube); c, refractive index, n^{25}D.

When recovered, partly racemized nopol of α^{22}D −26.3° (10-cm. tube) was again refluxed for 2.5 hours and the pyrolysis mixture fractionated, the β-pinene recovered showed α^{25}D −12.66° and the nopol recovered was −19.28°. The nopol recovered from this experiment contained about 6 to 8% alkyl cyclohexadiene carbinols, which, as derivatives of optically inactive V, are themselves optically inactive. Therefore, the true rotation of the recovered unreacted nopol was about −21.5°.

The major pyrolysis product, boiling about 18° above nopol, is dipentene-7-carbinol (IV) as shown by comparison of its infrared spectrum with that of limonene (Fig. 1) and the fact that the infrared spectrum of IV is identical with that of the product produced by dehydrochlorination of 1,8-dichloro-*p*-menthane-7-carbinol.[1] The structure of IV was further confirmed by its partial hydrogenation to carvomenthene-7-carbinol (VI) and its complete hydrogenation to *p*-menthane-7-carbinol (VII) which was oxidized to the known[13] *p*-menthane-7-carboxylic acid.

The alloöcimenecarbinol (V) boiling about 6° above IV showed λ_{max} 278 mμ, α 241 as compared to the values obtained in the course of this investigation for alloöcimene, λ_{max} 277 mμ, α 313. In Fig. 1 is shown the infrared spectrum of mixed A and B alloöcimene isomers as ordinarily recovered from the fractionation of an α-pinene pyrolysis mixture and the spectrum of the alloöcimenecarbinol (V).

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(13) D. M. Oldroyd, G. S. Fisher and L. A. Goldblatt, THIS JOURNAL, **72**, 2407 (1950).

The presence of three double bonds in V was confirmed by its hydrogenation to the corresponding saturated acyclic alcohol.

Esters of nopol isomerize readily to esters of IV and V accompanied by cyclization products and polymer of esters of V, but do not yield β-pinene or other hydrocarbons at 235 to 245° as does nopol itself.

Experimental

Spectra.—Ultraviolet spectra were obtained with a Beckman DU spectrophotometer. Isoöctane was employed as the solvent except where otherwise noted.

Infrared spectra presented in Fig. 1 were determined on the homogeneous liquid samples by Samuel Sadtler & Son who employed a Baird spectrophotometer equipped with a sodium chloride prism. Other infrared data were obtained in this Laboratory using a Perkin-Elmer 12-C instrument.

Isomerization of Nopol.—Commercial grade nopol was fractionated to obtain a constant boiling product, b.p. 110.5° (10 mm.), $\alpha^{23}\mathrm{D}$ −35.86° (10-cm. tube). This material showed no $\lambda_{\max}$ above 220 mμ in the ultraviolet region. The purified product was refluxed at 760 mm. pressure and 225 to 240°. Samples were taken at intervals for infrared and ultraviolet analysis. Some typical results of the latter are shown in Fig. 2. A strong absorption appeared, $\lambda_{\max}$ 278 mμ and the extinction coefficient increased for 2.5 hours then began to decrease. At the end of 13 hours of heating, the $\lambda_{\max}$ in this region was very weak and had shifted from 278 to about 274 mμ and a second and now much stronger $\lambda_{\max}$ had appeared at about 241 mμ. After 20 hours of refluxing, there remained only a barely discernible inflection in the region 265 to 275 mμ, probably due to the presence of alkyl cyclohexadienecarbinols. This last sample also showed $\lambda_{\max}$ at about 240 mμ and a new $\lambda_{\max}$ at about 230 mμ had developed. During the course of the isomerization, the boiling point gradually rose from about 225 to 240°. Examination of the infrared spectrum of the material at the end of the 20-hour heating period showed that nopol was absent. Since neither nopol, β-pinene nor dipentene-7-carbinol shows an absorption maximum in the ultraviolet region above 220 mμ, their presence in the reaction mixture had little or no effect on the ultraviolet spectra of pyrolysis mixtures or on distilled fractions.

A large batch of nopol was heated at reflux at 230–240° for 2.5 hours in order to secure a maximum concentration of the material absorbing at 278 mμ then fractionated through a 100 cm. by 50 mm. Stedman column at 10 mm. pressure and at 10:1 reflux ratio with the results shown in Fig. 3.

Formaldehyde was recovered in appreciable quantities as paraformaldehyde from the reflux condenser employed in the isomerization step and from the fractions boiling at about 48°. It was identified by mixed m.p. with an authentic sample, but no attempt was made to estimate it quantitatively.

β-Pinene (I) was the chief constituent of the fractions boiling below 110°, mainly at 48°, and was obtained on refractionation of these fractions in high purity; $n^{25}\mathrm{D}$ 1.4769, $\alpha^{25}\mathrm{D}$ −15.9° (10-cm. tube). The infrared spectrum was identical with that of high purity β-pinene isolated from gum turpentine, $n^{25}\mathrm{D}$ 1.4769, $\alpha^{25}\mathrm{D}$ −18.6° (10-cm. tube). Neither α-pinene nor other terpenes could be detected.

Nopol (II) was identified by infrared analysis as the chief component of fractions boiling in the range 110–113° but traces of impurities were present in even the purest samples. These impurities exhibited absorptions in the ultraviolet region, $\lambda_{\max}$ 265 mμ, of the same type as is shown by α-terpinene and other alkyl cyclohexadienes having both double bonds in the ring. Their amount was estimated from infrared and ultraviolet absorption data not to exceed about 3% of any recovered nopol fraction and it is believed that they consist of two or more alkyl cyclohexadiene carbinols resulting from cyclization of alloöcimenecarbinol (V). The purest nopol cuts showed $\alpha^{25}\mathrm{D}$ −26.3° (10-cm. tube). Since the quantity of impurities present was too small to affect the rotation appreciably, there was no doubt that the nopol had racemized.

Dipentene-7-carbinol (IV) was recovered almost pure as fractions boiling in the range 128–129° though slight absorptions in the region 270–278 mμ showed the presence of traces of alloöcimenecarbinol. The infrared spectra of the fractions showed a strong resemblance to that of limonene and comparison with spectra of "menthadiene-7-carbinol"[1,8] produced by vapor phase pyrolysis of nopol showed that the two carbinols were identical. As further proof of the suggested structure (IV) for this carbinol, 1,8-dichloro-7-*p*-menthane-carbinol[1] was dehydrochlorinated by hot dilute sodium hydroxide and the product was shown to have all characteristic bands of IV, but this dehydrochlorination product was not further purified and was obviously crude. The best sample of IV obtained by liquid phase pyrolysis showed $n^{25}\mathrm{D}$ 1.4981 and $\alpha^{25}\mathrm{D}$ +6.2° (10-cm. tube), d^{25}_{4} 0.958.

Alloöcimenecarbinol (V) was most concentrated in fractions boiling at about 132 to 134° which were refractionated to yield constant boiling material, b.p. 134.7° at 10 mm. The recovery of pure V by fractionation is not quantitative because of its tendency to polymerize. The purest fractions showed $\alpha^{25}\mathrm{D}$ 0 (10-cm. tube); $n^{25}\mathrm{D}$ 1.5580 to 1.5590; d^{25}_{25} 0.9079; $M\mathrm{D}$ calcd. 52.02, found 58.7. The character of the ultraviolet absorption spectrum is practically identical with that of alloöcimene, showing the same $\lambda_{\max}$, 277 mμ, but somewhat smaller extinction coefficient, α 241. The infrared spectrum of V also shows strong similarities to that of alloöcimene. No attempt was made to separate V into the *cis–trans* forms probably present.

A sample of V of 84.5% purity, the remainder IV, was hydrogenated at 30–60 pounds pressure using platinum oxide catalyst. Allowing for absorption of hydrogen by the IV present to form carvomenthene-7-carbinol, the V absorbed 97% of the hydrogen required for three double bonds.[1] The 7-methyl-3-ethyloctanol produced was fractionated to yield the pure material, b.p. 114.5° at 10 mm., $n^{25}\mathrm{D}$ 1.4398, d^{25}_{4} 0.8354.

Anal. Calcd. for $C_{11}H_{24}O$: C, 76.67; H, 14.04. Found: C, 76.49; H, 14.31.

Pyrolysis of Partly Racemized Nopol.—The purest fractions of recovered, partly racemized nopol, $\alpha^{25}\mathrm{D}$ −26.3° (10-cm. tube), were combined and heated at reflux at 760 mm. pressure for 2.5 hours. Results of fractionation were similar to those shown in Fig. 3. The β-pinene was recovered in at least 98% purity but now showed $\alpha^{25}\mathrm{D}$ −12.66° (10-cm. tube). The purest nopol recovered showed $n^{25}\mathrm{D}$ 1.4920 and $\alpha^{25}\mathrm{D}$ −19.3° (10-cm. tube). It contained about 6 to 8% impurities possessing $\lambda_{\max}$ 265 mμ, probably alkyl cyclohexadienecarbinols, but this quantity of impurity is not sufficient to affect the conclusion that the nopol had suffered further racemization during this second heating period. The dipentene-7-carbinol fractions contained about 2 to 4% of V but were otherwise pure and showed $n^{25}\mathrm{D}$ 1.4980, $\alpha^{25}\mathrm{D}$ +4°, indicating that as might be expected, partly racemized nopol yields IV of lower rotation.

β-Pinene was shown to undergo no racemization at the temperatures employed here for decomposition of nopol to formaldehyde and β-pinene. Pure β-pinene, $n^{25}\mathrm{D}$ 1.4771, $\alpha^{23}\mathrm{D}$ −18.61° was heated in a sealed tube immersed in boiling nopol at 225–240° for 3 hours. The contents of the tube became cloudy when cooled and possessed $n^{25}\mathrm{D}$ 1.4774 and $\alpha^{23}\mathrm{D}$ −19.88°. Infrared analysis showed the presence of about 1% limonene and about 98% β-pinene. When this product was fractionated, pure β-pinene, $n^{25}\mathrm{D}$ 1.4770, and $\alpha^{23}\mathrm{D}$ −18.58° was recovered.

In a second experiment conducted under approximately the same conditions but at a slightly higher average temperature, β-pinene yielded a cloudy mixture which was filtered to remove myrcene polymer. The filtrate contained 8% limonene, a trace of myrcene and about 91% β-pinene. After purification by fractionation, the β-pinene showed $n^{25}\mathrm{D}$ 1.4769 and $\alpha^{23}\mathrm{D}$ −18.54°.

It is evident from these experiments that the partly racemic β-pinene recovered from pyrolysis of nopol does not indicate racemization of β-pinene but does indicate the partial racemization of nopol prior to its decomposition to formaldehyde and partly racemic β-pinene.

Carvomenthene-7-carbinol (VI) was produced by hydrogenation of IV at 30 to 60 pounds pressure using platinum oxide catalyst. Only one mole of hydrogen could be added readily under these conditions. The product was fractionated at 10 mm., b.p. 126°; $n^{25}\mathrm{D}$ 1.4826; d^{25}_{4} 0.9289. The presence of approximately one double bond was shown by bromine titration. Evidence of the structure of the product was apparent from comparison of its infrared spectrum with that of carvomenthene produced by partial hydrogenation of *d*-limonene. The two compounds show the same strong infrared absorption band at 11.03 μ and the same medium strength bands at 8.05 and 8.18 μ.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.41; H, 12.07.

***p*-Menthane-7-carbinol (VII)** was produced by hydrogenation of a mixture of about 75% IV and 25% V using Raney nickel at 1500–2000 pounds pressure. After removal of 7-methyl-3-ethyloctanol resulting from the hydrogenation of V at 110–116° at 10 mm., VII distilled at 126° at 10 mm., n^{25}_{D} 1.4700, d^{25}_{4} 0.9117. It was identified by oxidation with chromic acid–acetic acid to a mixture which partly solidified. The solid acid after several recrystallizations from pentane melted at 77–78° and its infrared spectrum was identical with that of a known[13] sample of *p*-menthane-7-carboxylic acid kindly furnished by Dr. L. A. Goldblatt. The liquid acids are thought to be a mixture of the *cis–trans* isomers of this acid which indicates that the VII is a mixture of the two possible *cis–trans* alcohols.

Alloöcimene dimer[7] is readily produced by heating alloöcimene at about 200° and its ultraviolet spectrum has been studied.[10] This work was repeated. Alloöcimene was heated at 205° for 10 hours and 40 minutes at which time the product contained about 17% unchanged alloöcimene by ultraviolet absorption analysis. This result was in good agreement with Fuguitt[14] who reported 19% unchanged alloöcimene after heating alloöcimene under the same conditions of time and temperature. The partly polymerized product was distilled at about 5 mm. pressure through a short column and fractions of dimer, b.p. 155–156°, were collected and examined. All fractions showed λ_{max} 241–242 mμ and the extinction coefficient (α) of the fractions ranged from 88 to 110.6. The dimer is further characterized by infrared absorption bands at 10.15, 10.36, 11.54, 11.63 and 11.87 μ.

Alloöcimenecarbinol (V) was polymerized by heating at 205° for 10 hours and 40 minutes. The viscous product was shown by infrared analysis to have retained the hydroxyl group. Its ultraviolet spectrum was determined in methanol since the product was partly insoluble in isoöctane. The spectrum showed two absorption maxima, λ_{max} 242, α 65, and λ_{max} 276, α 78. From these data and the known extinction coefficient for V, it was calculated that the partly polymerized V contained approximately 31% unreacted V and 69% polymerized V, and that the polymerized V possessed an extinction coefficient, α, of about 79. The infrared spectrum of this crude mixture of V and its polymer showed with certainty only one absorption band which appeared to be common with that of alloöcimene dimer, a band at 10.15 μ.

Isomerization of Nopyl Acetate.—Nopyl acetate was heated at 240° for 5.5 hours. The isomerized product contained free acetic acid equivalent to decomposition of about 0.8% of the nopyl acetate. The product was fractionated at 10 mm. and the fractions were analyzed by ultraviolet and infrared methods.

There was formed no β-pinene or other low boiling terpenes. The first fractions boiling over the range 109–132.5° were rich in acetates showing λ_{max} 264 mμ and believed to be alkyl cyclohexadiene carbinol acetates resulting from cyclization of alloöcimenecarbinol acetate. The quantity of these conjugated cyclic acetates was estimated to be 10% of the original nopyl acetate. There was also present in these fractions nopyl acetate amounting to 5% of the starting material.

Dipentene-7-carbinol acetate was obtained in about 55% yield, b.p. 134° at 10 mm., n^{25}_{D} 1.4775. Its identity was apparent from comparison of its infrared spectrum with that of limonene and dipentene-7-carbinol, all of whose major absorption bands are common except, of course, for the acetate or hydroxyl absorptions.

Alloöcimenecarbinol acetate was obtained in about 15% yield; b.p. 140° at 10 mm., n^{25}_{D} 1.526; extinction coefficient for the purest fraction, α 173, λ_{max} 279 mμ. The major infrared absorption bands of the acetate coincide with those common to alloöcimene and alloöcimene carbinol. It was estimated from spectrophotometric data that purity of the best fraction was only about 85%, the remainder chiefly dipentene-7-carbinol acetate.

The distillation residue amounted to 15% of the charge and was estimated to contain 28% alloöcimenecarbinol acetate and 15% alloöcimenecarbinol polymer acetate, the latter showing λ_{max} 241.

Acknowledgment.—The authors wish to express their appreciation to Dr. Philip Sadtler for providing the infrared absorption spectra shown in Fig. 1.

JACKSONVILLE, FLORIDA

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(14) R. E. Fuguitt, Thesis, University of Florida, May, 1943.

[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

The Preparation of Some 1-Alkylamino- and Dialkylaminoalkylaminothiaxanthones[1]

BY S. ARCHER AND C. M. SUTER

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The preparation of an extensive series of 1-alkyl and dialkylaminoalkylaminothiaxanthones was undertaken as part of a study on the chemotherapy of schistosomiasis. The compounds were prepared by condensing a 1-chlorothiaxanthone with a substituted alkylenediamine at atmospheric pressure. The required 1-chlorothiaxanthones were obtained by (a) condensing a thio- or dithiosalicylic acid with a 1-halo-4-methylbenzene; (b) treating a chlorothiophenol with an appropriately substituted *o*-chlorobenzoic acid followed by ring closure of the resulting *o*-arylmercaptobenzoic acid with sulfuric acid and (c) condensing 2,4-dichloronitrobenzene with a thiosalicyclic acid, followed by conversion of the resulting acid to the corresponding acid chloride and cyclizing with the aid of aluminum chloride. A modified mechanism for the condensation of dithiosalicylic acid with benzene and its congeners is proposed.

Several years ago it became of interest to prepare a sample of Miracil D (II), a new orally effective schistosomicidal drug, which was developed in Germany during the recent war. The method of preparation[2] consisted of condensing diethylaminoethylamine with 1-chloro-4-methylthiaxanthone (I). The intermediate chlorothiaxanthone, I, was obtained mixed with the 4-chloro-1-methylthiaxanthone according to the procedure of Ullmann and Glenck[3] who treated thiosalicylic acid with *p*-chlorotoluene in sulfuric acid. The 1-chloro isomer, I, is sufficiently reactive to condense with an amine at elevated temperatures.

When this work was repeated it was found that in small scale runs it was possible to duplicate the results already reported; however, on a larger scale

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[1] The numbering system of the thiaxanthones used throughout this paper follows current *Chemical Abstracts* usage. This differs from the system used by the English and German workers in that the sulfur atom is numbered 5 in one case and 10 in the other. The compound which Mauss (ref. 4) named 1,6-dichloro-4-methylthioxanthone corresponds to 1,7-dichloro-4-methylthiaxanthone here. The minor difference in spelling should be noted.

[2] Office of the Publication Board, Department of Commerce, Washington, D. C., Report No. 981.

[3] F. Ullmann and O. v. Glenck, *Ber.*, **49**, 2487 (1916).