[Contribution from the Chemical Laboratories of Northwestern University]

The Reactions of Terpenes with Thiourea and Acid. II.[1] Preparation, Properties, and Evidence for the Structure of 1(S),8(N)-*p*-Menthyleneisothiourea, a New Ring System

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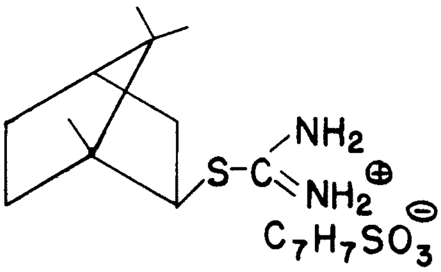
When pinene and certain related terpenes react with thiourea and *p*-toluenesulfonic acid, the principal reaction product is a cyclic adduct wherein thiourea is attached to the 1 and 8 positions of the *p*-menthane nucleus forming 1(S),8(N)-*p*-menthyleneisothiourea. In this paper the preparation and properties of 1(S),8(N)-*p*-menthyleneisothiourea and its derivatives are described. The data leading to the assignment of the 1(S),8(N)-*p*-menthyleneisothiourea structure are presented and discussed.

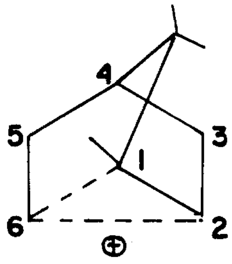
In the first paper of this series[1] it was shown that camphene and certain related terpenes react with thiourea and acid to give isobornylisothiuronium *p*-toluenesulfonate (I). This reaction product was obtained in high yield. The complete course of the reaction for formation of this compound could be rationalized if one assumed, (a) that a bridged ion structure II was involved as an intermediate, (b) that the bridged ion II reacted with reagent thiourea in a stereospecific manner at C-2 with inversion and displacement of the 2,6-hybrid bond, and (c) that any attack on C-1 by reagent thiourea was reversible.

In terms of this interpretation one might expect to obtain some bornylisothiouronium *p*-toluenesulfonate (III) when reagent thiourea reacts at C-1 with the bridged ion (IV) which might be formed from pinene in acidic solution. When this reaction was tried, a compound having the properties of III was obtained in small amounts. However, the principal reaction product was an amine salt (VI), which was subsequently shown to be the *p*-toluenesulfonate salt of 1(S),8(N)-*p*-menthyleneisothiourea (V).

In this paper the preparation and properties of V and the data leading to the assignment of structure for this substance are described in some detail.



I



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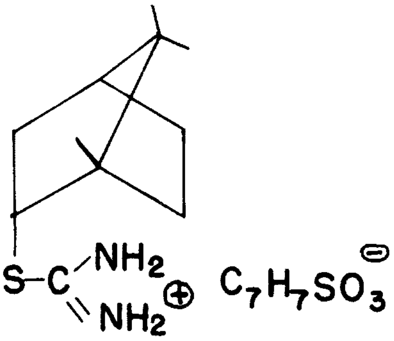

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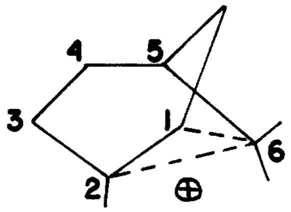

IV

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[1] For paper I in this series see Subluskey and King, *J. Am. Chem. Soc.*, **73**, 2647 (1951).

[2] From the Ph.D. Theses of Lee A. Subluskey (1950) and Eric W. Stern (1954).

When α-pinene was heated with *p*-toluenesulfonic acid and thiourea two crystalline products and a glass-like substance were produced. The principal crystalline product, $C_{18}H_{28}N_2S_2O_3$, m.p. 240°, accounted for 30% of the total yield and was the *p*-toluenesulfonate salt (VI) of 1(S),8(N)-*p*-menthyleneisothiourea (V). The other crystalline product $C_{18}H_{28}N_2S_2O_3$, m.p. 176–178° was obtained in 4.4% yield; the glass was obtained in 50% yield. Both the crystalline product, m.p. 176–178°, and the glass were shown to be S-alkylisothiuronium salts, by conversion to mercaptans with aqueous base. The crystalline compound, m.p. 176–178°, was an isomer of isobornylisothiuronium *p*-toluenesulfonate (I) and gave camphane on reduction with Raney Nickel. On the basis of these observations it was tentatively identified as bornylisothiuronium *p*-toluenesulfonate (III). Desulfurization of the glass gave a mixture of hydrocarbons of which camphane was identified. Further separation of the glass into its constituents was not accomplished.

The *p*-toluenesulfonate salt VI was also obtained from β-pinene, dipentene, *d*-limonene, α-terpineol, β-terpineol, terpin hydrate, terpinolene, 1,8-cineol, and from limonene dihydrochloride. These reactions and their yield data are summarized in Table I. The highest yield of VI, 44%, was obtained from 1,8-cineol. Each time VI was prepared in the course of this sequence of reactions it was characterized by conversion to the free base V and by conversion to one or more derivatives of the free base. These derivatives are described in the experimental part of this paper. Neither 1(S),8(N)-*p*-menthyleneisothiourea nor its *p*-toluenesulfonate salt were optically active even when prepared from optically active terpenes.

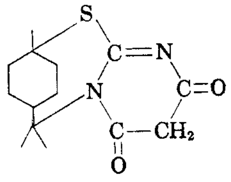
TABLE I

PREPARATION OF THE HYDROTOSYLATE OF 1(S),8(N)-*p*-MENTHYLENEISOTHIOUREA

Starting Substance Name	$[\alpha]^{24}_D$	Hydrotosylate Yield, %	M.p., °C.	$[\alpha]^{24}_D$
α-Pinene	31.2	30	236–238	0
β-Pinene	−20.9	—	238–240	0
Dipentene	0.0	21	237–238	0
d-Limonine	118.9	43	238–240	0
α-Terpineol	—	26	236–238	0
β-Terpineol	—	30	237–238	0
Terpin hydrate	0.0	40	236–238	0
1,8-Cineole	0.0	44	233–235	0
Terpinolene	—	37	238–239	0
Limonine dihydrochloride	0.0	43	232–233	0

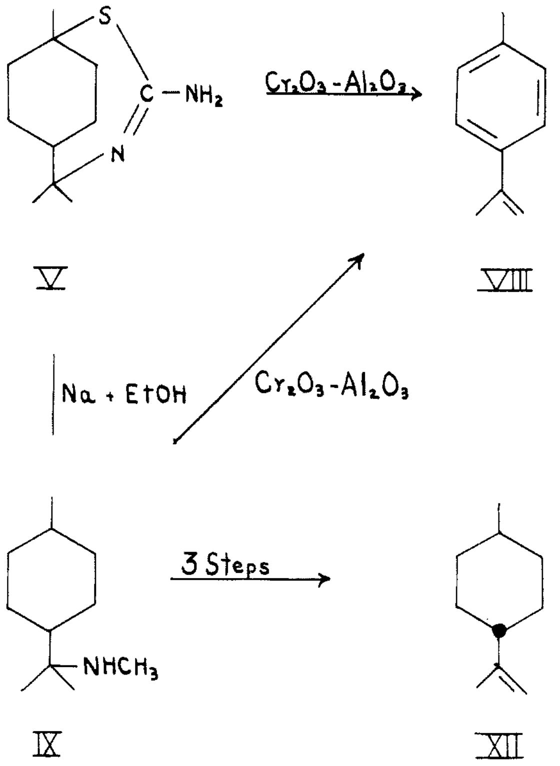
The free base V was characterized as a monobasic primary amine, pK_b 5.08, by conversion to a number of amide derivatives and by a consideration of the solubility of its benzenesulfonamide.

Examination of the infrared spectrum of V showed a medium band at 6.1 μ which was indicative of the C=N—group. On reaction with malonic ester compound V gave N,N′-malonyl-1(S),8(N)-*p*-menthyleneisothiourea (VII), a pyrimidine.[3] This fact was taken as evidence for the —N=C—NH$_2$ group in the molecule.



VII

Early in the course of this investigation it was postulated that V was a cyclic adduct of thiourea and *p*-menthane. The plan of attack therefore, centered around (a) removal of all heteroatoms in order to demonstrate the carbon skeleton, and (B) cleavage of the heterocyclic ring to give substituted *p*-menthanes. Identification of these would then indicate the positions at which thiourea was attached to the *p*-menthane nucleus.



Removal of the heterocyclic portion of the molecule was accomplished by passing V, in pentane solution, over chromia-alumina catalyst at 480°. Hydrogen sulfide and ammonia were detected in the effluent gases. The product oil decolorized aqueous potassium permanganate, and its infrared spectrum was identical with that of 1-methyl-4-isopropenylbenzene[4] (VIII).

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(3) Masters and Bogert, *J. Am. Chem. Soc.*, **64**, 2709 (1942).

(4) Murrary and Galloway, *J. Am. Chem. Soc.*, **70**, 3867 (1948).

The appearance of the double bond in the side chain of VIII was taken as evidence that in V the carbon corresponding to the 8-position of the *p*-methane nucleus was a point of substitution. An independent experiment indicated that *p*-cymene when passed over chromia-alumina catalyst at 500–600° was unchanged.

The second objective, degradation of V to substituted *p*-menthanes, presented several difficulties. A number of reactions proved unsuitable before a workable method of degradation was found. Some of these will be discussed since the reactions give some information on the stability of V.

Raney nickel failed to desulfurize V under conditions which gave 91% yield of camphane from isobornylisothiuronium *p*-toluenesulfonate.[1]

The reaction of V with bromine using the procedure of Gabriel[5] for degradation of thiazolines, gave the hydrobromide of V plus a tarry substance, presumably the N-bromoamine, which regenerated V on heating with acetone.

Desulfurization finally was accomplished by treatment of V with sodium in absolute ethanol. Ammonia was evolved during the course of the reaction and the product was a secondary amine (IX), subsequently shown to be 8-methylamino-*p*-menthane.[6]

The amine IX when passed over the chromia-alumina catalyst at 480° gave 1-methyl-4-isopropenylbenzene (VIII). In view of this observation it is apparent that IX is 8-methylamino-*p*-menthane and hence, that the nitrogen in V is attached to the carbon in the 8 position of the *p*-menthane nucleus.

The attachment of the nitrogen to the 8 position of the *p*-menthane carbon skeleton in compound V was further confirmed in the following manner:

Reductive methylation of the amine IX gave a tertiary amine X which on reaction with methyl iodide gave the quaternary salt XI. The salt XI was converted to the quaternary hydroxide[7] and subsequently to *trans*-8(9)-*p*-menthene (XII).[8]

The 4 position of *p*-menthane as a possible site of substitution for nitrogen can be discarded on the basis of the above observation, since Hofmann elimination of nitrogen attached to the 4 position would result in either 3(4)-*p*-menthene or in 4(8)-*p*-menthene. In any case, no *trans*-8(9)-*p*-menthene would be formed.

The possibility that *trans*-8(9)-*p*-menthene is produced by rearrangement of a *p*-menthene which was produced by the Hofmann reaction itself is ruled out by the recent work of Pines and Eschinazi.[9]

From the evidence presented the structure of V is established as a *p*-menthane skeleton with a nitrogen substituted at position 8. Since the second nitrogen is present as a primary amine the position of attachment of the sulfur atom to the *p*-menthane skeleton remains to be determined.

Compound V showed no optical activity even when prepared from highly active terpenes. This indicates that V is symmetrical or a racemic mixture. If the latter situation exists, V should be resolvable. The *d*-camphorsulfonate salt of V was prepared and resolution was attempted by crystallization from a variety of solvents. No resolution was observed. The compound V, therefore is symmetrical and the 2,3,5, and 6 positions of the *p*-menthane carbon skeleton are ruled out as sites for substitution of the sulfur atom.

If sulfur were attached at the 4 position of the *p*-menthane skeleton compound V would be a thiazoline. The infrared spectra of 2-aminothiazoline and some of its derivatives, show a large absorption peak at 9.8–10.2 μ. This peak also is found in the spectrum of 2-phenyl-2-thiazoline.[10] This band is absent in the infrared absorption of compound V, Figure 1.

On the premise that the 9.8–10.2 μ band is characteristic of thiazoline, the 4 position of the *p*-menthane skeleton of compound V is eliminated as a point of attachment for the sulfur atom. It would also be difficult to rationalize attachment at position 4 on mechanistic grounds.

The 1 position of the *p*-menthane skeleton is the only place left for attachment of sulfur to the *p*-menthane skeleton, that can be rationalized in terms of the method of preparation and all the degradation data. Thus, compound V is 1(S),8(N)-*p*-menthyleneisothiourea.

Acknowledgment. We wish to thank the National Cancer Institute of the U. S. Public Health Service (L. A. S.), and Swift and Company (E. W. S.), for research grants.

EXPERIMENTAL[11]

Starting materials. α-Pinene,[12] b.p. 98.5°/100 mm., n_D^{30} 1.4507, $[\alpha]_D^{24}$ 31.2°. β-Pinene,[12] b.p. 98.5°/100 mm., n_D^{30} 1.4741, $[\alpha]_D^{24}$ −20.9°. Terpinolene,[12] n_D^{25} 1.4678, estimated purity 80–83%. Dipentene,[13] practical grade, b.p. 78–80°/35 mm. *d*-Limonene,[13] b.p. 67–68°/2 mm., $[\alpha]_D^{25}$ 118.9°. α-Terpineol,[13] a practical grade, was frozen, allowed to warm to room temperature, and the liquid was decanted.

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(5) Gabriel, *Ber.*, **22**, 1141 (1889).

(6) The infrared spectrum indicated the presence of some primary amine in this preparation. However, analysis of the preparation and its derivatives indicated a single product. These derivatives are described in the Experimental Part.

(7) Weinstock and Boekelheide, *J. Am. Chem. Soc.*, **75**, 2546 (1953).

(8) *Trans*-8(9)-*p*-menthene was synthesized by reduction of dihydrocarvone and shown to be identical with the degradation product XII. Kishner, *J. Russ. Phys.-Chem. Soc.*, **43**, 951 (1911).

(9) Pines and Eschinazi, *J. Am. Chem. Soc.*, **78**, 1176 (1956); *J. Am. Chem. Soc.*, **78**, 1178 (1956).

(10) Randall, Fowler, Fuson, and Dangl, *Infrared Determination of Organic Structure*, Van Nostrand Co., 1949, p. 211.

(11) All melting points were observed on a Fisher-Johns block. Analyses by H. Beck, J. Sorensen, and C. White.

(12) Research sample obtained from Hercules Powder Company.

(13) From Eastman Kodak.

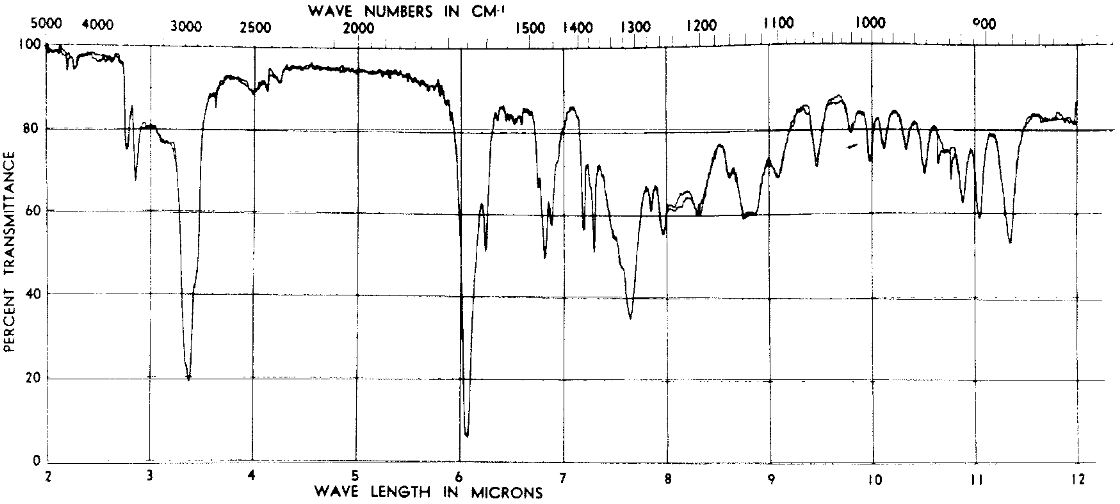

Fig. 1. INFRARED SPECTRUM OF 1(S),8(N)-*p*-MENTHYLENEISOTHIOUREA. 100 mg. in 2.0 cc. of $CHCl_3$. Sample cells, 0.1 mm.

The crystalline residue, m.p. 30–32°, was used. β-Terpineol, a student preparation, n^{25}_D 1.4724 was used. Terpin Hydrate,[13] was used as supplied. 1,8-Cineol,[13] the fraction, b.p. 52–54°/6 mm., n^{25}_D 1.4555, was used.

Limonene dihydrochloride. The high-melting form of the dihydrochloride was prepared according to the directions of Simonsen and Owen.[14]

Reaction of α-pinene with thiourea and p-toluenesulfonic acid. α-Pinene (100 g., 0.735 mole), 165 g. (0.835 mole) of *p*-toluenesulfonic acid monohydrate, and 85 g. (1.12 moles) of thiourea were stirred and heated on the steam-bath for 3 days. The reaction mixture was cooled, washed with ether, and then with water. The ether extract contained 4.4% of oily material with a strong lemon-like odor.

The gummy material remaining after washing with ether and water was leached with acetone and 83 g. of white crystals, m.p. 236–238°, VI, which were insoluble in the acetone were collected. The crystals VI, after crystallization from ethanol, melted at 238–240°, $[\alpha]^{24}_D$ 0°.

Anal. Calc'd for $C_{18}H_{28}N_2O_3S_2$: C, 56.25; H, 7.31; N, 7.29. Found: C, 56.48; H, 7.10; N, 7.22.

This product is the *p*-toluenesulfonate salt of 1(S),8(N)-*p*-menthyleneisothiourea, V.

Continued concentration of the acetone leachings gave 11.8 g., 4.4%, of a second salt III which melted at 176–178° after crystallization from ethanol.

Anal. Calc'd for $C_{18}H_{28}N_2O_3S_2$: C, 56.25; H, 7.31; N, 7.29. Found: C, 56.58; H, 7.41; N, 7.28.

After no more crystalline material could be separated by further concentration of the acetone leachings, the remainder of the acetone was removed in *vacuo*. A clear, hard, light brown glass-like substance remained; yield 50.5%.

Anal. Calc'd for $C_{18}H_{28}N_2O_3S_2$: C, 56.25; H, 7.31; N, 7.29. Found: C, 56.87; H, 7.68; N, 7.83.

Reaction of other terpenes with thiourea and p-toluenesulfonic acid. In general, the reaction procedures were identical with that described above except that only compound VI was isolated in pure form. Maximum yields of VI were obtained by heating the terpene, thiourea, and *p*-toluenesulfonic acid mixture for three days. Longer heating periods did not improve the yield.

Preparation VI was optically inactive even when starting materials were active. Detailed yield data for the preparation of VI are shown in Table I.

Preparation of VI from limonene dihydrochloride. A mixture consisting of 26 g. of limonene dihydrochloride and 20 g. of thiourea was heated on the steam-bath for three days. The resinous product was dissolved in hot water and the solution was cooled and extracted with ether. The aqueous solution then was treated with a solution of *p*-toluenesulfonic acid whereupon VI separated. After washing with water and acetone 20.5 g. (43%) of VI, m.p. 232–233°, was obtained.

1(S),8(N)-p-Menthyleneisothiourea (V). The salt VI was warmed for 20 minutes with an excess of 4 *M* sodium hydroxide and the resulting slurry was cooled and filtered. The precipitate when crystallized from petroleum hexane (Skellysolve B) gave white needles, m.p. 116.5–117°, pK_b 5.08 (in 30% alcohol). Equivalent weight 222 by titration with hydrochloric acid. Molecular weight 220 in boiling acetone.

Anal. Calc'd for $C_{11}H_{20}N_2S$: C, 62.26; H, 9.43; N, 13.20. Found. C, 62.53; H, 9.45; N, 13.49.

Hydrochloride. Crystallized from ethanol-ether; m.p. 258–259°.

Anal. Calc'd for $C_{11}H_{21}ClN_2S$: C, 53.09; H, 8.51; N, 11.26. Found: C, 53.56; H, 8.53; N, 11.95.

Hydrobromide. Recrystallized from water, m.p. 240–241°.

Anal. Calc'd for $C_{11}H_{21}BrN_2S$: C, 45.66; H, 7.17; N, 9.56. Found: C, 45.79; H, 7.35; N, 9.41.

Picrate. Recrystallized from ethanol, m.p. 196–197°.

Anal. Calc'd for $C_{17}H_{23}N_5O_7S$: C, 46.26; H, 5.22; N, 15.87. Found: C, 46.36; H, 5.17; N, 16.41.

d-Camphorsulfonate. Recrystallized from several solvents, melts at 176–181°, solidifies and remelts at 196–197°.

Anal. Calc'd for $C_{21}H_{36}N_2O_4S_2$: C, 56.76; H, 8.11; N, 6.31. Found: C, 57.31; H, 8.32; N, 6.19.

Acetamide. Crystallized from isopropyl ether, m.p. 145–147°.

Anal. Calc'd for $C_{13}H_{22}N_2OS$: C, 61.42; H, 8.66; N, 11.02. Found: C, 61.80; H, 8.87; N, 11.14.

Benzenesulfonamide. Crystallized from ethanol, m.p. 204–205°.

Anal. Calc'd for $C_{17}H_{24}N_2O_2S_2$: C, 57.95; H, 6.82; N, 7.95. Found: C, 58.45; H, 6.90; N, 8.19.

Treatment with base gave the sodium salt as a white precipitate, m.p. over 300°. On acidification, the white precipitate was converted to the benzenesulfonamide above, m.p. 204–205°.

Phenylthiourea. Crystallized from ethanol, m.p. 142–144°.

Anal. Calc'd for $C_{18}H_{25}N_3S_2$: C, 62.25; H, 7.20; N, 12.10. Found: C, 61.75; H, 7.36; N, 11.62.

Camphane from hydrogenolysis of III. The salt III iso-

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(14) Simonsen and Owen, *The Terpenes*, 2nd ed., The University Press, Cambridge, 1947, page 159.

lated from the reaction of α-pinene with thiourea and *p*-toluenesulfonic acid as described above, was treated with freshly prepared standard Raney nickel and camphane was isolated as described by Subluskey and King.[1] The crude camphane, m.p. 143–150°, was sublimed; yield 1.1 g. (41%), m.p. 148–151° (sealed tube).

Camphane from hydrogenolysis of the glass. The reaction was carried out as described above. The product was a dark oil from which a small amount of camphane, m.p. 143–150°, was obtained on sublimation.

N,N′-Malonyl-1(S),8(N)-p-menthyleneisothiourea. A solution of 5.3 g. of 1(S),8(N)-*p*-menthyleneisothiourea in ethanol,[3] was added to sodiomalonic ester in alcohol. The solution was refluxed for three hours, then cooled and acidified with hydrochloric acid. The precipitate was washed to remove salt and was crystallized from ethanol, m.p. 249–249.5°.

Anal. Calc'd for $C_{14}H_{20}N_2O_2S$: C, 60.00; H, 7.14; N, 10.00. Found: C, 60.68; H, 7.13; N, 10.32.

1-Methyl-4-isopropenylbenzene (VIII). (a) *By dehydrogenation of V.* A solution of 6 g. of V in 780 ml. of pentane was passed over a chromia-alumina catalyst (activated with ceric and potassium nitrates) in a vertical constant temperature furnace set at 480°.[15] The hourly liquid space velocity was 0.78.

The solvent was removed at atmospheric pressure and the residual oil was distilled in a vacuum. The infrared spectrum of the fraction, b.p. 68–69°/11 mm., n^{26}_D 1.5192, was identical with that of 1-methyl-4-isopropenylbenzene.[4]

(*b*) *By dehydrogenation of the amine* IX. The amine IX produced by sodium reduction of V in alcohol, *vide infra,* was dehydrogenated over a chromia-alumina catalyst in the same manner as described above. The product was 1-methyl-4-isopropenylbenzene (VIII), identical with that described above.

Attempted dehydrogenation of p-cymene. p-Cymene (25 g.) was shaken with 100 ml. of ferrous ammonium sulfate solution, acidified with sulfuric acid until a peroxide test was negative. The *p*-cymene was separated and dried over magnesium sulfate. Several samples of 10 ml. each were passed over a chromia-alumina catalyst at 500–600°. The infrared spectrum samples before and after passage over the catalyst were identical. The strong absorption at 11.2 μ, typical of styrene did not appear.

Reaction of V *with sodium and alcohol.* A solution of 15 g. (0.071 mole) of V in 175 ml. of absolute ethanol was brought to the reflux and treated with 15 g. of clean sodium. The reaction flask was swept with nitrogen and the effluent gases were bubbled through standard hydrochloric acid. After all the sodium was used up, the sweeping was continued for two hours. A total of 0.0366 mole of hydrochloric acid was consumed indicating 51% of the nitrogen had been removed from the compound.

Water was added to the reaction mixture and the solution was steam-distilled. The first portion of the steam-distillate was clear; later, an oily layer separated. The steam-distillate was saturated with potassium hydroxide and extracted with ether. The ether extract was dried over potassium hydroxide. The solvent was removed from the above extracts and the residual oil was fractionated. The major portion of the distillate, 5.69 g., boiled at 79–80°/10 mm., n^{24}_D 1.4570. This distillate was basic to litmus and contained no sulfur. Its infrared spectrum indicated a primary amine but no carbylamine test could be obtained. Reaction with nitrous acid in acetic acid solution gave a nitrosoamine. A green precipitate was obtained on treatment with nickel chloride, carbon disulfide, and ammonium hydroxide.[16] All derivatives prepared from this amine correspond to derivatives of 8-methylamino-*p*-menthane.

Derivatives of 8-methylamino-p-menthane. The amine preparation IX referred to above was used as starting material for each of the following preparations.

Hydrochloride. Recrystallized from 6 *M* HCl, m.p. 229–230°.

Anal. Calc'd for $C_{11}H_{24}ClN$: C, 64.20; H, 11.76; N, 6.81. Found: C, 64.13; H, 11.55; N, 7.18.

Picrate. Recrystallized from ethanol-water, m.p. 184–185°.

Anal. Calc'd for $C_{17}H_{26}N_4O_7$: C, 51.25; H, 6.58; N, 14.06. Found: C, 50.98; H, 6.40; N, 14.46.

Benzamide. Crystallized from cyclohexane and from ethanol, m.p. 157.5–158°.

Anal. Calc'd for $C_{18}H_{27}NO$: C, 79.07; H, 9.96; N, 5.12. Found: C, 79.45; H, 9.78; N, 5.48.

Benzenesulfonamide. Crystallized from ethanol-water, m.p. 105–106°.

Anal. Calc'd for $C_{17}H_{27}NO_2S$: C, 65.98; H, 8.80; N, 4.53. Found: C, 66.03; H, 8.53; N, 4.93.

Phenylthiourea. Crystallized from ethanol-water, m.p. 123–124°.

Anal. Calc'd for $C_{19}H_{28}N_2S$: C, 71.00; H, 9.27; N, 9.20. Found: C, 70.62; H, 8.99; N, 9.98.

8-Dimethylamino-p-menthane (X). The Eschweiler-Clark[17] modification of the Leuckart reductive methylation was used. A solution consisting of 11.7 g. of IX, 23 g. of 88% formic acid, and 14 g. of 35% formaldehyde was heated on the steam-bath for four hours and then was acidified. The acidic solution was evaporated to remove excess reagent. The residue was made alkaline and extracted with ether. The ether solution was dried, the solvent removed, and the residue fractionated, b.p. 98–99°/10 mm., yield 6.2 g.

Picrate. Crystallized from ethanol, m.p. 177–178°.

Anal. Calc'd for $C_{18}H_{28}N_4O_7$: C, 52.42; H, 6.84; N, 13.59. Found: C, 52.31; H, 6.64; N, 13.58.

8-p-Menthyltrimethylammonium iodide (XI). A solution of 6.2 g. of the 8-dimethylamino-*p*-menthane (X) and 20 g. of methyl iodide in methanol was allowed to stand overnight; yield 10.3 g. (97%) of substance melting at 215–240° with decomposition.

Anal. Calc'd for $C_{13}H_{28}IN$: N, 4.31. Found: N, 4.32.

trans-8(9)-p-Menthene (XII). A solution of 5.0 g. of 8-*p*-menthyltrimethylammonium iodide (XI) in 85 ml. of water was passed over Amberlite IRA-400-OH and eluted until the eluate was not basic. This aqueous solution (350 ml.) was heated at reflux for eight hours. Trimethylamine was evolved and an oily layer separated. The oily layer was separated with pentane, dried, and the solvent was evaporated, yield 2.5 g. (98% of the crude product).

On fractionation, the entire product distilled between 52–56°/12 mm. with the major portion coming over at 53–54°/10 mm., n^{26}_D 1.4490.

Anal. Calc'd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.54; H, 12.82.

This compound was identical with *trans*-8(9)-*p*-menthene prepared by reduction of dihydrocarvone according to the method of Kishner.[18]

Attempted resolution of 1(S),8(N)-p-menthyleneisothiourea. Compound V was converted to the *d*-camphorsulfonate and this product was fractionated from a series of solvents in an attempt to resolve it. The following solvents were used: ethyl acetate, ethanol, isopropyl alcohol, methyl ethyl ketone, dimethylformamide, and pyridine. No resolution was accomplished. When the amine was regenerated in each case it was identical with starting material, m.p. 116.5–117°, $[\alpha]^{24}_D$ 0.0.

EVANSTON, ILLINOIS

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(15) H. Pines, *Laboratory Manual. Teaching Unit of the Ipatieff Catalytic Laboratory,* Northwestern University, p. 6.

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