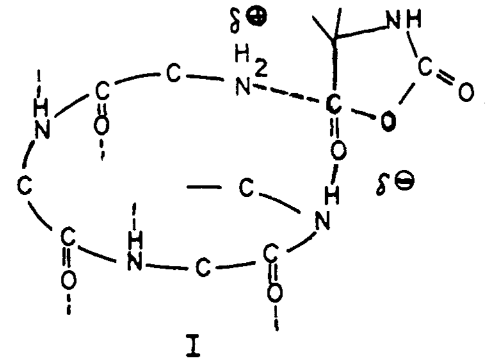
give products without the formation of an intermediate complex. Several other mechanisms can be envisioned such as the one discussed below; however none can be selected or rejected on the basis of our present knowledge.



I

The faster reaction which is first order in [R'-NH$_2$], reaction 3, is a somewhat more interesting source of speculation. If we accept the suggestion of Doty and Lundberg[5] that this reaction involves an α-peptide and add the suggestion that NCA's can hydrogen-bond to the peptide,[14] a reaction proceeding through I becomes immediately attractive. In I, a transition state or intermediate, the negative charge generated on the carbonyl oxygen is distributed into the peptide by resonance. When I decomposes by rearranging electrons, the next unit added to the peptide is already hydrogen-bonded into the chain.

If we re-examine Table II in light of the preceding discussion, a consistent rationale begins to appear. Glycine NCA with only a hydrogen in the R position should readily form α-peptide and polymerize by the fast first-order reaction. A fast first-order rate is observed. L-Isomers should also form α-peptides since they can arrange their side chains in such a way that they do not sterically interact with each other. They would be expected to polymerize by the fast first-order reaction. A fast first-order rate is again observed. DL-Alanine NCA with a small R group, CH$_3$-group, could conceivably form an α-peptide in spite of its racemic properties. Again a fast first-order rate is observed. The mixed-order reaction begins to appear with DL-α-amino-iso-butyric NCA where R is CH$_3$CH$_2$–, and continues throughout the rest of the series. The anhydrides proceeding by a mixed-order reaction, (1) and (2) above, are presumably producing β-peptide.

DAYTON, OHIO

[14] D. G. H. Ballard and C. H. Bamford, *Nature*, **177**, 477 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Amine Oxides. V. Olefins from N,N-Dimethylmenthylamine and N,N-Dimethylneomenthylamine Oxides[1,2]

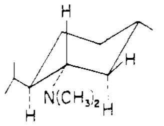
BY ARTHUR C. COPE AND EDWARD M. ACTON[3]

RECEIVED JULY 17, 1957

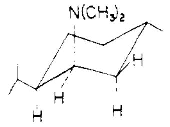
N,N-Dimethylneomenthylamine oxide forms pure 2-menthene on thermal decomposition. This observation provides additional evidence that the amine oxide pyrolysis proceeds by *cis* elimination of a β-hydrogen atom and the amine oxide function through a cyclic transition state. N,N-Dimethylmenthylamine oxide under similar conditions forms an olefin mixture (85%) containing 64.8% of 2-menthene and 35.2% of 3-menthene, both of which can be formed by *cis* elimination from this amine oxide.

This paper describes an additional test of the steric course of the conversion of amine oxides to olefins by study of the thermal decomposition of N,N-dimethylneomenthylamine oxide and N,N-dimethylmenthylamine oxide. Previous evidence that this type of reaction is a *cis* elimination process was obtained by pyrolysis of the oxides of *threo-* and *erythro*-2-(N,N-dimethylamino)-3-phenylbutane, which formed almost exclusively the conjugated olefins produced by *cis* elimination.[4]

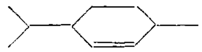
N,N-Dimethylmenthylamine (I) could give either 2-menthene (III) or 3-menthene (IV) by *cis* elimination from the amine oxide, whereas application of the Hofmann method could form only 2-menthene by *trans* elimination. On the other hand, *cis* elimination from the oxide of N,N-dimethylneomenthylamine (II) could give only 2-menthene, while formation of either 2- or 3-menthene would be possible from the quaternary base.



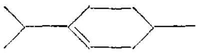
I



II



III



IV

By using the optically active amines, the olefinic products could be analyzed by preferential acid-catalyzed racemization of 3-menthene.[5-7]

l-Menthylamine was prepared by reduction of *l*-menthone oxime with sodium in alcohol and characterized as *l*-menthylamine hydrochloride.[8] *d*-Neomenthylamine was prepared from *l*-menthone

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[1] Sponsored by the Office of Ordnance Research, U. S. Army, under contract No. DA-19-020-ORD-3226, Project TB 2-0001(1112).

[2] Paper IV in this series, THIS JOURNAL, **79**, 4729 (1957).

[3] National Science Foundation Fellow, 1954–1955; National Institutes of Health Fellow, 1955–1956.

[4] D. J. Cram and J. E. McCarty, THIS JOURNAL, **76**, 5740 (1954).

[5] W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

[6] N. L. McNiven and J. Read, *J. Chem. Soc.*, 153 (1952).

[7] N. L. McNiven and J. Read, *ibid.*, 2067 (1952); J. P. Wibaut, H. C. Beyerman and H. B. van Leeuwen, *Rec. trav. chim.*, **71**, 1027 (1952).

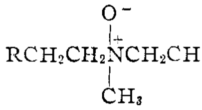
[8] E. S. Rothman and A. R. Day, THIS JOURNAL, **76**, 111 (1954).

by treatment with ammonium formate at 185° and characterized as the resulting formyl-*d*-neomenthylamine.[5,9]

l-Menthylamine and *d*-neomenthylamine were exhaustively methylated with methyl iodide.[10] N,N,N-Trimethyl-*l*-menthylammonium iodide and N,N,N-trimethyl-*d*-neomenthylammonium iodide were obtained in 69% yields after recrystallization. Treatment of N,N,N-trimethyl-*l*-menthylammonium iodide with lithium aluminum hydride in refluxing dioxane removed methyl iodide and formed N,N-dimethyl-*l*-menthylamine in 75% yield. N,N,N-Trimethyl-*d*-neomenthylammonium iodide was converted to N,N-dimethyl-*d*-neomenthylamine by the same method in 87% yield. Oxidation of the tertiary amines with peracetic acid afforded N,N-dimethyl-*l*-menthylamine oxide and N,N-dimethyl-*d*-neomenthylamine oxide, both of which were characterized as crystalline picrates. N,N,N-Trimethyl-*l*-menthylammonium hydroxide and N,N,N-trimethyl-*d*-neomenthylammonium hydroxide were prepared by treating the corresponding iodides in aqueous solution with silver oxide.

A test of *cis* elimination in the amine oxide pyrolysis is offered by N,N-dimethyl-*d*-neomenthylamine oxide, since the only *cis*-β-hydrogen atom is located on C_2, and 2-menthene should be the only olefin formed. This amine oxide decomposed on heating at 90–160° and 7 mm. to give 77% of an olefin. N,N-Dimethyl-*d*-neomenthylamine, formed by loss of oxygen from the amine oxide, was recovered in 9% yield from an acid extract of the product. The olefin was identified as pure 2-menthene by the rotation of the pure liquid, $\alpha^{25}\mathrm{D}$ +109.06°, the highest value reported, and by gas chromatography, which indicated the presence of only a single component. Attempted racemization of the liquid resulted in a negligible drop in the rotation to $\alpha^{25}\mathrm{D}$ +108.44°, corresponding to a racemization of 0.6% of the material present. Calculation[11] indicates that this may be due to conversion of some 2-menthene to an optically inactive substance, rather than racemization of 3-menthene.

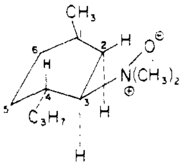
N,N-Dimethyl-*l*-menthylamine oxide was pyrolyzed at 100–180° and 8 mm. A mixture of menthenes was formed in 85% yield. Racemization experiments indicated that the olefin consisted of 64.8% 2-menthene and 35.2% 3-menthene. Pyrolysis of a number of aliphatic amine oxides of the type



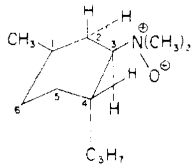
$$\mathrm{RCH_2CH_2}\underset{\underset{\displaystyle \mathrm{CH_3}}{|}}{\overset{\overset{\displaystyle \mathrm{O^-}}{|+}}{\mathrm{N}}}\mathrm{CH_2CHR_2}$$

R = hydrogen
or alkyl

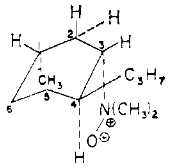
has shown that the two possible olefins are formed in a roughly statistical ratio approximating the ratios of the number of β-hydrogen atoms in the alkyl groups, with a slight favoring of the more highly substituted olefin in certain cases.[12] A similar result might have been expected for N,N-dimethyl-*l*-menthylamine oxide; however, a statistical ratio of olefins in this case would have been 2-menthene/3-menthene = 1/1, since C_2 and C_4 each have one *cis*-β-hydrogen atom. The actual ratio of 2-menthene/3-menthene (65/35) favors the least highly substituted olefin. This result may be related to the fact that eclipsing of the bonds about the α- and β-carbon atoms in an amine oxide is necessary for these atoms to participate in a planar five-centered transition state, along with the nitrogen and oxygen atoms and the β-hydrogen atom. In N,N-dimethyl-*l*-menthylamine oxide, eclipsing could occur either between the bonds about C_3 and C_2 (V), or between the bonds about C_3 and C_4 (VI or VII). The two possible transition states differ in that if C_4 were part of the *quasi* five-membered ring (VI or VII), the isopropyl group attached to C_4 would be involved in eclipsing with the C_3–H bond. On the other hand, if the bonds about C_3 and C_2 were eclipsed, as in the transition state leading to 2-menthene (V), the C_3–H bond would be eclipsed with the C_2–H bond. These arguments are illustrated in drawings showing the boat form of the cyclohexane ring; the pseudo-chair conformation (as in cyclohexene) is equally (or more) probable, and the arguments are the same. To the extent that eclipsing with a carbon–hydrogen bond is favored over eclipsing with a carbon–isopropyl bond, 2-menthene might be expected to predominate over 3-menthene. It might be noted that the pyrolysis of *l*-menthyl acetate[7] also appears anomalous when compared with pyrolyses of aliphatic acetates. 3-Menthene, the most highly substituted olefin, predominated in the product, although aliphatic acetates form principally the least highly substituted olefins.[13]



V



VI



VII

N,N,N-Trimethyl-*l*-menthylammonium hydroxide decomposed on heating at 120–180° and 8 mm. A menthene mixture was formed in 80% yield, and 11% of N,N-dimethyl-*l*-menthylamine was recovered from an acid extract of the product. Racemization experiments showed that the mixture contained 87.4% of 2-menthene and 12.6% of 3-menthene. These results are in essential agreement with those of McNiven and Read[6] who isolated an olefin mixture (in 30% yield) that contained 96% of 2-menthene and 4% of 3-menthene. 2-Menthene is the only product that could be formed in this reaction by *trans* elimination, and the formation of 3-menthene must therefore be ex-

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[9] J. Read and G. J. Robertson, *J. Chem. Soc.*, 2209 (1926).

[10] J. Read and J. A. Hendry, *Ber.*, **71**, 2544 (1938).

[11] See Experimental section.

[12] A. C. Cope, N. A. LeBel, H. H. Lee and W. R. Moore, THIS JOURNAL, **79**, 4720 (1957).

[13] W. J. Bailey and C. King, *ibid.*, **77**, 75 (1955).

TABLE I

RESULTS OF AMINE OXIDE AND QUATERNARY BASE PYROLYSES

			Analysis by racemization, %			Analysis by gas chromatography, %	
			2-Menthene	3-Menthene			
Compound pyrolyzed	Amine recovd., %	Olefin yield, %	Calcd. for $\alpha_2 = 109.06°$	Calcd. by difference	Calcd. for $\alpha_3 = +88.0°$	2-Menthene	3-Menthene
Dimethyl-*d*-neomenthylamine oxide	9	77	(99.4% unaffected)			100	0
Dimethyl-*l*-menthylamine oxide	1	85	64.8	35.2	34.8	64	36
Trimethyl-*l*-menthylammonium hydroxide	11	80	87.4	12.6	12.8	86	14
Trimethyl-*d*-neomenthylammonium hydroxide	0	94	9.6	90.4	89.9	8	92

plained by another mechanism. Migration of the double bond seems to be ruled out as an explanation for the formation of 3-menthene by the fact that heating a mixture of 2- and 3-menthene with tetramethylammonium hydroxide for 48 hours at 150° resulted in a conversion of a maximum of 4% of the 2-menthene present into 3-menthene, as calculated from a drop in rotation from 106.34 to 105.64°. Since *trans* elimination in N,N,N-trimethyl-*l*-menthylammonium hydroxide to form 2-menthene requires ring transition of the molecule, converting the ring substituents from the normal all-equatorial to the less stable all-axial form, this Hofmann decomposition might be expected to be a more drastic process than most quaternary base pyrolyses. This fact probably accounts for the recovery of a considerable quantity of tertiary amine, which could result from attack by hydroxide ion on the quaternary ammonium group in its normal equatorial orientation, removing a methyl group to form methanol and N,N-dimethyl-*l*-menthylamine.

Pyrolysis of N,N,N-trimethyl-*d*-neomenthylammonium hydroxide occurred at 150–170° and 10 mm. to give 94% of a mixture of menthenes. No N,N-dimethyl-*d*-neomenthylamine whatever was recovered. Racemization experiments identified 9.6% of 2-menthene and 90.4% of 3-menthene in the olefin mixture. McNiven and Read had isolated 86% of an olefin mixture containing 10.5% and 89.5% of 2- and 3-menthene, respectively. The high yield of olefin obtained is not surprising since the conformation of the molecule, with an axial quaternary ammonium group and two *trans* axial hydrogen atoms, should facilitate elimination. The marked predominance of 3-menthene over 2-menthene in accordance with the Saytzeff rather than the Hofmann rule is perhaps more surprising. Competitive elimination of the same two hydrogen atoms in the pyrolysis of N,N-dimethyl-*l*-menthylamine oxide formed 2- and 3-menthene in the ratio 65/35. It has been pointed out[12] that if the acidity of the β-hydrogen atoms is the controlling factor in determining the course of elimination, the results of the Hofmann and amine oxide decompositions involving the same two hydrogen atoms should parallel each other. This obviously is not the case in the menthyl series. The presence of double bond character and hyperconjugative stabilization in the transition state for the Hofmann reaction may account in part for the preponderance of 3-menthene obtained from N,N,N-trimethyl-*d*-neomenthylammonium hydroxide. A similar interpretation for this result has been advanced by Brown and Moritani.[14] The results of these degradations are compiled in Table I.

Experimental[15]

***l*-3-*p*-Menthylamine.**—This compound was prepared as its hydrochloride starting from *l*-menthol.[8,6] The commercial *l*-menthol used had $[\alpha]^{25}\text{D}$ −50.21° (24% in absolute ethanol). Subsequent conversions to *l*-menthone and *l*-menthone oxime occurred in 90–92% yields. The most convenient procedures for preparing the oxime and reducing it to *l*-menthylamine were those described for cyclohexanone oxime and cyclohexylamine.[16] The *l*-menthylamine hydrochloride obtained was recrystallized from water to constant rotation, $[\alpha]^{25}\text{D}$ −36.3° (7% in water), in 52% yield. The highest value reported is $[\alpha]^{25}\text{D}$ −36.6° (5% in water).[8] Treatment of the hydrochloride in 10% aqueous solution with excess sodium hydroxide solution regenerated the free amine, which was used directly in the next step after extraction with pentane, drying over magnesium sulfate, and removing of the solvent under reduced pressure.

N,N,N-Trimethyl-*l*-menthylammonium Iodide.—*l*-Menthylamine was treated three times with 1.5 molar equivalents of methyl iodide in the presence of sodium methoxide in methanol.[10] Recrystallization of the product from acetone to constant rotation gave the quaternary ammonium iodide (69% based on amine hydrochloride), $[\alpha]^{25}\text{D}$ −40.5° (5% in water), melting sharply forming a cloudy melt at 192.3–192.5° (dec., introduced at 175° with a temperature rise of 2°/min.). Literature values are $[\alpha]^{25}\text{D}$ −37.6° (3% in water), m.p. 193–194°,[6] and $[\alpha]^{25}\text{D}$ −39.3° (2% in water), m.p. 190° (dec.).[10]

N,N-Dimethyl-*l*-menthylamine.—N,N,N-Trimethyl-*l*-menthylammonium iodide (16.2 g.) was added to a stirred mixture of 500 ml. of purified dioxane and 6.7 g. of lithium aluminum hydride. Stirring was continued while the reaction mixture was heated under gentle reflux for 24 hours. The mixture was cooled to 10°, and 7 ml. of water was added dropwise with stirring, followed by 7 ml. of 15% sodium hydroxide solution and another 25-ml. portion of water. The solids were separated by filtration and washed with ether (150 ml.) until dry. The combined filtrate was acidified to *p*H 2 with 10% hydrochloric acid and concentrated under reduced pressure to a semi-solid residue. Water (200 ml.) was added and the insoluble material removed by filtration. After removal of colored material by extraction with two 50-ml. portions of ether, the filtrate was made alkaline (*p*H 12) by the addition of 40% sodium hydroxide solution, and the amine that separated was extracted with five 25-ml. portions of pentane. The extracts were dried over magnesium sulfate, filtered, and distilled, first through a Vigreux column at 75 mm. to remove pentane. The residue was distilled through a semimicro column (30 × 0.7-cm.). A 75% yield (6.8 g.) of N,N-dimethyl-*l*-menthylamine was obtained, b.p. 85° (7 mm.), $n^{25}\text{D}$ 1.4552, $\alpha^{25}\text{D}$ −51.20° (pure liq., l = 1 dm.) (lit.values[10] $n^{17}\text{D}$ 1.4584, $\alpha^{17}\text{D}$ −51.18°).

Pyrolysis of N,N-Dimethyl-*l*-menthylamine Oxide.—N,N-Dimethyl-*l*-menthylamine (5.49 g.) was oxidized with 40% peracetic acid according to a described procedure.[17] After decomposition of the excess peracetic acid, the amine oxide

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[14] H. C. Brown and I. Moritani, THIS JOURNAL, **78**, 2203 (1956).

[15] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

[16] "Organic Syntheses," 2nd ed., Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 314, 319.

[17] A. C. Cope and H. H. Lee, THIS JOURNAL, **79**, 964 (1957).

was obtained as a sirupy residue upon concentration of the chloroform solution. The amine oxide picrate was prepared by treating a small portion of the amine oxide in methanol with an equivalent amount of picric acid in 50% aqueous methanol saturated at 55°. The solid that formed on slow cooling was recrystallized from aqueous methanol, m.p. 115.0–115.8°.

Anal. Calcd. for $C_{12}H_{28}O_8N_4$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.73; H, 6.88; N, 13.33.

Pyrolysis of N,N-dimethyl-*l*-menthylamine oxide was accomplished by heating in a round-bottomed flask, which was equipped with a capillary nitrogen inlet and connected through a Vigreux column (1.2 × 15-cm.) to 2 traps in series, cooled in a Dry Ice–acetone mixture. The nitrogen atmosphere was evacuated to 8 mm. and most of the amine oxide decomposed during 30 minutes at a bath temperature of 100–130°. Decomposition and distillation of the products were completed by heating to 180°.

The contents of the traps were allowed to melt, combined, and diluted with 40 ml. of pentane. The pentane solution was extracted with three 10-ml. portions of water to remove N,N-dimethylhydroxylamine. Extraction with 10 ml. of 1 *N* hydrochloric acid removed any recovered amine; the free amine (0.05 g.) regenerated from the acid extract with sodium hydroxide corresponded to 1% of dimethyl-*l*-menthylamine. The extracted pentane solution, after washing with 10 ml. of 1% sodium bicarbonate solution and 10 ml. of water, was dried over magnesium sulfate and filtered. The solvent was removed by distillation through a Vigreux column (27 × 1-cm.) at 80 mm., and the residue was distilled through a semimicro column (30 × 0.7-cm.) to give 3.50 g. of menthene (85%), b.p. 95° (73 mm.), $n^{25}\mathrm{D}$ 1.4487, $\alpha^{25}\mathrm{D}$ +96.72° (pure liq., l = 1 dm.). After redistillation, the menthene mixture (64.8% 2-menthene and 35.2% 3-menthene) had $n^{25}\mathrm{D}$ 1.4488–1.4490, $\alpha^{25}\mathrm{D}$ +101.28° (pure liq., l = 1 dm.).

***d*-Neomenthylamine** was prepared and characterized as its formamide from the Leuckart reaction.[8,9] The *l*-menthone used in this reaction is apparently equilibrated with *d*-isomenthone under the conditions involved, and it has been stated that formyl-*d*-neomenthylamine is more easily obtained when the ketone has already been partially equilibrated.[9] Consequently, 90 g. of *l*-menthone was dissolved briefly in 90 ml. of concentrated sulfuric acid, poured over cracked ice, and extracted at once with pentane. The dried, filtered pentane solution was distilled to give 81 g. of the partially inverted ketone, b.p. 80–82° (6.5 mm.), $[\alpha]^{25}\mathrm{D}$ +12.7° (pure liq., l = 1 dm.), presumably a mixture of *l*-menthone and *d*-isomenthone. This material was mixed with 100 g. of ammonium formate and heated under reflux at 180° for 48 hours. The aqueous layer was then separated, and the organic layer was distilled at 125–135° (1.5 mm.) after separation of the forerun. To obtain the crystalline product, it was necessary to seed the distillate with formyl-*d*-neomenthylamine obtained from partially purified *d*-neomenthylamine which had been prepared by hydrogenation of *l*-menthone oxime, recrystallization of the resulting amine hydrochloride from hexane, and treatment of the regenerated free amine with formic acid.[18] The solid was recrystallized from ether until the rotation and melting point were constant, to give 25.8 g. of formyl-*d*-neomenthylamine (28%), m.p. 117.2–118.2°, $[\alpha]^{25}\mathrm{D}$ +59.9° (5% in absolute ethanol). The highest reported values are m.p. 117–118°, $[\alpha]^{20}\mathrm{D}$ +62.4° (1% in absolute ethanol).[8,10] Some formyl-*l*-menthylamine also was recovered from the mother liquors, m.p. 101.8–103.2° after recrystallization from ether (5% yield) (lit.[17] m.p. 102–103°).

Formyl-*d*-neomenthylamine was hydrolyzed with concentrated hydrochloric acid.[10] The resulting amine hydrochloride was converted to *d*-neomenthylamine by treatment with sodium hydroxide solution as was done with the *l*-menthyl isomer.

N,N,N-Trimethyl-*d*-neomenthylammonium Iodide.—*d*-Neomenthylamine was treated with methyl iodide according to the procedure used above.[10] After recrystallization from acetone, N,N,N-trimethyl-*d*-neomenthylammonium iodide (69% based on the formamide) was obtained, $[\alpha]^{25}\mathrm{D}$ −20.2° (5% in water), melting sharply at 159.0–159.5° (dec., introduced at 145° with a temperature rise of 2°/min.). This compound also gave a cloudy melt. Reported values are $[\alpha]^{17}\mathrm{D}$ −19.5° (2% in water), m.p. 160.5° (dec.).[10]

N,N-Dimethyl-*d*-neomenthylamine.—The procedure followed for preparing N,N-dimethyl-*l*-menthylamine was also used for the preparation of this compound from its methiodide. N,N-Dimethyl-*d*-neomenthylamine (87%) was obtained, b.p. 89–90° (7 mm.), $n^{25}\mathrm{D}$ 1.4600–1.4602, $\alpha^{25}\mathrm{D}$ +52.82° (pure liq., l = 1 dm.) ($n^{17}\mathrm{D}$ 1.4597, $\alpha^{17}\mathrm{D}$ +36.16° have been reported[10]).

Pyrolysis of N,N-Dimethyl-*d*-neomenthylamine Oxide.—N,N-Dimethyl-*d*-neomenthylamine was oxidized and the resulting amine oxide pyrolyzed as described above for the *l*-menthyl derivative. N,N-Dimethyl-*d*-neomenthylamine oxide picrate had m.p. 124.2–125.4° after recrystallization from aqueous methanol.

Anal. Calcd. for $C_{18}H_{28}O_8N_4$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.73; H, 6.73; N, 13.27.

Pyrolysis at 7 mm. of the amine oxide obtained from 5.85 g. of N,N-dimethyl-*d*-neomenthylamine occurred mainly at 90–130°, but heating to 160° was necessary to complete distillation of the pyrolysate. From the hydrochloric acid extract of the product in pentane on treatment with excess sodium hydroxide solution, 0.54 g. of N,N-dimethyl-*d*-neomenthylamine (9%) was recovered, b.p. 87–92° (10 mm.), $n^{25}\mathrm{D}$ 1.4582–1.4600. The extracted pentane solution yielded 3.38 g. of menthene (77%), b.p. 97–98° (80 mm.), $n^{25}\mathrm{D}$ 1.4458–1.4475, $\alpha^{25}\mathrm{D}$ +106.98° (pure liq., l = 1 dm.). Redistillation afforded pure 2-menthene, $n^{25}\mathrm{D}$ 1.4482, $\alpha^{25}\mathrm{D}$ +109.06° (pure liq., l = 1 dm.).

Pyrolysis of N,N,N-Trimethyl-*d*-neomenthylammonium Hydroxide.—N,N,N-Trimethyl-*d*-neomenthylammonium iodide (19.5 g.) in 200 ml. of water was stirred with 14.0 g. of silver oxide for 12 hours. The precipitate was separated by filtration and washed with water (150 ml.) until the washings were neutral to litmus. The filtrate was concentrated under reduced pressure at 30–40° to a sirup, which was decomposed in the apparatus used for the amine oxide pyrolyses. The nitrogen atmosphere was evacuated to 10 mm. Heating removed the final traces of water, leaving the solid quaternary base which decomposed at 150–170°. The products collected in the traps were allowed to melt, 60 ml. of pentane was added, and the aqueous layer was separated. The pentane solution was extracted with 25 ml. of 1 *N* hydrochloric acid, 25 ml. of 1% sodium bicarbonate and 25 ml. of water. No tertiary amine was recovered from the acid extract. The pentane solution was then dried over magnesium sulfate, filtered, and concentrated through a Vigreux column at 90 mm. The residue was distilled through a semimicro column giving 7.82 g. (94%) of menthene, b.p. 98–101° (90 mm.), $n^{25}\mathrm{D}$ 1.4480–1.4498, $\alpha^{25}\mathrm{D}$ +86.28° (pure liq., l = 1 dm.). On redistillation the menthene mixture (9.6% 2-menthene, 90.4% 3-menthene) had $n^{25}\mathrm{D}$ 1.4494–1.4498, $\alpha^{25}\mathrm{D}$ +89.62° (pure liq., l = 1 dm.).

Pyrolysis of N,N,N-Trimethyl-*l*-menthylammonium Hydroxide.—N,N,N-Trimethyl-*l*-menthylammonium iodide (30.74 g.) was converted to the quaternary base which was pyrolyzed as described above. N,N,N-Trimethyl-*l*-menthylammonium hydroxide also became solid on concentration, and decomposed at 120–180° and 8 mm. The hydrochloric acid extract of the product in pentane solution was made basic with sodium hydroxide and the liberated amine was distilled, giving 1.85 g. (11%) of N,N-dimethyl-*l*-menthylamine, b.p. 86–87° (8 mm.), $n^{25}\mathrm{D}$ 1.4552. The pentane solution yielded 10.48 g. of menthene (80%), b.p. 97° (80 mm.), $n^{25}\mathrm{D}$ 1.4480–1.4483, $\alpha^{25}\mathrm{D}$ +106.19° (pure liq., l = 1 dm.). This menthene mixture (87.4% 2-menthene and 12.6% 3-menthene) after redistillation had $n^{25}\mathrm{D}$ 1.4483, $\alpha^{20}\mathrm{D}$ +106.55° (pure liq., l = 1 dm.).

Analysis of Menthenes. (a) Racemization Experiments.—The composition of mixtures of *d-trans-p*-2-menthene and *d-p*-3-menthene was determined by the method of Hückel[5] as modified by McNiven and Read.[6] Portions of the olefin mixtures (2 ml.) were refluxed for 4.5 hours with 2.8 ml. of a solution of 29.4 g. of *p*-toluenesulfonic acid in 100 ml. of ethanol. Water (15 ml.) and pentane (25 ml.) were added, and the aqueous layer was separated. The pentane layer was washed with 5 ml. of 1% sodium carbonate solution, 5 ml. of water, and then dried over magnesium sulfate and filtered. Pentane was removed by concentration through a Vigreux column, and the partly racemized menthenes were distilled through a semimicro column. Rotations were determined after redistillation to remove traces of solvent.

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(18) O. Wallach, *Ann.*, **276**, 296 (1893).

In calculating the compositions of the menthene mixtures, the relation $\alpha_{obs} = \alpha_3 x + \alpha_2 y$ was used,[19] where α_{obs} = observed rotation; α_3 and α_2 = rotations of pure *d-p*-3-menthene and pure *d-trans-p*-2-menthene, respectively; x and y = mole fractions of 3-menthene and 2-menthene, respectively. After racemization of the 3-menthene present, $\alpha_{obs} = \alpha_2 y$. The 2-menthene obtained from N,N-dimethyl-*d*-neomenthylamine oxide had α_D +109.06°; since this is the highest value reported and vapor-phase chromatography indicated this 2-menthene was pure, $\alpha_2 = +109.06°$ was used subsequently in the calculation of its mole fraction, y. Then, x can be calculated as $1 - y$, or as $\alpha_3 x$ = the drop in rotation on racemization of 3-menthene, using $\alpha_3 = +88.0°$. Pure *d-p*-3-menthene has not been prepared, and this value is one which was calculated by Hückel.[5] The results are listed in Table I, and show values of x in excellent agreement when calculated by both methods.

It will be observed that there was a small loss of rotation on treatment of pure 2-menthene with alcoholic *p*-toluenesulfonic acid, which corresponds to a value of 0.994 for y. By difference, $x = 0.006$ for the material racemized. The rotation of the material racemized can be calculated as α_3 = drop in rotation/x, giving $\alpha_3 = 103.2°$. Since this is nearly the rotation of 2-menthene, it may mean that a small amount of the 2-menthene was racemized rather than indicating the presence of 3-menthene. Correction of the other results to allow for 0.6% racemization of 2-menthene does not appreciably change the figures. Composition of the menthenes given in Table I was calculated from the rotations listed in Table II.

Analysis of Menthenes. (b) Gas Chromatography.—Approximately 0.005 ml. samples of the olefin mixtures were injected into a column (200 × 0.6-cm.) containing 48–100 mesh firebrick impregnated in a 5/2 ratio with tetraethylene glycol that had been saturated with silver nitrate at 100°. The column was heated to 88° and equipped with a preheater at 150°. The carrier gas was helium at a pressure of 12.7 p.s.i. A thermal conductivity cell was used as detector. The composition of each olefin mixture was computed from a chromatogram by determining the ratio of individual peak areas, obtained from the product of the peak height and its half-band width.[12] The 2-menthene obtained from N,N-dimethyl-*d*-neomenthylamine oxide showed only a single peak. The olefins obtained from the other three pyrolyses showed but two peaks, those for 2-menthene and 3-menthene, varying only in relative size.

TABLE II

OPTICAL ROTATION OF MENTHENES FORMED BY PYROLYSES

Compound pyrolyzed	Rotations of menthenes produced (α^{25}_D, pure liq., l = 1 dm.) Before racemization	After racemization
Dimethyl-*d*-neomenthylamine oxide	109.06°	108.44°
Dimethyl-*l*-menthylamine oxide	101.28	70.64
Trimethyl-*l*-menthylammonium hydroxide	106.55	95.31
Trimethyl-*d*-neomenthylammonium hydroxide	89.62	10.50

Attempted Isomerization of 2-Menthene to 3-Menthene—A mixture of 2- and 3-menthene (3 ml.), having α^{25}_D + 106.34° (pure liq., l = 1 dm.), was heated in a sealed tube with 0.5 ml. of 50% aqueous tetramethylammonium hydroxide at 150° for 2 days. The reaction mixture was diluted with 50 ml. of pentane, the aqueous phase was separated, and the pentane solution was dried over magnesium sulfate. Distillation and redistillation of the olefin obtained afforded a menthene mixture having α_D +105.64° (pure liq., l = 1 dm.). Calculations based on values of α_3 = 88.0° for *d*-3-menthene, and α_2 = 109.06° for *d*-2-menthene, indicated that the composition of the mixture was shifted from 87.1% 2-menthene and 12.9% 3-menthene to 83.8% 2-menthene and 16.2% 3-menthene. If the drop in rotation was caused by double-bond migration, this corresponds to a conversion of 4% of the 2-menthene originally present into optically inactive 3-menthene. Apparently 2-menthene is not appreciably converted into 3-menthene under the conditions of the Hofmann decomposition.

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[19] H. Landolt, "Optical Rotating Power of Organic Substances and Its Applications," 2nd ed., Chemical Publishing Co., Easton, Pa., 1902 (translated), p. 240.

[CONTRIBUTION FROM AVERY LABORATORY, THE UNIVERSITY OF NEBRASKA]

Esters of β-Diazopropionic Acid. A New Synthesis of β-Aryloxypropionic Acids[1,2]

BY LOREN L. BRAUN[3] AND J. H. LOOKER

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Ethyl and benzyl β-diazopropionate have been prepared *ex situ* from the corresponding nitrosocarbamate by a novel procedure. Reaction of several phenolic and enolic compounds with the diazopropionic ester in methanolic ether has led to the β-aryloxypropionic ester, which upon acid hydrolysis (or hydrogenolysis when appropriate) gave the corresponding β-aryloxypropionic acid. Cyclization of β-(6-bromo-2-naphthoxy)-propionic acid with polyphosphoric acid resulted in 8-bromo-1-benzo[f]chromanone.

Esters of diazoacetic acid and their application to a variety of organic syntheses are well-known.[4] However, diazo esters in which diazo and carbonyl functions are separated by one or more methylene groups appear to have been prepared infrequently.[5] The present paper describes the preparation of ethyl and benzyl β-diazopropionate by a simple but novel *ex situ* procedure which does not involve a distillation step, and the utility of these diazo esters in syntheses of β-aryloxypropionic acids and esters.

The synthesis of diazopropionic esters was investigated by both *in situ* and *ex situ* procedures.[6] The necessary starting material in each case was the N-nitrosocarbamate ($C_2H_5O_2CN(NO)CH_2CH_2CO_2R$, R = C_2H_5 or $CH_2C_6H_5$), which was obtained by nitrosation of ethyl or benzyl N-carbethoxy-β-aminopropionate (N-carbethoxy-β-alanine ethyl or benzyl ester) and used without purification. A classical *in situ* procedure[7] utilizing

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[1] Abstracted from a portion of a thesis submitted in partial fulfillment of requirements for the Ph.D. degree at the University of Nebraska by Loren L. Braun, 1956.

[2] Financial support of this investigation through a Frederick Gardner Cottrell Grant to the University of Nebraska by the Research Corporation of New York is gratefully acknowledged.

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[4] (a) N. C. Hancox, *Roy. Australian Chem. Inst. J. and Proc.*, **16**, 282 (1949); (b) C. D. Gutsche in "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 364; (c) R. Huisgen, *Angew. Chem.*, **67**, 439 (1955).

[5] Ethyl 6-diazohexanoate has been prepared *in situ* by D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 184 (1939).

[6] For a discussion of the terms *in situ* and *ex situ*, see reference 4b, p. 394.

[7] For a discussion of the various procedures available for the synthesis of diazoalkanes, see reference 4; also, W. E. Bachmann and