# **563.** *Stereochemical Investigations of Cyclic Bases. Part III.* An Example of Wagner–Meerwein Elimination with a Quaternary Ammonium Salt.*

By J. McKenna and J. B. Slinger.

Pyrolysis of dry bornyltrimethylammonium hydroxide yields pure bornylene, and this hydrocarbon is also the chief decomposition product of *neo*bornyltrimethylammonium hydroxide or of the corresponding epimeric amine oxides. Nearly pure camphene is obtained by heating neutral or alkaline aqueous or glycol solutions of *neo*bornyltrimethylammonium iodide: the rate of hydrocarbon formation is independent of alkali concentration, but camphene of high optical purity is obtained only from the alkaline degradations. Hot alkaline solutions of bornyltrimethylammonium iodide yield only the tertiary base by methanol elimination, a reaction which also proceeds more slowly with the epimeric salt.

Both $E1$ and $E2$ mechanisms have been established kinetically for a wide range of variables X and Y in the elimination reaction involving the process (A). However, Hofmann elimination of quaternary ammonium salts ($Y = Alk_3N^+$) usually proceeds by the $E2$ process, although there are[1] a few examples † where the alternative mechanism seems

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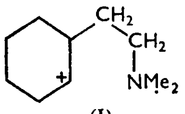
* Part II, *J.*, 1958, 2209.

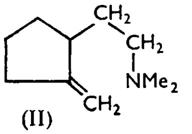
† We thank a referee for drawing our attention to these examples.

[1] Norcross and Openshaw, *J.*, 1949, 1174; Pailer and Bilek, *Monatsh.*, 1948, **79**, 135.

probable, although it has not been fully established. Ease of unimolecular elimination is enormously increased if a combination of polar and stereoelectronic factors facilitates rearrangement of the developing carbonium ion, but we are unaware of any previous adequate demonstration (*i.e.*, structural and kinetic) of Wagner–Meerwein rearrangement during a Hofmann elimination reaction of a quaternary ammonium salt. King and Booth have suggested [2] however, that thermal degradation (by the conventional experimental



(I)



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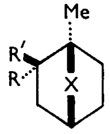

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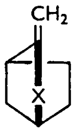

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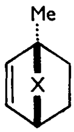

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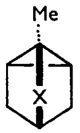
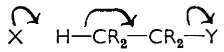


(VI)

(A):



$X = CMe_2$

procedure) of *trans*-octahydro-1-methylindole methohydroxide proceeds with rearrangement *via* the related secondary carbonium ion (I), yielding the methine (II), but little evidence was adduced in support of this mechanism, which would involve charge-transfer towards the developing primary carbon atom. An example of Wagner–Meerwein rearrangement effected under suitable conditions in the structurally favourable case of quaternary salts derived from *neo*bornyldimethylamine (III; $R = H$, $R' = NMe_2$) is described in this paper, together with related work.

The preparation and characterisation, from (+)-camphor,‡ of (+)-bornylamine (III; $R = NH_2$, $R' = H$), (−)-*neo*bornylamine (III; $R = H$, $R' = NH_2$) and their *NN*-dimethyl derivatives is described in the Experimental section; three of these bases have been prepared before, but our work includes improvements in preparative methods and some correction and extension of data in previous literature. Of some theoretical interest is the isolation of camphor during formaldehyde–formic acid methylation of either primary amine: as this result suggests the equilibrium of intermediates $>CH{\cdot}N{:}CH_2 \rightleftharpoons >C{:}N{\cdot}CH_3$, formation of some epimeric tertiary base might be expected, but our work indicates that (as in some related examples in the literature [3,4]) no appreciable epimerisation does in fact occur. *cyclo*Pentylamine and *cyclo*hexylamine gave much lower yields of ketone during methylation, with no significant [5] preferential formation of *cyclo*pentanone.

Ionic eliminations with 2-substituted camphanes usually yield mainly camphene (IV) together with varying proportions of bornylene (V) and tricyclene (VI). When conditions strongly favour *E*2 elimination the chief product is bornylene, which can be obtained, for example,[6] with 93% purity (7% of camphene) from bornyl halides and potassium pentyloxide in dry pentanol at 190—230°. However, Ruzicka's thermal degradation [7] of what was evidently a mixture of bornyl- and *neo*bornyl-trimethylammonium hydroxides has been the only elimination process previously claimed to yield pure bornylene directly from a 2-substituted camphane, although Shriner and Sutherland have stated,[8] without experimental evidence, that the olefinic product contains *ca.* 4% of camphene. Neither

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‡ For the absolute configuration of (+)-camphor and related compounds see Birch, *Ann. Reports*, 1950, **47**, 191, and Prelog and Meier, *Helv. Chim. Acta*, 1953, **36**, 320. All active terpenes described in this paper are configurationally related to (+)-camphor.

[2] King and Booth, *J.*, 1954, 3798.

[3] Parham, Hunter, Hanson, and Lahr, *J. Amer. Chem. Soc.*, 1953, **74**, 5646; Grob, Kny, and Gagneux, *Helv. Chim. Acta*, 1957, **40**, 130.

[4] Cope and Bumgardner, *J. Amer. Chem. Soc.*, 1957, **79**, 960.

[5] Cf. Brown, *J. Org. Chem.*, 1957, **22**, 439.

[6] Meerwein and Joussen, *Ber.*, 1922, **55**, 2529.

[7] Ruzicka, *Helv. Chim. Acta*, 1920, **3**, 748.

[8] Shriner and Sutherland, *J. Amer. Chem. Soc.*, 1938, **60**, 1314.

Shriner and Sutherland nor Ruzicka investigated the degradation of both individual epimeric quaternary salts, or the effect of changing the reaction conditions.

When dry bornyl- or *neo*bornyl-trimethylammonium hydroxide or a mixture of the two was heated at temperatures up to 180°, the quaternary bases remained solid, and bornylene slowly distilled together with some tertiary amine. Experiments in which mixtures of the epimeric quaternary hydroxides were pyrolysed indicated that bornyltrimethylammonium hydroxide decomposed more slowly than its epimer, but gave a higher proportion of the related tertiary amine. Ruzicka also obtained a tertiary base by pyrolysis of a mixture of the quaternary hydroxides; he characterised the base by conversion into the methiodide, which was incorrectly regarded, however, as being mainly the *neo*(or *iso*)-epimer. The bornylene obtained by pyrolysis of dry bornyltrimethylammonium hydroxide appeared to be quite pure, but the *neo*-hydroxide yielded a hydrocarbon containing some tricyclene. Bornyltrimethylammonium hydroxide when not quite dry was molten at 180°, and at that temperature yielded a hydrocarbon containing a trace of camphene; this may explain the slight discrepancy between the results of Ruzicka and of Shriner and Sutherland. In spite of the great ease of rearrangement of the camphane carbon framework, it is evident that the Wagner–Meerwein elimination cannot compete effectively with the normal $E2$ and $S_N2$ reactions in the extremely strongly basic conditions obtaining when the Hofmann degradation is carried out in the conventional manner [9] (*i.e.*, evaporation of aqueous quaternary hydroxide,* followed by pyrolysis), and it appeared desirable to study the elimination at moderate dilutions in ionising solvents.

Distillation of an alkaline solution of (−)-*neo*bornyltrimethylammonium iodide in aqueous glycol yielded some tertiary base and (+)-camphene; the latter, although containing traces of bornylene and tricyclene, was of higher optical purity than was obtainable by any other elimination process from a 2-substituted camphane, either directly or even after further purification. Similar treatment of bornyltrimethylammonium iodide yielded no hydrocarbon, but only tertiary base. Complete alkaline decomposition of approximately equimolar mixtures of the epimeric methiodides gave camphene, and, in the basic fraction, mainly bornyldimethylamine; nearly pure samples of this tertiary base were obtained from mixed methiodide degradations in glycol which was only weakly alkaline. These results are chiefly due to the much more rapid conversion of the *neo*-salt into hydrocarbon; the rate of this reaction in glycol, as in water, is probably alkali-independent (see below) while the rates of the competitive methanol-elimination reactions are probably alkali-dependent ($S_N2$). Camphene was also obtained by dry pyrolysis of *neo*bornyltrimethylammonium iodide at 180°; at this temperature the epimeric salt was stable, but at 250° it gave bornyldimethylamine and a neutral oil containing some camphene.

Experiments in which methiodide mixtures were partly (*ca.* 20%) decomposed in alkaline solution showed that the methanol-elimination (reversion to tertiary base) with the bornyl quaternary salt (less hindered N) was slightly faster than with the epimer. This rather unexpected result indicates that relief of strain at the quaternary nitrogen atoms during formation of the transition state is not the controlling factor in determining the relative rates of the methanol-elimination with this particular pair of quaternary salts. Bornyl and *neo*bornyl epimers, however, do not differ considerably in degree of steric compression at the functional groups.

That the conversion of (−)-*neo*bornyltrimethylammonium iodide into (+)-camphene is a conventional (carbonium ion) Wagner–Meerwein rearrangement was demonstrated by experiments in aqueous solution at 140°: the rate of formation of hydrocarbon was independent of hydroxide-ion concentration. The camphene from neutral degradations was found to be partly racemised, and was significantly (no $E2$ reaction) free from bornylene.

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* We did this *in vacuo* at room temperature for manipulative convenience, but solutions of the quaternary hydroxide decompose only very slowly at 100° (see Experimental section).

[9] Cf. Weinstock, *J. Org. Chem.*, 1956, **21**, 540.

Racemisation appears to occur during, and not after, formation of hydrocarbon, and is possibly related to the longer life in neutral solution of the related carbonium ion, which is an intermediate in either of the two possible racemisation mechanisms.[10] Elimination of methanol from *neo*bornyltrimethylammonium hydroxide was not observed even in strong aqueous alkali; the reaction is more readily suppressed in water than in glycol, probably because water is such a favourable solvent for the competitive rearrangement.

Degradation of alicyclic amine oxides to olefins and alkylhydroxylamines assumes a *cis*-steric course,[11] and we have found that pyrolysis of the *N*-oxides of (+)-bornyl- and (−)-*neo*bornyl-dimethylamine affords hydrocarbon mixtures similar to those obtained from the mechanistically related pyrolysis of the xanthate esters of borneol and *neo*borneol, which yield[12] respectively bornylene contaminated with a little tricyclene, and a mixture of equal parts of bornylene and camphene; not so much camphene, however, is formed on pyrolysis of *neo*bornyldimethylamine oxide. These pyrolyses also yielded some tertiary base, less with the *neo*bornyl than with the bornyl epimer.

By a combination of reactions described in this paper samples of nearly pure optically active camphene and quite pure active bornylene may rapidly and conveniently be prepared from the active camphor of related configuration. This is converted into a mixture of epimeric trimethylammonium iodides, which on distillation with alkaline glycol yields camphene and mainly bornyldimethylamine; this base is then converted into quaternary hydroxide, dry distillation of which gives bornylene.

## EXPERIMENTAL

Except where stated otherwise, optical rotations refer to EtOH solutions at room temperature (17—23°) at concentrations of 0·5—2% (usually nearer the higher value) in 2 dm. tubes of internal diameter 6 mm.

*(+)-Bornylamine.*—Reduction of (−)-camphor oxime with sodium in pentanol gave a mixture containing (optical rotation) (+)-bornylamine (70%) and (−)-*neo*bornylamine (30%). Several successive recrystallisations of this mixture from dilute hydrochloric acid gave (+)-bornylamine hydrochloride, m. p. 330°, $[\alpha]_D$ +23° (Found: C, 63·3; H, 10·5; N, 7·4; Cl, 18·9. Calc. for $C_{10}H_{20}NCl$: C, 63·3; H, 10·6; N, 7·4; Cl, 18·7%). The base had m. p. 159°, $[\alpha]_D$ +46° (Found: C, 78·4; H, 12·5; N, 9·1. Calc. for $C_{10}H_{19}N$: C, 78·3; H, 12·4; N, 9·2%). The *N*-benzoyl derivative, m. p. 138°, $[\alpha]_D$ −23° (Found: C, 79·2; H, 9·0; N, 5·5. Calc. for $C_{17}H_{23}ON$: C, 79·3; H, 9·0; N, 5·5%), picrate, m. p. 245—247° (decomp.) (Found: C, 50·3; H, 5·9; N, 14·5. Calc. for $C_{16}H_{22}O_7N_4$: C, 50·3; H, 5·8; N, 14·7%), and *picrolonate*, needles (from ethanol), m. p. 260° (decomp.) (Found: C, 57·6; H, 6·6; N, 16·7. $C_{20}H_{27}O_5N_5$ requires C, 57·5; H, 6·5; N, 16·8%), were prepared. The physical constants for previously known compounds agree with those quoted in the literature.[13]

*(+)-Bornyldimethylamine and (−)-Bornyltrimethylammonium Iodide from (+)-Bornylamine.*—(a) *Formaldehyde–formic acid method.* A mixture of (+)-bornylamine (820 mg.), 40% aqueous formaldehyde (2·5 c.c.), and 98% formic acid (6 c.c.) was heated under reflux for 12 hr. on the steam-bath, and the products were separated into (+)-camphor (138 mg.), m. p. and mixed m. p. 174°, $[\alpha]_D$ +50° (in $Et_2O$) [dinitrophenylhydrazone, m. p. and mixed m. p. 174·5° (Found: C, 57·8; H, 6·0; N, 16·9. Calc. for $C_{16}H_{20}O_4N_4$: C, 57·8; H, 6·0; N, 16·9%)], and (+)-*bornyldimethylamine* (800 mg.), b. p. 216°/744 mm., $[\alpha]_D$ +27°, increased to +34° on purification by the countercurrent process described below (p. 2764), $n_D^{26}$ 1·4772 (Found: C, 79·7; H, 12·8; N, 7·6. $C_{10}H_{23}N$ requires C, 79·5; H, 12·8; N, 7·7%). Forster[14] records b. p. 210—212°/763 mm., $[\alpha]_D$ +48·7° (in EtOH), but this value of $[\alpha]$ is criticised by later workers[15] who give $[\alpha]_D$ +34·86° (but no analysis) for the liquid base. The *hydrochloride* was obtained

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[10] Roberts and Yancey, *J. Amer. Chem. Soc.*, 1953, **75**, 3165.

[11] *Inter al.*, Cope, Pike, and Spencer, *ibid.*, p. 3212, and other papers by Cope and his collaborators.

[12] Tschugaeff and Budrich, *Annalen*, 1912, **388**, 280; Henderson and Caw, *J.*, 1912, **101**, 1416; Shavrygin, *J. Gen. Chem.* (*U.S.S.R.*), 1940, **10**, 807 (*Chem. Abs.*, 1941, **35**, 2491).

[13] Josephy and Radt (Ed.), "Encyclopaedia of Organic Chemistry," Elsevier, Amsterdam, 1948, Vol. 12A, pp. 609—611.

[14] Forster, *J.*, 1899, **75**, 934.

[15] Ives and Nettleton, *J.*, 1948, 1085.

as needles (from chloroform–ether), m. p. 220°, $[\alpha]_D$ +9° (Found: N, 6·4. $C_{12}H_{24}NCl$ requires N, 6·4%): Forster [14] records m. p. >300°, $[\alpha]_D$ +37·2° (in EtOH). The *picrate*, yellow rods (from ethanol), had m. p. 213—214°, not depressed on admixture with the salt from preparations (b) and (c) (Found: C, 52·8; H, 6·5; N, 13·6. $C_{18}H_{26}O_7N_4$ requires C, 52·7; H, 6·4; N, 13·7%). With methyl iodide in boiling methanol the tertiary base prepared by method (a) was converted into (−)-bornyltrimethylammonium iodide, leaflets, m. p. (from ether–methanol) 276°, after discoloration at 270°, $[\alpha]_D$ −3·6° (Found: C, 48·3; H, 8·1; N, 4·1; I, 39·1. Calc. for $C_{13}H_{26}NI$: C, 48·3; H, 8·1; N, 4·2; I, 39·3%). Forster,[14] who prepared the methiodide from (+)-bornylamine with methyl iodide and alcoholic sodium hydroxide, records m. p. >250°, $[\alpha]_D$ −3·9° (in EtOH).

(b) Via N-*methylbornylamine.* (+)-Bornylamine (1·37 g.) was treated with 98% formic acid (5 c.c.) at 100° for 12 hr., neutral and basic products were separated, and the base was again treated with formic acid. The crude *N*-formyl derivative (1·12 g.) in boiling ether (500 c.c.) was reduced with lithium aluminium hydride (0·6 g.) for 4 hr. The secondary amine was isolated as the *hydrochloride* (1·2 g.) which formed rectangular plates, m. p. >300°, $[\alpha]_D$ +38°, after crystallisation from ethanol (Found: C, 64·6; H, 11·0; N, 6·8; Cl, 17·3. $C_{11}H_{22}NCl$ requires C, 64·8; H, 10·9; N, 6·9; Cl, 17·4%). Forster [14] records m. p. >250°, $[\alpha]_D$ +31° (in EtOH), and gives no analysis. The *N*-benzoyl derivative had m. p. 126° (lit.,[14] 127°) (Found: C, 79·4; H, 9·2; N, 5·3. Calc. for $C_{18}H_{25}ON$: C, 79·7; H, 9·2; N, 5·2%). Methylation of the secondary base with formaldehyde and formic acid yielded no camphor; the (+)-bornyldimethylamine was characterised as the hydrochloride, $[\alpha]_D$ +7·7°, and the picrate, m. p. 209—210°.

(c) *By methylation with methyl iodide.* A mixture of (+)-bornylamine hydrochloride (7·8 g.), potassium carbonate (6 g.), methyl iodide (25 c.c.), and acetone (750 c.c.) was refluxed overnight, and the quaternary salt isolated in chloroform; it had m. p. 276° (decomp. at 270°) and $[\alpha]_D$ −3·7° (Found: C, 48·1; H, 8·1; N, 4·2; I, 39·6. Calc. for $C_{13}H_{26}NI$: C, 48·3; H, 8·1; N, 4·2; I, 39·3%). The *X*-ray powder photograph and infrared absorption spectrum of this methiodide were identical with those obtained with the salt prepared by method (a). Reduction of the methiodide (1·48 g.) by refluxing it in tetrahydrofuran (125 c.c.) with lithium aluminium hydride [4] (1·8 g.) for 84 hr. gave (+)-bornyldimethylamine (740 mg.), $n_D^{25}$ 1·4775 (Found: C, 79·6; H, 12·7; N, 8·0. Calc. for $C_{12}H_{23}N$: C, 79·5; H, 12·8; N, 7·7%), from which the hydrochloride, $[\alpha]_D$ +7·1°, and the picrate, m. p. and mixed m. p. 213—214°, were prepared.

(−)-neo*Bornylamine.*—This amine was obtained as hydrochloride by application of Goodson's technique [16] (distribution between ether and dilute hydrochloric acid in separating funnels) to the residual hydrochlorides from the oxime reduction (after crystallisation of bornylamine hydrochloride) or to a mixture of (−)-*neo*bornylamine hydrochloride (65%) and (+)-bornylamine hydrochloride (35%) derived from (+)-camphor by the Leuckart reaction. The *neo*-epimer (weaker base [17]) was preferentially extracted by the ether. The oxime reduction residues also appeared to contain some dibornylamine or an isomer. (−)-*neo*-Bornylamine hydrochloride after recrystallisation from chloroform–ether had m. p. 324° and $[\alpha]_D$ −48° (Found: C, 63·1; H, 10·4; N, 7·4; Cl, 18·5. Calc. for $C_{10}H_{20}NCl$: C, 63·3; H, 10·6; N, 7·4; Cl, 18·7%). Goodson [16] gives $[\alpha]_D$ −49°.

(−)-neo*Bornyldimethylamine and* (−)-neo*Bornyltrimethylammonium Iodide.*—(*a*) Methylation of (−)-*neo*bornylamine (590 mg.) with 40% aqueous formaldehyde (1·95 c.c.) and 98% formic acid (4·7 c.c.) at 100° overnight gave camphor (100 mg.), m. p. 172° (dinitrophenylhydrazone, m. p. and mixed m. p. 174°), and (−)-*neo*bornyldimethylamine (510 mg.) from which the hydrochloride, $[\alpha]_D$ −60°, and the picrate, m. p. 194°, were prepared, identical with the compounds prepared by methods (*b*) and (*c*).

(*b*) A mixture of (−)-*neo*bornylamine hydrochloride (260 mg.), potassium carbonate (5 g.), methyl iodide (5 c.c.), and acetone (60 c.c.) was refluxed overnight. The resulting (−)-neo-*bornyltrimethylammonium iodide* (204 mg.) separated from ether–methanol in rods, m. p. 242° (with some preliminary decomp.), $[\alpha]_D$ −34° (Found: C, 48·4; H, 8·2; N, 4·2; I, 39·1. $C_{13}H_{26}NI$ requires C, 48·3; H, 8·1; N, 4·3; I, 39·3%). Reduction of this methiodide with lithium aluminium hydride in tetrahydrofuran by the method described for the epimeric salt yielded (−)-*neo*bornyldimethylamine which gave the hydrochloride, $[\alpha]_D$ −64°, and the picrate, m. p. 194°.

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[16] Goodson, *J.*, 1927, 930.

[17] Girault-Vexlearschi, *Bull. Soc. chim. France*, 1956, 589.

(*c*) A mixture of *N*-formylbornylamine and *N*-formyl*neo*bornylamine derived from a Leuckart reaction with (+)-camphor (7 g.) was reduced in ether (500 c.c.) with lithium aluminium hydride (2 g.) for 12 hr. and the resulting mixture of secondary amines (5·8 g.) converted into mixed tertiary bases (6·0 g.), $[\alpha]_D$ −30° (Found: C, 79·8; H, 12·8; N, 7·7. Calc. for $C_{12}H_{23}N$: C, 79·5; H, 12·8; N, 7·7%), with formaldehyde and formic acid. Separation of the tertiary bases was most readily achieved by countercurrent distribution in a Craig apparatus between ether and a phosphate buffer (pH 6·6), the *neo*-base again being preferentially extracted by the ether. This process yielded (+)-bornyldimethylamine, $[\alpha]_D$ +34° (hydrochloride, $[\alpha]_D$ +9°), and (−)-*neobornyldimethylamine*, b. p. 210°/744 mm., $n_D^{26}$ 1·4792, $[\alpha]_D$ −61° (Found: C, 79·5; H, 12·4. $C_{12}H_{23}N$ requires C, 79·5; H, 12·8%) which gave a *hydrochloride*, needles from (chloroform–ether), m. p. 243°, $[\alpha]_D$ −63° (Found: C, 66·1; H, 10·5; N, 6·8. $C_{12}H_{24}NCl$ requires C, 66·2; H, 11·1; N, 6·4%), and a *picrate*, rods (from ethanol), m. p. 194° (Found: C, 52·5; H, 6·2; N, 13·4. $C_{18}H_{26}O_7N_4$ requires C, 52·7; H, 6·4; N, 13·7%). The methiodide from the tertiary base was identical with that obtained directly from (−)-*neo*bornylamine by method (*b*), having m. p. 242° (preliminary decomp.) and $[\alpha]_D$ −33° (Found: C, 48·5; H, 8·0; N, 4·2; I, 39·7. Calc. for $C_{13}H_{26}NI$: C, 48·3; H, 8·1; N, 4·3; I, 39·3%).

*Methylation of* cyclo*Hexyl- and* cyclo*Pentyl-amine*.—After gradual heating (exothermic reaction), a mixture of *cyclo*hexylamine (25 g.), 98% formic acid (45 c.c.), and 40% aqueous formaldehyde (40 c.c.) was kept at 100° for 1 hr. Dilution with water and extraction with light petroleum (b. p. 40—60°) yielded a neutral oil (262 mg.) which yielded *cyclo*hexanone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 158° (Found: C, 51·3; H, 5·5; N, 20·1. Calc. for $C_{12}H_{14}O_4N_4$: C, 51·8; H, 5·1; N, 20·1%). *cyclo*Hexyldimethylamine (19·2 g.), b. p. 158°, was obtained from the acid solution.

From *cyclo*pentylamine (16·2 g.) were likewise obtained crude *cyclo*pentanone (376 mg.) [2 : 4-dinitrophenylhydrazone, m. p. 140°; lit., 146°] and *cyclo*pentyldimethylamine (9·0 g.), b. p. 131°, which yielded the picrate,[18] m. p. 176—177° (Found: C, 45·5; H, 5·2; N, 16·4. Calc. for $C_{13}H_{18}O_7N_4$: C, 45·6; H, 5·3; N, 16·4%). Some basic resinous by-products were formed during each methylation.

*Infrared Spectra of Camphene, Tricyclene, and Bornylene*.—The infrared spectra of these hydrocarbons and of mixtures from the elimination reactions were observed usually in Nujol mulls or occasionally in carbon disulphide, band positions under either conditions being almost the same. Our curves for camphene and tricyclene covered a slightly different range, but otherwise agreed closely with those of Swann and Cripwell,[19] showing bands in Nujol at (for camphene), 670, 747, 760, 810, and 877 cm.$^{-1}$ and (for tricyclene) 815, 843, and 854 cm.$^{-1}$. Swann and Cripwell did not publish a curve for bornylene but indicated that the hydrocarbon showed strong absorption at 717 cm.$^{-1}$. We have confirmed this, and find other bands in the spectrum (Nujol) of the pure hydrocarbon at 691, 749 (but not also a band of comparable strength *ca.* 10 cm.$^{-1}$ higher; cf. camphene), 798, 841 (but not also a comparable band at 854 cm.$^{-1}$; cf. tricyclene), and 874 cm.$^{-1}$. The extremely strong 717 cm.$^{-1}$ band exhibited by bornylene made easy the identification of this hydrocarbon in admixture (even in traces) with camphene, while camphene admixed with larger proportions of bornylene was identified by its bands at 670 and 760 cm.$^{-1}$. A small proportion of tricyclene in bornylene or in camphene was identified mainly by its bands at 815 and 854 cm.$^{-1}$, or at 843 and 854 cm.$^{-1}$ respectively.

*Pyrolysis of Bornyltrimethylammonium Hydroxide*.—(+)-Bornyltrimethylammonium iodide (1·67 g.) was converted by the silver oxide method into an aqueous solution of quaternary hydroxide, which was evaporated at room temperature in a vacuum-desiccator. The dry waxy residue decomposed slowly at 140—160° (bath)/0·3 mm. in a distillation apparatus with a cold trap ($CO_2$); the quaternary base remained solid during the degradation. The distillate was treated with excess of dilute acetic acid, and the (−)-bornylene (324 mg.) was separated by filtration. After being dried between filter papers and sublimed it had m. p. 111—112° $[\alpha]_D$ −21° (Found: C, 88·0; H, 12·0. Calc. for $C_{10}H_{16}$: C, 88·2; H, 11·8%). The infrared spectrum gave no indication of presence of traces of camphene or tricyclene. Bornyldimethylamine was obtained from the acetic acid solution, being isolated as the hydrochloride (298 mg.), $[\alpha]_D$ +5·6°.

A slightly damp sample of quaternary hydroxide (from 3·2 g. of methiodide) melted at 180° (bath) and decomposed completely in 3 min. at that temperature at 0·01 mm., yielding

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[18] Mousseron, Jacquier, and Zagdoun, *ibid.*, 1952, 197.

[19] Swann and Cripwell, *Ind. Chemist*, 1948, 573.

bornylene (600 mg.), m. p. 108°, $[\alpha]_D$ −19°, slightly contaminated (infrared spectrum) with camphene, and bornyldimethylamine [isolated as hydrochloride (652 mg.), a sample of which yielded the picrate, m. p. and mixed m. p. 213°].

*Pyrolysis of* neo*Bornyltrimethylammonium Hydroxide.*—Quaternary base from the (−)-iodide (2 g.) when treated as above at 150—160° yielded *neo*bornyldimethylamine (146 mg.) and bornylene (363 mg.), m. p. 106°, $[\alpha]_D$ −19°, containing (infrared spectrum) a little tricyclene.

*Pyrolysis of a Mixture of Bornyl and* neo*Bornyltrimethylammonium Hydroxides.*—Quaternary base from mixed methiodide (30% of bornyl- and 70% of *neo*bornyl-trimethylammonium iodide; 16·4 g.) was almost completely decomposed (without fusion) when heated at 150—210°/0·3 mm. during several hours. The residue in the pyrolysis flask was treated with potassium iodide and sodium hydroxide solutions and extracted with chloroform, evaporation of which yielded nearly pure bornyltrimethylammonium iodide (135 mg.), m. p. (from ether–methanol) 277° (following decomp. at 270°), $[\alpha]_D$ −2·4°. The infrared absorption curve (potassium bromide disc) and the *X*-ray powder photograph were identical with those from pure bornyltrimethylammonium iodide ($[\alpha]_D$ −3·7°) and entirely different from those of the *neo*-epimer ($[\alpha]_D$ −34°). The distillate was separated into basic (1·21 g.) and neutral (2·4 g.) fractions. The basic fraction, $[\alpha]_D$ +3·2° (Found: C, 79·9; H, 12·8; N, 7·6. Calc. for $C_{12}H_{23}N$: C, 79·5; H, 12·8; N, 7·7%), yielded a hydrochloride, $[\alpha]_D$ −2·4° and appeared from the optical rotatory data to consist of 70—80% of bornyl- and 20—30% of *neo*bornyl-dimethylamine; the mixture with picric acid gave bornyldimethylamine picrate, m. p. 213—214°. After further distillation the neutral fraction had m. p. 109—110°, $[\alpha]_D$ −20°; purification by Henderson and Caw's method [12] (hydrogen peroxide–acetic acid) gave bornylene, m. p. 111—112°, $[\alpha]_D$ −21°, the infrared spectrum of which indicated no contamination with camphene or tricyclene.

*Degradation of (−)-Bornyltrimethylammonium Iodide in Alkaline Glycol.*—A mixture of the quaternary salt (2·5 g.) and ethylene glycol (33 c.c.) was treated with potassium hydroxide (13 g.) in water (13 c.c.), and the whole reduced to one-third of the volume by distillation. The distillate contained (+)-bornyldimethylamine (1·37 g.), $[\alpha]_D$ +26°, $n_D^{26}$ 1·4772 (Found: C, 79·7; H, 12·8; N, 8·1. Calc. for $C_{12}H_{23}N$: C, 79·5; H, 12·8; N, 7·7%), from which the picrate, m. p. 214°, was obtained. No hydrocarbon fraction was obtained.

*Degradation of (−)-*neo*Bornyltrimethylammonium Iodide in Alkaline Glycol.*—The quaternary salt (800 mg.) when treated as above gave the tertiary base (72 mg.; identified as the picrate, m. p. 194°) separated with dilute acetic acid from a neutral fraction (225 mg.), m. p. 49°, identified as camphene by its infrared spectrum which indicated contamination with a little bornylene and tricyclene. A more detailed examination of the hydrocarbon was made on samples obtained from degradations in alkaline glycol of the more readily accessible mixtures of bornyl- and *neo*bornyl-trimethylammonium iodide (following paragraph); it is evident that the camphene from such experiments is derived from the (−)-*neo*-quaternary salt.

*Degradation of Mixtures of Bornyl- and* neo*Bornyl-trimethylammonium Iodides in Alkaline Glycol.*—(*a*) A mixture ($[\alpha]_D$ −18·5°; approximately equimolar) of the methiodides (3·02 g.), when completely decomposed as described above, yielded (+)-camphene (350 mg.), m. p. 49°, $[\alpha]_D$ +104° (in EtOH), +112° (in $C_6H_6$) (Found: C, 88·3; H, 11·8. Calc. for $C_{10}H_{16}$: C, 88·2; H, 11·8%). The infrared spectrum indicated presence of traces of tricyclene and bornylene. For (+)-camphene prepared by the usual type of elimination reaction a range of optical rotatory values has been recorded up to +99·6° (in EtOH), +107·7° (in $C_6H_6$), and +103·9° (in $Et_2O$); [20] the more elaborate procedure of Bain and his collaborators [21] yielded (−)-camphene considered by these authors to be optically pure; it had m. p. 49·1°, $[\alpha]_D$ −113·5° (in $Et_2O$), −117·5° (in toluene). Our basic reaction product (880 mg.) (Found: C, 79·6; H, 12·7; N, 7·6. Calc. for $C_{12}H_{23}N$: C, 79·5; H, 12·8; N, 7·7%) had $n_D^{25}$ 1·4778, $[\alpha]_D$ +15°; it yielded a hydrochloride, $[\alpha]_D$ +0·2°, and on treatment with picric acid afforded bornyldimethylamine picrate, m. p. 213°. The indications are that the recovered tertiary base contains *ca.* 10—20% of *neo*bornyl- and 80—90% of bornyl-dimethylamine.

(*b*) Decomposition of a methiodide mixture ($[\alpha]_D$ −16°; 610 mg.) by distillation of its solution in glycol containing only 1 mol. of potassium hydroxide yielded camphene (42 mg.), $[\alpha]_D$ +98°, and bornyldimethylamine (170 mg.), isolated as the hydrochloride, $[\alpha]_D$ +10°.

(*c*) An approximately equimolar mixture of methiodide ($[\alpha]_D$ −18·5°; 1·01 g.) was heated under reflux with potassium hydroxide (0·45 g.) in glycol (8 c.c.) and water (2 c.c.) for 5 min.

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[20] Rodd (Ed.), " Chemistry of Carbon Compounds," Elsevier, Amsterdam, 1953, Vol. IIB, p. 586.

[21] Bain, Best, Hampton, Hawkins, and Kitchen, *J. Amer. Chem. Soc.*, 1950, **72**, 3124.

at 186° (bath); the mixture was cooled, extracted with ether, treated with saturated aqueous potassium iodide (100 c.c.), and extracted with chloroform. The chloroform extract contained nearly pure (−)-bornyltrimethylammonium iodide (317 mg.), $[\alpha]_D$ −3·0°, m. p. 284°.

(*d*) Mixed methiodides ($[\alpha]_D$ −18°; 4·7 g.), when heated in glycol (50 c.c.) with potassium hydroxide (9·5 g.) at 100° for 2 hr., yielded a tertiary basic mixture isolated as hydrochloride ($[\alpha]_D$ −7·6°; 252 mg.) and some camphene; treatment of the glycol solution with potassium iodide and extraction with chloroform resulted in the recovery of mixed methiodides ($[\alpha]_D$ −15·7°; 3·6 g.). These figures indicate that 23% of the methiodide mixture was decomposed, that the original and the final methiodide mixtures contained respectively 52% and 59% of the bornyl epimer, and that the hydrochloride mixture isolated contained 77% of the bornyl epimer. It may be calculated that 0·32 g. of bornyltrimethylammonium iodide is decomposed; as this yields only tertiary base, the recovered hydrochloride should contain 83% of the bornyl epimer, so that the internal consistency of the figures is satisfactory for an essentially qualitative experiment. A further experiment, in which 16% of the original, approximately equimolar, methiodide mixture was allowed to decompose, again indicated the preferential loss of methanol from the bornyl epimer.

*Competition of Bornyl- and* neo*Bornyl-dimethylamine for Methyl Iodide.*—When a mixture of tertiary amines (4·3 g.) containing (optical rotation) 62% of the bornyl epimer was treated in ether (100 c.c.) with methyl iodide (2·4 c.c.) at 5° the first fraction (110 mg.) of methiodide which separated contained (optical rotation) 87% of bornyltrimethylammonium iodide. Neither quaternary iodide is appreciably soluble in ether.

*Stability of Camphene, Bornylene, and Tricyclene to the Reaction Conditions.*—None of the hydrocarbons was altered appreciably in infrared spectrum, m. p., or specific rotation when refluxed for some time with alkaline glycol and then recovered by distillation. Tricyclene was likewise unaltered overnight in glacial acetic acid at room temperature. These experiments indicate that camphene or bornylene, when isolated in the above experiments, is not an artefact derived from either of the other hydrocarbons by isomerisation. Camphene, m. p. 47°, $[\alpha]_D$ +101°, was unaltered on being heated with water at 150° for 12 hr. with or without addition of one mol. of trimethylamine hydriodide; this fact is relevant to the interpretation of the results described in the following paragraph.

*Degradation of Mixed Methiodides in Neutral Aqueous Solution.*—An approximately equimolar mixture of (−)-bornyl- and (−)-*neo*bornyl-trimethylammonium iodides ($[\alpha]_D$ −17°; 2 g.) in water (14·5 c.c.) was heated in a sealed tube at 160° for 12 hr.; the mixture was then cooled and treated with dilute acetic acid, and the solid (202 mg.) was filtered off. This had m. p. 49—50°, raised to 54° on sublimation, $[\alpha]_D$ +52·5°; it was (infrared spectrum) essentially camphene (Found: C, 88·5; H, 11·3. Calc. for $C_{10}H_{16}$: C, 88·2; H, 11·8%); it contained a little tricyclene, but there was an unidentified band at 789 cm.$^{-1}$. There was no trace of the powerful 717 cm.$^{-1}$ band exhibited by bornylene, and the tricyclene bands at 843 and 854 cm.$^{-1}$ were just clearly visible, and very much weaker than in the spectrum of a 1 : 1 mixture of (+)-camphene and tricyclene. The low optical rotation of the degradation hydrocarbon is therefore not due in the main to its tricyclene content. The filtration apparatus and acetic acid filtrate when washed with benzene yielded a further 106 mg. of hydrocarbon, as estimated from the optical rotation of the extract.

The filtrate from the hydrocarbon was evaporated to dryness, and the residue was dissolved in aqueous sodium hydroxide and extracted several times with ether. Addition of picric acid to the ether extract yielded trimethylamine picrate (370 mg.), m. p. and mixed m. p. 216° depressed to *ca.* 185° on admixture with bornyldimethylamine picrate (Found: C, 37·2; H, 4·3; N, 19·3. Calc. for $C_9H_{12}O_7N_4$: C, 37·6; H, 4·2; N, 19·4%). Saturation of the alkaline solution with potassium iodide and extraction with chloroform yielded bornyltrimethylammonium iodide (910 mg.), m. p. and mixed m. p. 280°, hot aqueous solutions of which therefore decompose much more slowly than those of the *neo*-epimer.

*Degradation of Aqueous (−)-Bornyltrimethylammonium Iodide.*—A saturated aqueous solution of (−)-bornyltrimethylammonium iodide (1 g.) was heated at 210° for 5 days, yielding an oily neutral insoluble fraction (360 mg.) and a mixture (640 mg.) of bornyldimethylamine hydriodide and (presumably) trimethylamine hydriodide which on basification, extraction with ether, evaporation of the extract, and treatment of the residue with ethereal picric acid gave bornyldimethylamine picrate (400 mg.), m. p. and mixed m. p. 213—214°. The alkaline aqueous solution on saturation with potassium iodide and extraction with chloroform gave unchanged bornyltrimethylammonium iodide (74 mg.), m. p. and mixed m. p. 281°. The neutral oil partially crystallised; the solid, m. p. 45°, was identified by its infrared spectrum as camphene containing a little tricyclene.

*Degradation of* (−)-neo*Bornyltrimethylammonium Iodide in Aqueous Solutions of Varying Alkali Concentration.*—(*a*) A solution of the methiodide (200 mg.) in aqueous 10% potassium hydroxide (6 c.c.) was heated in a sealed tube at 155° for 12 hr., cooled, and extracted with benzene. The extract was shaken with dilute hydrochloric acid, and the mixture evaporated to dryness. The residual hydrochloride (12 mg.) was converted into the picrate, m. p. 216°, alone or mixed with authentic trimethylamine picrate of m. p. 216°, but depressed to *ca.* 175° on admixture with *neo*bornyldimethylamine picrate (m. p. 194°). The reaction mixture contained no residual methiodide.

(*b*) Four sealed tubes each containing methiodide (*ca.* 30 mg.) and varying amounts of potassium hydroxide in water (1·8 c.c.) were heated at 140° for 40 min. and cooled. The contents of each tube were treated with aqueous 30% potassium hydroxide (10 c.c.) and saturated with potassium iodide, and all residual methiodide was extracted with chloroform (4 × 10 c.c.); the chloroform extract was evaporated and the residue washed (with negligible loss in weight) with ether. The recovered quaternary iodide was identified by its infrared spectrum. The following results were obtained:

| Tube no. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Weight of methiodide taken (mg.) | 31·15 | 28·7 | 33·0 | 29·75 |
| Mols. of alkali | 70 | 35 | 2 | 0 |
| Weight of methiodide recovered (mg.) | 11·5 | 11·95 | 12·25 | 9·6 |
| Reaction (%) | 63 | 58·5 | 63 | 67·5 |

*Pyrolysis of Bornyl- and* neo*Bornyl-trimethylammonium Iodide.*—When the *neo*-methiodide was heated at 170—190°/0·1 mm. for 3 hr., it was apparently completely decomposed into trimethylamine hydriodide (which partly sublimed during the reaction), m. p. 230—240° (Found: I, 68·3. Calc. for $C_3H_{10}NI$: I, 67·9%), the infrared spectrum of which (in a potassium bromide disc) was identical with that from an authentic specimen, and camphene, m. p. 40°, containing (infrared spectrum) some tricyclene.

The epimeric quaternary salt lost no weight at 200°/17 mm. in 70 min., but when kept at 250°/0·005 mm. for 8 hr. afforded a mixture of bornyldimethylamine and (presumably) trimethylamine hydriodides, from which the picrate of the former base was prepared (m. p. and mixed m. p. 215°), and a small quantity of neutral oily distillate, which was dissolved in carbon disulphide. The only bands in the infrared spectrum of this solution sufficiently prominent for characterisation were at 670 and 877 cm.$^{-1}$; these correspond in position to the two strongest camphene bands.

*Degradation of* (+)-*Bornyldimethylamine Oxide.*—(+)-Bornyldimethylamine (450 mg.) in methanol (40 c.c.) was treated with 30% hydrogen peroxide (4 c.c.), the solution was refluxed for 14 hr., and excess of peroxide was then decomposed by treatment with manganese dioxide. The crude crystalline ether-insoluble oxide had m. p. 76—82°, $[\alpha]_D$ +3·7°; it was characterised as the *picrate*, needles (from methanol), m. p. 225° (decomp.), depressed to <200° on admixture with bornyldimethylamine picrate (Found: C, 50·8; H, 6·4; N, 13·3. $C_{18}H_{26}O_8N_4$ requires C, 50·7; H, 6·2; N, 13·1. Calc. for $C_{18}H_{26}O_7N_4$: C, 52·7; H, 6·4; N, 13·7%).

The crude amine oxide (163 mg.), when distilled with ethylene glycol, yielded volatile neutral and basic products. The former (30 mg.) had m. p. 102—104°, $[\alpha]_D$ −20° ± 5° (microtube), and was identified (infrared spectrum) as bornylene containing some tricyclene and a trace (just visible band at 670 cm.$^{-1}$) of camphene. An ether extract of the basic product was washed with water, the ether was evaporated, and the residual bornyldimethylamine (83 mg.), $[\alpha]_D$ +34°, $n_D^{25}$ 1·4778 (Found: C, 79·4; H, 12·6; N, 7·5. Calc. for $C_{12}H_{23}N$: C, 79·5; H, 12·8; N, 7·7%), was characterised as the picrate, m. p. 212—213°.

Pyrolysis of the amine oxide at 120° (bath)/0·4 mm. also yielded crude bornylene, m. p. 105—106°, $[\alpha]_D$ −16°, and tertiary base (hydrochloride, $[\alpha]_D$ +9°); the amine oxide tended to sublime under these conditions.

*Degradation of* (−)-neo*Bornyldimethylamine Oxide.*—The crude oxide, prepared as described above from the (−)-tertiary base, had m. p. 66—70°, $[\alpha]_D$ −35°; it was characterised as the *picrate*, m. p. 180°, not in this case depressed on admixture with the tertiary amine picrate of m. p. 194° (Found: C, 50·5; H, 6·3; N, 13·1. $C_{18}H_{26}O_8N_4$ requires C, 50·7; H, 6·2; N, 13·1. Calc. for $C_{18}H_{26}O_7N_4$: C, 52·7; H, 6·4; N, 13·7%).

The amine oxide (180 mg.) was distilled with ethylene glycol, and the distillate was examined as described above. It contained *neo*bornyldimethylamine (16 mg.) identified as the picrate, m. p. and mixed m. p. 194°. The neutral product, after sublimation, had m. p. 96°, $[\alpha]_D$ 0° ± 5° (micro-tube); the infrared absorption curve indicated bornylene with some admixture with camphene, the 670 and 760 $cm.^{-1}$ bands of the latter hydrocarbon being prominent. The m. p.[6] and $[\alpha]_D$ of the hydrocarbon mixture (Found: C, 88·0; H, 12·2. Calc. for $C_{10}H_{16}$: C, 88·2; H, 11·8%) suggest that it contains *ca.* 20% of camphene.

Pyrolysis of the amine oxide at 120° (bath)/0·4 mm. gave similar products, the hydrocarbon (Found: C, 88·0; H, 11·8%) again having m. p. 96°.

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