

warmed to -78° and the vessel was charged with 3 mmoles of OF_2 . Stirring was initiated and the blue color of the nitroso monomer appeared immediately. Upon completion of the oxidation, the solvent and nitroso monomer were transferred out of the reaction flask, concentrated, and analyzed by vapor phase chromatography (silicon 710, 146°). Based on the OF_2 consumed (63%), v.p.c. analysis indicated essentially quantitative conversion to 2-methyl-2-nitrosopropane. The infrared spectrum was identical with that of an authentic sample. *t*-Butylammonium fluoride (0.302 g., 3.2 mmoles, 85% yield), identified by its infrared spectrum, remained as a nonvolatile residue.

Oxidation of Cyclopropylamine on Chromosorb P.—Cyclopropylamine (0.86 g., 15 mmoles) was dispersed on 5 g. of Chromosorb P and degassed. The mixture was cooled to -42° and 5 mmoles of OF_2 was admitted to the reactor. The OF_2 was completely consumed within 30 min. The volatile components were pumped out of the reactor and condensed at -80° giving a bright blue liquid which dimerized to 0.121 g. (34% yield) of a colorless solid, m.p. $78-79^\circ$. The solid melted to a blue solution which sublimed to another crystalline solid, m.p. $68-69^\circ$.

Both solids produce blue solutions in organic solvents showing characteristic absorption for both monomer ($-\text{N}=\text{O}$), 1515 cm^{-1} , and dimer, 1266 and 1177 cm^{-1} (CCl_4).

The n.m.r. spectrum of the dimer shows a single proton (multiplet) centered at $4.9\ \delta$ and two groups of two protons each as multiplets centered at 1.0 and $1.4\ \delta$.

Anal. Calcd. for $\text{C}_3\text{H}_5\text{NO}$: C, 50.69; H, 7.09; N, 19.71. Found: C, 50.63; H, 7.25; N, 19.36.

Oxidation of *t*-Octylamine.—A solution of *t*-octylamine (2.0 g., 15 mmoles) in 15 ml. of Freon 11 was treated with 4 mmoles of OF_2 at -78° . The work-up was similar to that described for *t*-butylamine and yielded 0.5 g. (88% yield) of nitroso-*t*-octane identified by its infrared and ultraviolet spectra. The nonvolatile

residue consisted of 1.01 g. (85%) of *t*-octylammonium fluoride, identified by infrared spectrum and neutralization to *t*-octylamine.

Oxidation of Cyclohexylamine.—A solution of freshly distilled cyclohexylamine (1.0 g., 10 mmoles) in 10 ml. of Freon 11 was repeatedly degassed and was treated with 3 mmoles of OF_2 . The reaction was essentially complete after 2 hr. at -78° . The solvent was removed and the residue extracted with 50 ml. of anhydrous ether. The ether-insoluble material was cyclohexylammonium fluoride, 0.54 g. (76% yield), m.p. 129° dec., identified by its infrared spectrum. The ether solution was evaporated to yield a colorless oil which upon crystallization from petroleum ether at -80° gave 0.224 g. (66% yield after purification) of cyclohexanone oxime as a colorless solid, m.p. $85-87^\circ$. The melting point and the infrared spectrum were identical with that of an authentic sample.

Oxidation of Ethylamine.—A solution of 12 mmoles of ethylamine in 10 ml. of Freon 11 was degassed and treated at -78° with 4 mmoles of OF_2 for 16 hr. The usual work-up yielded 0.103 g. (44% yield) of acetaldoxime identified by comparison of its infrared spectrum with that of an authentic sample. An ether-insoluble, water-soluble, hygroscopic, colorless solid was also isolated and presumed to be ethylammonium fluoride.

Warning.—Oxygen difluoride has proved to be somewhat treacherous and adequate precautions against explosions must be taken.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

ortho-Substitution Rearrangement and Other Reactions of α -Substituted Benzyltrimethylammonium Ion-Alcohols with Potassium Amide in Liquid Ammonia^{1a}

BY WALTER H. PUTERBAUGH^{1b} AND CHARLES R. HAUSER

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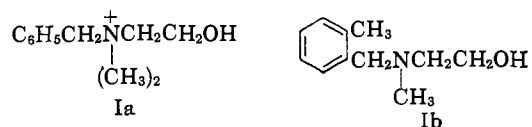
A series of α -substituted benzyltrimethylammonium ions, which have hydroxyl and other substituents β to the quaternary nitrogen, underwent with excess potassium amide in liquid ammonia not only the *ortho*-substitution rearrangement, but also in most cases certain other types of reaction. The β,β -diphenyl quaternary ion IIa and the cyclopentyl quaternary ion IV exhibited almost exclusively the rearrangement to give aminocarbinols Va and VII, whereas the cyclohexyl quaternary ion III underwent mainly cyclization to form epoxide XI. These results are ascribed to steric factors. The β,β -dimethyl quaternary ion IIc underwent more cyclization and cleavage than rearrangement. The cyclization afforded epoxide IX, and the cleavage gave 2-methylbenzyltrimethylamine (X) and presumably acetone. Amine X resulted from rearrangement of intermediate benzyltrimethylammonium ion. The β -phenyl quaternary ion IIb underwent, besides rearrangement, a β -elimination type of reaction to form desoxybenzoin (VIII). Quaternary ion II'd apparently exhibited similar results. The monoanion of quaternary ion III underwent cyclization to form epoxide XI, whereas the monoanion of quaternary ion IIa failed to cyclize. Mechanisms for certain of these reactions are considered.

The benzyl type quaternary ammonium ion-alcohol Ia has recently been shown to undergo the *o*-substitution rearrangement with excess sodium amide in liquid ammonia to form Ib.² β -Elimination, which occurs to a considerable extent with the benzyl-*n*-propyldimethylammonium ion,³ failed to occur appreciably with Ia apparently because of deactivation of the β -hydrogen by the negative charge on the intermediate alkoxide ion. Rather surprisingly, no intramolecular cyclization of the alkoxide ion of Ia to form ethylene oxide or benzyl β -dimethylaminoethyl ether was observed.

(1) (a) Supported in part by Army Research Office (Durham); (b) National Science Foundation Science Faculty Fellow, on leave from Thiel College.

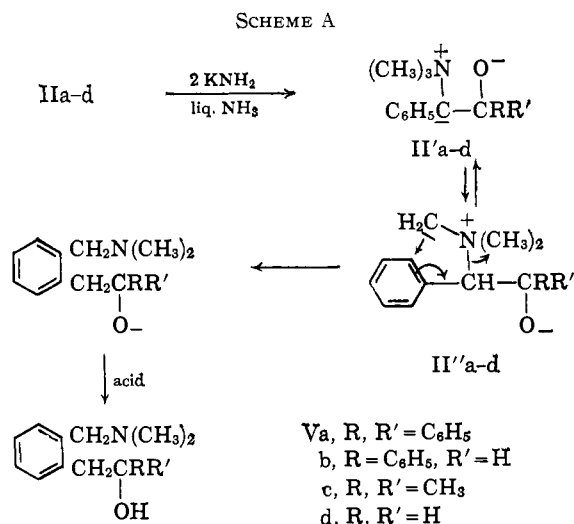
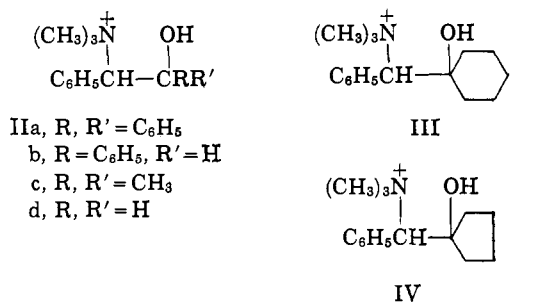
(2) G. C. Jones and C. R. Hauser, *J. Org. Chem.*, **27**, 806 (1962).

(3) C. R. Hauser and A. J. Weinheimer, *J. Am. Chem. Soc.*, **76**, 1264 (1954).

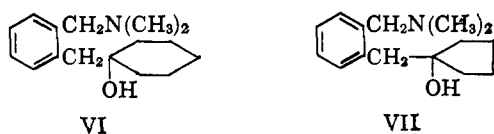


The α -substituted benzyltrimethylammonium ions IIa-d, III, and IV, which have hydroxyl and other substituents β to the quaternary nitrogen, have now been found to exhibit, with excess potassium amide in liquid ammonia, not only the *o*-substitution rearrangement but also, in most cases, certain other types of reaction.

The rearrangements of quaternary ion-alcohols IIa-d afforded aminocarbinols Va-d in yields of 88, 51, 17, and 37%, respectively. Presumably II'a-d and II''a-d would be intermediates (Scheme A).⁴



Similarly, the rearrangement of quaternary ion-alcohol III apparently afforded aminocarbinol VI (13%), and that of IV produced aminocarbinol VII in 77% yield.



The structures of the rearranged aminocarbinols were supported by analysis (except VI) and by infrared spectra which showed a strong peak in the 853–837 cm^{-1} region attributable to the dimethylaminomethyl group.⁵ The spectra of aminocarbinols Vc, Vd, and VII each showed a peak near 740 and no absorption in the 690–710 cm^{-1} region, indicating an *o*-disubstituted rather than a monosubstituted aromatic ring.⁶ Compounds Va and Vb also showed peaks near 740 cm^{-1} , but the assignment of the *o*-substituted ring, while indicated, is less certain because of the presence of additional aromatic rings.

The structures of aminocarbinols Va–c were confirmed by independent syntheses from 2-methylbenzyl-dimethylamine and the appropriate carbonyl compound (Scheme B).⁷

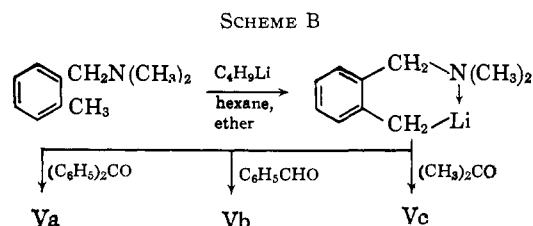
Incidentally, amino alcohol Vb obtained by both methods melted over a 10° range even after repeated recrystallizations, yet its analysis was satisfactory and its vapor phase chromatogram showed a single peak.

(4) See W. H. Puterbaugh and C. R. Hauser, *J. Am. Chem. Soc.*, **86**, 1105 (1964).

(5) W. Q. Beard, Jr., and C. R. Hauser, *J. Org. Chem.*, **25**, 334 (1960).

(6) See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 77.

(7) The details of this method will be published soon. For deuteration at the 2-methyl position through metalation, see F. N. Jones, M. F. Zinn, and C. R. Hauser, *J. Org. Chem.*, **28**, 663 (1963).

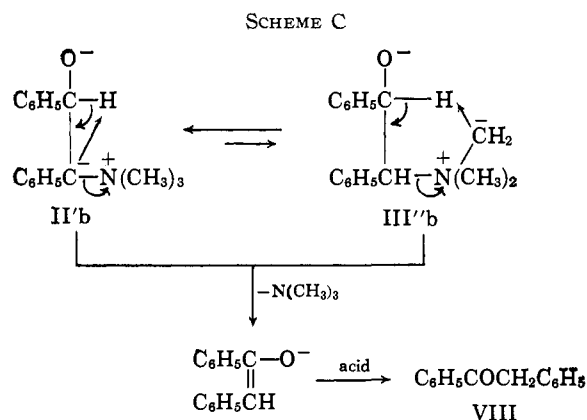


Its methiodide and picrate, obtained in high yields, melted sharply.

The structure of amino alcohol VII was confirmed as an *o*-rearrangement product by oxidation to *o*-phthalic acid. Amino alcohol VI was indicated by vapor phase chromatography (see Experimental).

Besides the *o*-substitution rearrangement, a β -elimination type of reaction was observed with quaternary ion-alcohols IIb and apparently IIc, and cyclization and cleavage reactions were exhibited by quaternary ion-alcohols IIc and III.

The elimination reaction afforded desoxybenzoin (VIII, 30%) and apparently phenylacetaldehyde (obtained as polymer) from IIb and IIc, respectively. Two possible mechanisms for the elimination in IIb are illustrated in Scheme C. In these mechanisms, intermediates II'b or III'b (see Scheme A) are assumed to undergo a 1,2-shift of the β -proton, or removal of the β -proton through a five-atom ring, respectively. The former would occur through the more predominant carbanion, whereas the latter is similar to the α',β -elimination mechanism previously demonstrated in certain cases.⁸



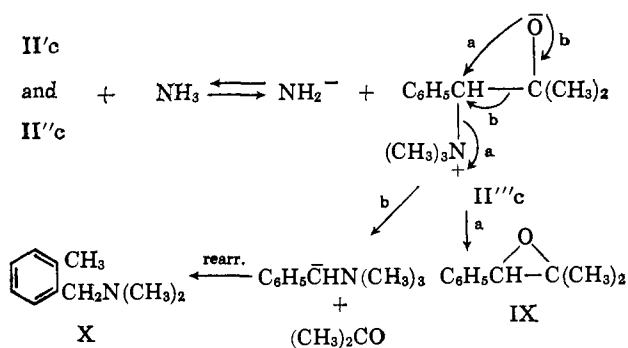
The cyclization and cleavage reactions of quaternary ion-alcohol IIc afforded epoxide IX and rearranged amine X in yields of 28 and 31%, respectively. The formation of these products is illustrated in Scheme D by courses a and b, respectively. In this scheme, these reactions are considered to involve monoanion II'c (see Discussion), which presumably would be in equilibrium with dianions II'c and II''c, though the dianions themselves might possibly undergo these reactions.

The structure of epoxide IX was established by its infrared spectra, which showed peaks at 1250 and 910 cm^{-1} indicative of an epoxy ring,⁹ and by the reactions represented in Scheme E.

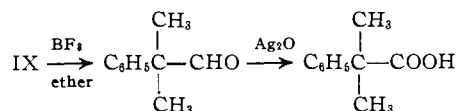
(8) G. Wittig and R. Polster, *Ann.*, **599**, 13 (1956); G. Wittig and T. F. Burger, *ibid.*, **632**, 85 (1960); see also A. C. Cope, N. A. LeBel, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **83**, 3861 (1961); F. N. Jones and C. R. Hauser, *J. Org. Chem.*, **27**, 1542 (1962).

(9) Reference 6, pp. 118–119.

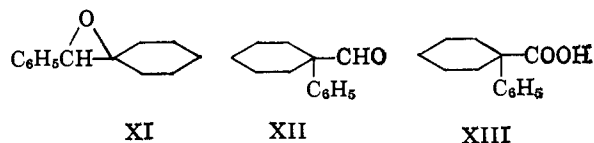
SCHEME D



SCHEME E



Similarly, quaternary ion-alcohol III afforded epoxide XI and rearranged amine X in yields of 64 and 10%, respectively. The structure of XI was established by its infrared spectra which showed absorptions for an epoxy ring at 1250 and 915 cm.⁻¹, and by its rearrangement to aldehyde XII which was oxidized to acid XIII.



In Table I are summarized the yields of all products isolated from quaternary ion-alcohols IIa-d, III, and IV on treatment with 3 molecular equivalents of potas-

TABLE I

YIELDS OF PRODUCTS FROM QUATERNARY ION-ALCOHOLS IIa-d, III, AND IV WITH EXCESS POTASSIUM AMIDE IN LIQUID AMMONIA

Quaternary ion-alcohol	<i>o</i> -Rearr. yield, %	β -Elim. yield, %	Cyclization yield, %	Cleavage yield, %
IIa	88 (Va)
IIb	51 (Vb)	30 (VIII)
IIc	17 (Vc)	...	28 (IX)	31 (X)
IId	37 ^a (Vd)	26 ^b
III	13 (VI)	...	64 (XI)	10 (X)
IV	77 (VII)

^a An additional 14% of polymeric amine residue was left after distillation of amine Vd. ^b Estimated from the neutral fraction which appeared to have arisen through phenylacetaldehyde (see Experimental).

sium amide for 6 hr. in liquid ammonia. In addition to the products listed, small amounts of unidentified neutral material were also obtained in most cases (see Experimental).

Discussion

Table I shows that the β,β -diphenyl quaternary ion-alcohol IIa and the cyclopentyl quaternary ion-alcohol IV underwent almost exclusively the *o*-substitution rearrangement, whereas the cyclohexyl quaternary ion-alcohol III exhibited mainly cyclization. This remarkable difference in the main course of reaction of IIa and IV *vs.* III appears to be ascribable to steric factors.

With regard to the *o*-rearrangement, a consideration of Stuart-Briegleb models indicates that free rotation around the bond connecting the benzylic carbon to the quaternary nitrogen is possible in IIa and IV, but not in III. Thus, any one of the three methyl groups of IIa or IV should be available for rearrangement, but only one methyl group of III would have access to the aromatic ring.

With regard to the cyclization, the models indicate that free rotation around the bond connecting the benzylic carbon to the β -carbon is possible in III, but not in IIa and IV. Thus, backside displacement of trimethylamine by the alkoxide ion may occur readily in III, but not in IIa or IV. In each of the two latter cases, the most favorable rotamer appears to be one in which the alkoxide ion is not backside to the trimethylammonium group. These indications were supported by experiments with the monoanions III' and II''a, which were prepared by treating III and IIa each with only one molecular equivalent of potassium amide in liquid ammonia. After 6 hr., III' afforded epoxide XI in 82% yield, whereas II''a produced none of the corresponding epoxide. Instead, 74% of IIa was recovered. Incidentally, monoanion II''a underwent some cleavage to form benzophenone (24%) and rearranged amine X (see Scheme D).

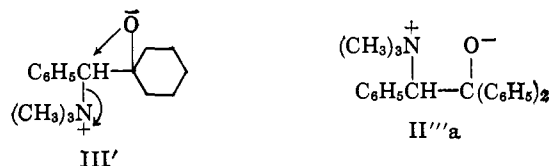
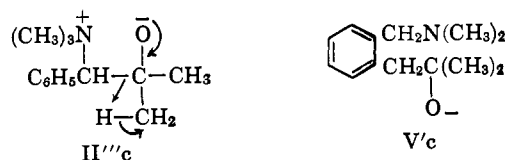


Table I further shows that the β,β -dimethyl quaternary ion-alcohol IIc underwent more cyclization and cleavage than *o*-rearrangement. The failure to exhibit much rearrangement appears not to be due to steric factors, since the model indicates little restriction around the benzylic carbon to quaternary nitrogen bond. The fact that more cleavage was observed in this case than in any of the others suggests that one of the six methyl hydrogens is involved in either the transition state as indicated below in II''c, or in an intermolecular mechanism. The possibility that cleavage took place *after* *o*-rearrangement was ruled out by treating Vc (the *o*-rearrangement product of IIc) with excess potassium amide to form V'c. After 3 hr. in liquid ammonia, 90% of aminocarbinol Vc was recovered, and no 2-methylbenzyl dimethylamine (X) was found.



Finally, Table I shows that the β -phenyl quaternary ion-alcohol IIb and also apparently IId underwent considerable elimination reaction. This result with IIb is not surprising, since deactivation of the β -hydrogen by the negative charge on the adjacent oxygen may be offset by activation of this hydrogen by the β -phenyl group.¹⁰ However, the result with IId

was not expected in view of the essential absence of elimination observed previously with quaternary ion-alcohol Ia.^{2,11}

Experimental¹²

Quaternary Ammonium Ion-Alcohols.—The iodides of quaternary ion-alcohols IIa-c, III, and IV were prepared as described previously¹³ by metalation of benzyltrimethylamine with phenylsodium followed by condensation with the appropriate carbonyl compound and treatment with methyl iodide.

Quaternary ion-alcohol II d was prepared by the following adaptation of this method. A suspension of α -sodiobenzyltrimethylamine was prepared by metalating 19.9 g. (0.147 mole) of benzyltrimethylamine with phenylsodium prepared from 9.67 g. (0.42 mole) of dispersed sodium and 21.6 g. (0.192 mole) of chlorobenzene in 125 ml. of benzene and 35 ml. of octane. After refluxing for 3 hr., the red suspension was immersed in a water bath and maintained at 20–30° while gaseous formaldehyde, generated by heating 22.5 g. (0.75 mole) of paraformaldehyde in a stream of nitrogen,¹⁴ was passed over the reaction mixture during 15 min. The resultant brown suspension was stirred 4 hr. at room temperature and then worked up as described previously to afford 11.9 g. (49%) of β -(N,N-dimethylamino)-phenethyl alcohol, b.p. 92–94° at 1.5 mm.; lit. b.p. 135–138° at 15 mm.,^{15a} 148.5° at 16 mm.^{15b} The infrared spectrum showed principal peaks at 3400, 2940, 2790, 1460, 1100, 1035, 853, 755, 745, and 700 cm.⁻¹. This amino alcohol (14.3 g., 0.087 mole) in 90 ml. of acetonitrile was treated with 0.176 mole of methyl iodide for 5 hr. at room temperature followed by 1 hr. at reflux. Ether (150 ml.) was added and the resultant mixture, which contained the methiodide as a viscous oil, was heated to reflux and then cooled and scratched to induce crystallization. The solvent was decanted and the solid was rinsed with two portions of dry ether. The residual solvent was removed by drying *in vacuo* over phosphorus pentoxide to leave 25.3 g. (94%) of α -(hydroxymethyl)-benzyltrimethylammonium iodide (II d) as a white powder, m.p. 92–95°.¹⁶ This compound is very hygroscopic and was kept under anhydrous conditions during its subsequent use.

Reaction of Quaternary Ammonium Ion-Alcohols IIa-d, III, and IV with Excess Potassium Amide.—The appropriate solid methiodide was added to a stirred solution of 3 molecular equivalents of potassium amide in 400–600 ml. of liquid ammonia.¹⁷ After 6 to 6.5 hr. the reaction mixture was poured into a solution of 3 molecular equivalents of ammonium iodide in 150 ml. of liquid ammonia. The ammonia was evaporated on the steam bath as 200–300 ml. of ether was added. Water (100–150 ml.) was added and the layers were separated. The ether layer was washed with water and combined with an ethereal extract of the aqueous layer after the latter had been made strongly basic with sodium hydroxide. The ethereal solution was extracted with sufficient portions of 2 M hydrochloric acid to remove the basic products and combined with an ether washing of the acidic extracts. The ethereal solution was washed with saturated sodium chloride solution and dried over sodium sulfate, and the solvent was removed to leave the residual neutral fraction. The acidic extract was made basic with sodium hydroxide solution (cooled and stirred) and the resulting mixture was extracted with ether. The ether extract was dried and the solvent was removed to leave the residual basic fraction.

(10) Since quaternary ion-alcohol II b consisted of an approximately equal mixture of diastereoisomers (see ref. 12), the possibility exists that rearrangement may be the preferred course for one pair, and elimination the preferred course for the other pair. This is to be investigated.

(11) As suggested by the referee, II d may be more prone than Ia to undergo β -elimination since the former leads to an enolate ion stabilized by a phenyl group whereas the latter does not.

(12) Melting points were taken on a Fisher-Johns melting point stage which had been calibrated with standard samples. Analyses were by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were taken on a Perkin-Elmer Model 237 Infracord using the potassium bromide pellet method for solids, and the neat liquid between sodium chloride plates for liquids. Vapor phase chromatography was carried out on an F and M Model 500 gas chromatograph using a 2-ft. silicone gum rubber column unless otherwise specified.

(13) W. H. Puterbaugh and C. R. Hauser, *J. Org. Chem.*, **28**, 3465 (1963).

(14) H. Gilman and W. E. Catlin, *Org. Syntheses*, **1**, 188 (1932).

(15) (a) M. Tiffeneau and E. Forneau, *Bull. soc. chim. France*, [4] **13**, 979 (1913); (b) Y. de Lestrangé and J. Levy, *Bull. Sci. Pharmacol.*, **36**, 35 (1929).

(16) Previously reported as amorphous,¹⁴ and m.p. 100°.¹⁵

(17) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

The residual *basic* and *neutral fractions* obtained in each experiment were treated as described below.

(A) **Reaction of II a.**—From 23.0 g. (0.05 mole) of II a there was obtained on removal of solvent from the *basic fraction*, 14.7 g. (88%) of 2-(dimethylaminomethyl)-benzylphenylcarbinol (Va), m.p. 122.5–125°, which was recrystallized and identified as described previously.⁴ The *neutral fraction* contained 1.1 g. of yellow partial solid which was not identified.

(B) **Reaction of II b.**—From 20.7 g. (0.054 mole) of II b there was obtained on removal of solvent from the *basic fraction*, 7.0 g. (51%) of 2-(dimethylaminomethyl)-benzylphenylcarbinol (Vb), m.p. 62–80°. Three recrystallizations from hexane gave Vb, m.p. 81–90°. A v.p.c. at 210° of an acetone solution of Vb showed, besides the solvent peak, a single peak with a retention time of 2.9 min. No other peak was obtained on programming to 300°.

Anal. Calcd. for C₁₇H₂₁NO: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.89; H 8.02; N 5.48.

The infrared spectrum was identical with that of a sample of Vb, m.p. 84–92°, independently synthesized through metalation of 2-methylbenzyltrimethylamine with *n*-butyllithium and condensation with benzophenone.⁷ The spectrum showed principal peaks at 3055, 2940, 2810, 1490, 1470, 1445, 1350, 1200, 1170, 1105, 1060, 1005, 837, 775, 760, and 700 cm.⁻¹.

The picrate of Vb, obtained in 85% yield, melted at 143–143.5° after recrystallization from 95% ethanol.

Anal. Calcd. for C₂₃H₂₄N₄O₈: C, 57.02; H, 4.99; N, 11.57. Found: C, 57.09; H, 5.28; N, 11.71.

The methiodide of Vb, obtained in 92% yield, melted at 141–143° and at 142.5–144.5° after recrystallization from ethanol-ether. The m.p. was not depressed on admixture with the methiodide⁷ prepared from the independently synthesized sample of Vb. The infrared spectra were identical.

The *neutral fraction* obtained from II b was scratched to set up a partial solid which was recrystallized from methanol to afford 2.5 g. (24%) of desoxybenzoin (VIII), m.p. 53–56° and at 55–57° on admixture with an authentic sample. A v.p.c. (5-ft. Apiezon L column) on the filtrate from the recrystallization showed it to contain an additional 0.6 g. (6%) of VIII, identified by enhancement.

(C) **Reaction of II c.**—From 16.3 g. (0.0486 mole) of II c there was obtained 3.9 g. of *basic fraction* and 3.5 g. of *neutral material*.

A v.p.c. at 150° of the *basic fraction* showed it to contain 2.2 g. (31%) of 2-methylbenzyltrimethylamine (X) and 1.7 g. (17%) of α,α -dimethyl-2-(dimethylaminomethyl)-phenethyl alcohol (Vc), identified by enhancement with authentic samples of X and Vc.⁷ Distillation afforded X, b.p. 71–73° at 8 mm., and Vc, b.p. 75–77° at 0.2 mm. The picrate of X melted at 112–113°, undepressed on admixture with an authentic sample. The infrared spectrum of Vc was identical with that of the independently synthesized sample,⁷ and showed principal peaks at 3350, 3125, 2950, 2800, 1470, 1360, 1255, 1175, 1130, 1015, 970, 840, 740, and 720 cm.⁻¹.

The methiodide of Vc melted at 175.5–176.5° after recrystallization from acetonitrile. The m.p. was not depressed on admixture with the methiodide⁷ prepared from the independently synthesized sample of Vc.

A v.p.c. at 100° of the *neutral fraction* from II c showed it to contain 2.0 g. (28%) of β,β -dimethylstyrene oxide (IX, for identification see below) and 1.5 g. of unidentified material¹⁸ with retention times of 3.2 and 6.0 min., respectively. Distillation afforded 1.9 g. of IX, b.p. 87–91° at 15 mm., lit.¹⁹ b.p. 87–90° at 13 mm., and 1.3 g. of the unidentified fraction, b.p. 114–116° at 15 mm. The infrared spectrum of IX showed peaks at 1250 and 910 cm.⁻¹ indicative of an epoxy ring, along with peaks at 740 and 700 cm.⁻¹ for a monosubstituted aromatic ring.

A solution of 1.8 g. of IX in 50 ml. of dry ether was isomerized by treating with 7 ml. of boron trifluoride etherate²⁰ for 1 hr. at room temperature. The reaction mixture was poured into ice water and the layers separated. The ethereal layer was washed with saturated sodium bicarbonate and sodium chloride solutions and dried over sodium sulfate. The solvent was removed to leave 1.6 g. of α -methylhydratropaldehyde, whose infrared spectrum showed aldehydic hydrogen peaks at 2800 and 2700 cm.⁻¹ and

(18) The infrared spectrum of this material showed a strong band at 3450 cm.⁻¹ indicative of a hydroxy group. Treatment with boron trifluoride etherate for 1 hr. at room temperature yielded a polymer.

(19) J. Levy and A. Tabart, *Bull. soc. chim. France*, [4] **49**, 1783 (1931).

(20) See H. O. House, *J. Am. Chem. Soc.*, **76**, 1235 (1954).

carbonyl absorption at 1710 cm^{-1} .²¹ The semicarbazone melted at 176–177°, lit.¹⁹ m.p. 176–177°.

A solution of 0.66 g. of the α -methylhydratropaldehyde in 8 ml. of 95% ethanol was added to a suspension of silver oxide prepared from 1.8 g. of sodium hydroxide and 2.55 g. of silver nitrate in 15 ml. of water, and the resulting mixture was stirred for 5 hr. The mixture was filtered and the filtrate, after washing with ether, was acidified. The precipitate was recrystallized from hexane to give α -methylhydratropic acid, m.p. 77.5–78.5°, lit.²² m.p. 76.5–78°. The m.p. was not depressed on admixture with an authentic sample.

Reaction of II_d.—From 25.0 g. (0.0814 mole) of II_d there was obtained 8.3 g. of basic fraction and 2.5 g. of neutral material.

A v.p.c. at 150° of the *basic fraction* showed only a trace of 2-methylbenzylidimethylamine (X). Distillation afforded 5.4 g. (37%) of 2-(dimethylaminomethyl)-phenethyl alcohol (V_d), b.p. 95–96° at 0.3 mm., and left 2.0 g. of polymeric residue. Redistillation gave the analytical sample of V_d, b.p. 92° at 0.25 mm. The infrared spectrum showed principal peaks at 3350, 2940, 2820, 1470, 1075, 1050, 1020, 840, 755, and 727 cm^{-1} .

Anal. Calcd. for $\text{C}_{11}\text{H}_{17}\text{NO}$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.97; H, 9.59; N, 7.98.

The methiodide of V_d melted at 202.5–203.5° after recrystallization from acetonitrile.

Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{INO}$: C, 44.87; H, 6.28; N, 4.36. Found: C, 44.78; H, 6.22; N, 4.17.

The *neutral fraction* from II_d was a viscous orange gum, which is believed to have arisen through polymerization of phenylacetaldehyde. A blank run was made by treating 12.0 g. (0.10 mole) of phenylacetaldehyde with 0.21 mole of potassium amide for 4 hr. in liquid ammonia. The bright red reaction mixture was neutralized and worked up under the same conditions employed in the reaction of II_d with excess potassium amide. No phenylacetaldehyde was recovered. Instead, there was obtained 5.7 g. of orange, viscous neutral material whose appearance, odor, and infrared spectrum were very similar to those of the neutral material obtained from II_d. Since only about half of the starting weight of phenylacetaldehyde was recovered as neutral products, the extent of β -elimination in II_d may possibly be twice the value reported in Table I.

That the neutral fraction obtained from II_d did not arise from styrene oxide (formed through cyclization) was indicated by a similar blank experiment using 12.0 g. (0.10 mole) of styrene oxide and 0.21 mole of potassium amide. There was obtained only 0.3 g. of neutral product along with 3.3 g. of basic material as a viscous oil.

(E) Reaction of III.—From 12.6 g. (0.0336 mole) of III there was obtained 1.6 g. of basic fraction and 4.6 g. of neutral material.

A v.p.c. at 200° of the *basic fraction* showed it to contain 0.5 g. (10%) of 2-methylbenzylidimethylamine (X, identified by enhancement technique), and 1.1 g. (13%) of presumably 1-(*o*-dimethylaminobenzyl)-cyclohexanol (VI). The latter compound showed a retention time of 2.8 min., which is in the range expected by comparison with the retention time (2.4 min.) observed for the corresponding rearranged cyclopentylamine carbinoI VII (see below) under these conditions.

Distillation of the *neutral fraction* afforded 4.0 g. (64%) of 2-phenyl-1-oxaspiro[2.5]octane (XI), b.p. 140–142° at 15 mm., lit.²³ b.p. 135° at 15 mm. The infrared spectrum of XI showed absorption at 1250, 910, and 830 cm^{-1} indicative of an epoxy ring.

A 3.4-g. sample of epoxide XI was isomerized with boron trifluoride etherate as described above under C to afford 2.2 g. (65%) of 1-phenylcyclohexanecarboxaldehyde (XII), b.p. 150–153° at 14 mm., lit.²³ b.p. 144–145° at 19 mm. The semicarba-

zone of XII melted at 210–211° after recrystallization from 95% ethanol; lit.²³ m.p. 219°.

A 0.94-g. sample of aldehyde XII was oxidized with silver oxide as described above under C to afford, after recrystallization from hexane, 1-phenylcyclohexanecarboxylic acid (XIII), m.p. 123–124°, lit.²⁴ m.p. 123–124°; neut. equiv. calcd. 204.3, found 205.3.

(F) Reaction of IV.—From 21.7 g. (0.06 mole) of IV there was obtained 11.2 g. of basic fraction and 1.9 g. of neutral material.

A v.p.c. of the basic fraction indicated the absence of amine X. Distillation afforded 10.7 g. (77%) of 1-(*o*-dimethylaminomethylbenzyl)-cyclopentanol (VII), b.p. 114–118° at 0.3 mm. Redistillation afforded the analytical sample, b.p. 115° at 0.3 mm. The infrared spectrum showed principal peaks at 3150, 2945, 2860, 2830, 1470, 1365, 1315, 1255, 1170, 1090, 1040, 1010, 890, 840, and 740 cm^{-1} .

Anal. Calcd. for $\text{C}_{15}\text{H}_{23}\text{NO}$: C, 77.20; H, 9.94; N, 6.00. Found: C, 77.13; H, 9.87; N, 5.83.

The methiodide of VII melted at 182–183° after recrystallization from ethanol.

Anal. Calcd. for $\text{C}_{16}\text{H}_{26}\text{INO}$: C, 51.20; H, 6.98; N, 3.73. Found: C, 51.19; H, 6.96; N, 3.72.

The picrate of VII melted at 125–126° after recrystallization from ethanol.

Anal. Calcd. for $\text{C}_{21}\text{H}_{26}\text{N}_4\text{O}_8$: C, 54.54; H, 5.67; N, 12.12. Found: C, 54.78; H, 5.81; N, 12.09.

Oxidation of 2.3 g. of VII was effected by refluxing for 9 hr. with 24 g. of potassium permanganate (added in 3-g. increments as the color disappeared) in 100 ml. of 1 *M* sodium hydroxide. There was obtained 0.7 g. (42%) of *o*-phthalic acid, m.p. 209–210°, undepressed on admixture with an authentic sample. The infrared spectra were identical.

Distillation of the *neutral fraction* obtained from IV afforded 1.2 g. of material, b.p. 127–131° at 7 mm. That this material was not an epoxide was indicated by the absence of peaks near 1250, 910, and 830 cm^{-1} in its infrared spectrum. The latter showed a strong band at 3450 cm^{-1} suggestive of a hydroxyl group. Treatment of a sample of this material with boron trifluoride etherate gave mainly polymeric material. Oxidation with acidic dichromate solution failed to yield an identifiable product.

Treatment of III with 1 Equivalent of Potassium Amide to Form XI.—To a solution of 0.081 mole of potassium amide in 250 ml. of liquid ammonia was added 28.1 g. (0.075 mole) of III. The flocculent gray suspension was stirred 6 hr. and then neutralized and worked up as described above for the experiments employing excess potassium amide. Distillation of the neutral fraction afforded 11.5 g. (82%) of epoxide XI, b.p. 95–97° at 0.6 mm. The infrared spectrum of this product was identical with that of epoxide XI obtained as described above under E. This compound solidified on standing and was recrystallized from 95% ethanol to give XI, m.p. 37°.

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.93; H, 8.57. Found: C, 82.95; H, 8.51.

Treatment of II_a with 1 Equivalent of Potassium Amide.—To a solution of 0.079 mole of potassium amide in 250 ml. of liquid ammonia was added 33.5 g. (0.073 mole) of II_a. The mixture containing a white suspension was stirred 6 hr. and then neutralized with ammonium iodide. The ethereal suspension left after removal of the ammonia was stirred with 100 ml. of water. The precipitate that remained was filtered and dried *in vacuo* to afford 24.8 g. (74%) of recovered II_a, m.p. 178–180°, and at 182–183° on admixture with a sample of starting II_a. The filtrate after removal of II_a was worked up as described above for the reactions employing excess potassium amide. From the *neutral fraction* there was obtained 3.5 g. (25%) of benzophenone, m.p. 47–48.5°, undepressed on admixture with an authentic sample. From the *basic fraction* there was obtained 0.5 g. (5%) of 2-methylbenzylidimethylamine (X) which was identified by v.p.c. (enhancement technique).

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