Tetrahedron, 1965, Vol. 21, pp. 2365 to 2373. Pergamon Press Ltd. Printed in Northern Ireland

QUATERNARY BENZYLAMMONIUM ION REARRANGEMENTS WITH ORGANOLITHIUM COMPOUNDS—I

SIMPLE TERTIARY AMINES FROM THE ATTACK OF N-BUTYLLITHIUM ON BENZYLTRIMETHYLAMMONIUM IODIDE

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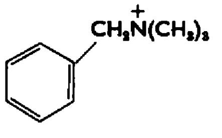
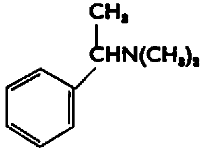
(*Received* 31 *March* 1965; *in revised form* 5 *May* 1965)

Abstract—Benzyltrimethylammonium (I) iodide reacts with n-butyllithium to produce α,N,N-trimethylbenzylamine (II) and *o*,N,N-trimethylbenzylamine (III) in a monomeric rearrangement process. A 51% total yield of the two simple tertiary amines contained II and III in the ratio of 1:3·8. Separation of the reaction products by gas chromatography and identification by IR and PMR indicated the absence of other rearrangement products [i.e. N-benzyl-N-ethylmethylamine (IV) and β-phenethyldimethylamine (V)] from the methyl ylide of I. The failure of V to be consumed in the presence of n-butyllithium eliminated secondary reactions as the feature limiting the number of observed products. The products II and III have previously been reported separately in other rearrangements of I.

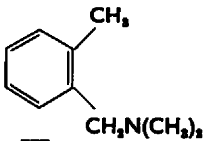
THE benzyltrimethylammonium ion (I) was shown to undergo rearrangement when treated with certain basic reagents. Either a Stevens or a Sommelet rearrangement occurred giving the respective products II[1] and III[2] depending on the base employed.



I



II



III

The Stevens rearrangement, a 1,2- or alpha shift, produced α,N,N-trimethylbenzylamine (II) when the bromide of I was reacted with phenyllithium in anhydrous ether.[1] Although no yields were determined, a neutral product, 1,1,2-triphenylethane, but no additional amine was reported in this reaction.

The *ortho* shift or Sommelet rearrangement produced *o*,N,N-trimethylbenzylamine (III) when sodium amide was reacted with the iodide of I in liquid ammonia.[2] The amine (III) was quantitatively obtained under these conditions. The identification of the *ortho* methyl group in III as the benzyl methylene in I was made[3] using $C.^{14}$

Since related reactions[4–6] of benzylammonium salts have been shown to give several

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[1] G. Wittig, R. Mangold and G. Fellestschin, *Liebigs Ann.* **560**, 116 (1948).

[2] S. W. Kantor and C. R. Hauser, *J. Amer. Chem. Soc.* **73**, 4122 (1951).

[3] F. N. Jones and C. R. Hauser, *J. Org. Chem.* **26**, 2979 (1961).

[4] L. P. A. Fery and L. van Hove, *Bull Soc. Chim. Belg.* **68**, 65 (1959); **69**, 63 (1960).

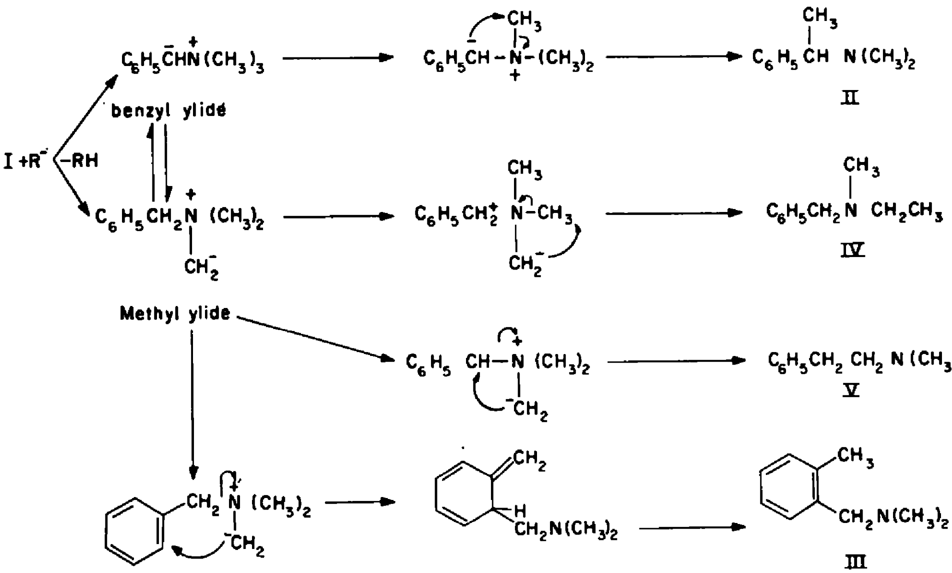
[5] L. P. A. Fery and L. Wilputte-Steinert, *Bull. Soc. Chim. Belg.* **73**, 154 (1964).

[6] C. L. Bumgardner, *J. Amer. Chem. Soc.* **85**, 73 (1963).

simple rearrangement products, we have reinvestigated the rearrangement of I using n-butyllithium as a base.

RESULTS AND DISCUSSION

The abstraction of a proton adjacent to the quaternary nitrogen in I can occur in two ways (Diagram A). The removal of a proton from the benzyl methylene gives a benzyl ylide while loss of a proton from one of the methyl groups leaves a methyl ylide. The benzyl ylide is the postulated intermediate for formation of II by a direct methyl group migration from quaternary nitrogen to the adjacent carbanion. The hypothesized route to III goes through the methyl ylide. At −80° using potassium amide in liquid ammonia, Puterbaugh and Hauser[7] have formed the benzyl ylide of I. The existence of the ylide was demonstrated by reaction with benzophenone to get a 73% yield of 2-hydroxy-1,2,2-triphenylethyltrimethylammonium iodide. However when the ylide formed in this fashion was warmed to −33°, a 87% yield of III was obtained. They interpreted this data as an indication of equilibrium between the two ylides and limitation of the reaction to the *ortho* rearrangement at the temperature used.



The methyl ylide undergoes a five-atom-ring displacement by attack of the carbanion at the *ortho* aromatic position. Bond making and breaking should then produce the unstable exomethylenecyclohexadiene.[8] The rearrangement of the proton on the sp^3 ring carbon atom to the germinal methylene then gives III. Alternatively the proton could be abstracted by base which would give the *ortho* methylene carbanion of III on an electronic shift toward aromatization. This known carbanion[9] would be detected as III when the reaction mixture is quenched with water.

At least two other rearrangement products seem plausible if one applies the mechanisms thus far discussed. Both of these products arise from the methyl ylide and involve a 1,2-shift. Either of the two groups on nitrogen could migrate to the carbanion via a

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[7] W. H. Puterbaugh and C. R. Hauser, *J. Amer. Chem. Soc.* **86**, 1105 (1964).

[8] cf. C. R. Hauser and D. N. van Eenam, *J. Amer. Chem. Soc.* **79**, 5512, 5520, 6277, 6280 (1957).

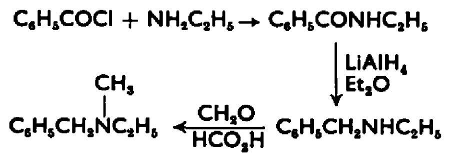
[9] F. N. Jones, M. F. Zinn and C. R. Hauser, *J. Org. Chem.* **28**, 663 (1963).

three atom ring displacement mechanism. The shift of one of the methyl substituents should give N-benzyl-N-ethylmethylamine (IV). While if the benzyl group was transferred, phenethyldimethylamine (V) should result. Wittig and Felletschin,[10] in studies on the fluorene ylide, observed only benzyl group rearrangement when both benzyl and methyl groups were substituents on nitrogen. Methyl group migration did not occur even with 9-(trimethylammonium)fluorene ylide. However, at higher temperature, 55–65% methyl migration was observed[11] from this trimethyl ylide. Thus the benzyl shift giving V should be more probable than IV formation. Similar information[11] on temperature effects in the rearrangement of dibenzyldimethylammonium ions indicated that an increase in temperature favored an *alpha* rather than an *ortho* shift. With sodamide in liquid ammonia however, cleavage of an analog to V from the rearrangement of benzyldimethylanilinium ion occurred.[12]

Migrations analogous to that required for the formation of IV have only been observed on anilinium and other structurally limited compounds. Trimethylanilinium bromide on treatment with phenyllithium produced 20% of ethylmethylaniline.[13] Similarly a number of benzyne additions of tertiary amines give related rearrangements which are postulated to pass through ylide intermediates.[14]

When 2,2,2-triphenylethyltrimethylammonium iodide was reacted with potassium amide in liquid ammonia, a 97% conversion to 3,3,3-triphenylpropyldimethylamine occurs.[15] The size of the triphenylmethyl group in the ethyl substituent was postulated to limit methyl migration and give rise to the abnormal rearrangement. In general, however, alpha shifts have been observed only to the most acidic carbon attached to quaternary nitrogen.

The compounds II–V were prepared by unequivocal routes for comparison with the reaction products. *o*,N,N-trimethylbenzylamine was synthesized by the method of Kantor and Hauser.[2] α-Bromo-*o*-xylene was condensed with hexamethylenetetraimine and then reduced with formic acid giving 67% of III. II was prepared in 43% yield by a similar treatment of 1-bromoethylbenzene. This method was essentially comparable with the reported[16] formation of II by the Clark-Eschweiler method. Phenethyldimethylamine (V) was prepared by the action of formaldehyde and formic acid on β-phenethylamine. The method was analogous to a well tested synthesis[17] of V. N-Benzyl-N-ethylmethylamine (IV) was obtained starting with benzoyl chloride and



$$C_6H_5COCl + NH_2C_2H_5 \rightarrow C_6H_5CONHC_2H_5$$

$$\Big\downarrow \text{LiAlH}_4,\ \text{Et}_2\text{O}$$

$$C_6H_5CH_2\overset{CH_3}{N}C_2H_5 \xleftarrow[HCO_2H]{CH_2O} C_6H_5CH_2NHC_2H_5$$

IV

Diagram B

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[10] G. Wittig and G. Felletschin, *Liebigs Ann.* **555**, 133 (1944).

[11] C. R. Hauser, R. M. Manyik, W. R. Brasen and P. L. Bayliss, *J. Org. Chem.* **20**, 1119 (1955).

[12] G. C. Jones, W. Q. Beard and C. R. Hauser, *J. Org. Chem.* **28**, 199 (1963).

[13] F. Weygand, A. Schroll and H. Daniel, *Chem. Ber.* **97**, 857 (1964).

[14] G. Wittig, *Angew. Chem.* **63**, 15 (1951); G. Wittig and T. Polster, *Liebigs Ann.* **599**, 13 (1956), **612**, 102 (1958); G. Wittig and E. Benz, *Chem. Ber.* **92**, 1999 (1959).

[15] E. Grovenstein, Jr. and L. C. Rogers, *J. Amer. Chem. Soc.* **86**, 854 (1964).

[16] D. J. Cram, L. K. Gaston and H. Jager, *J. Amer. Chem. Soc.* **83**, 2183 (1961); A. C. Cope, E. Ciganek, L. J. Fleckenstein and M. A. P. Meisinger, *Ibid.* **82**, 4651 (1960).

[17] R. N. Icke, B. B. Wisegarver and G. A. Alles, *Org. Syntheses* **III**, 723 (1955).

ethylamine (Diagram B). The N-ethylbenzamide from this reaction was reduced to N-benzylethylamine with LAH. Formaldehyde–formic acid methylation of this amine[18] produced IV. The synthetic materials were used to establish criteria for the separation and identification of products from the rearrangements of I.

The two column gas chromatography (GC) method previously reported[19] was used as the first step in qualitative identification of reaction products. An appreciable difference in liquid phase interaction with amines was obtained with silicon oil, GE SF-96, and polycarbinol, 20 M Carbowax, columns. The order of compound emergence from the non-polar GE SF-96 column (Table 1) was essentially in the order of b.p. The Carbowax column retention for amines and the tailing of their peaks were decreased by the addition of potassium hydroxide. Using a long Carbowax column, it was possible to clearly distinguish between the several compounds which have only small differences in their retention ratios (II, III and IV). Of the tertiary amines possible from rearrangement, gas chromatography of the acid soluble portion of reaction mixtures showed only two peaks. The retention ratios of these two peaks agreed with II and III. No peaks having retentions appropriate for IV, V or benzyldimethylamine were apparent even when large (·25 ml) samples of the amine reaction concentrate were injected into the GC. For quantitative evaluations, separations were excellent on the longer Carbowax column and the mass to peak area relationship[19] held when benzyldimethylamine was used as an internal standard.

TABLE 1. GAS CHROMATOGRAPHY RETENTION RATIOS OF COMPOUNDS RELATED TO THE BENZYLTRIMETHYLAMMONIUM HALIDE REARRANGEMENTS

Compound	Structure	Retention ratio 20% GE-SF 96 Column[a]	 20% 20 M Carbowax +5% KOH Column[b]
Benzyldimethylamine		1·00[c]	1·00[d]
Dimethylamiline		1·25	2·20
β-Phenethylamine		1·31	2·23
α,N,N-Trimethylbenzylamine	II	1·47	1·27
N-Benzyl-N-ethylmethylamine	IV	1·53	1·34
o,N,N-Trimethylbenzylamine	III	1·55	1·39
Phenethyldimethylamine	V	1·83	1·70

[a] ¼ in × 5 ft column, 142°, 28 ml/min He flow; ratios are ±0·02

[b] ¼ in × 12 ft column, 125° up at 0·4°/min, 30 ml/min He flow, and ¼ in × 18 ft column, 135°, 72 ml/min He flow; ratios are ±0·005

[c] Retention time for standard 26 ± 4 min, peak width at half height 2·2 ± 0·4 min.

[d] 12 ft column, retention time for standard 30 ± 5 min, peak width at half height 1·4 ± 0·2 min; 18 ft column, retention time for standard 20 ± 1 min, peak width at half height 0·70 ± 0·05 min.

Confirmation of the GC identifications was accomplished by collecting and determining the physical properties of emerging compounds. The IR and PMR spectra of the collected samples were compared with those of synthetic materials. The spectra of the first and second GC peak corresponded to II and III, respectively. In the IR, the general finger print of each compound is characteristic.

The PMR absorptions (Table 2) give excellent association with structure. All hydrogens of the methyl groups on nitrogen absorb at higher field than those from the

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[18] J. S. Buck and R. Baltzly, *J. Amer. Chem. Soc.* **63**, 1964 (1941).

[19] A. R. Lepley, *Analyt. Chem.* **34**, 322 (1962).

TABLE 2. PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF COMPOUNDS RELATED TO BENZYLTRIMETHYLAMMONIUM HALIDE REARRANGEMENTS[a]

Proton	Classification	Chemical shifts					
Group	Attached to	$C_6H_5N(CH_3)_2$	$C_6H_5CH_2N(CH_3)_2$	$C_6H_5\underset{\underset{CH_3}{\vert}}{C}HN(CH_3)_2$ II	o-$CH_3C_6H_4CH_2N(CH_3)_2$ III	$C_6H_5CH_2\underset{\underset{CH_3}{\vert}}{N}CH_2CH_3$ IV	$C_6H_5CH_2CH_2N(CH_3)_2$ V
CH_3	C			1·23 d (3)		1·04 t (3)	
	NC		2·13 s (6)	2·10 s (6)	2·12 s (6)	2·09 s (3)	2·16 s (6)
	Ar				2·30 s (3)		
	NAr	2·78 s (6)					
CH_2	C, N					2·37 q (2)	2·47 m (2)[b]
	C, Ar						2·68 m (2)[b]
	N, Ar		3·31 s (2)			3·38 s (2)	
CH	C, N, Ar			3·12 q (1)			
H	Ar	6·60 m (3) 7·08 m (2)	7·20 m (5)	7·20 m (5)	7·04 m (4)	7·18 m (5)	7·11 m (5)

[a] All peaks are relative to TMS in parts per million; splitting s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, all J values are 6·9 ± 0·1 c/s; ( ) values are integrated relative peak area ratios in compound.

[b] Complex A_2B_2 splitting centered at 2·57 ppm with nine peaks in each group at ±c/s from integral centers of 3·5, 5·8, 9·4, 12·0, 15·0, 19·2, 21·2, 28·8 and 37·6.

p–π conjugatively deshielding in dimethylaniline. The least methyl shielding in II–V is afforded by direct attachment of a CH_3 group to the aromatic ring in III. All the methyl on tertiary aliphatic nitrogen values are $\delta = 2{\cdot}12 \pm 0{\cdot}4$ ppm. However the chemical shift of 1·23 ppm for CH_3 on carbon indicates a long range coupling with the aromatic ring[20] in II. The $\delta = 1{\cdot}04$ ppm for the same group in IV is in the normal region for the unperturbed absorption. Methylenes with both nitrogen and aromatic ring attachment are noticeably deshielded. These chemical shifts are almost 1·0 ppm downfield from the normal methylene absorptions. Since the complex multiplets of the aromatic protons in II–V have not been clearly split (cf. dimethylaniline), long range coupling of nitrogen with the aromatic ring is not marked if present.

The GC, IR and PMR comparison of the monomeric tertiary amine rearrangement products from I and from authentic samples of II–V indicated the formation of II and III in the current reactions. The GCs for extracted amines from the reaction mixture and for the crude quenched reaction mixture were identical in the region of interest. Under the conditions employed for the rearrangements, small amounts of neutral and acidic (base soluble) material were separated by extraction. In a typical n-butyllithium reaction in ether, these fractions accounted for approximately 5·5 and 0·5% respectively of the total recovered mass. No attempt was made to analyze these materials. Similarly only rearrangement monomers were determined even though cleavage and higher mol. wt. products which would account for these fractions and the imbalance in the mass of materials have been previously reported. The ammoniacal odor was postulated as trimethyl amine and 1,1,2-triphenylethane was a previously reported[1] neutral species. In the related rearrangement of *o*,N,N-tetramethylbenzylammonium iodide, Kantor and Hauser[2] identified by-products including amine dimers and trimers and dimeric hydrocarbons.

These secondary reactions could account for the absence of other possible products if they were particularly sensitive to further reaction. Therefore, the rearrangement compound which was not observed but whose formation seemed most favorable, V, was subjected to reaction conditions. Compound V was mixed with n-butyllithium in hexane at a 1:2 molar ratio; and the concentration of V was determined after 1, 4 and 24 hr. No change in the amount of V was observed at any time. It was not determined if metallation similar to that with benzyldimethylamine or III[9] occurred. The water quench procedure employed in this reaction would regenerate V from any of its possible carbanions. The constancy of recovered V does, however, rule out particular sensitivity to cleavage[21] or elimination by reactions paralleling the butyllithium attacks on ethers.[22] This experiment reinforced the GC evidence that V was not produced under any of the conditions studied.

In summary, a method has been developed for the separation and identification of simple rearrangement products from the action of base on benzyltrimethylammonium (I) halides. The gas chromatographic, IR and PMR data for known and postulated reaction products are used in the separation and identification procedures. Although α,N,N-trimethylbenzylamine (II) or *o*,N,N-trimethylbenzylamine (III) was reported as the only product on treatment with phenyllithium[1] or sodium amide,[2,3,7] respectively,

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[20] R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds* p. 82, J. Wiley, New York, N.Y. (1963).

[21] cf. Ref. 12.

[22] R. L. Burwell, Jr., *Chem. Revs.* **54**, 615 (1954).

both of these products were formed when the iodide of I was treated with n-butyllithium in ether. Two other rearrangement products, which might be formed from a methyl ylid of I, were absent. Since the most probable of these compounds, phenethyldimethylamine (V) was quantitatively recovered after treatment with butyllithium, the disappearance of this compound from the reaction mixture due to cleavage, elimination or higher mol. wt. product formation was not supported. It was therefore concluded that II and III but no other monomeric rearrangement products are formed in this reaction. On the basis of these observations a further study of the reaction and its variables seems possible and desirable. We soon hope to report the results of such an investigation.

EXPERIMENTAL

Physical constants. PMR spectra were measured on a Varian A-60 NMR spectrometer as 20% by volume solutions in CCl_4 with approximately 1% tetramethylsilane as an internal standard. Chemical shifts are given as δ in ppm relative to TMS; splitting is indicated as s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet with $J = 6{\cdot}9 \pm 0{\cdot}1$ c/s unless otherwise indicated.

IR measurements were made on the pure liquids or on KBr disks of the solids, using a Perkin-Elmer Infracord Spectrophotometer. The frequencies are given in cm^{-1}; intensities indicated relative to the most intense peak (*) as equivalent to 100% are s: strong 76–100%, m: medium 51–75%, w: weak 26–50% and vw: very weak 10–25% (very weak bands are given only when quite sharp and characteristic).

Refractive indices were measured with a Zeiss Abbe' Refractometer. Calibration[18] using water in the range 20 to 30° gave n_D values $\pm 0{\cdot}0001$.

M.ps and b.ps are uncorrected.

Gas chromatography. Separations on a non-polar substrate were accomplished on an Aerograph A-90P using a 5 ft colum of 20% GE-SF96 on 60–80 mesh firebrick. Analyses were carried out at 142° with 28 ml/min He flow. The reproducibility of retention ratios on the A-90P without a flow controller was $\pm 0{\cdot}02$.

Column packing for polar separations was prepared by dissolving 5 g KOH in hot abs. EtOH and adding 95 g of 40–60 mesh acid washed firebrick. The EtOH was vacuum evaporated to dryness on a hot water bath using a Rinco rotating evaporator. To this mixture was added a solution of 25 g 20 M carbowax in hot EtOH and evaporation was carried out as before. The resulting solid was sized to 40–60 mesh.

Polar separations were run on a F and M Model 500 gas chromatograph using 12 and 18 ft columns of 20% 20 M Carbowax on 40–60 mesh firebrick which has been precoated with 5% KOH. Operation of the 12 ft column was at 125° programmed to increase at 0·4°/min with a He flow of 30 ml/min. The longer, 18 ft, column was operated at 135° fixed temp and a He flow of 72 ml/min. Two stage press. regulation and a flow controller in the F and M 500 gave a retention ratio reproducibility of $\pm 0{\cdot}005$, for runs over an interval of several months. Consecutive analyses had a normal retention ratio reproducibility $\pm 0{\cdot}002$.

Quantitative analyses were carried out on the 18 ft Carbowax column using samples prepared by adding a weighed amount of product mixture to a weighed amount of benzyldimethylamine and diluting with ether. The ratio of peak areas[19] was used to determine the wt. of products in the mixtures.

Chemicals. α-Bromo-*o*-xylene, 1-bromoethylbenzene and β-phenethylamine were obtained from Eastman Kodak. Benzyldimethylamine was a product of Miles Chemical Company. n-Butyllithium was obtained from Foote Mineral Company.

Benzyltrimethylammonium (I) *iodide.* The iodide was prepared by reaction at room temp of equimolar amounts of benzyldimethylamine (100 g, 0·74 mole) and MeI (105 g) in 200 ml anhydrous ether. After 2 weeks the salt was collected and recrystallized from abs. EtOH. On vacuum drying the salt had a m.p. of 178–178·5° (Lit.[8] 178–179°).

α,N,N-*Trimethylbenzylamine* (II). Equimolar amounts (0·4 mole) of 1-bromoethylbenzene and hexamethylenetetramine in 200 ml $CHCl_3$ were refluxed for 30 min after the initial reaction subsided. The solution was vacuum evaporated and 200 ml of 50% formic acid was added and cautiously heated

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[18] A. I. Vogel, *Elementary Practical Organic Chemistry* p. 360, J. Wiley, New York (1958).

until evolution of CO_2 ceased. After 2 hr reflux, the solution was evaporated to 100 ml, neutralized with Na_2CO_3 and extracted with ether. The ether layer was dried over Na_2CO_3 and vacuum distilled. This gave 26 g, 43% yield, of II b.p. 70·5–72°/12 mm. (Lit[24] 71°/11 mm), n_D^{22} 1·5050 (Lit[15] n_D^{25} 1·5002–1·5007). The IR spectrum had bands at 703 s*, 741 w, 759 m, 777 w, 824 w, 915 w, 959 m, 1043 w, 1080 w, 1100 w, 1152 w, 1212 w, 1263 w, 1352 w, 1370 w, 1450 s, 1490 m, 2775 s, 2845 m, 2870 m, 2985 s and 3080 w cm^{-1}.

o,N-N-*Trimethylbenzylamine* (III)[8]. Equimolar amounts (0·4 mole) of α-bromo-*o*-xylene and hexamethylenetetramine were treated as in the preparation of II. This gave 40 g, 67% yield, of III b.p. 87–88·5°/20 mm. (lit.[8] 80–81°/14 mm), n_D^{22} 1·5040. The IR spectrum had bands at 744 s*, 765 m, 846 m, 858 w, 871 w, 941 w, 975 s, 1047 m, 1100 w, 1113 w, 1150 w, 1176 m, 1258 m, 1364 m, 1460 s, 1492 w, 2780 s, 2820 m, 2860 m, 2960 s and 3030 w cm^{-1}.

N-*Benzyl*-N-*ethylmethylamine* (IV). Benzoyl chloride (1 mole) was slowly added to 100 g cooled, rapidly stirred ethylamine. When reaction ceased, the product was washed with three 150 ml aliquots 6 N NaOH and then two 150 ml portions water. The yield of the air dried crude solid was 86%, 129 g. Half of the amide (0·43 mole) was added with stirring to a slurry of 15·4 g LAH in 500 ml anhydrous ether. After 16 hr reflux, 10 ml water was cautiously added followed by 200 ml 6 N NaOH. The ether layer was separated and the ether was vacuum evaporated from the wet amine. Formic acid (2·2 mole of 90%) was added to the amine with cooling. Then 2·6 mole formaldehyde (36% aqueous solution) was added and the mixture was refluxed for 16 hr. Volatile acidic and neutral material were removed by vacuum evaporation of the solution after addition of 60 ml (0·7 mole) conc. HCl. The mixture was made strongly alkaline by adding solid NaOH slowly with stirring and cooling. The amine was extracted with ether, dried over KOH pellets, decanted, and the ether flash evaporated. The center cut of the distillation 28 g, 44% yield, had a b.p. 84–85°/18 mm (Lit.[16] 80°/16 mm) and showed only a single GC peak, n_D^{20} 1·5052 (Lit.[25] n_D^{20} 1·5068). The IR spectrum of IV had peaks at 700 s, 738 s*, 831 w, 953 vw, 1033 m, 1046 m, 1065 w, 1079 w, 1098 vw, 1137 w, 1173 m, 1205 w, 1225 w, 1258 vw, 1300–1310 w, 1350 w, 1369 m, 1385 w, 1455 s, 1495 w, 1605 vw, 2800 s, 3000 s and 3035 w cm^{-1}.

β-Phenethyldimethylamine (V). 2-Phenethylamine (0·4 mole), 36% formaldehyde and 50% formic acid were mixed in a 1:2:5 molar ratio and, after cessation of the initial reaction, heated at 100° overnight. A slight excess (35 ml) conc. HCl over that needed to form the amine salt was added and the solution was vacuum evaporated to half the original volume. The solution was made strongly basic with solid NaOH and the amine was extracted with ether. The ether layer was dried over BaO. On vacuum distillation, 22 g (38% yield) of V was obtained b.p. 102–104°/19 mm (Lit.[17] 97–98/22 mm), n_D^{25} 1·4990. The IR spectrum of V had bands at 698 s*, 746 m, 866 w, 1018 w, 1042 m, 1055 m, 1078 w, 1095 w, 1137 w, 1170 w, 1222 w, 1263 w, 1368 w, 1455 s, 1490 m, 1600 w, 2770 s, 2810 m, 2860 m, 2940 s and 3030 m cm^{-1}.

Reaction of benzyltrimethylammonium (I) *iodide with n-butyllithium.* The dry, finely powdered iodide of I (5·4 g, 20 mmole) was rapidly added to a vigorously stirred solution of 26 ml (40 mmole) of 1·6 N n-butyllithium in hexane and 74 ml anhydrous diethyl ether under an atm. of dry N_2. The mixture was stirred at 20–30° during the entire reaction. After 2 hr all the solid had dissolved and after 4 hr precipitate began to appear. The reaction was quenched with ice after 24 hr. The ether and alkaline aqueous layers were separated.

The aqueous layer was washed once with ether and then made strongly acidic by slow addition of conc. HCl. The acidified aqueous solution was extracted with 3 portions of ether. After drying over $MgSO_4$, the evaporation of this ether extract gave 11 ± 0·5 mg of nonvolatile organic material.

The original ether solution and aqueous alkali ether extract were combined and extracted with two 50 ml portions of 6 N HCl. The ether layer was dried over $MgSO_4$ and then evaporated on a steam bath giving 0·18 ± 0·02 g of neutral organic material.[1] The aqueous acid layer was made strongly alkaline by the slow addition of NaOH pellets while cooling and stirring. The oil which separated was recovered by extracting with two portions of ether, drying the ether layer over BaO and evaporation of the ether at 50°. The recovered amines, 2·15 ± 0·10 g, were analyzed by GC for monomeric rearrangement products. Two peaks were observed in the thermal conductivity trace. These materials were collected after separation on the 18 ft Carbowax column. The GC retention ratios, and IR and PMR spectra of the first and second compounds were identical with α,N,N,-trimethylbenzylamine (II) and

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[24] A. C. Cope, T. T. Foster and P. H. Towle, *J. Amer. Chem. Soc.* 71, 3929 (1949).

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o,N,N-trimethylbenzylamine (III), respectively. The total amount of II plus III in the recovered amines accounted (by GC) for 1·52 g (51% yield, and 71% of all basic material recovered). The molar ratio of II:III produced was 1:3·8.

Attempted cleavage of β-phenethyldimethylamine (V). A solution of 1·5 g (10 mmole) V and 13 ml (20 mmole) 1·6 N n-butyllithium in hexane was mixed at 20–30°. After 1, 4 and 24 hr intervals, 1 ml samples were removed and quenched with ice. Analyses of the organic layer by GC indicated no apparent decrease in the amount of V present. Quantitative recovery was observed in all cases.

Acknowledgement—This investigation was supported by Public Health Service Research GM-09136, from the National Institute of General Medical Sciences.

APPENDIX A. PROTON MAGNETIC RESONANCE CHEMICAL SHIFT ASSIGNMENTS

Group	Attached to	Chemical shift range[a] (ppm)	No. compounds[b]
CH_3	C { N	0·85–1·20	6
	ArN	1·20–1·50	3
	NC	2·00–2·20	14
	Ar	2·20–2·35	5
	NAr	2·40–2·90	11
CH_2	C,NC	2·35–2·50	3
	C,Ar	2·65–2·80	2
	NC,Ar	3·20–3·50	10
	C,NAr	2·85–3·85(3·15–3·45)	9(7)
	Ar,Ar	4·00–4·10	2
	NAr,Ar	3·90–4·40	4
CH	C,N,Ar	3·10–3·55	3
	C,C,NAr	3·7 ± 0·1	2
	N,Ar,Ar	4·00–4·20	2
	C,Ar,NAr	5·05 ∓ 0·1	1
H	ArN	6·60–7·00	13
	Ar	7·00–7·30	21

[a] Relative to tetramethysilane.

[b] Tertiary amines from the unpublished works of A. R. Lepley, A. G. Giumanini, A. B. Giumanini and W. A. Khan.