

Quaternary Benzylammonium Ion Rearrangements with Organolithium Compounds. V. Reaction of *N,N*-Dimethyl-*N*-benzylanilinium Halides^{1a,b}

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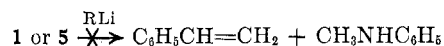
A new rearrangement product, *N*-methyl-*N*-(α -phenethyl)aniline (4), and a new cleavage product, *N*-methyl-*N*-benzylaniline (3), have been observed in reactions of *N,N*-dimethyl-*N*-benzylanilinium ion (1) with organolithium bases. *N*-Methyl-*N*-(β -phenethyl)aniline (5) was directly isolated from reaction mixtures, whereas it is destroyed by sodium amide. The Sommelet rearrangement product, *N*-methyl-*N*-(*o*-xylyl)aniline (6), was observed in very small quantities because of the benzylation of its *o*-Li precursor by the starting salt, to give a dimeric product. Cleavage reactions of the quaternary benzylanilinium salt with potassium hydroxide and sodium ethoxide in refluxing ethanol also gave 3 in addition to the principal products, *N,N*-dimethylaniline (2) and ethyl benzyl ether. Analogous cleavage products were observed with organolithium reagents plus significant amounts of *trans*-stilbene (8). The effects of concentration, ether-hexane solvent mixtures, and anion of the salt on the ratios of rearrangement and cleavage products were studied for *n*-butyllithium reactions and are interpreted in terms of dianion and radical pair mechanisms.

N,N-Dimethyl-*N*-benzylanilinium chloride is known²⁻⁴ to undergo ortho substitution rearrangement (Sommelet) on treatment with sodium amide in liquid ammonia. In the most comprehensive study of this reaction,⁴ indirect evidence of a 1,2 shift (Stevens) was also observed. The latter type of reaction generally occurs readily^{1a,5-7} on treatment of benzylic quaternary ammonium salts with organolithium reagents; the effect of base on the distribution of the competing rearrangement processes has been compared for *N*-benzyltrimethylammonium ion.⁸

We have now observed that the *N,N*-dimethyl-*N*-benzylanilinium ion (1), when treated with organolithium reagents, produces *N,N*-dimethylaniline (2), *N*-methyl-*N*-benzylaniline (3), *N*-methyl-*N*-(α -phenethyl)aniline (4), *N*-methyl-*N*-(β -phenethyl)aniline (5), *N*-methyl-*N*-(*o*-xylyl)aniline (6), a dimeric amine (7), and *trans*-stilbene (8). Hot ethanolic hydroxide or ethoxide caused displacement of substituents on quaternary nitrogen of 1 Cl⁻ with 2, 3, and benzyl ethyl ether formation (Table I, expt 1 and 2). Lower yields

of 2 and 3 resulted with the lithium reagents in aprotic media, but significant amounts of the rearrangement products 4, 5, and 6 were obtained with 1,2 shifts predominating (Table I, expt 3-7). In addition to the effect of halide and solvent on the 1,2-shift ratio of 4/5 (Table II), the ratio was 0.8 in a 2:1 v/v solution of ether-hexane with *n*-butyllithium. The best mass balance, 90% obtained when a 2.2:1 mixture of *n*-butyllithium:1 Br⁻ reacted in hexane, gave 47% 2, 7.4% 3, 11.3% 4, 14.4% 5, 1.5% 6, 8.5% 7, 18% 8, and 3.4% *n*-pentylbenzene.

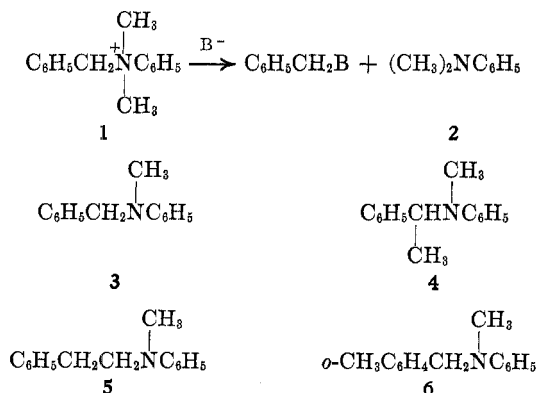
We did not observe *N*-methylaniline or styrene, evidence of cleavage in the β -phenethyl product,⁴ even when pure 5 was treated with *n*-butyllithium. Ethyl-



benzene was absent in experiments with methyllithium; toluene may be present in several cases, but we were unable to collect an adequate sample from gas chromatography (gc) for characterization. Separation characteristics and physical properties of separately synthesized materials were determined⁹ (Table III) and used in product identification and analysis.

Discussion

General trends due to base, solvent, and halide ion may best be considered in reference to earlier studies on this and related rearrangements. The reaction conditions certainly have a distinct effect. Earlier sodium amide rearrangements²⁻⁴ were at temperatures 50-60° below the current ambient organolithium experiments or as much as 110° below our reactions in refluxing ethanol. Hauser and coworkers¹⁰ noted that benzylammonium salt reactions in related Stevens rearrangement predominate at high temperatures and Sommelet migration is almost exclusive at low temperatures. These rearrangements are very base and solvent dependant as well and, for benzyltrimethylammonium ion at least, almost exclusive ortho migration can be observed within the temperature range currently used.^{1a,8,11} The low ortho conversions ob-



(1) (a) Part IV: A. R. Lepley and T. A. Brodof, *J. Org. Chem.*, **32**, 3234 (1967). (b) This investigation was supported in part by U. S. Public Health Service Grant GM-09136 from the National Institute of General Medical Sciences and was presented in part before the X Congresso Nazionale della Societa Chimica Italiana, Padova, Italy, June 1968. (c) To whom reprint requests should be sent, Marshall University. (d) Fulbright student, State University of New York at Stony Brook, 1962-1964.

(2) E. J. Gaughan, *Diss. Abstr.*, **22**, 1827 (1961).

(3) L. P. A. Fery, *Bull. Soc. Chim. Belges*, **71**, 376 (1962).

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(11) K. P. Klein and C. R. Hauser, *ibid.*, **31**, 4276 (1966).

TABLE I
 REACTIONS OF *N,N*-DIMETHYL-*N*-BENZYLANILINIUM (1) CHLORIDE WITH SEVERAL BASES

Expt no.	1	2	3	4	5	6	7
Base concn (<i>M</i>)	KOH, 1.3	NaOEt, 1.9	MeLi, 0.8	C ₆ H ₅ Li, 0.6	<i>n</i> -BuLi, 0.3	<i>n</i> -BuLi, 1.1	<i>n</i> -BuLi, 0.5
Molar ratio of base/1	2.1:1	3.2:1	3.3:1	1.4:1	0.4:1	4.4:1	1.9:1
Solvent	EtOH	EtOH	C ₆ H ₁₄	C ₆ H ₁₄ -C ₆ H ₆ - Et ₂ O, 7:3:1	C ₆ H ₁₄	C ₆ H ₁₄	C ₆ H ₁₄
Time (hr), temp	24, reflux	12, reflux	24, ambient	14, ambient	24, ambient	24, ambient	24, ambient
Products							
Amines							
<i>N,N</i> -Dimethylaniline (2)	42	59	22	39.5	10.3	4.9	29
<i>N</i> -Methyl- <i>N</i> -benzylaniline (3)	5.8	5.3	2.2	4.0	3.1	9.7 ^a	5.3
<i>N</i> -Methyl- <i>N</i> -(α -phenethyl)aniline (4)	<i>b</i>	<i>b</i>	39.5	30	6.2	2.7	2.4
<i>N</i> -Methyl- <i>N</i> -(β -phenethyl)aniline (5)	<i>b</i>	<i>b</i>	8.4	3.9	8.7	14.8	12.7
<i>N</i> -Methyl- <i>N</i> -(<i>o</i> -xylyl)aniline (6)	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	2.5 ^c	2.1
Neutral compd							
C ₆ H ₅ CH ₂ B (B = radical from base)	45 ^d	63	<i>b</i>	0.9	<i>e</i>	0.6	2.1
<i>trans</i> -Stilbene (8)	<i>e</i>	<i>b</i>	<i>e</i>	10.1	<i>e</i>	<i>a</i>	>10
Overall ^f	51	69	72	82	28	33	60 ^g
Ratios							
4/5 (α/β rearrangement)			4.7	7.7	0.7	0.2	0.2
2/3 (benzyl/methyl loss)	7.0	11.1	9.7	9.9	3.3	0.5	5.5

^a Probably a mixture of 3 and 8, but calculated as pure 3. ^b Not observed. ^c At 60 hr, this material was not detected in 24-hr sample. ^d Ethyl benzyl ether. ^e Not determined. ^f Calculated on the basis of C₆H₅N or C₆H₅CH₂ groups accounted for depending on which was the greatest. ^g Includes 8.3% of the dimeric material 7.

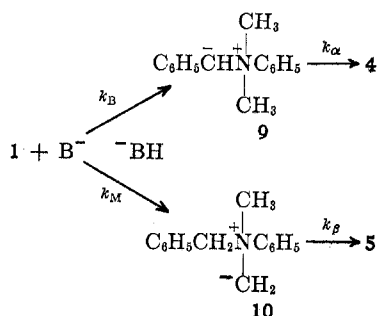
 TABLE II
 HALIDE ANION EFFECTS ON STEVENS REARRANGEMENT
 PRODUCTS FROM *N,N*-DIMETHYL-*N*-BENZYLANILINIUM (1)
 CATION WITH ORGANOLITHIUM BASES

Base-solvent	Base:1 ratio	Anion, X ⁻	α/β product ratio, 4/5
C ₆ H ₅ Li-7:3:1 hexane: benzene:ether	1.4:1	Cl	7.7
		Br	7.2
<i>n</i> -BuLi-5.5:1 ether:hexane	1:1	Cl	1.3
		Br	1.6
<i>n</i> -BuLi-hexane	1.9:1	I	1.0
		Cl	0.2
<i>n</i> -BuLi-hexane	0.4:1	Br	0.8
		Cl	0.7
		Br	1.3

served are, therefore, not totally attributable to temperature effects; *vide infra*.

Base and solvent effects were not completely distinct. The cleavage observed in ethanolic hydroxide (Table I) was accompanied by 27% rearrangement with 5.8 4/5, between that of methyl- and phenyllithium, when 1 Cl was heated with solid KOH at 100°. ¹² No ortho migration product was evident in any of these reactions until a solvent change to hexane with *n*-butyllithium as base gave detectable 6.

Both cleavage and rearrangement products show comparable trends with base variation. If proton abstraction giving ylides 9 and 10, as evident in the


 TABLE III
 GAS CHROMATOGRAPHIC RETENTION RATIOS OF SOME
 NEUTRAL AND BASIC COMPOUNDS RELATED TO THE
 FRAGMENTATION AND DISPLACEMENT REACTIONS OF
N,N-DIMETHYL-*N*-BENZYLANILINIUM (1) HALIDES

Compd	Retention ratio	
	GE-SF96 ^a	Carbowax, KOH ^b
Toluene		0.129
Ethylbenzene		0.178
Styrene		0.280
<i>N,N</i> -Dimethylbenzylamine	0.659	0.445
Ethyl benzyl ether	0.827	0.627
<i>N</i> -Methylaniline	0.907	
<i>N,N</i> -Dimethylaniline ^c (2)	1.00	1.000
<i>n</i> -Pentylbenzene	1.47	0.635
<i>N,N</i> -Dimethyl- β -phenethylamine (5)	1.51	0.920

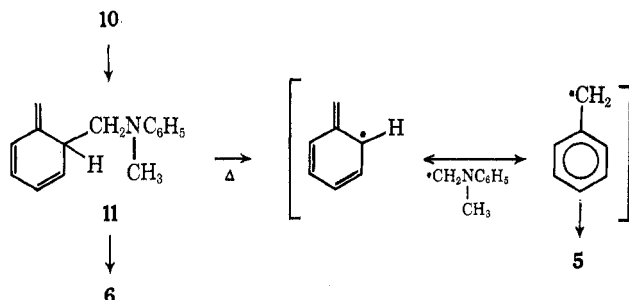
^a A 0.25 in. \times 5 ft column of 20% GE-SF96 on 60-80 mesh Chromosorb W at 122°, 62 ml/min He flow; ratios are \pm 0.005. ^b A 0.25 in. \times 5 ft column of 20% Carbowax 20M plus 5% KOH, on 40-60 mesh firebrick at 115°, 42 ml/min He flow; ratios are \pm 0.002. ^c On GE-SF96, retention time for calibration standard 19.3 \pm 0.6 min, peak width at half-height 1.6 \pm 0.1 min; on Carbowax-KOH, 44.0 \pm 0.7 min and 3.3 \pm 0.2 min, respectively.

α/β rearrangement ratio 4/5, was the controlling factor ($k_\alpha \gg k_B$, $k_\beta \gg k_M$), then less discrimination was evident with increasing base strength. However, the α/β ratio was lower than the statistical minimum of 2/6 in the butyllithium reaction where it reached 1/5. Butyllithium induced rearrangements of benzyltrimethylammonium ion also exceed statistical distributions.⁸ These data seem to preclude a prerearrangement equilibrium, $9 \rightleftharpoons 10$,¹³ unless one assumes the reverse of benzyl > methyl acidity or unless $k_\beta \gg k_\alpha \sim k_{9-10}$. The α/β ratios paralleled the α /ortho order for the benzyltrimethylammonium system;⁸ *i.e.*, for the lithium bases, RLi, the R group effect was

(12) A. G. Giumanini, *Chem. Ind. (London)*, 1140 (1967).

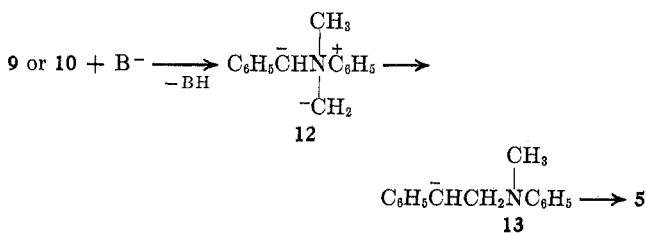
(13) In aprotic media even slow return to 1, k_B or k_M , does not furnish an equilibration path but exchange with 1, $1 + 9 \rightleftharpoons 10 + 1$, gives an alternate path.

phenyl > methyl > *n*-butyl. Such comparable changes could indicate a relationship between 5 and 6 and detectable amounts of 6 only appear when 5 increases. Baldwin and Brown¹⁴ suggest that β products are actually formed by a thermal Hauser rearrangement of the *exo*-methylenecyclohexadiene intermediate which precedes a Sommelet product. Thus a concerted [3,2]



sigmatropic migration in 10 would give 11 which undergoes proton loss to base yielding 6 on water quenching¹⁵ or which thermally breaks a C-C bond homolytically and collapses into 5. Carbonyl stabilized nitrogen ylides do not rearrange by a combination of concerted and radical pair mechanisms.¹⁶ The sulfur angular methyl analog of 11 also thermally forms a β -phenyl product *via* a radical pair.¹⁷ In the instance of 11 \rightarrow 5, only resonance stabilization of the benzyl radical is possible since the aniline fragment electron redistribution structures involve pentavalent nitrogen. Although the higher temperatures than in liquid ammonia, *vide supra*, drive the reaction to 5 rather than 6, the condition for the observed thermal rearrangements were in excess of 100°.^{14,17}

Greater proton abstraction at high base concentrations would tend to trap more 11 as 6, but 6 was not seen until after 4 and 5 buildup ceased. Furthermore, Pine has found that high base concentrations cause RLi addition to intermediates like 11.¹⁸ Thus 5 and 6 should decrease at very high base-salt ratios rather than increasing at the apparent expense of 4 (*cf.* Table I, expt 5-7). Another pathway to 5 and 6 are dianions of the type proposed by Hauser⁶ to account for effects in the presence of excess base. The most probable dianion, 12, could rearrange to anionic precursors of 4, 5,

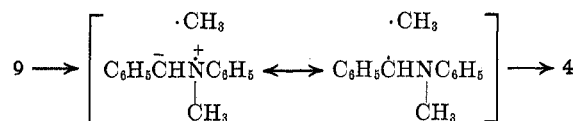


or 6 by homolytic or heterolytic benzyl CN cleavages.¹⁹ However, the only rearranged anion with resonance stabilization is 13. Thus as seen in Tables I and II, as the base-salt ratio increases the 4/5 value decreases

- (14) J. E. Baldwin and J. E. Brown, *J. Amer. Chem. Soc.*, **91**, 3647 (1969).
 (15) The analogous [1,3] sigmatropic shift is forbidden.
 (16) J. E. Baldwin, J. E. Brown, and R. W. Cordell, *Chem. Commun.*, **31** (1970).
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 (18) S. H. Pine, *Org. React.*, **18** (1970); S. H. Pine and B. L. Sanchez, *Tetrahedron Lett.*, 1319 (1969).
 (19) A. R. Lepley and A. G. Giuanini, in "Mechanisms of Molecular Migrations," Vol. 3, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1971.

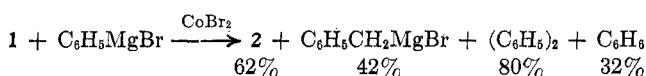
supporting the 9 \rightarrow 12 \rightarrow 13 \rightarrow 5 route. Dianions with aromatic ring deprotonation, either benzyl²⁰ or *N*-phenyl²¹ as with tertiary amines, may also account for the destruction of 1 but none of these species has been trapped as has the benzyl ylide of benzyltrimethylammonium,²² *cf.* 9, or isolated as have several phenacyl nitrogen ylides.²³ A number of other ion pair and carbene pathways could participate in the rearrangements of 1 but have been extensively discussed elsewhere.¹⁹ Therefore only the radical pair mechanisms based on the analogous benzyne amine reactions,⁹ Stevens rearrangements with CIDNP,^{16,17,23-27} and product evidence²³ are specifically applied to 1 \rightarrow 4.

Although the CIDNP producing rearrangements include sulfonium^{17,25} and aminimide^{16,26,27} results as well as ammonium salts,^{23,24} all the reactions invoke a caged radical pair state. In terms of the current system the conversion of 9 to 4 would involve homolytic



CH₃-N bond breaking and subsequent collapse of the radical pair after electron redistribution to the more stable neutral resonance contributor. This is exactly the same step as that which gave CIDNP in the benzyne formation of 4.⁹ Unfortunately, the heterogeneous reactions of 1 could not be accelerated to produce 4 under conditions for the direct observation of this phenomena. However, the close analogy with the other Stevens 1,2 shifts providing evidence for radical pairs is compelling. Since some escape from the cage might be anticipated,⁹ the cleavage product 3 would be expected to increase as 4 decreases as appears to be qualitatively true in the organolithium reactions (Table I).

A case for free-radical participation in cleavage reactions was presented when Kharasch, Williams, and Nudenberg²⁹ used cobalt salts to catalyze the reaction of 1 with phenylmagnesium bromide. The Grignard reagent in the absence of catalyst formed only 4%



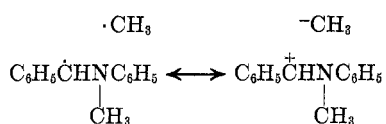
of 2. This radical participation in reactions of a number of other quaternary ammonium salts was also shown,²⁹ but investigators have not specifically tested such mechanisms with other bases.

- (20) W. H. Puterbaugh and C. R. Hauser, *J. Amer. Chem. Soc.*, **86**, 1394 (1964).
 (21) A. R. Lepley, W. A. Khan, A. B. Giuanini, and A. G. Giuanini, *J. Org. Chem.*, **31**, 2047 (1966).
 (22) W. H. Puterbaugh and C. R. Hauser, *J. Amer. Chem. Soc.*, **86**, 1105 (1964).
 (23) R. W. Jemison, S. Mageswaran, W. D. Ollis, S. E. Potter, A. J. Pretty, and I. O. Sutherland, *Chem. Commun.*, 1201 (1970).
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 (28) G. F. Hennion and M. J. Shoemaker, *J. Amer. Chem. Soc.*, **92**, 1769 (1970).
 (29) M. S. Kharasch, G. H. Williams, and W. Nudenberg, *J. Org. Chem.*, **20**, 937 (1955).

Although this last route might contribute to the current reactions, all the cleavage products observed are reasonable for direct displacement. Alternative pathways for the production of **8** were previously discussed.⁵

Displacements and rearrangements of **1** with hydroxide and phenoxide at high temperatures were first observed by Michler and Gradmann.³⁰ Benzyl alcohol and **2** were obtained by codistillation of sodium hydroxide and **1** until high temperatures were reached (220–230°); then higher molecular weight products, thought to be ring benzyl derivatives of **2** or methyl derivatives of **3**, were observed. These latter rearrangement products were probably the compounds recently identified¹² as **4** and **5**. Sodium phenoxide and **1** at 300°,³⁰ however, gave only **2** and benzyl phenyl ether. Ethyl benzyl ether was observed with **2** when **1** was "reduced" with sodium in ethanol.³¹ Only **2** and no ether was mentioned in a later work with sodium ethoxide,³² while reduction³³ with platinum-barium sulfate or platinum oxide gave toluene, **2**, and other more highly saturated products. Sodium derivatives of ethyl malonate and related compounds were also benzylated with **1** in good yields.³⁴ In addition, **2**,^{3,4} and **8**⁴ were observed as cleavage products of **1** with sodium amide. This latter base also caused product breakdown to *N*-methylaniline^{3,4} and styrene.⁴

No single reaction pathway for rearrangement or cleavage products allows the *a priori* prediction of the exact products which will be formed, let alone their quantitative distribution. Therefore, the suggestion made previously⁸ that two or more different types of intermediates are involved in the benzylammonium salt reaction is particularly applicable to the current case. The new products identified in the reaction of **1** support an ylide precursor **9** which rearranges *via* a radical pair to **4**. To accommodate known substituent effects in Stevens 1,2 shifts and the exchange properties of radical pairs,³⁵ a facile one-electron transfer process may occur for the caged pair. In addition, a



dianion is apparent in the production of **5**, but the intermediate interconversion of **12** to **13** needs further clarification.

Experimental Section³⁶

Chemicals.—Mono-free *N,N*-dimethylaniline from Fisher was dried over potassium hydroxide and vacuum distilled before use. Iodomethane, α -chloro- and α -bromotoluene, β -bromoethylbenzene, and hexamethylphosphoramide were obtained from Eastman. Deuterium oxide (99.5+%) was from Matheson Coleman and Bell. Hexane solutions of *n*-butyllithium and methylolithium and ether-benzene solution of phenyllithium were

from Footé Mineral. *N,N*-Dimethyl- β -phenethylamine³⁷ and *n*-pentylbenzene⁸ were available from previous work. Other compounds are described in ref 9.

Ethyl Benzyl Ether.—Sodium wire (7.5 g, 0.33 g-atom) was dissolved in 100 ml of absolute ethanol and 38 ml (0.33 mol) of α -chlorotoluene was very slowly added to the mixture at 60° with stirring. Sodium chloride separated from the bright yellow solution which was refluxed for 3 hr. After addition of 200 ml of water and 5 g of sodium chloride to the cooled reaction mixture, a deep red oil separated. The product was dried over potassium hydroxide and distilled to give a 65% yield (29 g) of a colorless oil, bp 83.5–84° (17 mm) [lit.³⁸ 70° (15 mm)], n_D^{25} 1.4903 [lit.³⁹ n_D^{25} 1.4934].

***N*-Methyl-*N*-(β -phenethyl)aniline (**5**).**—*N*-Methylaniline (36 ml, 0.33 mol) and 47 ml (0.33 mol) of β -bromoethylbenzene were mixed and heated on a steam bath for 24 hr. The brownish glass obtained was decomposed with warm (60°) concentrated potassium hydroxide solution (40 ml of water and 19 g KOH). The oily insoluble amine was dissolved in ether; the ether solution was separated, dried over potassium hydroxide, decanted, and distilled. The white crystalline product (58 g, 84% yield) was collected at 195–197° (24 mm) [lit.⁴⁰ 198–199° (18 mm)], mp 43.5–44° [lit.⁴⁰ 44°]. An additional 7.5 g, 11%, of product was obtained on heating the distillation forerun (1:1 mixture of starting material, gc) for an additional 15 hr on a steam bath.

The infrared spectrum had bands at 3040 w, 2940 w, 2880 w, 2810 vw, 1605 s, 1503 s*, 1448 w, 1374 m, 1355 m, 1275 vw, 1250 w, 1222 w, 1190 w, 1160 vw, 1114 w, 1078 vw, 1034 w, 992 w, 956 vw, 906 vw, 860 vw, 751 s, and 690–700 m cm⁻¹. Gc and pmr data on this material are given elsewhere.⁹

Attempted Cleavage of *N*-Methyl-*N*-(β -phenethyl)aniline (5**) with *n*-Butyllithium.**—The amine **5** (2.1 g, 10 mmol), dissolved in 10 ml of dry hexane, was added to 20 ml of 1.5 *M* (30 mmol) *n*-butyllithium in hexane at room temperature. The solution was clear and remained clear for the period of observation, 2 days. Gc analysis of quenched samples from the initial solution and at several intervals up to 48 hr showed that **5** concentration remained constant, within experimental error. No *N*-methylaniline was observed.

Preparation of *N,N*-Dimethyl-*N*-benzylammonium (1) Halides.

A. Chloride.—Equimolar amounts^{30,31,41} of *N,N*-dimethylaniline (255 ml, 2.0 mol) and of α -chlorotoluene (230 ml, 2.0 mol) were stored in the dark in a desiccator containing anhydrous magnesium sulfate for a month. The quantitatively produced solid was washed repeatedly with dry hexane to give a salt, mp 108°. Recrystallization from hot absolute ethanol raised the melting point to 110° [lit. 110°,^{30,42} 116°³¹]; the material was then vacuum dried for 2 hr at 75°, mp 150° for the colorless crystals.

Anal. Calcd for C₁₅H₁₈NCl: C, 72.72; H, 7.32; N, 5.65; Cl, 14.31. Found: C, 72.41; H, 7.45; N, 5.40; Cl, 14.06.

The infrared spectrum of the dried recrystallized product had bands at 3400–3300 m, 3070 w, 2985 m, 2960 m, 2982 m, 1630 vw, 1590 w, 1490 s, 1450 s, 1400 m, 1380 m, 1225 m, 1120 w, 1085 vw, 1030 w, 1000 m, 970 m, 935 w, 890 s, 845 m, 775, s, 760 s*, 710 s, and 700 s cm⁻¹. An additional 24 hr of vacuum drying at 75° had no appreciable effect on this spectrum. However, the initial drying period had caused a very large decrease (*ca.* fourfold) in the OH stretch, intensity at 3400–3300 cm⁻¹, an inversion of the intensity ratios for the weak 1630 and 1590 cm⁻¹ bands, an increase in intensity of the weak 1400 and 1380 cm⁻¹ bands, and a doubling in width of the strong bands at 775 and 760 cm⁻¹. The pmr spectrum of this salt in D₂O was comparable to the spectrum given for the bromide; *vide infra*.

B. Bromide.—An equimolecular mixture⁴³ of *N,N*-dimethylaniline (38.2 ml, 0.3 mol) and of α -bromotoluene (35.7 ml, 0.3 mol) was heated on a steam bath overnight. Colorless crystals were slowly formed from the solution, which rapidly turned bright blue. The crude product was quantitatively recovered, washed with dry acetone, dissolved in a minimum quantity of absolute alcohol, and reprecipitated with anhydrous ether. The colorless

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solid had mp 148–149° which increased to 153° (lit.⁴ mp 145–146°) after vacuum drying for 12 hr at 75–85°. The solid, and especially its solutions in protic solvents, were lacrimatory⁴⁴ even after repeated purification of the solid. Both the solid and its solutions develop a bright blue color on standing in contact with moist air.

Anal. Calcd for C₁₅H₁₈NBr: C, 61.65; H, 6.21; N, 4.79; Br, 27.35. Found: C, 61.38; H, 6.15; N, 4.82; Br, 27.14.

The pmr spectrum was measured in D₂O, using the water impurity at δ 4.52 ppm as a standard, and in hexamethylphosphoramide (HMPA) or in dimethyl sulfoxide (DMSO), using a tetramethylsilane standard (Table IV). The anion, chloride, bromide,

TABLE IV
SOLVENT EFFECTS ON PMR CHEMICAL SHIFTS OF
N,N-DIMETHYLBENZYLANILINIUM (1) BROMIDE

Protons of group	Multiplicity	Relative integral	—Chemical shifts, δ (ppm)—		
			D ₂ O ^a	DMSO ^b	HMPA ^b
CH ₃	Singlet	6	3.50	3.70	3.98
CH ₂	Singlet	2	4.82	5.32	5.75
Ar	Multiplets	5	7.19	7.28 ^c	7.31 ^d
		3	7.49 ^e	7.62 ^f	7.60 ^g
		2	7.49 ^e	8.03 ^f	8.43 ^g

^a Relative to H₂O impurity at 4.52 ppm. ^b Relative to TMS. ^c Center of integral of broad multiplet ca. 25 cps wide. ^d Broad singlet, width at half-height ca. 3 cps. ^e Center of integral of broad multiplet ca. 40 cps wide. ^f Centers of integrals of two well-separated multiplets ca. 13 cps wide. ^g As in footnote f but ca. 15 cps wide.

or iodide, had no appreciable effect on the pmr spectra. The ir spectrum of this salt had the same major peaks as given for the chloride above.

C. Iodide.—*N*-Methyl-*N*-benzylaniline (51.7 g, 0.27 mol) and 19 ml (0.3 mol) of iodomethane were warmed gently as described by Jones.⁴⁵ The salt was recrystallized twice from methanol, mp 147° (lit. 165°,⁴⁵ 155°⁴⁶).

The infrared spectrum contained no bands in the OH stretch region, indicating the absence of hydroxylic solvents. The spectra, ir and pmr, had bands comparable to those given above. The solid and especially its solutions were lacrimatory.⁴⁷

Reaction of *N,N*-Dimethylbenzylanilinium (1) Halides with *n*-Butyllithium.—Tables I and II summarize the results and variables in reactions with either chloride or bromide salts and *n*-butyllithium. A particular example, including product identification, is given here in some detail (cf. Table I, expt 7).

n-Butyllithium (0.30 M in 200 ml of hexane) was rapidly added to a vigorously magnet-stirred suspension of 40.0 g (0.16 mol) of finely powdered, vacuum dried 1 chloride in 100 ml of sodium-dried hexane. The three-necked reaction flask, equipped with calcium chloride drying tube, was flame dried and then swept with dry nitrogen during the butyllithium addition and kept at 30 \pm 2° for 36 hr before 50 ml of water was slowly added. The reaction was exothermic and an initial greenish-yellow color of the solution disappeared after 2 hr. The organic layer was separated and all materials boiling up to 100° were distilled off. The undistilled liquid was cooled to 0° and filtered, giving colorless crystals, which were washed with 5 ml of methanol, 2.9 g, mp 121–123°. The ir spectrum of the solid **8** in CS₂ was identical with that of *trans*-stilbene (yield 10.1%).

The liquid product mixture was then distilled; fractions were collected from 165 to 205° (1 atm), 58 to 130°, 133 to 190°, and 190 to 215° (1.5 mm). The first of these fractions contained predominantly two materials observed by gc analysis at 122°. The ir spectra in CS₂ of preparative gc samples were comparable with **2** (yield 29%) and *n*-pentylbenzene (2.1%).

The second and third distillation fractions both showed the same four gc peaks. Analysis of retention ratios and ir and pmr spectra gave the product yields: 5.3% **3**, 2.4% **4**, 12.7% **5**, and 2.1% **6**.

The last fraction, 3.5 g, was essentially pure **7** (8.3% yield based on *N*-methyl-*N*-[*o*-(β -phenethyl)benzyl]aniline⁴) and was

further purified (>99%) by preparative gc. The yellow oil had bp 200–204° (1.0 mm) [lit.⁴ 199–203° (1.10 mm)], *n*_D²⁰ 1.6037, *n*_D³⁰ 1.6018.

Anal. Calcd for C₂₂H₂₃N: C, 87.66; H, 7.69; N, 4.65. Found: C, 87.39; H, 7.99; N, 4.82.

The ir spectrum of a liquid film had bands at 3015 w, 2890 w, 1590 s, 1500 s*, 1445 w, 1370 w, 1340 w, 1255 w, 1210–1190 w, 1155 vw, 1115 w, 1035 w, 990 w, 953 vw, 860 vw, 752 m, and 695 m cm⁻¹. The pmr spectrum had absorption in three regions, centered near 2.5, at 4.12, and centered near 6.9 ppm with the relative integral intensities of 5.8:1.0:13.8, respectively. The first of these multiplets was composed of four distinguishable bands with peaks at 2.28, 2.45, 2.53, and 2.72 ppm but only the last two of these being of sufficient intensity to qualify as a CH₂ singlet attached to aromatic nitrogen; the remainder might be accounted for by an A₂B₂ link between two aromatic rings in the assigned structure. The singlet at 4.12 ppm would then be a benzylic methylene attached to aromatic nitrogen in the assigned structure, but its intensity was only half that required. The third region, that of the aromatic proton multiplet, was between 6.35 and 7.20 ppm with a broad singlet at 6.95 ppm accounting for more than two-thirds of the region's integrated area.

Reaction of *N,N*-Dimethylbenzylanilinium Bromide with Phenyllithium.—Results of a comparable reaction with the chloride are given in Table II. A solution of 40 ml of 1.7 M phenyllithium (0.68 mol) in 3:1 v/v benzene–ether was added to vigorously stirred suspension of 14.6 (50 mmol) of the finely powdered quaternary bromide at room temperature. The solution turned yellow and became warm in 25 min. After 14 hr, 20 ml of water was added slowly. The organic layer was reduced in volume to 29 ml by distillation and this product mixture was extracted with concentrated hydrochloric acid. The remaining organic phase had gc peaks at 168° with ir spectra for hydrocarbon product **8** and biphenyl present in the original phenyllithium solution. Diphenylmethane was not observed.

The acidic aqueous extract of the original organic layer was washed with ether and then made strongly alkaline with potassium hydroxide. The oil was collected by washing twice with 20-ml portions of ether. The extracts were evaporated and analyzed. *N,N*-Dimethylbenzylamine was used as a standard for analysis at 115° on a 20M Carbowax–KOH column after determining the absence of conflicting peaks. The single basic product observed on this column was **2** in 37% yield with a retention ratio of 2.20 relative to the standard used. The higher boiling amines were determined by analysis relative to *N,N*-dimethylbenzylhydramine at 168° as previously described.⁹ Only three product peaks were observed, retention ratios 1.49, 1.80, 2.28; these peaks were assigned to **3** (1.3%), **4** (23%), and **5** (3.9%), respectively. Products detected accounted for 65% of the starting salt.

Reaction of *N,N*-Dimethylbenzylanilinium (1) Chloride with Ethanol Potassium Hydroxide.—Powdered 1 chloride (23.6 g, 95 mmol) was added to a solution of 11.2 g (0.2 mol) of potassium hydroxide in 150 ml of absolute ethanol. The mixture was refluxed for 24 hr, and then, after cooling, 200 ml of water was added. The separated organic layer and an ether extract of the aqueous solution were combined and dried over potassium hydroxide. Gc analysis at 135° on an 18-ft 20M Carbowax–KOH column³⁷ gave two peaks which had retention ratios of 4.75 and 7.75 relative to toluene at 1.00 (retention time 4.0 min), and at 122° on a GE-SF96 column these two peaks had retention ratios of 0.546 and 0.660 relative to *N,N*-dimethyl- β -phenethylamine. Ir analysis on a preparative gc sample containing both products gave a spectrum which was a composite of ethyl benzyl ether (45%, gc) and **2** (42%, gc).

A single peak with a retention ratio of 1.48 relative to *N,N*-dimethylbenzylhydramine at 1.00 was observed in gc analysis at 168° on a GE-SF96 column. No trace of **8** was apparent in the ir of a preparative gc sample which was identical with that of commercial **3**, 5.8% yield.

Reaction of *N,N*-Dimethylbenzylanilinium (1) Chloride with Sodium Ethoxide.—The quaternary chloride (10.0 g, 40 mmol) was added to a solution which had been prepared by reacting 3.0 g (0.13 g-atom) of sodium with 70 ml of absolute ethanol. The solution was stirred at reflux for 24 hr. After cooling, 250 ml of water was added, and the solution was salted out with 10 g of sodium chloride and extracted with 20 ml of ether. The organic layer and a subsequent 50-ml ether extract were combined, dried over potassium hydroxide, and evaporated to 44 ml before analysis. The same three products and their characteristic gc retention ratios

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