of methyl iodide with the pyridinecarboxaldehyde in alcoholic solution under the conditions described. The solid products obtained were air dried.

Physical measurements. Infrared spectra were determined on a Perkin-Elmer 1R 21. The ultraviolet determinations were performed with a Beckman model DU spectrophotometer; concn. 5×10^{-5} *M*, temp. 23.5°, slit width 0.82 mm. The Beckman Model G *p*H meter was employed for potentiometric titration.

Acknowledgment. We wish to thank Mr. Omer O. Owens for having determined the rate of GB hydrolysis and Mr. Jacob Hanker for his assistance in the interpretation of the infrared spectra.

ARMY CHEMICAL CENTER, MD.

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(9) J. B. Adams, J. Cymerman Craig, C. Ralph, and D. Willis, *Austr. J. Chem.*, **8**, 392 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

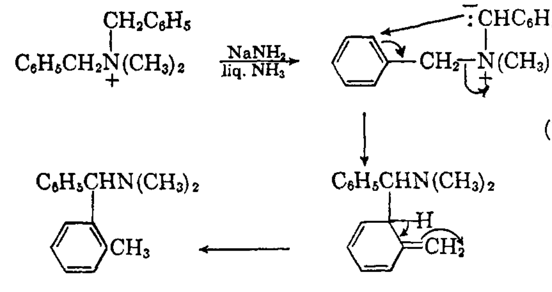
ortho-Substitution Rearrangement of Certain Substituted Dibenzyldimethylammonium Ions by Sodium Amide in Liquid Ammonia[1]

WILLIAM Q. BEARD, JR.,[2] AND CHARLES R. HAUSER

Received May 23, 1960

Several substituted dibenzyldimethylammonium ions were shown to undergo the *ortho*-substitution rearrangement with sodium amide in liquid ammonia to form substituted benzohydryldimethylamines. Each of the four 4,4'-disubstituted quaternary ions studied produced single rearranged amines, but each of the two unsymmetrical 4-substituted quaternary ions gave a mixture of rearranged amines. The unsymmetrical 2-chlorobenzylbenzyldimethylammonium ion yielded a single rearranged amine as the only isolated product. The structures of most of the rearranged amines were established.

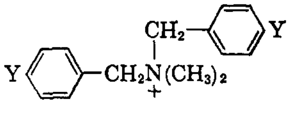
It has previously been observed[3] that the dibenzyldimethylammonium ion undergoes the *ortho*-substitution rearrangement with sodium amide in liquid ammonia to form 2,*N*,*N*-trimethylbenzohydrylamine in 95% yield. The mechanism has been assumed to involve the intermediate formation of the benzyl carbanion and the *exo*-methyleneamine (Equation 1).



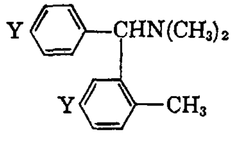
(1)

It has now been found that certain substituted benzyldimethylammonium ions likewise undergo this type of rearrangement. First, a study was made of the symmetrical 4,4'-substituted quaternary ions Ia–d, which underwent the rearrangement to form benzohydryldimethylamines IIa–d respectively.

These products presumably arose through the intermediate formation of the corresponding benzyl-type carbanions (see Equation 1). None of the possible *ortho*-substitution rearrangement products involving the intermediate formation of methyl carbanions or the Steven's 1,2-shift products were detected.



Ia. Y = CH_3
Ib. Y = OCH_3
Ic. Y = Cl
Id. Y = CN



IIa. Y = CH_3
IIb. Y = OCH_3
IIc. Y = Cl
IId. Y = CN

In Table I are summarized the results of the preparations of quaternary ions Ia–d, in Table II the results of the rearrangements of these ions to form rearranged amines IIa–d, and in Table III some infrared data on the rearranged amines. It can be seen from Table I that the yields of quaternary ions Ia–d from the appropriate 4-substituted benzyldimethylamines and benzyl halides were almost quantitative. It can be seen from Table II that the yields of the tertiary amines IIa–d from the rearrangements of the corresponding quaternary ions Ia–d were 89, 75, 21, and 11% respectively. The reaction with the chloro quaternary ion Ic was carried out by the inverse addition procedure in order to minimize the possible benzyne type of reaction of the rearranged tertiary amine with the alkali amide.[4] Even then there was obtained a considerable amount of amorphous, amine material, which apparently arose from the latter type of reaction. The reaction with the cyano quaternary ion Id appeared to be accompanied by a side reaction, since the recovered ether-insoluble organic salts could not be purified. Thus, the yield was not improved by a longer reaction time.

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[1] Supported in part by the National Science Foundation.

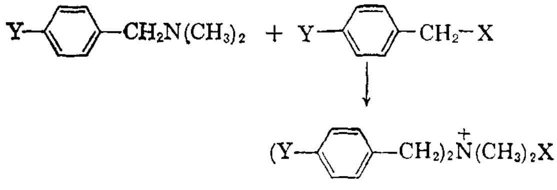
[2] Union Carbide Chemicals Company Fellow, 1956–58.

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

[4] See J. D. Roberts, H. Simmons, Jr., L. Carlsmith, and C. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953).

TABLE I

PREPARATION OF SOME SYMMETRICAL 4,4'-DISUBSTITUTED DIBENZYLDIMETHYLAMMONIUM SALTS (TYPE I)



Y	X	M.P.	Yield, %	Formula	Calculated			Found		
					C	H	N	C	H	N
CH_3	Br	208–209	97	$C_{18}H_{24}BrN$	64.68	7.24	4.19	64.64	7.41	4.10
CH_3O	Br	175–176	94	$C_{18}H_{24}BrNO_2$	59.02	6.60	3.82	58.87	6.40	3.78
Cl	Cl	204–205	98	$C_{16}H_{18}Cl_3N$	58.11	5.49	4.24	57.96	5.44	4.46
CN	Br	232.5–233.5	97	$C_{18}H_{18}BrN_3$	60.68	5.09	11.79	60.42	5.26	11.97

TABLE II

REARRANGEMENT OF QUATERNARY AMMONIUM IONS OF TYPE I BY SODIUM AMIDE TO FORM TERTIARY AMINES OF TYPE II

Quat. Ion	Product	Equiv. $NaNH_2$	Time, Hr.	Recryst. Solvent	Yield, %	M.P.	Formula	Calculated			Found		
								C	H	N	C	H	N
Ia	IIa	2	2	Hexane	89	53.5–54	$C_{18}H_{23}N$	85.32	9.15	5.53	85.56	9.39	5.89
Ib	IIb	2	2.5	Methanol	73	74–74.3	$C_{18}H_{23}NO_2$	75.75	8.12	4.91	75.65	7.92	4.87
Ic	IIc	1	1.5	Pet. ether	21[a]	97.5–97.8	$C_{16}H_{17}Cl_2N$	65.31	5.83	4.76	65.09	6.03	4.80
Id	IId	1	1.25	Methanol	11	132.5–133.5	$C_{18}H_{17}N_3$	78.51	6.22	15.26	78.26	6.06	15.09

[a] Run by inverse addition procedure.

Support for the structures of the rearranged amines IIa–d was obtained from their infrared data (Table III). Thus, all four of the amines showed bands of medium intensity in the region of 900–860 cm.$^{-1}$, which may be ascribed to the out-of-plane deformation frequency of the isolated hydrogen atom present in one of the aromatic rings of these structures.[5] Moreover, all four of the amines exhibited two strong bands in the region of 860–800 cm.$^{-1}$, which may be attributed to the two adjacent aromatic hydrogen atoms found in both of the aromatic rings of these structures.[6] It is not surprising that these bands are of unequal intensity, since one of the rings possesses two pairs of adjacent hydrogen which are equivalent and the other, only one pair. Present in each amine was one band of variable intensity in the region of 855–845 cm.$^{-1}$ which was presumably due to the benzyldimethylamine moiety.[7] The bands below 800 cm.$^{-1}$ were not identified.

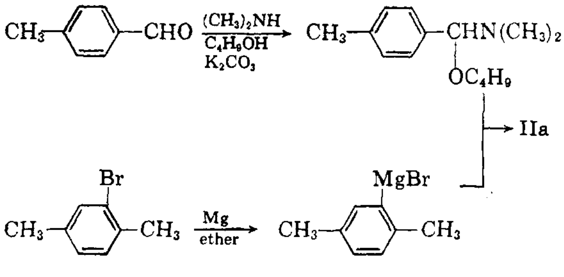
The structure of the rearranged amine from quaternary ion Ia was confirmed as IIa by an independent synthesis from the α-dimethylamino-*n*-butyl ether of *p*-tolualdehyde and the Grignard reagent of 2,5-dimethylbromobenzene (Equation 2).

TABLE III

INFRARED SPECTRA OF AMINES IIa–d FROM 900 TO 700 CM.$^{-1}$

IIa	IIb	IIc	IId
890 (M)[a]	885 (M)	887 (M)	890 (M)
855 (W)[b]	855 (M)	845 (M)	852 (S)
825 (S)[c]	835 (S)	830 (S)	830 (S)
810 (S)	815 (S)	815 (S)	825 (S)
790 (S)	797 (S)	789 (M)	765 (M)
. . .	782 (M)	. . .	. . .
736 (M)	735 (M)	737 (M)	. . .
. . .	716 (M)	. . .	. . .
. . .	713 (M)	. . .	. . .

[a] Medium intensity. [b] Weak intensity. [c] Strong intensity.



(2)

The structures of the rearranged amines from quaternary ions Ib and Ic were further established as IIb and IIc, respectively, by oxidations of both the methyl and dimethylaminomethylene groups to form the corresponding substituted *o*-benzoylbenzoic acids, which are known (Equation 3).

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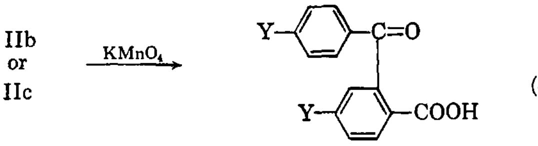
(5) See L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, N. Y., 1959, p. 79.

(6) See ref. 5, page 78.

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



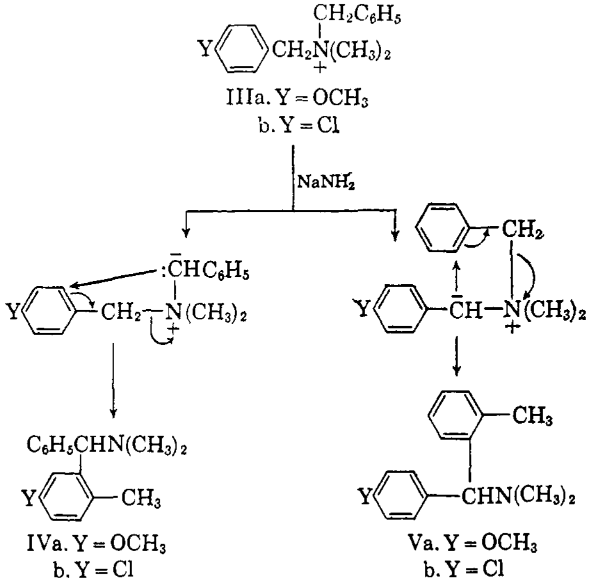
(3)

Y = OCH_3 or Cl

The structure of the rearranged amine from quaternary ion Id was not established chemically, but on the basis of the infrared data discussed above, structure IId may be assumed. Moreover, its infrared spectrum showed a strong band for the nitrile group at 2240 cm.$^{-1}$.[8]

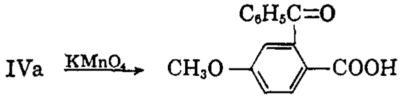
Next a study was made of the unsymmetrical 4-substituted quaternary ions IIIa-b, each of which might form two intermediate benzyl-type carbanions leading to the formation of two different types of rearranged tertiary amines, IVa-b and Va-b (Scheme A).

SCHEME A



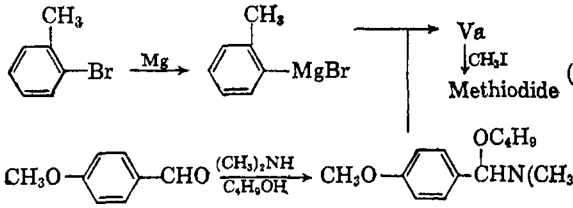
Treatment of quaternary ions IIIa-b with sodium amide in liquid ammonia produced amine fractions which, calculated on the basis of either or both of the isomeric amines, amounted to yields of 95% and 80% respectively. Special conditions were employed with quaternary ion IIIb (see experimental). Infrared spectra of each of the amine fractions indicated that both isomers were present. Thus, the spectrum of each showed two strong bands in the regions of 770-730 cm.$^{-1}$ and 710-690 cm.$^{-1}$ indicative of the five adjacent aromatic hydrogen atoms[9] present in the phenyl group of IVa-b, and a second strong band in the region of 770-730 cm.$^{-1}$ indicative of the four adjacent aromatic hydrogen atoms[10] present in the *ortho* disubstituted ring of amines Va-b.

Of the mixture of amines from quaternary ion IIIa 45% was crystallized in pure form, exhibiting a spectrum in agreement with structure IVa and yielding on oxidation 2-benzoyl-4-methoxybenzoic acid (Equation 4).



(4)

The remaining impure amine still possessed a strong band at 705 cm.$^{-1}$ for five adjacent aromatic hydrogen atoms,[9] indicating that it was still heavily contaminated by IVa, since the spectrum of authentic Va possessed no band in this region. This impure amine was treated with methyl iodide to give a 50% yield of the methiodide of Va, the structure of which was established by an independent synthesis from the Grignard reagent of *o*-bromotoluene and the dimethylamino-*n*-butyl ether of anisaldehyde (Equation 5). It should be mentioned

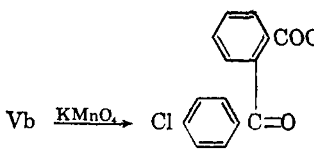


(5)

that no infrared bands were present in the spectrum of the crude product mixture from IIIa that were not accounted for in the spectrum of either IVa or Va.

The above results indicate that the mixture of amines obtained from the rearrangement of IIIa was predominantly IVa, formed from the benzyl carbanion (Scheme A) which should be a weaker base than the 4-methoxybenzyl carbanion and therefore be present in the greater concentration.

The mixture of isomeric rearranged amines from quaternary ion IIIb produced, on recrystallization, a 29% yield of amine Vb. This structure was supported by its infrared spectrum and by oxidation to form 2(4-chlorobenzoyl)benzoic acid (Equation 6).



(6)

Finally a study was made of the unsymmetrical quaternary ion VI, which might form two possible intermediate benzyl-type carbanions of considerably different basicity. The chlorine atom apparently greatly reduces the strength of the 2-chlorobenzyl carbanion[7] through its inductive effect. In accordance with the expected predominance of the 2-chlorobenzyl carbanion the crystallizable amine fraction obtained on treatment of VI with sodium

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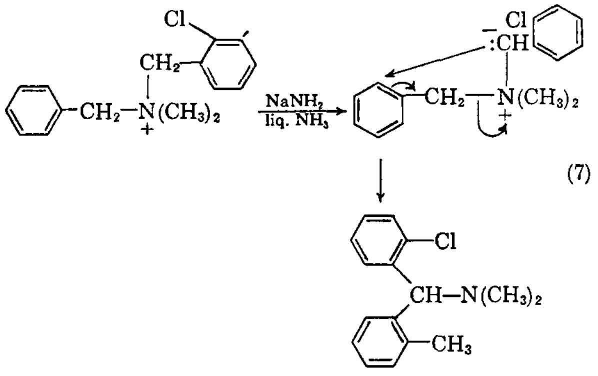
(8) See ref. 5, page 264.

(9) See ref. 5, page 76.

(10) See ref. 5, page 77.

amide in liquid ammonia appeared to consist of only rearranged amine VII (Equation 7).

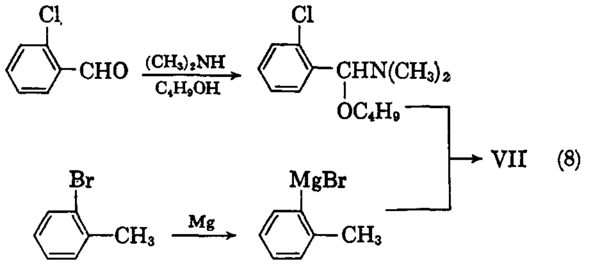


(7)

VII

There was also obtained some polymeric amine material, which may have arisen from the benzyne type of reaction between rearranged amine VII and the reagent. It seems unlikely that this material arose from the other possible rearranged amine since none of this isomer was isolated from runs of long or short duration.

The structure of the rearranged amine isolated was established as VII by an independent synthesis from the dimethylamino-*n*-butyl ether of *o*-chlorobenzaldehyde and the Grignard reagent of *o*-bromotoluene (Equation 8).



(8)

EXPERIMENTAL[11]

Preparation of 4-substituted benzyldimethylamines. These amines were obtained from the alkyl bromide or chloride and excess dimethylamine by the method of Eliel, *et al.*[12]

4-Methylbenzyldimethylamine, b.p. 92–93° at 22 mm., reported 196–197° at 760 mm.[13]

4-Methoxybenzyldimethylamine, b.p. 110–113° at 16 mm., reported 110–111° at 16 mm.[13]

4-Chlorobenzyldimethylamine, b.p. 96–98.5° at 14 mm., reported 90–95° at 9–11 mm.[12]

4-Cyanobenzyldimethylamine, yield 77%, b.p. 130–132° at 15 mm.

Anal. Calcd. for $C_{10}H_{12}N_2$: C, 74.96; H, 7.55; N, 17.49. Found: C, 75.16; H, 7.54; N, 17.35.

Preparation of dibenzyldimethylammonium salts. Equimolar quantities of the appropriate benzyl halide and the appropriate benzyldimethylamine were dissolved in acetonitrile (100 ml. per 0.1 mole of amine). The solution was allowed to stand overnight, the product then being precipitated by the addition of three to five volumes of dry ether. The product was collected on a suction filter, washed with dry ether, and dried in a vacuum desiccator.

Rearrangement of dibenzyl quaternary salts. A. General Procedure. To a suspension of 0.1–0.2 mole of sodium amide[14] in 500 ml. of liquid ammonia was added rapidly 0.1 mole of quaternary salt. The reaction mixture was neutralized after 1–3 hr. with 10.7 g. (0.2 mole) of ammonium chloride, and the ammonia was replaced by ether. Filtration removed the ether-insoluble salts. The ethereal solution was treated with three 100-ml. portions of 2*M* hydrochloric acid. The amine hydrochloride usually precipitated during the addition of the acid. The water layer containing the insoluble hydrochloride salt was made strongly basic with concentrated sodium hydroxide, cooled, and extracted with ether. The ethereal solution of amine was dried and evaporated leaving the crude amine which was frozen out of an appropriate solvent by cooling with Dry Ice.

B. Inverse addition procedure. A suspension of 0.11 mole of sodium amide in 200 ml. of liquid ammonia was added over a period of 10 min. to 0.10 mole of quaternary salt in 300 ml. of liquid ammonia. After expiration of the chosen reaction time the mixture was neutralized with 5.88 g. (0.11 mole) of ammonium chloride. The work-up was the same as that described above in the general procedure.

Independent synthesis of IIa. *A. p-Methyl-α-dimethylaminobenzyl n-butyl ether.* This amino ether was prepared from *p*-tolualdehyde, 1-butanol, and dimethylamine by Method A of Stewart and Hauser[15] in 69% yield. Its boiling point was 101–102° at 1.5 mm.

Anal. Calcd. for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33. Found: C, 76.07; H, 10.46; N, 6.49.

B. 2,4′,5,N,N-Pentamethylbenzohydrylamine (IIa). The above amino ether was coupled with 2,5-dimethylphenylmagnesium bromide in 44% yield by the general method of Stewart and Hauser for the reaction of amino ethers with Grignard reagents.[15] Its melting point was 54–54.5°. Admixture with the rearrangement product gave a melting point of 53.5–54°. The infrared spectrum was also identical with that of IIa.

Oxidation of IIb *to 4-anisoylanisic acid.* A mixture of 5.0 g. of amine IIb, 9.5 g. of potassium permanganate, and 1.4 g. of potassium hydroxide in 250 ml. of water was heated on a steam bath until the permanganate color had faded. Then 9.0 g. of potassium permanganate was added in 3.0 g. portions as the color of the preceding portion had faded. The mixture was filtered through a Supercell mat and the filtrate acidified with concentrated hydrochloric acid. The precipitated acid was filtered out and dried. A yield of 0.90 g. (18%) of 2-anisoylanisic acid, m.p. 207–208°, reported 208°,[16] was obtained. One recrystallization from ethanol raised the melting point to 209.5–210°.

Oxidation of IIa *to 4-chloro-2(4-chlorobenzoyl)benzoic acid.* A 2.0-g. portion of amine IIc was oxidized with 6.2 g. of potassium permanganate as described for the oxidation of IIb. The yield was 0.18 g. (9%) of 4-chloro-2-(4-chlorobenzoyl)benzoic acid, m.p. 193–195°, reported, 195–195.5°.[17] One recrystallization from a mixture of ethanol and hexane raised the melting point to 194.5–195°.

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[11] Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn. All melting points are corrected; boiling points are uncorrected.

[12] E. L. Eliel, T. Ferdinand, and Sr. M. Herrmann, *J. Org. Chem.*, **19**, 1693 (1954).

[13] M. M. Tiffeneau, *Bull. soc. chim. France*, [4] **9**, 827.

[14] R. Levine and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1770 (1944); J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1220 (1944).

[15] A. T. Stewart and C. R. Hauser, *J. Am. Chem. Soc.*, **77**, 1098 (1955).

[16] W. Baker and J. Enderby, *J. Chem. Soc.*, **1940**, 1094.

[17] Mosuke Hayashi and Naomiki Katsuki, *J. Chem. Soc. Ind. Japan*, **45**, 40 (1942); *Chem. Abstr.* **45**, 1570 (1951).

Benzyl-4-methoxybenzyldimethylammonium chloride (IIIa). This quaternary salt was prepared in 96% yield by the above general method from benzyl chloride and 4-methoxybenzyldimethylamine. Its melting point was 173–174°.

Anal. Calcd. for $C_{17}H_{22}ClNO$: C, 69.99; H, 7.60; N, 4.80. Found: C, 69.96; H, 7.65; N, 5.03.

Rearrangement of IIIa. The rearrangement was carried out as described in the general method above with 29.2 g. (0.10 mole) of IIIa and 0.2 mole of sodium amide. Reaction time was 1 hr. The acid work-up was omitted. Evaporation of the filtered ethereal solution yielded a colorless oil which partially crystallized. The mixture was triturated with 25 ml. of methanol and cooled in an ice bath. Filtration yielded 8.46 g. of amine IVa, m.p. 77–78.5°. The mother liquor was evaporated and cooled, producing second and third crops of crystalline amine IVa totalling 2.15 g. The total yield of IVa was 10.91 g. (43%). One recrystallization from methanol produced a melting point of 78°.

Anal. Calcd. for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.90; H, 8.32; N, 5.54.

The methiodide prepared from amine IVa and methyl iodide melted at 107–108°.

Anal. Calcd. for $C_{18}H_{24}INO$: C, 54.42; H, 6.09; N, 3.53. Found: C, 54.29; H, 6.28; N, 3.41.

The mother liquor from the above recrystallizations was evaporated and distilled yielding 13.57 g. (52%) of isomeric amines, b.p. 138–143°/0.6 mm.

Anal. Calcd. for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.57. Found: C, 79.67; H, 8.31; N, 5.57.

A 1.0-g. sample of this mixture of amines was allowed to stand overnight in the presence of excess methyl iodide in 5 ml. of acetonitrile. At the end of this time 10 ml. of acetone was added, and the solution was cooled. The white precipitate of quaternary salt was filtered out. A yield of 0.76 g. (50%) of the methiodide of Va was obtained. After one recrystallization from acetone the melting point was 206.5–207.5°.

Oxidation of IVa. A 1.5-g. sample of amine IVa was oxidized according to the procedure for oxidation of IIb with 5.6 g. of potassium permanganate. The yield was 0.22 g. (14%) of 4-methoxy-2-benzoylbenzoic acid m.p. 156–160°. The melting point was 159–159.5° after one recrystallization from water and ethanol. Recrystallization from benzene gave a melting point of 171°, reported, 172–174° (from benzene).[18]

Independent synthesis of Va *and methiodide. A. 4-Methoxy-α-dimethylaminobenzyl n-butyl ether.* This amino ether was prepared in 39% yield from anisaldehyde, dimethylamine and *n*-butyl alcohol by Method A of Stewart and Hauser.[15] Its boiling point was 114–118° at 0.7 mm. Since this amino ether decomposed fairly rapidly it was used in the next step immediately, and no analysis was obtained.

B. 2-Methyl-4-methoxy-N,N-dimethylbenzohydrylamine (Va). This amine was obtained in 73% yield from the above amino ether and *o*-tolylmagnesium bromide by the general method of Stewart and Hauser.[15] The melting point after one recrystallization from methanol was 56.5°.

Anal. Calcd. for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.89; H, 8.44; N, 5.41.

C. Methiodide of Va. A small sample of amine Va was allowed to react overnight with excess methyl iodide in acetonitrile. The product was precipitated by the addition of ether. After one recrystallization from acetone and 95% ethanol its melting point was 210–210.5°. Admixture with a sample obtained from the methylation of the impure amine fraction from the rearrangement of IIIa produced no depression of the melting point. The infrared absorption spectra of the two samples were identical.

Anal. Calcd. for $C_{18}H_{24}INO$: C, 54.42; H, 6.09; N, 3.53. Found: C, 54.29; H, 6.28; N, 3.41.

Benzyl-4-chlorobenzyldimethylammonium chloride (IIIb). This salt was prepared in 73% yield by the above general procedure for the preparation of dibenzyl quaternary salts from benzyldimethylamine and 4-chlorobenzyl chloride with a reaction time of only 2 hr. Its melting point was 205–206°.

Anal. Calcd. for $C_{16}H_{19}Cl_2N$: C, 64.87; H, 6.46; N, 4.73. Found: C, 64.81; H, 6.41; N, 4.81.

Rearrangement of IIIb. This rearrangement was carried out by a modification of the inverse addition procedure described above on 28.6 g. (0.1 mole) of benzyl-4-chlorobenzyldimethylammonium chloride (IIIb) with 0.20 mole of sodium amide. The addition time was 5 min., and the reaction time was only 5 min. No acid work-up was used. Evaporation of the resulting ethereal solution of the amine left a crude yield of 22.5 g. of amine. The amine was treated with 100 ml. of hot methanol and the solution filtered, leaving 1.5 g. of amorphous polymeric amine. The filtrate was evaporated to give 21 g. (80%) of a solid which showed infrared bands for the two probable isomeric products. This solid was allowed to stand at room temperature for 2 weeks in 30 ml. of methanol. The undissolved crystals were then collected on a suction filter and washed with methanol, yielding 7.2 g. (28%) of 4-chloro-2′,*N*,*N*-trimethylbenzohydrylamine (Vb), m.p. 79–79.5°.

Anal. Calcd. for $C_{16}H_{18}ClN$: C, 74.00; H, 6.98; N, 5.39. Found: C, 74.18; H, 7.18; N, 5.62.

Oxidation of a 1.0-g. sample of amine Vb with 4.07 g. of potassium permanganate by the usual method yielded 0.15 g. (15%) of 2-(4-chlorobenzoyl)benzoic acid, m.p. 146–147°, reported 147–148°.[19]

Benzyl-2-chlorobenzyldimethylammonium chloride (VI). This salt was prepared in 91% yield from 2-chlorobenzyl chloride and benzyldimethylamine by the general method described above. The hydroscopic crystals melted at 163–164°.

Anal. Calcd. for $C_{16}H_{19}Cl_2N$: C, 64.87; H, 6.46; N, 4.73. Found: C, 65.05; H, 6.52; N, 4.68.

Rearrangement of VI *to form 2-chloro-2′,N,N-trimethylbenzohydrylamine* (VII). To 14.8 g. (0.05 mole) of benzyl-2-chlorobenzyldimethylammonium chloride in 200 ml. of liquid ammonia was added a suspension of 0.1 mole of sodium amide in 200 ml. of liquid ammonia over a period of 30 min. After an additional 30 min., 5.35 g. (0.1 mole) of ammonium chloride was added and the ammonia replaced by ether. After filtration the ethereal solution was evaporated leaving a yellow solid, which was recrystallized twice from petroleum ether (b.p. 30–60°) at −70°. Much polymeric amine was insoluble in the petroleum ether and was filtered out. The yield of VII was 4.9 g. (38%), m.p. 92–94°. An additional recrystallization from methanol raised the melting point to 96–97°.

Anal. Calcd. for $C_{16}H_{18}ClN$: C, 74.00; H, 6.98; N, 5.39. Found: C, 74.02; H, 7.15; N, 5.54.

Independent synthesis of VII. *A. 2-Chloro-α-dimethylaminobenzyl n-butyl ether.* This compound was prepared in 52% yield by Method A of Stewart and Hauser[15] from *o*-chlorobenzaldehyde, *n*-butylalcohol and dimethylamine. The boiling point was 97–98° at 1 mm., n_D^{25} 1.4995.

Anal. Calcd. for $C_{13}H_{20}ClNO$: C, 64.58; H, 8.34; N, 5.80. Found: C, 64.57; H, 8.59; N, 5.96.

B. 2-Chloro-2′,N,N-trimethylbenzohydrylamine (VII). Treatment of the above amino ether with *o*-tolylmagnesium bromide by the general method of Stewart and Hauser[15] for solid amines produced amine VII, m.p. 96.5–97°, in quantitative yield. Admixture with the product of the rearrangement produced no depression of the melting point.

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(18) R. Melby, R. Crawford, D. McGreer, and R. B. Sandin, *J. Am. Chem. Soc.*, **78**, 3816–17 (1956).

(19) P. H. Groggins and R. H. Nagel, *Ind. Eng. Chem.*, **25**, 1083 (1933).