[Contribution from the Department of Chemistry, Duke University]

INFLUENCE OF STRUCTURE OF QUATERNARY AMMONIUM IONS ON ORTHO SUBSTITUTION REARRANGEMENT *VERSUS* 1,2-SHIFT WITH SODIUM AMIDE IN LIQUID AMMONIA. INFLUENCE OF TEMPERATURE.[1]

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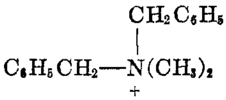
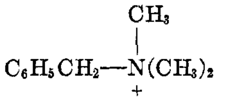
It was recently shown in this laboratory (1, 2) that a number of quaternary ammonium ions having a benzyl or related group undergo with sodium amide in liquid ammonia a rearrangement involving the *ortho* position of the aromatic ring rather than the more common Stevens 1,2-shift. Three typical quaternary ions that exhibit this *ortho* substitution rearrangement are I, II, and III which form tertiary amines IV, V, and VI in yields of 93%, 96%, and 88% respectively. The rearrangement of II, together with the subsequent rearrangement of the methiodide of V, has already found application in a useful method of synthesis of aromatic vicinal methyl derivatives (3). It should be mentioned that Sommelet (4) first showed that III may be rearranged to VI but the method, using sodium hydroxide in sunlight, appears not very satisfactory. Wittig and coworkers (5) found that III undergoes partly this type of rearrangement with phenyllithium, the 1,2-shift product also being formed.



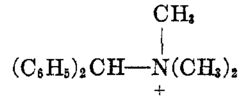
$$C_6H_5CH_2\overset{CH_2C_6H_5}{\overset{|}{\underset{+}{N}}}(CH_3)_2$$

I



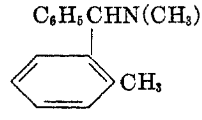
$$C_6H_5CH_2\overset{CH_3}{\overset{|}{\underset{+}{N}}}(CH_3)_2$$

II

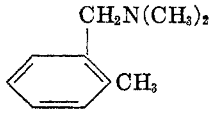


$$(C_6H_5)_2CH\overset{CH_3}{\overset{|}{\underset{+}{N}}}(CH_3)_2$$

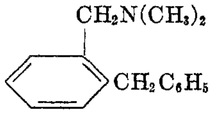
III



IV



V



VI

The mechanism for the *ortho* substitution rearrangement may be illustrated with quaternary ion III with which the reactive intermediate is carbanion or ylide VIII, rather than the predominant carbanion or ylide VII which cannot exhibit this type of rearrangement. The rearrangement of quaternary ion II similarly involves the less predominant carbanion arising from the ionization of a methyl hydrogen, but that of quaternary ion I involves the more predominant carbanion arising from the ionization of a benzyl hydrogen.

In the present investigation it has been found that certain related quaternary ammonium ions fail to exhibit the *ortho* substitution rearrangement even with sodium amide in liquid ammonia. Thus, the relatively complex benzhydrylbenzyl-

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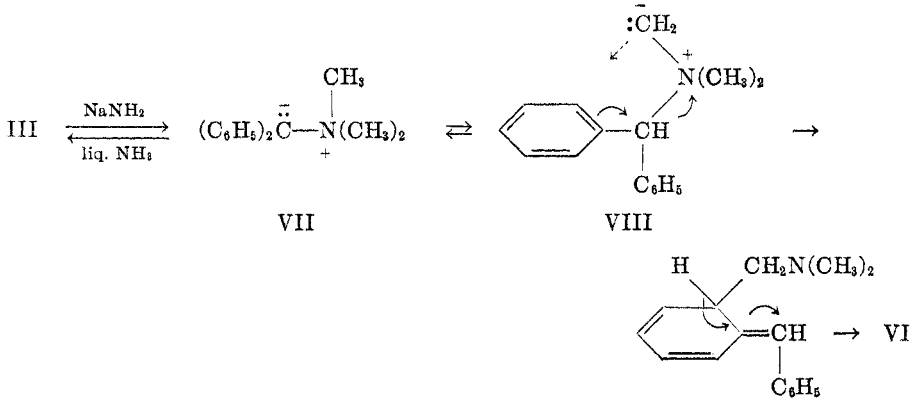
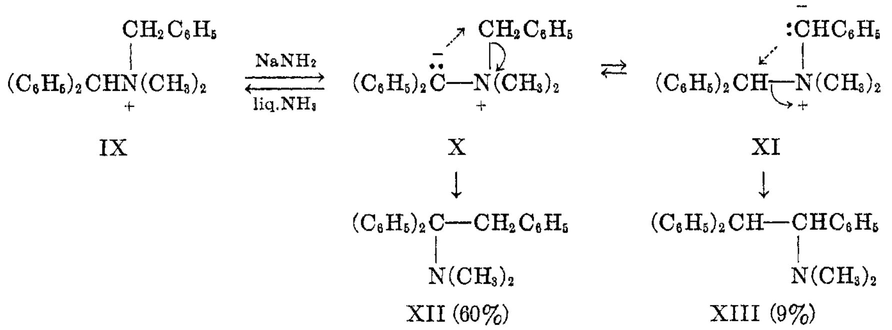
[1] Supported in part by the Office of Ordnance Research, U. S. Army.

[2] Carbide and Carbon Chemicals Company Fellowship, 1952–1953.

dimethylammonium ion (IX) undergoes, instead, two types of 1,2-shifts. The main 1,2-shift involves the migration of the benzyl group within carbanion X to form tertiary amine XII (60%), and the other 1,2-shift, the migration of the benzhydryl group within carbanion XI to form tertiary amine XIII (9%). No *ortho* substitution rearrangement product was isolated.

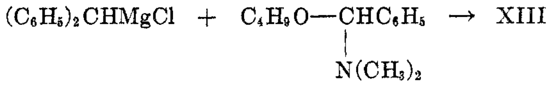




The main product from this reaction was shown to have arisen from a 1,2-shift without involving an aromatic ring by its reduction to 1,1,2-triphenylethane with sodium in liquid ammonia, and by its β-elimination to form 1,1,2-triphenylethylene by means of methyl *p*-toluenesulfonate in refluxing methanol. Its structure was definitely established as XII by an unequivocal synthesis from the methiodide of imine XIV and benzylmagnesium chloride. Imine XIV was synthesized satisfactorily from benzophenone and methylamine apparently for the first time.

$$(C_6H_5)_2C{=}O + H_2NCH_3 \xrightarrow{180^\circ} \underset{\text{XIV}}{(C_6H_5)_2C{=}NCH_3} \xrightarrow[\text{2. } C_6H_5CH_2MgCl]{\text{1. } CH_3I} \text{XII}$$

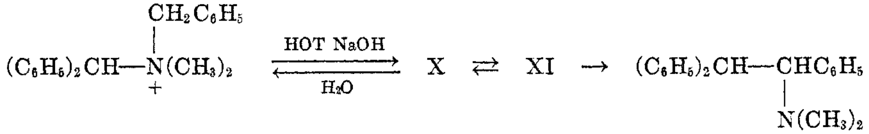
The structure of the other product from quaternary ion IX was established as XIII by an unequivocal synthesis from benzhydrylmagnesium chloride and α-amino ether XV which was carried out recently in connection with another investigation (6).



$$(C_6H_5)_2CHMgCl + C_4H_9O\text{—}\underset{\displaystyle N(CH_3)_2}{\underset{|}{C}}HC_6H_5 \rightarrow \text{XIII}$$

XV

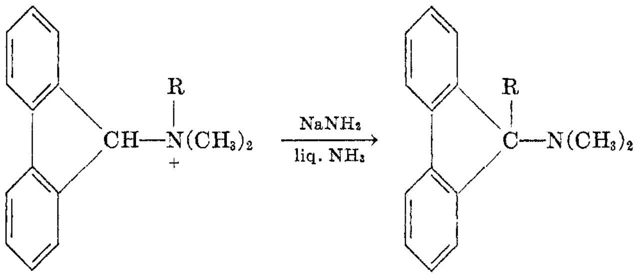
Although tertiary amine XIII is merely a minor product from quaternary ion IX with sodium amide in liquid ammonia, it is apparently the only rearrangement product (35%) from this quaternary ion with hot aqueous sodium hydroxide, with which the common displacement reaction predominates. This rearrangement was reported many years ago (7) but at that time the product was erroneously assumed to have structure XII. Since both tertiary amines are now available from unequivocal syntheses as well as from the rearrangements of IX, their structures may be considered as definitely established.



$$(C_6H_5)_2CH\text{—}\overset{\displaystyle CH_2C_6H_5}{\underset{+}{\overset{|}{N}}}(CH_3)_2 \underset{H_2O}{\overset{\text{HOT NaOH}}{\rightleftarrows}} \text{X} \rightleftarrows \text{XI} \rightarrow (C_6H_5)_2CH\text{—}\underset{\displaystyle N(CH_3)_2}{\underset{|}{C}}HC_6H_5$$

IX XIII (35%)

Also the fluorenylbenzyldimethylammonium ion (XVIA) and the difluorenyldimethylammonium ion (XVIB) were found to undergo with sodium amide in liquid ammonia only the Stevens 1,2-shift to form in high yields tertiary amines XVIIA and XVIIB respectively. The structures of these tertiary amines were established by comparisons with samples of the products prepared by effecting the 1,2-shifts of quaternary ions XVIA and XVIB with sodium methoxide, which Wittig and Felletschin (8) have shown to bring about this type of rearrangement.

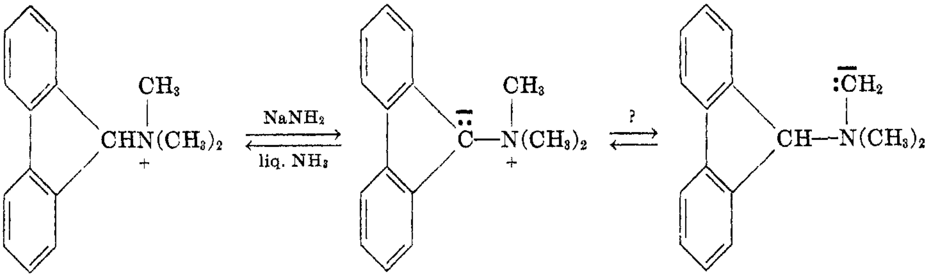


XVIA (R = benzyl)
XVIB (R = fluorenyl)

XVIIA (R = benzyl)
XVIIB (R = fluorenyl)

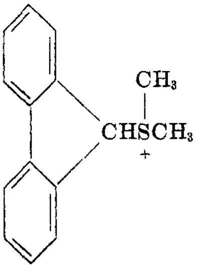
The fact that the relatively complex quaternary ammonium ions IX, XVIA, and XVIB exhibit with sodium amide in liquid ammonia the 1,2-shift instead of the *ortho* substitution rearrangement appears to be associated with a steric factor which interferes with the operation of the five-atom ring mechanism of the latter rearrangement but facilitates the 1,2-shift. In line with this is the observation that the difluorenyl ion XVIB, which is the most complex quaternary ion studied, underwent some of the 1,2-shift even during its preparation from 9-bromofluorene and 9-dimethylaminofluorene.

On the other hand, the fluorenyltrimethylammonium ion (XVIII) failed to undergo either type of rearrangement with sodium amide in liquid ammonia, and was largely recovered. Evidently carbanion XIX was formed since the reaction mixture was colored but the formation of carbanion XX, in equilibrium with XIX, is uncertain. Carbanion XIX was not expected to undergo the 1,2-shift of a methyl group in liquid ammonia since Wittig and Felletschin (8) have shown that the lithium derivative of this carbanion is stable even at 100°. However, carbanion XX might be expected to exhibit either the *ortho* substitution rearrangement, which occurs with the analogous carbanion VIII, or the 1,2-shift of the fluorenyl group like that observed with the difluorenyl quaternary ion XVIB. The fact that neither of these rearrangements was realized indicates that an appreciable concentration of carbanion XX was not present. At least its concentration should be less than that of carbanion VIII since the difference in basicity between XX and XIX is presumably greater than that between VIII and VII.

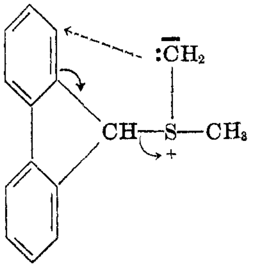


XVIII XIX XX

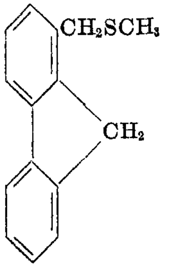
It is possible that even if carbanion XX were formed it might not exhibit the *ortho* substitution rearrangement because of steric strain. Pinck and Hilbert (9) have observed that the analogous carbanion XXII from sulfonium ion XXI does undergo this type of rearrangement to form sulfide XXIII with liquid ammonia at room temperature or with sodium hydroxide in ethanol. However, in this



XXI



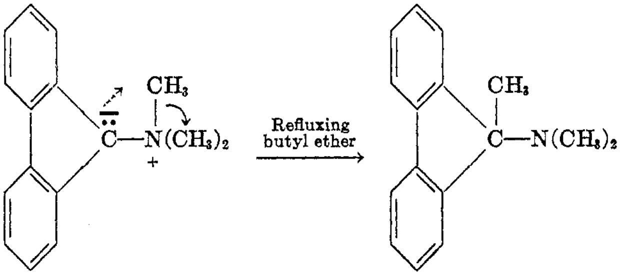
XXII



XXXIII

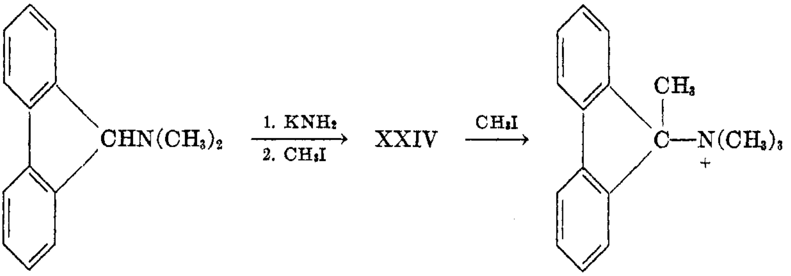
case, the presence of the larger sulfur atom should allow more freedom for the operation of the five-atom ring mechanism. Precedents for this comparison are the facts that dibenzyl sulfide undergoes the *ortho* substitution rearrangement with potassium amide (10) whereas dibenzyl ether exhibits the 1,2-shift with this reagent (11).

Influence of temperature. Although carbanion XIX from quaternary ion XVIII and sodium amide is stable in liquid ammonia and even in refluxing ethyl ether, it was found to undergo the 1,2-shift of a methyl group to form tertiary amine XXIV (55–65%) in refluxing butyl ether.



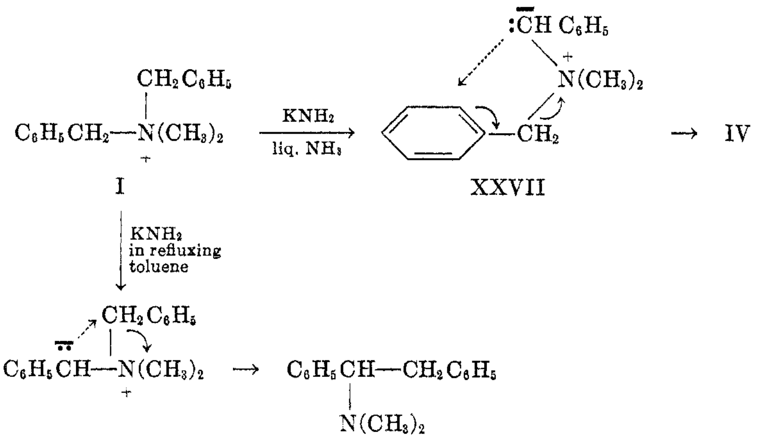
XIX XXIV

The structure of the product was established as XXIV not only by the Emde reduction of its methiodide to form 9-methylfluorene but also by an independent synthesis involving the methylation of 9-dimethylaminofluorene (XXV) by means of potassium amide. Incidentally this appears to be the first alkylation of such a tertiary amine, which was realized in 65% yield, although Wittig and Felletschin (8) have methylated the methiodide of this amine to form quaternary ion XXVI employing phenyllithium. We obtained quaternary ion XXVI on treating tertiary amine XXIV with methyl iodide.

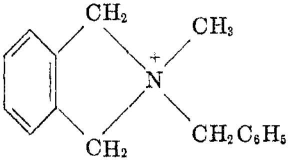


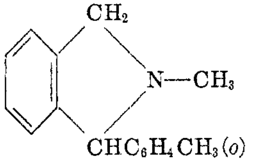
XXV XXVI

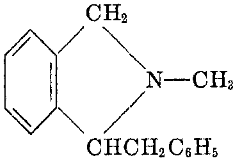
In general the elevation of temperature favors the 1,2-shift over the *ortho* substitution rearrangement. Thus, whereas quaternary ion I undergoes exclusively the latter rearrangement with sodium amide in liquid ammonia (1), Thompson and Stevens (12) have shown that I exhibits only the 1,2-shift with fused sodium amide at 140–150°. We have likewise found that I undergoes the *ortho* substitution rearrangement to form IV (93%) with potassium amide in liquid ammonia, but the 1,2-shift to give XXVIII (59%), with this base in refluxing toluene. Under the latter conditions, some (37%) of I was recovered as its picrate. It is to be noted that these two different types of rearrangement involve the same intermediate carbanion or ylide XXVII.


I XXVII XXVII XXVIII

Similarly, Wittig and Streib (13) have shown that quaternary ion XXIX undergoes the *ortho* substitution rearrangement to form XXX (69%) with phenyllithium in ethyl ether at 20–30°, but the 1,2-shift to give XXXI (41%) with this reagent in butyl ether at 120°. Incidentally the former rearrangement was realized in better yield (87%) with sodium amide in liquid ammonia (13).


XXIX


XXX


XXXI

EXPERIMENTAL[3]

Rearrangement of quaternary ion IX *with sodium amide in liquid ammonia.* Benzhydrylbenzyldimethylammonium bromide was prepared from 0.4 mole each of benzhydryl bromide and benzyldimethylamine in 50 ml. of acetonitrile essentially as described previously (7). After the mixture had stood at room temperature for 3 hours, the crystalline salt was collected, and dissolved in the minimum of boiling chloroform. An equal volume of hot acetonitrile was added, and, after boiling off the chloroform, two volumes of acetone were added. Crystallization was induced by scratching to give a 99% yield of the salt which melted at about 116°. The *mono hydrate*, which was obtained by recrystallization from water, melted at 130–131°; reported m.p. about 125° (7). The *picrate*, recrystallized from dilute ethanol, melted at 148–149° dec.; reported m.p. 149° dec. (7).

The *anhydrous salt* (0.05 mole) was added to a stirred suspension of sodium amide (0.11 mole) in 500 ml. of liquid ammonia, and the red (rust) colored mixture was stirred for 15

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[3] Melting points and boiling points uncorrected. Analyses by Clarke Microanalytical Laboratory, Urbana, Ill.

minutes. Ammonium chloride (0.11 mole) then was added, followed by ether (300 ml.), and the ammonia was allowed to evaporate. Water was added, and after filtering, the ether layer of the filtrate was extracted with 6 *N* hydrochloric acid. The acid extract was made basic with sodium hydroxide solution and the liberated amine was taken up in ether. The solvent was removed, and the oily residue was recrystallized from approximately 50 ml. of methanol to give 9.1 g. (60%) of 1,1,2-triphenylethyldimethylamine (XII), m.p. 96.5–97.5°. This melting point was not depressed on admixture with a sample of amine XII prepared by the independent synthesis described below.

Anal. Calc'd for $C_{22}H_{23}N$: C, 87.66; H, 7.69; N, 4.65.
Found: C, 87.65; H, 7.69; N, 4.51.

The *picrate*, crystallized from ethanol, melted at 158–159°, which was not depressed by admixture with the picrate of the authentic sample of amine XII.

Anal. Calc'd for $C_{28}H_{26}N_4O_7$: C, 63.39; H, 4.94; N, 10.56.
Found: C, 63.63; H, 5.09; N, 10.56.

The methanolic mother liquor from the recrystallization of the oily residue described above was boiled until essentially free from solvent, and petroleum ether then was added. Scratching induced crystallization to give 1,2,2-triphenylethyldimethylamine (XIII) which, after recrystallization from methanol, melted at 126.5–127.5°; yield, 1.4 g. (9%). The melting point was not depressed on admixture with a sample of amine XIII prepared by the unequivocal synthesis described previously (6). The picrate melted at 225–226° dec., which was not depressed on admixture with the picrate of the authentic amine XIII.

When the reaction of one equivalent of quaternary ion IX with two equivalents of sodium amide in liquid ammonia was allowed to proceed for 4 hours the yield of tertiary amine XII was somewhat lower (40%) and considerable gummy material was obtained.

Similar results were obtained with two equivalents of potassium amide, the yield of tertiary amine XII being 46% after one hour and 35% after 4 hours. Gummy material was obtained in both cases. Evidently the excess base caused decomposition of the product since one equivalent of potassium amide gave after one hour a 40% yield of tertiary amine XII and only little gummy material, 28% of the quaternary salt being recovered.

When the reaction was carried out with two equivalents of sodium amide at −70° for 3 hours, a 23% yield of tertiary amine XII was obtained, and 65% of the quaternary salt was recovered.

Reduction and β-elimination of tertiary amine XII *from quaternary ion* IX. A sample (1.3 g.) of the tertiary amine (XII) obtained from the rearrangement of quaternary ion IX was added to a solution of 0.5 g. of sodium in liquid ammonia and the reaction mixture was swirled until the blue color had changed to red. Ammonium chloride was added, followed by ether, and the ammonia was evaporated. After separating the solids the ether solution was evaporated to give 1,1,2-triphenylethane which, after recrystallizing from petroleum ether (cooled in ice-bath), melted at 55–55.5° (sintering at 54.5°); reported m.p. 54.5° (14).

A sample of the tertiary amine (XII) was refluxed with methyl *p*-toluenesulfonate in absolute ethanol to give triphenylethylene melting at 65–67°; reported m.p. 68–69° (15). The mixture melting point with an authentic sample of triphenylethylene was 66–69°.

Independent synthesis of tertiary amine XII. *A. Preparation of imine* XIV. Benzophenone (133 g., 0.73 mole) was heated to 180° and a rapid stream (1 to 2 bubbles per sec.) of dry methylamine was passed into the melt until no more water distilled over (4–5 hours). After distillation of the crude material under reduced pressure, the mixture was dissolved in ether and extracted with 500 ml. of ice-cold 2 *M* hydrochloric acid. The acid extract was washed with ether and the imine was liberated by neutralization of the acid solution with an excess of cold 40% sodium hydroxide. The oily imine was taken up in 30–60° petroleum ether and dried over potassium hydroxide. Removal of the solvent and distillation of the residue yielded 69.2 g. (49%) of pure N-methyl benzophenone imine (XIV), b.p. 93° at 0.4 mm., n_D^{25} 1.5985.

Anal. Calc'd for $C_{14}H_{13}N$: C, 86.12; H, 6.71; N, 7.17.
Found: C, 86.25: H, 6.72; N, 7.11.

On shaking one drop of imine XIV with 2 ml. of 2 *N* hydrochloric acid, there was obtained a clear solution which became cloudy only after 5–10 minutes at room temperature. This serves as a useful test for the purity of the imine since, when benzophenone is present, the initial clear solution is not obtained.

B. *Reaction of methiodide of imine* XIV *with benzylmagnesium chloride.* A solution of 9.7 g. (0.05 mole) of imine XIV in 10.8 g. (0.075 mole) of methyl iodide was allowed to stand for three hours after which time a heavy oily layer of the quaternary salt had formed. Crystallization of the methiodide salt was effected by scratching, the excess methyl iodide was removed, and the solid was washed by decantation with anhydrous ether.

The methiodide was added in one portion to a solution of benzylmagnesium chloride prepared from 1.2 g. of magnesium and 6.35 g. of benzyl chloride in 200 ml. of ether. The mixture was stirred under reflux for ten hours, and then was decomposed with an ammonium chloride solution. The ether layer was extracted with acid, and the acid extract was made basic. The solid was collected on a funnel and recrystallized from methanol to give 5.5 g. (37%) of tertiary amine XII, m.p. 96.5–97.5°.

Anal. Calc'd for $C_{22}H_{23}N$: C, 87.66; H, 7.69.
Found: C, 87.65; H, 7.75.

The *picrate*, recrystallized from ethanol, melted at 158–159°.

Anal. Calc'd for $C_{28}H_{26}N_4O_7$: C, 63.39; H, 4.94; N, 10.56.
Found: C, 63.63; H, 5.05; N, 10.52.

Imine XIV itself formed a precipitate with benzylmagnesium chloride in ether but, on working up the reaction mixture after refluxing 5 hours, 86% of the imine was recovered.

Rearrangement of quaternary ion IX *with sodium hydroxide.* Following the general procedure described previously (7), 0.05 mole of benzhydrylbenzyldimethylammonium bromide was shaken with 0.055 mole of silver oxide in 100 ml. of water for 36 hours. After filtering, 1.0 mole of solid sodium hydroxide was added, and the mixture was heated on the steam-bath for one hour. The cooled mixture was extracted with ether, and the ether solution was extracted with 6 *N* hydrochloric acid. The acid extract was made basic, and the solid was collected and recrystallized twice from methanol to give 1,2,2-triphenylethyldimethylamine (XIII), m.p. 127.5–128°; yield, 35%. The melting point was not depressed on admixture with a sample of amine XIII prepared by the unequivocal synthesis described previously (6). The picrate melted at 225–226° dec., which was not depressed on admixture with the picrate of the authentic amine. The melting points reported previously (7) were 128° for the amine, and 226° dec., for the picrate.

Rearrangement of quaternary ions XVIA *and* XVIB *with sodium amide in liquid ammonia.* 9-Fluorenylbenzyldimethylammonium bromide (XVIA) and di-9-fluorenyldimethylammonium bromide (XVIB) were prepared as described previously (8) from 9-bromofluorene and dimethylbenzylamine and 9-fluorenyldimethylamine respectively.

Finely powdered bromide XVIA was added to a suspension of an excess of sodium amide in liquid ammonia. After three hours the reaction mixture was decomposed with ammonium chloride and worked up to give an 87% yield of 9-benzyl-9-dimethylaminofluorene XVIIA. The melting point and mixture melting point with an authentic sample prepared by effecting the rearrangement with sodium methoxide (8) was 98–99.5°.

In a similar manner quaternary ion XVIB was rearranged to give about the same yield of XVIIB which was identified by its melting point and mixture melting point with an authentic sample.

Treatment of quaternary ion XVIII *with sodium amide. Rearrangement in butyl ether.* 9-Fluorenyltrimethylammonium bromide (XVIII) was prepared from 9-bromofluorene and trimethylamine as described previously (8). This quaternary salt failed to rearrange with sodium amide in liquid ammonia or in refluxing ethyl ether, and 63–65% of it was recovered. Rearrangement was effected as described below.

The finely powdered bromide (30.4 g., 0.1 mole) was added to stirred sodium amide (0.2 mole) in liquid ammonia, followed by 150–200 ml. of di-*n*-butyl ether to yield a yellow-green suspension. Ammonia was evaporated to give a yellow suspension which was heated to the refluxing temperature (140°), the color changing to orange at about 120°. After refluxing for 24 hours, the orange-colored butyl ether suspension was decomposed with water, and the mixture was extracted with hydrochloric acid. The acid extract was made basic with alkali, and the liberated amine was taken up in ether. The solvent was removed, and the residue was distilled *in vacuo* to give a 55–65% yield of 9-dimethylamino-9-methylfluorene (XXIV), b.p. 192–199° at 10 mm., m.p. 64.5–67.5°. Recrystallization from petroleum ether (cooling in a Dry Ice-acetone bath) raised the melting point to 69–70° which was not lowered by admixture with a sample of 9-dimethylamino-9-methylfluorene prepared by the alkylation of 9-dimethylaminofluorene as described below.

Anal. Calc'd for $C_{16}H_{17}N$: C, 86.05; H, 7.68; N, 6.27.
Found: C, 86.00; H, 7.46; N, 6.48.

A sample of the amine, on treatment with methyl iodide, gave (9-methylfluorenyl)-9-trimethylammonium iodide (XXVI), m.p. 153° (dec.); reported m.p. 151° (dec.) (8).

Anal. Calc'd for $C_{17}H_{20}IN$: N, 3.84. Found: N, 3.85.

This methiodide gave, on reduction in aqueous solution with 5% sodium amalagam (16), 9-methylfluorene melting at 46–47°. A mixture melting point with an authentic sample of 9-methylfluorene was the same.

Independent synthesis of tertiary amine XXIV. *Methylation of 9-dimethylaminofluorene.* To a stirred solution of 0.05 mole of potassium amide in liquid ammonia was added an ether solution of 0.044 mole of 9-dimethylaminofluorene (XXV) prepared from 9-bromofluorene and dimethylamine. An immediate red color was produced. The liquid ammonia was evaporated, and the resulting ether suspension was treated with an ether solution of 0.05 mole of methyl iodide, the color changing from red to yellow. The reaction mixture was decomposed carefully with water, and worked up to give a 65% yield of 9-dimethylamino-9-methylfluorene (XXIV), b.p. 154° at 4 mm., m.p. 63–65°. Recrystallization from petroleum ether (cooling in a Dry Ice-acetone bath) raised the melting point to 68–69°.

Rearrangement of quaternary ion I *with potassium amide. A. In liquid ammonia.* This reaction was carried out essentially as described previously (1) for sodium amide in liquid ammonia employing 26.2 g. (0.1 mole) of dibenzyldimethylammonium chloride, m.p. 92.5–93°, and 0.22 mole of potassium amide in 300 ml. of liquid ammonia. The chloride was added to the stirred reagent during 15 minutes (producing a red color immediately). After 3 hours, the reaction mixture was decomposed with ammonium chloride (10 g.) to give 21 g. (93%) of 2-methylbenzhydryldimethylamine (IV), m.p. 47.0–49.5°. One recrystallization from ethanol-water raised the melting point to 48.0–48.5° which was not depressed by admixture with an authentic sample of IV (1).

When the reaction was stopped after one hour, the yield of IV was 86%.

B. In toluene. Potassium amide (0.12 mole) was prepared in liquid ammonia, and this solvent was replaced by 250 ml. of dry toluene. To the resulting suspension was added, with stirring, 0.10 mole of dibenzyldimethylammonium chloride, and the mixture (which became orange-colored within 30 minutes) was refluxed for 34 hours. After standing at room temperature for 40 hours longer, the reaction mixture was decomposed cautiously with water, and the toluene layer was extracted with hydrochloric acid. The acid extract was made basic with sodium hydroxide, and the liberated amine was taken up in ether. The solvent was removed, and the residue was distilled *in vacuo* to give, after a small forerun, 13.1 g. (59%) of 1,2-diphenylethyldimethylamine (XXVIII), b.p. 110–111° at 1 mm. The picrate of this amine, after two recrystallizations from absolute ethanol, melted at 156–157°; reported m.p. 156–157° (12). Treatment of the original aqueous layer from the reaction mixture with picric acid precipitated 16.8 g. (37%) of the picric acid salt of quaternary ion I, which melted at 147–148°; reported, m.p. 148–150° (12).

SUMMARY

1. In contrast to a number of benzyl type quaternary ammonium ions, the relatively complex benzhydrylbenzyldimethylammonium ion (IX) and the

fluorenyl quaternary ions XVIA, XVIB, and XVIII failed to undergo the *ortho* substitution rearrangement with sodium amide in liquid ammonia which has been the most suitable reagent known for this purpose. Instead, they exhibited the Stevens 1,2-shift, except XVIII which was recovered.

2. The benzhydrylbenzyldimethylammonium ion (IX) underwent two types of 1,2-shifts with sodium amide in liquid ammonia, and one type with hot alkali. The structures of the products were established by independent syntheses.

3. Although quaternary ion XVIII is stable with sodium amide in liquid ammonia or in refluxing ethyl ether, it underwent the 1,2-shift with this base in refluxing butyl ether. The resulting tertiary amine (XXIV) was prepared more conveniently by the methylation of 9-dimethylaminofluorene (XXV) by means of potassium amide.

4. The dibenzyldimethylammonium ion (I) exhibited the *ortho* substitution rearrangement with potassium amide in liquid ammonia, but the 1,2-shift, with this base in refluxing toluene.

5. N-Methyl benzophenone imine (XIV) was prepared conveniently from benzophenone and methylamine.

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