Anal. Calcd. for $C_2H_3N_3S_2$: S, 48.15. Found: S, 47.80.

5-Benzylmercapto-1,2,3,4-triatriazole (**V. R = $C_6H_5CH_2$**).—The procedure was similar to that described above except that the sodium nitrite solution was added over a period of 1.5 hr. and the mixture stirred for an additional 4 hr. The product was recrystallized from acetone and water. The melting point of the purified product was found to be 65–67°.

Anal. Calcd. for $C_8H_7N_3S_2$: S, 30.58. Found: S, 30.10.

Salts of Thiatriazolinethione (**VIII**). (a) **Metallic Salts.**—The following general procedure was adopted. The heavy metal salts were prepared by the interaction of aqueous solutions containing freshly prepared thiatriazolinethione and aqueous solutions containing the appropriate metallic ion. After filtration and washing, a portion of the precipitate so obtained was set aside (in a vacuum desiccator over phosphorous pentoxide) for analysis and the remainder of the specimen preserved by suspending in white mineral oil and maintaining below −20°. These precautions were found to be essential due to the explosive instability of the heavy metallic salts. The mineral oil suspensions were utilized for the determination of the infrared absorption spectra at the earliest possible moment. In the same manner the analyses were carried out as early as possible after their preparation.

Silver thiatriazolinethionate (**VIII. M = Ag^+**; n = 1) was a white, slightly photosensitive solid. It was not recrystallized before analysis.

Anal. Calcd. for CN_3S_2Ag: Ag, 47.73. Found: Ag, 47.61.

Lead thiatriazolinethionate (**VIII. M = Pb^{++}**; $n = 2$) was obtained in the form of a light greenish yellow solid which was not purified further.

Anal. Calcd. for $C_2N_6S_4Pb$: 46.76. Found: Pb, 46.60.

(b) **Organic Nitrogen Salts. Ammonium Thiatriazolinethionate** (**VIII. M = NH_4^+**; n = 1). This compound was by prepared by neutralization of II[1] with ammonium hydroxide and isolated as a white crystalline solid by evaporation in a vacuum desiccator over phosphorus pentoxide at 5°, m.p. 110–115° dec.

Anal. Calcd. for $CH_4N_4S_2$: S, 47.09. Found: S, 46.78.

Guandininum Thiatriazolinethionate (**VIII. M = $(NH_2)_3C^+$**; n = 1).—This compound was prepared by adding thiatriazolinethione still moist, to an aqueous solution of guanidine carbonate until no further evolution gas was observed to take place. The turbid liquid was filtered, and the filtrate concentrated *in vacuo* over phosphorus pentoxide at 5°. After several days the crystalline material so obtained was recrystallized from water. The colorless crystals melted at 90–91° with decomposition.

Anal. Calcd. for $C_2H_6N_6S_2$: S, 35.99. Found: S, 36.05.

Anilinium Thiatriazolinethionate (**VIII. M = $C_6H_5NH_3^+$**; n = 1).—To a solution of benzene and aniline was added freshly prepared thiatriazolinethione, still moist. An oil separated, which was removed and shaken with dry benzene (to remove excess aniline). The oil so isolated was concentrated *in vacuo* over phosphorus pentoxide at 5°. After 2 hr. the solid yellow crystalline product was removed, washed with benzene, and allowed to dry, m.p. 70–72°.

Anal. Calcd. for $C_7H_8N_4S_2$: S, 30.21. Found: S, 30.27.

Benzylammonium Thiatriazolinethionate (**VIII. M = $C_6H_5CH_2NH_3^+$**; n = 1).—This compound was prepared by adding moist III to an ether solution of benzylamine. As aqueous lower layer appeared that was removed and washed several times with benzene. The aqueous layer so obtained was chilled and the product crystallized. This slightly yellow, crystalline product was removed from its aqueous suspension by filtration and washed several times with benzene. The decomposition point was found to be 99°.

Anal. Calcd. for $C_8H_{10}N_4S_2$: S, 28.34. Found: S, 28.18.

Degradative Studies. (a) **Reference Compounds.**—These were prepared by methods described in the literature and are summarized in Table III. The triphenylmethyl thiocyanate of Elbs[19] turned out to be triphenylmethyl isothiocyanate.[24,41,44] The procedure of Wheeler[42] for diphenylmethyl thiocyanate and diphenyl isothiocyanate gave mixtures[24] of these two compounds.

(b) **Pyrolysis of 5-(Thiocyano)-1,2,3,4-thiatriazole** (**V. R = CN**).—Approximately 5 g. of the substance was refluxed in carbon disulfide for 3 hr. After the reflux period, the carbon disulfide was distilled and the distillate allowed to evaporate to dryness at room temperature. A white crystalline product was obtained having a melting point of 60°. This was identified as sulfur dicyanide by mixture melting point with an authentic specimen[18] and by comparative infrared absorption spectroscopy.

(c) **General Procedure for Thermal Degradation.**—About 0.04 mole of the thiatriazole was refluxed in benzene for 2 hr. at which time a sufficient quantity of ligroin was added to cause precipitation of the degradation product on cooling. The products so obtained, after recrystallization (see Table III for melting point data), were examined by infrared absorption spectroscopy to determine whether the degradative product, so obtained, was a normal thiocyanate or an isothiocyanate. The data obtained are summarized in Table III.

(d) **Degradation in Basic Solution.**—1:2 mole ratio of III and sodium hydroxide, in 200 ml. of water, was gently warmed on a hot plate until the evolution of nitrogen gas had ceased. During the process of heating the solution turned from yellow to a bright orange-red color. Carbon disulfide was identified by the detection of sodium thithiocarbonate. The other degradation products identified were thiocyanate ion, azide ion, and sulfide ion.

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[44] A. Iliceto, A. Fava, and U. Mazzuccatv, *J. Org. Chem.*, **25**, 1445 (1960).

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ortho Substitution–Rearrangement and Other Reactions of the Benzyldimethylanilinium Ion by Sodium Amide in Liquid Ammonia[1]

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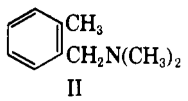
Whereas the benzyltrimethylammonium ion (I) undergoes exclusively the *ortho* substitution–rearrangement with sodium amide in liquid ammonia, the related benzyldimethylanilinium ion (III) exhibits, with this reagent, not only this type of rearrangement but also two other courses of reaction. One of the two latter courses of reaction involves a Stevens 1,2-shift, and the other self-condensation. The products formed from these two courses of reaction underwent β-elimination to give methylaniline and styrene, and dimethylaniline and stilbene, respectively. Also the self-condensation product underwent some rearrangement to produce apparently a dimeric amine. The *o*-xylyldimethylanilinium (XIV) ion exhibited similar reactions with sodium amide in liquid ammonia.

It has previously been shown[3] that the benzyltrimethylammonium ion I undergoes exclusively the *ortho* substitution–rearrangement with sodium amide in liquid ammonia to form tertiary amine II.

$$C_6H_5CH_2\overset{+}{N}(CH_3)_3$$

I



II

It has now been found that the related benzyldimethylanilinium ion (III) reacts with this reagent to give not only the *ortho* substitution–rearrangement

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

[2] Tennessee Eastman Fellow, 1959–1960.

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

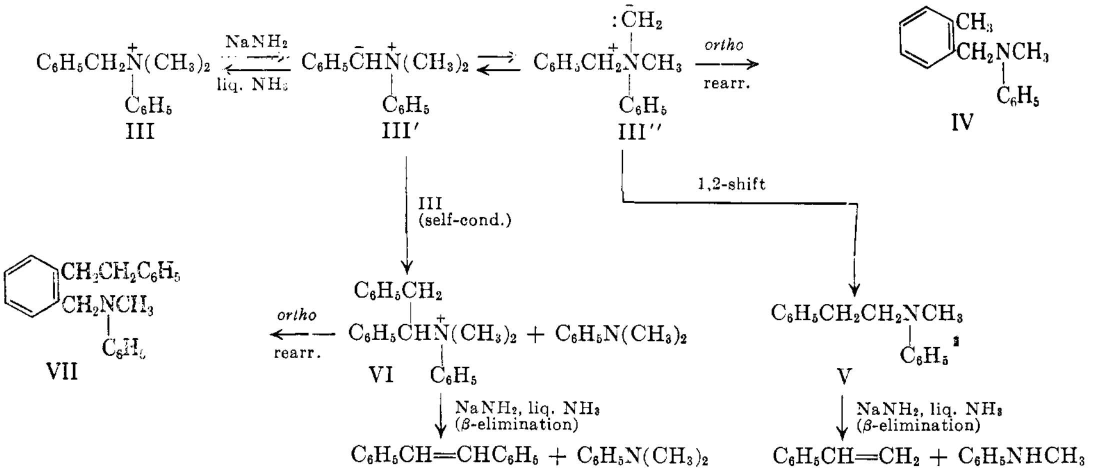
TABLE I

YIELDS OF PRODUCTS FROM 0.1 MOLE OF QUATERNARY ION III WITH 0.2 MOLE OF SODIUM AMIDE IN LIQUID AMMONIA UNDER VARIOUS CONDITIONS

Exp. no.	Liq. ammonia, total volume, ml.	Mode of addition	Addition time, min.	Total reaction time, min.	*ortho* product IV yield, %	*N*-Methylaniline yield, %	Styrene yield, %	*N,N*-Dimethylaniline yield, %	Stilbene yield, %	Dimeric product VII yield, %
1	1000	Direct	30	180	69	11	14	Trace		
2[a]	1000	Direct	30	150	69	6	10[d]	Trace		
3[b]	100	Direct	2	180	40	Trace		16	9	
4[c]	200	Direct	5	90	59			12[e]	2	
5	700	Inverse	7	180	50			6[e]	Trace	5
6	400	Inverse	25	210	27	Trace		30	3	31
7[c]	400	Inverse	30	300	50			22	8	14

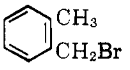
[a] In this experiment 0.3 mole of reagent was used. [b] In this experiment 0.087 mole of III and 0.23 mole of reagent were employed. [c] Lithium amide (0.2 mole) was used instead of sodium amide. [d] Neutral material not identified but calculated as styrene. [e] Contains *N*-methylaniline.

Scheme A



product IV[4] but also methylaniline, dimethylaniline, styrene, stilbene, and apparently dimeric amine VII. These products may be accounted for by Scheme A; their yields, obtained with two molecular equivalents of the reagent under various conditions, are summarized in Table I.

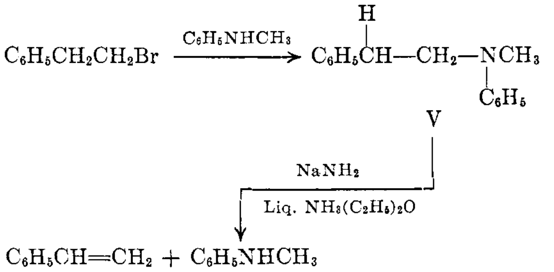
The structure of the *ortho* substitution–rearrangement product IV, which arose through the intermediate formation of the methyl carbanion III″, was established by independent synthesis from *o*-xylyl bromide and methylaniline (equation 1).



$$\xrightarrow{C_6H_5NHCH_3} \text{IV} \qquad (1)$$

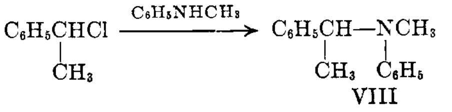
The methylaniline and styrene obtained from quaternary ion III (see Scheme A) evidently arose through a Stevens 1,2-shift of the benzyl group within the methyl carbanion III″ to form amine V, which then underwent β-elimination. That amine V can undergo such a β-elimination to form methylaniline and styrene under similar conditions was demonstrated employing an authentic sample of this amine (Scheme B). Liquid ammonia–ether was used as a solvent for this reaction since amine V appeared to be insoluble in liquid ammonia alone. When amine V was produced from III, it presumably underwent immediate β-elimination without precipitating.

Scheme B



Incidentally this appears to be one of the first demonstrated examples of β-elimination observed with an amine and an alkali amide in liquid ammonia, though this type of reaction is common with quaternary ammonium ions.

That methylaniline and styrene did not arise through amine VIII, which might have been formed by a Stevens 1,2-shift of a methyl group within the benzyl carbanion III′, was indicated by the failure of an authentic sample of VIII (equation 2) to afford these products with sodium amide under similar conditions.



$$C_6H_5\underset{\displaystyle CH_3}{CHCl} \xrightarrow{C_6H_5NHCH_3} \underset{\text{VIII}}{C_6H_5\underset{\displaystyle CH_3}{CH}-\underset{\displaystyle C_6H_5}{NCH_3}} \qquad (2)$$

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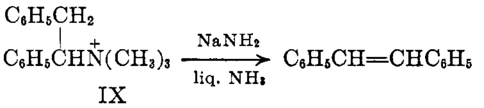
[4] After this manuscript on the bromide of III had been submitted for publication, our attention was called to a communication by L. P. A. Fery [*Bull. soc. chim. Belges*, **71**, 376 (1962)] who obtained amine IV, dimethylaniline, and methylaniline on treatment of the chloride of III with the reagent in yields of 85–90, 5, and 2%, respectively. Also E. J. Gaughan [Ph.D. thesis, Fordham University (1961) supervised by Dr. D. Hennessy] obtained amine IV in 82% yield from the chloride of III.

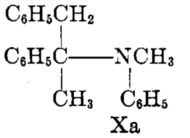
Although the Stevens 1,2-shift product V was not isolated from the reaction mixture of quaternary ion III with the alkali amide, evidence was obtained for its presence in the amine IV fraction of experiment 1 (see Table I and Experimental). Thus the vapor phase chromatogram[5] of this fraction showed not only a large peak for amine IV but also a small shoulder for a compound having the same retention time as the authentic sample of V and different from that found for the authentic sample of amine VIII. Moreover, a chromatogram[5] obtained on the amine fraction after further treatment (3 hr.) with sodium in liquid ammonia failed to show the shoulder; instead there appeared peaks for methylaniline and styrene, which are the β-elimination products of V.

The dimethylaniline and stilbene obtained from quaternary ion III (see Scheme A) presumably arose by self-condensation of this quaternary ion through the benzyl carbanion III′ to form quaternary ion VI, which underwent β-elimination. That the self-condensation product VI can undergo such a β-elimination is indicated by an earlier observation[6] that the related quaternary ion IX exhibits mainly β-elimination under similar conditions to form stilbene (73%) and presumably trimethylamine (equation 3).



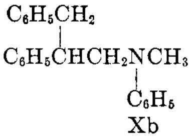
$$\begin{array}{l} C_6H_5CH_2 \\ \quad | \\ C_6H_5CH\overset{+}{N}(CH_3)_3 \\ \quad \textbf{IX} \end{array} \xrightarrow[\text{liq. NH}_3]{NaNH_2} C_6H_5CH{=}CHC_6H_5 \qquad (3)$$

The dimeric amine VII obtained from quaternary ion III apparently arose through self-condensation to form VI, which underwent an *ortho* substitution–rearrangement (see Scheme A). The analysis of this product fitted not only VII, but also the isomeric Stevens products Xa and Xb, which might have been formed from VI through 1,2-shifts of a methyl group and the 1,2-diphenylethyl group, respectively.



$$\begin{array}{l} C_6H_5CH_2 \\ \quad\ | \\ C_6H_5C\text{——}NCH_3 \\ \quad\ | \qquad | \\ \quad CH_3 \quad C_6H_5 \end{array}$$

Xa



$$\begin{array}{l} C_6H_5CH_2 \\ \qquad | \\ C_6H_5CHCH_2NCH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\ C_6H_5 \end{array}$$

Xb

The nuclear magnetic resonance spectrum of the product supports structure VII, not Xa or Xb. Thus the spectrum showed, in addition to an aromatic background, three single peaks at τ values of 7.33, 7.23, and 5.85, which may be assigned to the groups in VII: methyl on nitrogen, methylene between phenyls, and methylene between nitrogen and phenyl, respectively. The relative areas of these peaks were approximately 3:4:2, respectively. Moreover the spectrum of the *ortho* substitution–rearrangement product IV, to which VII is related, showed peaks at 7.29 and 5.83 τ. The observed spectrum for the dimeric amine is not the spectrum that would be expected for amine Xb since the methylene and methinyl hydrogens of Xb should couple, thereby producing multiplets which were not observed. Neither should the observed spectrum fit a structure Xa since the peak for the methyl on carbon in the related compound VIII did not appear in the 7.2–7.4 region.

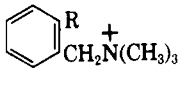
As might be expected the infrared spectrum of dimeric amine VII was similar to that of IV. However, the spectrum of VII showed bands at 690 and 700 cm.$^{-1}$, whereas, that of IV exhibited a single band at 690 cm.$^{-1}$. This is not surprising since these bands are probably due to five adjacent aromatic hydrogens[7] and VII has two such systems while IV has only one. Both spectra showed a broad band centering at 748 cm.$^{-1}$ due in part to five adjacent aromatic hydrogens and in part to four adjacent aromatic hydrogens.

Discussion

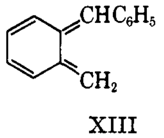
Although quaternary ion III underwent mainly the *ortho* substitution–rearrangement in most of the experiments listed in Table I, it also exhibited to an appreciable extent the Stevens 1,2-shift and self-condensation. The Stevens 1,2-shift was observed when the reaction was carried out in a relatively large amount of liquid ammonia (experiments 1 and 2), whereas, self-condensation occurred in a relatively small amount of liquid ammonia especially when the inverse addition procedure was employed (experiments 3–7). This favorable effect of the use of more concentrated solution[8] on the intermolecular self-condensation was anticipated since the *ortho* rearrangement and Stevens 1,2-shift are intramolecular.

The fact that quaternary ion III undergoes two courses of reaction besides the *ortho* substitution-rearrangement is interesting, since the related quaternary ion I exhibits only the last type of reaction to form II in 96% yield.[9] Evidently the phenyl group attached to nitrogen in III permits some Stevens 1,2-shift to occur by decreasing the rate of the *ortho* rearrangement, and allows some self-condensation to take place by furnishing a better leaving group (dimethylaniline compared to trimethylamine in I).

The self-condensation of III to form VI (see Scheme A) appears to be the first unambiguous example of such a self-alkylation of a quaternary ion by an alkali amide in liquid ammonia. Certain ring-substituted benzyltrimethylammonium ions, for example, the 2-methylbenzyltrimethylammonium ion XI, react with this reagent to form dimeric and higher polymeric amines and hydrocarbons besides the *ortho* substitution–rearrangement product.[3] However, these polymeric products might possibly arise not only through self-alkylation but also through an elimination reaction involving the 2-methyl group and the aromatic ring.[10] Indeed the 2-benzylbenzyltrimethylammonium ion (XII) undergoes exclusively the latter type of reaction to form poly-



XI. R = CH_3
XII. R = $CH_2C_6H_5$



XIII

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(5) A column packed with one part LAC-2R-446 on four parts Johns-Manville Chromasorb W (30–60 mesh) by weight was used.

(6) C. R. Hauser, W. Q. Beard, and D. N. van Eenam, *J. Org. Chem.*, **26**, 2062 (1961).

(7) See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 76.

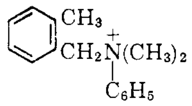
(8) Since the same amount of bromide III was used in most of the experiments, it presumably would be more concentrated in the smaller volumes of liquid ammonia than in the larger volumes, though its actual solubility was not ascertained (see Experimental).

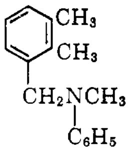
(9) F. N. Jones has observed that a v.p.c. of this product shows but a single peak indicating that it is uncontaminated with even a trace of the possible isomeric Stevens 1,2-shift product[5] or other by-products.

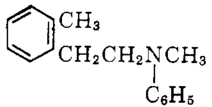
(10) See C. R. Hauser, W. Q. Beard, Jr., and F. N. Jones, *J. Org. Chem.* **26**, 4790 (1961).

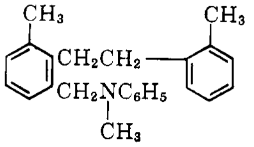
meric material, XIII presumably being an intermediate.[10]

Result with *o*-Xylyldimethylanilinium Bromide (XIV).—Similar to quaternary ion III, the related quaternary ion XIV reacted with sodium amide in liquid ammonia to form a mixture of five amines, which were shown by v.p.c. to be present in the relative proportions of about 13.8:1.0:7.0:10.0:trace. The last two of these amines were identified as dimethylaniline and methylaniline, respectively. Assuming the same courses of reaction to be operative for XIV that were indicated for III, the first three amine products would be the *ortho* substitution–rearrangement product XV, the Stevens 1,2-shift product XVI, and the higher boiling dimeric amine XVII, in that order. Some neutral material was also obtained.


XIV


XV


XVI


XVII

In view of the result with quaternary ion III under similar conditions (dilute solution) the relatively large amount of dimethylaniline and dimeric amine produced might seem surprising. In contrast to III, however, quaternary ion XIV might have afforded dimethylaniline not only through self-condensation but also by an elimination reaction as described above for XI, though the dimeric amine appears to have arisen only through self-condensation.

Experimental[11]

Benzyldimethylanilinium Bromide (III).—To a stirred solution of 51.3 g. (0.30 mole) of benzyl bromide in 200 ml. of acetonitrile was slowly added 36.3 g. (0.30 mole) of carefully purified *N*,*N*-dimethylaniline in 100 ml. of acetonitrile. After stirring for 5 hr., the reaction solution was allowed to stand overnight. Anhydrous ether (500 ml.) was slowly added with stirring to precipitate the quaternary salt, which was washed with dry ether, and dried in a vacuum desiccator to give 86.3 g. (98%) of bromide III, m.p. 153–155° on a Fisher–Johns block, 145–146° in sealed capillary on Mel-Temp (lit., m.p. 98°,[12] 129°,[13] 145°,[14] 203°[15]).

Anal. Calcd. for $C_{15}H_{18}NBr$: C, 61.65; H, 6.21; N, 4.79. Found: C, 61.51; H, 6.19; N, 4.88.

Because this quaternary salt appears to be unstable in certain solvents, for example, chloroform,[16] the following experiment was performed to ascertain its stability in liquid ammonia. A solution of 14.6 g. (0.05 mole) of the salt in 500 ml. of liquid ammonia was stirred for 3 hr., and 200 ml. of anhydrous ether was then added. The ammonia was evaporated, and the resulting ethereal suspension was filtered to recover 14.4 g. (99%) of unchanged bromide III, m.p. 145–146° (sealed tube). The ethereal filtrate was shown by v.p.c. to contain no organic solute.

Reactions of Bromide III with Sodium Amide.—These reactions were carried out several times employing direct and inverse addition procedures in relatively large and relatively small amounts of liquid ammonia. Generally 0.1 mole of the salt III and 0.2 mole of sodium amide were used. The conditions of reaction and yields of products are summarized in Table I. General directions for the two procedures are described below.

(A) **Direct Addition Procedure.**—To a stirred suspension of 0.2 mole of sodium amide in an appropriate amount of commercial, anhydrous liquid ammonia[17] (Dry Ice–acetone condenser) was added 0.1 mole of bromide III to produce immediately a bright yellow color that generally faded during the reaction period. The stirring was continued for an appropriate time, and 0.2 mole of solid ammonium chloride was then added. Anhydrous ether (200–300 ml.) was added and the liquid ammonia was evaporated overnight. The resulting ethereal suspension was filtered, and the ethereal filtrate extracted with excess 6 *N* hydrochloric acid. The remaining ethereal solution was dried over anhydrous magnesium sulfate and the solvent removed to give neutral products. The acid extract was made strongly basic with sodium hydroxide (cooling and stirring), and the liberated amines were extracted several times with ether. The combined ethereal extract was dried over anhydrous magnesium sulfate, and the solvent removed leaving a crude mixture of amines. After an indication of the composition of this crude mixture was obtained by v.p.c. on a small sample (*ca.* 0.05 g.), the mixture was fractionally distilled and each of the resulting fractions chromatographed. Identifications of the products are described below.

(B) **Inverse Addition Procedure.**—To a stirred suspension of 0.1 mole of the bromide of III in an appropriate amount of liquid ammonia (Dry Ice–acetone condenser) was added a suspension of 0.2 mole of sodium amide in an appropriate amount of liquid ammonia through a stopcock attached to the bottom of a flask. The resulting yellow mixture was stirred for an appropriate time (yellow color faded), and then worked up essentially as described above under (A). Identifications of the products are described below.

Identification of *N*,*o*-dimethyl-*N*-phenylbenzylamine (IV).—In all experiments there was obtained amine IV, b.p. 123–126° at 0.4 mm., at 130–131° at 0.6 mm., or at 162.5–164.5° at 5.4 mm., (lit.,[18] b.p. 200° at 35 mm.).

Anal. Calcd. for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.28; H, 7.99; N, 6.68.

The picrate of amine IV, after one recrystallization from ethanol, melted at 134–135° (lit.,[18] m.p. 110°).

Anal. Calcd. for $C_{21}H_{20}N_4O_7$: C, 57.27; H, 4.58; N, 12.72. Found: C, 57.23; H, 4.45; N, 12.71.

This picrate was also obtained with m.p. 112–113°. When a solution of this substance in ethanol was cooled and seeded with a sample, m.p. 134–135°, the picrate that crystallized had m.p. 134–135°.

Independent synthesis of amine IV was effected with 10.7 g. (0.10 mole) of *N*-methylaniline and 18.5 g. (0.10 mole) of *o*-xylyl bromide in 100 ml. of acetonitrile (refluxed overnight). After 95 ml. of acetonitrile was removed by distillation, 100 ml. of ether was added, and the mixture extracted with two 100-ml. portions of 3 *N* hydrochloric acid. The acid extracts were made strongly basic with concentrated sodium hydroxide solution (ice bath). The basic mixture was extracted with three 100-ml. portions of ether, the extracts dried over anhydrous magnesium sulfate, and the ether removed. The residue was distilled, giving 13.95 g. (66%) of amine IV, b.p. 130–134° at 0.5–0.6 mm. The picrate, after one recrystallization from ethanol, melted at 134–135°. On admixture with a sample of the picrate prepared from amine IV obtained from quaternary ammonium ion III, there was no depression of melting point. The infrared spectra of the two samples of amine IV were identical.

Identification of Other Products. (A) *N*-Methylaniline and Styrene.—The lower boiling amine fraction from experiments 1 and 2 (see Table I) was shown by v.p.c. to consist of *N*-methyl-

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(11) Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn. All melting points and boiling points are uncorrected. All vapor phase chromatography, unless otherwise indicated, was carried out on a column packed with one part polypropylene glycol on four parts Johns-Manville Chromasorb W (30–60 mesh) by weight. Infrared spectra were produced on either a Perkin–Elmer 21 spectrophotometer or a Perkin–Elmer Infracord; all solids were run in potassium bromide pellets, liquids on sodium chloride plates.

(12) M. S. Kharasch, G. H. Williams, and W. Nudenberg, *J. Org. Chem.*, **20**, 937 (1955).

(13) E. Wedekind, *Ber.*, **39**, 481 (1906).

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aniline contaminated by a trace of *N*,*N*-dimethylaniline. The main peak was only enhanced by an authentic sample of *N*-methylaniline. The infrared spectrum of this fraction was essentially the same as that of *N*-methylaniline. The fraction from experiments 1 and 2 boiled at 39–40° at 0.55 mm. and 62–64° at 4–5 mm., respectively (lit.,[19] b.p. for *N*-methylaniline 46.8° at 1.0 mm. and 67.7° at 5 mm.). The picrate of the fraction had a m.p. and mixed m.p. 145–148° (not clear) (lit.,[20] m.p. 144.5°).

The neutral product from experiments 1 and 2 was evidently mainly styrene, which partly polymerized. Its infrared spectrum closely resembled that of styrene; and its dibromide, recrystallized from dilute ethanol, melted at 67–70° (lit.,[21] m.p. 74.0–74.5°). The dibromide when mixed with an authentic sample showed no depression of melting point.

(**B**) ***N*,*N*-Dimethylaniline and Stilbene.**—The lower boiling amine fraction from experiments 3–7 was shown by v.p.c. to consist of *N*,*N*-dimethylaniline contaminated, in certain cases (see Table I), with *N*-methylaniline. The main peak was only enhanced by an authentic sample of *N*,*N*-dimethylaniline. The infrared spectrum of the fraction was essentially the same as that of *N*,*N*-dimethylaniline. The fraction boiled at 66–67° at 7–8 mm., 64–65° at 6.0–6.5 mm., or 62.5° at 5.8 mm. (lit.,[19] b.p. 61.6° at 5 mm., 64.5° at 6 mm., and 67° at 7 mm.). The picrate of this fraction had a m.p. and mixed m.p. 157–160° (not clear) (lit.,[22] m.p. 163–164°).

From the neutral fraction from experiments 3–7 was isolated stilbene, m.p. 122–123° after recrystallization from methanol (lit.,[23] m.p. 124°). On admixture with an authentic sample of stilbene the melting point was not depressed. The infrared spectrum of the product was essentially the same as that of stilbene, and like authentic stilbene it fluoresced under ultraviolet light.

(**C**) **Amine VII.**—In experiments 5–7 there was obtained a dimeric (higher boiling) amine, b.p. 190–192° at 0.55 mm., 198–199° at 0.7 mm., and 199–203° at 1.10 mm.

Anal. Calcd. for $C_{22}H_{23}N$: C, 87.66; H, 7.69; N, 4.65. Found: C, 87.84; H, 7.73; N, 4.73.

The picrate of amine VII, after one recrystallization from ethanol, melted at 134–135°.

Anal. Calcd. for $C_{28}H_{26}N_4O_7$: C, 63.39; H, 4.94; N, 10.56. Found: C, 63.61; H, 4.96; N, 10.73.

The melting point of this picrate was depressed to 115–120° when mixed with the picrate of amine IV. However, the infrared spectrum of amine VII was quite similar to that of amine IV (see Discussion).

The n.m.r. spectrum of amine VII was obtained with a HR-60 Varian spectrometer at room temperature (30°) using a solution of approximately one part of amine VII to one part carbon tetrachloride by volume and tetramethylsilane as an internal standard (for details, see Discussion).

***N*-Methyl-*N*-phenylphenethylamine (V) and *N*,α-Dimethyl-*N*-phenylbenzylamine (VIII).**—A solution of 21.4 g. (0.20 mole) of *N*-methylaniline and 27.0 g. (0.15 mole) of β-phenylethyl bromide in 200 ml. of acetonitrile was refluxed for 20 hr. After the acetonitrile was removed, 200 ml. of ether was added, the mixture was extracted with 3 *N* hydrochloric acid. The combined acid extract was made basic with a concentrated solution of sodium hydroxide (cooled). The basic mixture was extracted with ether. The ether extract was dried over anhydrous magnesium sulfate, and the solvent removed. The residue was distilled, yielding 8.63 g. (40%) of *N*-methylaniline and 14.68 g. (48%) of *N*-methyl-*N*-phenylethylamine (V), b.p. 131–134° at 0.75 mm. (lit.,[24] b.p. 198–199° at 18 mm., m.p. 42–43° (lit.,[24] m.p. 44°).

Similarly a solution of 16.0 g. (0.15 mole) of *N*-methylaniline and 21.5 g. (0.15 mole) of α-phenylethyl chloride in 150 ml. of acetonitrile was refluxed for 20 hr. There was isolated 7.14 g. (23%) of *N*,α-dimethyl-*N*-phenylbenzylamine (VIII), b.p. 121–124° at 0.6 mm. (lit.,[25] b.p. 158–165° at 7.0 mm.); 57% of the *N*-methylaniline was recovered.

Treatment of Amine V and VIII with Sodium Amide.—To a stirred suspension of 0.044 mole of sodium amide in 125 ml. of liquid ammonia (Dry Ice–acetone condenser) was added during 5 min., 4.2 g. (0.02 mole) of amine V in 125 ml. of anhydrous ether. The resulting green solution was stirred 3.25 hr. and 2.33 g. (0.044 mole) of solid ammonium chloride was added. The ammonia was allowed to evaporate and a dilute solution of sodium hydroxide was added to the resulting stirred ethereal suspension. The two layers were separated. The ethereal layer, combined with an ethereal extract of the aqueous layer, was dried over anhydrous magnesium sulfate and the solvent removed. The residue was distilled at 0.5–0.6 mm. giving 0.37 g. (17%) of *N*-methylaniline, b.p. 44–46°; 0.26 g. of mid-fraction, b.p. 46–134°; and 2.18 g. (52%) of unchanged amine V, b.p. 134–137°. The mid-fraction was shown by v.p.c. to consist mainly of *N*-methylaniline raising the total yield of this amine to approximately 29%. There was left 0.3–0.5 g. of residue, which presumably contained polystyrene.

When amine V was treated with sodium amide in liquid ammonia (without ether) for 3 hr., a trace of *N*-methylaniline and styrene were obtained as indicated by v.p.c. Most of amine V was recovered. The lack of appreciable reaction was presumably due to the insolubility of amine V in liquid ammonia in which it solidified.

When amine VIII was treated with sodium amide in either liquid ammonia, in which VIII was not soluble, or in liquid ammonia–ether, in which VIII was soluble, it gave only a trace of styrene and *N*-methylaniline as indicated by v.p.c. Most of VIII was recovered.

***o*-Xylyldimethylanilinium Bromide (XIV).**—Bromide XIV was prepared essentially as described by Wittig.[26,27] *o*-Xylyl bromide (3.7 g. 0.02 mole) and *N*,*N*-dimethylaniline (2.4 g., 0.02 mole) were mixed and allowed to stand overnight. The mixture was warmed slightly on a steam bath, and triturated with ethyl acetate. The white crystals thus produced were filtered, washed with anhydrous ether, and dried in a vacuum desiccator to constant weight, 6.0 g. (98%), m.p. 86–88° (lit.,[26] m.p. 87–88°).

Reactions of Bromide XIV with Sodium Amide.—To a stirred suspension of 0.033 mole of sodium amide in 500 ml. of liquid ammonia (Dry Ice–acetone condenser) was added during 5 min., 5.0 g. (0.016 mole) of bromide XIV. The initial green color of the reaction mixture was rapidly discharged. After 4 hr. the reaction mixture was neutrallized with 1.75 g. (0.033 mole) of solid ammonium chloride. Dry ether (400 ml.) was added and the liquid ammonia was evaporated overnight. After the salts were removed by filtration, the ethereal filtrate was extracted with two 50-ml. portions of 6 *N* hydrochloric acid and dried over anhydrous magnesium sulfate. On evaporation of the ether there remained 0.20 g. of unidentified neutral material. The combined acid extract was made strongly basic with sodium hydroxide pellets (cooling and stirring). The basic mixture was extracted with two 100-ml. portions of ether. The combined ether extract was dried over magnesium sulfate, and the ether evaporated leaving 0.9 g. of basic material which was subjected to vapor phase chromatography using a silicone rubber column (see Discussion). Of the five compounds indicated to be present only *N*,*N*-dimethylaniline and *N*-methylaniline were identified (enhancement technique). The infrared spectrum of the salt material (5.53 g.), which was removed by filtration, was practically identical with that of bromide XIV.

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