a chloroform solution of the product gave the isomeric composition. These results are summarized in Table I.

Attempted Addition of Phenylsodium to Triphenylethene.—Phenylsodium was prepared according to the above method from 8.75 g (0.38 g-atom) of sodium and 31.4 g (0.20 mole) of bromobenzene. To the phenylsodium suspension was added 5.9 g (0.08 mole) of *t*-butyl alcohol to prepare the phenylsodium–sodium *t*-butoxide complex *in situ* followed by the addition of 12.8 g (0.05 mole) of triphenylethene. The reaction was run under the same conditions which are described in the preceding section. After 10 hr, the reaction was hydrolyzed and the organic layer was separated from the aqueous layer. Vpc analysis of the organic layer showed that triphenylethene was recovered and that a trace (*ca.* 1%) of a compound formed which had an identical vpc retention time with an authentic sample of IV. It was found that sodium could not be in excess in this system since the sodium added across the double bond of triphenylethene to give, after hydrolysis, triphenylethane. A slight deficiency of sodium was therefore used in this experiment.

Two Types of Rearrangement of Benzhydryltrimethylammonium Ion by Sodium Amide in Liquid Ammonia[1]

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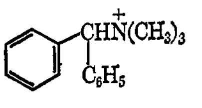
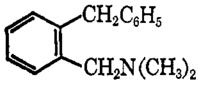
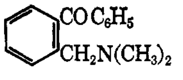
Previously,[2] the product from the reaction of the benzhydryltrimethylammonium ion (I) with sodium amide in liquid ammonia was thought to consist exclusively of the tertiary amine II, which arose through the *ortho*-substitution rearrangement.


I


II

We have now found by vapor phase chromatography that the distilled reaction product from I, obtained in 85–88% yield, boiling over 2°, consists not only of II (80–85%), but also of the isomeric amine III (15–20%), which presumably arose through a Stevens 1,2 shift; none of the isomeric amine IV, which also would have been a Stevens 1,2-shift product, was detected. Similar results were obtained with the crude reaction product. Also, some of solid amine V, which arose through alkylation of II with unchanged quaternary ion I, was isolated from the crude product. These reactions may be represented by Scheme I; the conversion of I′ to I″ might occur intra- or intermolecularly.

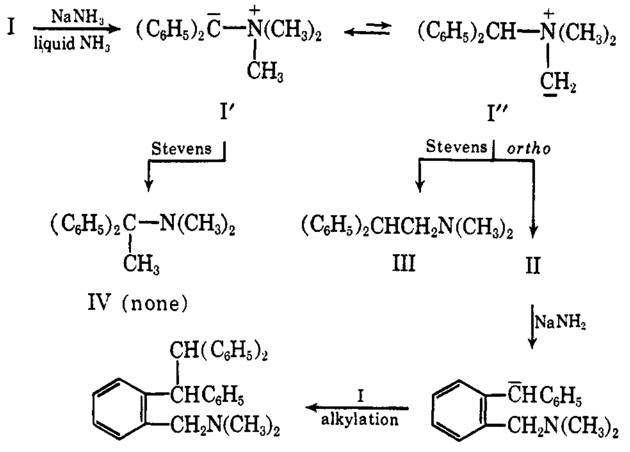
Authentic samples of isomeric amines II, III, and IV employed in the vpc determinations were prepared by Wolff–Kishner reduction of amino ketone VI,[3] by lithium aluminum hydride reduction of amide VII,[4] and by addition of methylmagnesium iodide to imminium iodide VIII,[5] respectively.


VI

$(C_6H_5)_2CHCON(CH_3)_2$
VII

$(C_6H_5)_2C{=}\overset{+}{N}(CH_3)_2I^-$
VIII

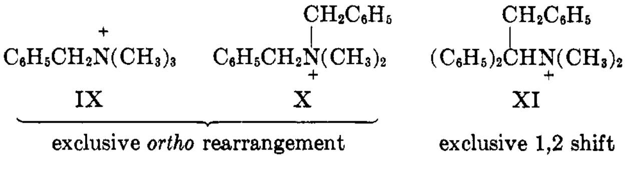
SCHEME I



The formation of Stevens product III from the less predominant ylid I″, rather than Stevens product IV from the more predominant ylid I′, may be rationalized by equilibration of I′ with I″ (see Scheme I) and migration of the benzhydryl group of I″ rather than a methyl group of I′. This more facile 1,2 shift of the benzhydryl group should be expected whether the S_{Ni}[6] or an elimination–readdition[7] mechanism operates.

The formation of some of amine V is not surprising since, not only is the *ortho*-rearrangement product II probably converted to its sodio salt II′ in the reaction mixture (see Scheme I), but quaternary ion I should be capable of alkylating II′.

Interestingly, the observance of both the *ortho* rearrangement and the Stevens 1,2 shift with quaternary ion I places it in an intermediate position between quaternary ions IX (or X) and XI in their reactions with sodium amide in liquid ammonia, since IX and X undergo exclusively the *ortho*-substitution rearrangement,[2] whereas XI exhibits exclusively the Stevens 1,2 shift (two types).[8]



$$\underbrace{\underset{\text{IX}}{C_6H_5CH_2\overset{+}{N}(CH_3)_3} \qquad \underset{\text{X}}{C_6H_5CH_2\overset{+}{N}(CH_2C_6H_5)(CH_3)_2}}_{\text{exclusive } ortho \text{ rearrangement}} \qquad \underbrace{\underset{\text{XI}}{(C_6H_5)_2\overset{+}{C}HN(CH_2C_6H_5)(CH_3)_2}}_{\text{exclusive 1,2 shift}}$$

IX X XI

exclusive *ortho* rearrangement exclusive 1,2 shift

Since consideration of molecular models indicates that the relative ease of the *ortho* rearrangement by the originally proposed cyclic mechanism (S_{Ni}′)[2a] should decrease in the order, IX > X > I > XI, the occurrence of the Stevens 1,2 shift with sodium amide in liquid ammonia appears to be dependent on retardation of the *ortho* rearrangement.

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[1] Supported by the Army Research Office (Durham).

[2] (a) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951); (b) W. R. Brasen and C. R. Hauser, *ibid.*, **77**, 4157 (1955).

[3] R. L. Vaulx and C. R. Hauser, unpublished results.

[4] T. Morikawa, *Yakugaku Zasshi*, **80**, 475 (1960); *Chem. Abstr.*, **54**, 19589c (1960).

[5] C. R. Hauser and D. Lednicer, *J. Org. Chem.*, **24**, 46 (1959).

[6] See C. R. Hauser and S. W. Kantor, *J. Am. Chem. Soc.*, **73**, 1437 (1951).

[7] See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 229.

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

Experimental Section[9]

Rearrangement of Quaternary Ion I to Form II and III.—To a stirred suspension of 0.05 mole of sodium amide in 300 ml of liquid ammonia was added 8.85 g (0.025 mole) of benzhydryltrimethylammonium iodide (I).[2a] After 3 hr, the red suspension was neutralized with 1.65 g (0.03 mole) of ammonium chloride, and the ammonia was replaced by an equal volume of ether. The ether was decanted from the solid residue which was washed twice with ether. The ether solutions were combined and dried over magnesium sulfate and the solvent was removed. The residue was distilled to give 4.80 g (85%) of a mixture of 2-benzylbenzyldimethylamine (II) and 2,2-diphenylethyldimethylamine (III), bp 126–128° (1.5 mm), in the ratio of 80–85:15–20,[10] determined by vpc on two different columns (see footnote 9). These amines were identified by the enhancement technique employing authentic samples.[3,4] Slight traces (<1%) of two unidentified amines were indicated, but none of amine IV was detected; an authentic sample of IV[5] showed a peak that was not present in the chromatogram of the product from I. Amine II has previously been isolated as a derivative.[2]

In another experiment, vpc determinations were made on a sample of the crude product, which gave essentially the same results. The precipitate that formed when the crude product was allowed to stand was removed by filtration and recrystallized from ethanol to give approximately 0.1 g (<1%) of 1-[2-(dimethylaminomethyl)phenyl]-1,2,2-triphenylethane (V), mp 175–176° (lit.[11] mp 177.5–179.5°), melting point undepressed upon admixture with an authentic sample prepared from the reaction of quaternary ion I with *n*-butyllithium.[12] The nmr spectrum of V (determined in deuteriochloroform) exhibited a singlet at 138 ± 1, a quartet[13] centered at 193 ± 1, with a coupling constant of 13, and a chemical-shift difference between these AB protons of 43, doublets at 283 and 342 ± 1 with a coupling constant of 12, and a multiplet centered at 433 ± 1 cps attributable to the N-methyl, benzylic, methylene, and aromatic protons, respectively.

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[9] Melting and boiling points are uncorrected. Vapor phase chromatograms were obtained on F and M Model 500 and 700 gas chromatographs using 6-ft silicone gum rubber and 5-ft Apiezon L columns.

[10] These values are reported as a range because of the small difference in the retention times of amines II and III.

[11] G. Wittig, R. Mangold, and G. Felletschin, *Ann.*, **560**, 116 (1948).

[12] K. P. Klein, D. N. Van Eenam, and C. R. Hauser, unpublished results.

[13] See J. C. Randall, J. J. McLeskey, III, P. Smith, and M. E. Hobbs, *J. Am. Chem. Soc.*, **86**, 3229 (1964).

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ortho-Substitution Rearrangement of Benzyltrimethylammonium Ion by the Methylsulfinyl Carbanion[1]

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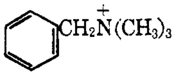
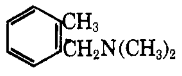
The *ortho*-substitution rearrangement of the benzyltrimethylammonium ion (I) to form II has previously been effected in high yield only by sodium amide[2] and potassium amide[3] in liquid ammonia at −33°. The yield with sodium amide is 90–95%.[2b]



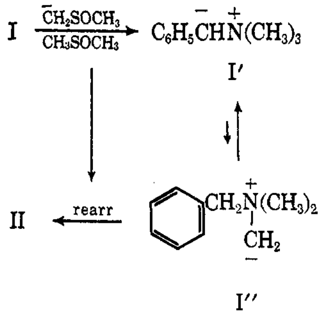
I



II

This rearrangement has now been brought about satisfactorily with the methylsulfinyl carbanion in dimethyl sulfoxide at 15–65°. The reaction presumably involves the intermediate formation of the benzyl and methyl carbanions, I′ and I″, respectively (Scheme I). In the analogous reaction with potassium amide in liquid ammonia, the intermediate benzyl carbanion I′ has been isolated as its benzophenone adduct.[3]

SCHEME I



In Table I are summarized the yields of rearranged amine II obtained from I with the sodium and lithium methylsulfinyl carbanions, which were prepared as described by Corey and Chaykovsky[4] by means of sodium hydride and *n*-butyllithium, respectively. The only other products detected were traces of a higher boiling amine and of a neutral fraction.

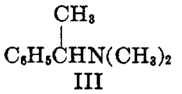
TABLE I

ortho-SUBSTITUTION REARRANGEMENT OF QUATERNARY ION I BY THE METHYLSULFINYL CARBANION IN DIMETHYL SULFOXIDE

Base	Temp, °C	Time, min	Yield of II, %
$NaCH_2SOCH_3$	15–20	60	85
$NaCH_2SOCH_3$	25–30	60	82
$NaCH_2SOCH_3$	25–30	10	81
$NaCH_2SOCH_3$	60–65	60	82
$LiCH_2SOCH_3$	25–30	60	85

Table I shows that the yields of II were 81–85%. Since the yield with the sodium methylsulfinyl carbanion was 81% after 10 min, the reaction appeared to be essentially complete after this time or, as indicated by a color change, within 2 min (see the Experimental Section). The rearrangement of I by sodium amide in liquid ammonia has similarly been observed to be very rapid.[2]

The rearranged amine II, obtained in the yields and under the conditions indicated in Table I, was pure by vpc; it was uncontaminated with the isomeric tertiary amines III and IV, the formations of which were possible through Stevens 1,2 shifts within ylids I′ and I″, respectively.



$$C_6H_5\overset{CH_3}{\overset{|}{C}}HN(CH_3)_2$$

III

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[1] Supported by the National Science Foundation.

[2] (a) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951); (b) W. R. Brasen and C. R. Hauser, *Org. Syn.*, **34**, 61 (1954).

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

[4] E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1345 (1965).