Ethyl β-Phenylcinnamate (II).—Ethyl acetate was condensed with benzophenone by means of lithium amide to form ethyl 3-hydroxy-3,3-diphenylpropionate,[13] which was dehydrated with formic acid to give ethyl 3,3-diphenylacrylate (II),[14] b.p. 144–147° at 0.8 mm., $n^{30}\text{D}$ 1.5892.

Ethyl β-Phenylcinnamate-α-d_1.—To a solution of 0.015 mole of sodium ethoxide (prepared from 0.35 g., 0.015 g. atom of sodium) in 22 g. (0.047 mole) of deuterioethanol was added 10 g. (0.04 mole) of ethyl β-phenylcinnamate. The resulting solution was refluxed for 60 hr., and then cooled to room temperature. The solvent was removed, and the residue was distilled to give 4.3 g. (43%) of recovered ester (slightly discolored), b.p. 143° at 1 mm. Redistillation gave colorless product IIa, b.p. 146–148° at 1.1 mm., $n^{25}\text{D}$ 1.5910. Analysis,[15] 4.97, 4.93 atom per cent. excess deuterium, indicated that the product contained 79% of IIa. No impurities were indicated by vapor phase chromatography.

Attempted Deuteration of Ethyl α-Phenylcinnamate (III).—α-Phenylcinnamic acid[16] was esterified with ethanol employing azeotropic removal of water with toluene[17] to give ethyl α-phenylcinnamate, b.p. 149–154° at 0.9–1.1 mm., $n^{26}\text{D}$ 1.5962–1.5993.

To a solution of 0.009 mole of sodium ethoxide (prepared from 0.20 g., 0.009 g. atom of sodium) in 22 g. (0.47 mole) of deuterioethanol was added 10 g. (0.04 mole) of ethyl α-phenylcinnamate and the solution refluxed for 60 hr. Distillation gave 9.6 g. (96%) of recovered ethyl α-phenylcinnamate, b.p. 135° at 0.6 mm., $n^{26}\text{D}$ 1.5989. Analysis[15] indicated no uptake of deuterium within the limit of accuracy of the method (0.02 D atom/molecule). The infrared spectrum of the recovered ester was essentially identical with that of an authentic sample.

Chalcone-α-d_1 (IV).—To a solution of 0.01 mole of sodium ethoxide (prepared from 0.01 g. atom of sodium) in 42 g. (0.9 mole) of deuterioethanol maintained at 0° was added 19.0 g. (0.09 mole) of chalcone in 75 ml. of anhydrous ether. After standing at 0° for 48 hr., the ether and the deuterioethanol were removed under reduced pressure. The residue was taken up in 100 ml. of anhydrous ether and filtered. The ethereal solution was washed rapidly with three portions of cold water, and dried over magnesium sulfate. The solvent was removed under reduced pressure to leave a yellow solid, which was recrystallized from 25 ml. of absolute ethanol to give 8.0 g. (42%) of recovered chalcone, m.p. 53–57°. Analysis,[12] 6.33 atom per cent excess deuterium, indicated that the product contained 76% of IV. Vapor phase chromatography indicated that the material was pure.

Cinnamonitrile-α-d_1.—To a solution of 0.01 mole of sodium ethoxide (prepared from 0.25 g., 9.01 g. atom of sodium) in 49 g. (1.05 mole) of deuterioethanol was added 13.5 g. (0.01 mole) of *trans*-cinnamonitrile. After stirring 4 days at room temperature, the ethanol was removed under reduced pressure. The residue was taken up in anhydrous ether and the mixture was filtered. The ethereal filtrate was washed with cold water, and dried over magnesium sulfate. The solvent was removed, and the residue was distilled to give 8.1 g. (60%) of recovered nitrile, b.p. 110–116° at 8.5–10 mm. During the course of the distillation the refractive index decreased. Vapor phase chromatography of the product indicated the presence of two principal components having the same retention times as *cis*- and *trans*-cinnamonitriles. Analysis,[12] 10.7 atom per cent excess deuterium, indicated that the product contained 75% of the deuterionitriles.

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[13] W. R. Dunnevant and C. R. Hauser, *J. Org. Chem.*, **25**, 1693 (1960).

[14] W. S. Johnson and H. J. Glenn, *J. Am. Chem. Soc.*, **71**, 1087 (1949).

[15] Dr. Josef Nemeth, Urbana, Ill.

[16] R. E. Buckles and K. Bremer, *Org. Syntheses*, **33**, 70 (1953).

[17] See V. M. Micovic, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 264.

[CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM & HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA]

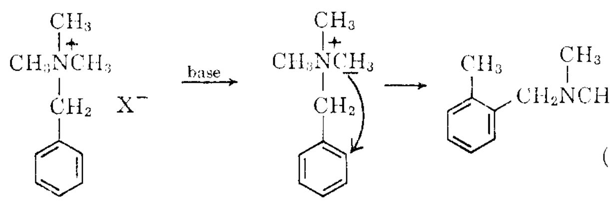
Sommelet–Hauser Rearrangement of Allylbenzyldimethylammonium Bromide and Cyclopropylcarbinylbenzyldimethylammonium Bromide. Evidence for Carbanion Stabilization by the Cyclopropane Ring[1]

BY CARL L. BUMGARDNER

RECEIVED AUGUST 27, 1962

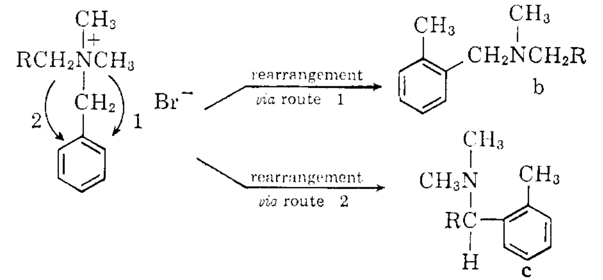
Treatment of cyclopropylcarbinylbenzyldimethylammonium bromide (Ia) with sodium amide in liquid ammonia gives mainly cyclopropyl-*o*-tolylcarbinyldimethylamine (Ic) along with small amounts of cyclopropylcarbinylmethyl-*o*-xylylamine (Ib) and benzylcyclopropylcarbinyldimethylamine (IV). Similar treatment of 3-phenylpropylbenzyldimethylammonium bromide (IIa) results in a mixture consisting of approximately 74% of 3-phenylpropyl-*o*-xylylmethylamine (IIb) and 26% of β-phenylethyl-*o*-tolylcarbinyldimethylamine (IIc). Allylbenzyldimethylammonium bromide (IIIa) under similar conditions yields *o*-tolylvinylcarbinyldimethylamine (IIIc), allylphenylcarbinyldimethylamine (V), benzylvinylcarbinyldimethylamine (VI) and 4-phenylbutyraldehyde. These results are rationalized by postulating that the carbanion derived from the cyclopropylcarbinyl group is stabilized by the cyclopropane ring.

The Sommelet or *ortho* substitution rearrangement is illustrated in eq. 1 using benzyltrimethylammonium halide as an example. Hauser and co-workers,[2] who



(1)

recently have elucidated the nature of this reaction, observed that sodium or potassium amide in liquid ammonia is a particularly effective reagent for promoting rearrangement into the *o*-position. If one of the methyl groups in benzyltrimethylammonium halide is replaced by a different substituent, rearrangement can proceed by different pathways which lead to isomers. These competing rearrangements, therefore, afford an opportunity to study the relative reactivity of different types of carbanions. To compare the carbanion derived from the cyclopropylcarbinyl group with saturated and unsaturated carbanions, we have studied the reaction of sodium amide in liquid ammonia with the following compounds: cyclopropylcarbinylbenzyldimethylammonium bromide (Ia), 3-phenylpropylbenzyldimethylammonium bromide (IIa) and allylbenzyldimethylammonium bromide (IIIa).



I, R = cyclopropyl
II, R = β-phenylethyl
III, R = vinyl

[1] Sponsored under Army Ordnance Contract DA-01-021-ORD-11878. A portion of this work was presented at the Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., November 3–5, 1960.

[2] (a) C. R. Hauser, R. M. Manyik, W. R. Brasen and P. L. Bayless, *J. Org. Chem.*, **20**, 1119 (1955); (b) C. R. Hauser, A. J. Weinheimer, *J. Am. Chem. Soc.*, **76**, 1264 (1954); (c) S. W. Kantor and C. R. Hauser, *ibid.*, **73**, 4122 (1951); (d) W. Q. Beard, Jr., and C. R. Hauser, *J. Org. Chem.*, **25**, 334 (1960); (e) W. Q. Beard, Jr., and C. R. Hauser, *ibid.*, **26**, 371 (1961); (f) F. N. Jones and C. R. Hauser, *ibid.*, **27**, 1542 (1962).

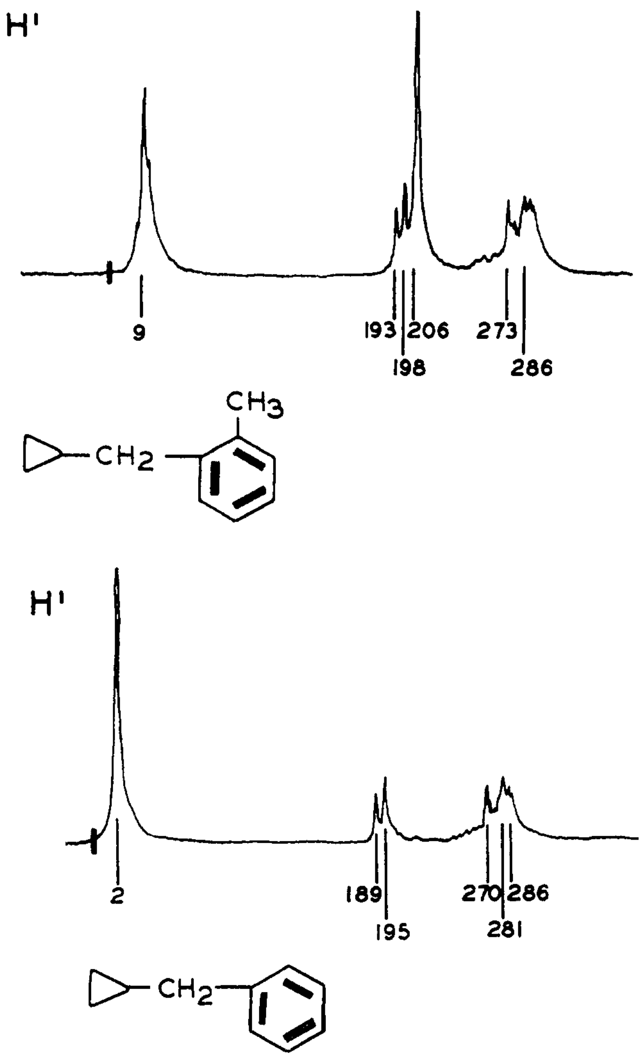


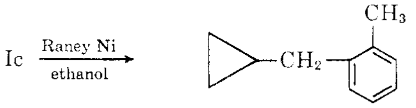
Fig. 1.—N.m.r. spectrum of cyclopropyl-*o*-tolylmethane and cyclopropylphenylmethane.

Cyclopropylcarbinylbenzyldimethylammonium bromide was prepared by treating cyclopropylcarbinyldimethylamine in benzene with benzyl bromide. The tertiary amine was obtained by methylation of cyclopropylcarbinylamine[3] with formic acid and formaldehyde. The n.m.r. spectrum of cyclopropylcarbinyldimethylamine prepared in this way indicates that no isomerization occurred during reductive methylation (see Experimental). 3-Phenylpropylbenzyldimethylammonium bromide (IIa) was available from a previous study.[4] Allylbenzyldimethylammonium bromide (IIIa) was prepared from allyl bromide and benzyldimethylamine.

Results

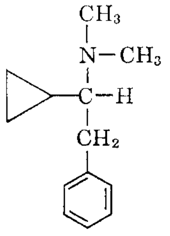
Treatment of bromide Ia with sodium amide in liquid ammonia produced a mixture of three isomeric amines in 88% yield. The mixture was resolved by gas phase chromatography and the components isolated. The major isomer, accounting for 73% of the mixture, was found to be cyclopropyl-*o*-tolylcarbinyldimethylamine (Ic). The n.m.r. spectrum of this amine shows signals at −11 c.p.s.[5] (phenyl), 176 and 179 c.p.s. (methyls) and 262 c.p.s. (cyclopropyl). Signal areas indicate that the ratio of N-methyl to C-methyl protons is 2:1, respectively. The infrared spectrum has bands at 3110 cm.$^{-1}$ (cyclopropyl hydrogen) and 1030 cm.$^{-1}$ (cyclopropyl ring) but no absorption in the double bond region.

Degradation of amine Ic by hydrogenolysis substantiated the n.m.r. analysis (eq. 2). Since the dimethylamino group is benzylic, it should be cleaved readily from amine Ic by treatment with Raney nickel.[6] Cyclopropyl-*o*-tolylmethane, the expected hydrocarbon, was obtained and characterized by comparing its n.m.r. spectrum with that of cyclopropylphenylmethane[7] (Fig. 1). Figure 1 shows that the two spectra are essentially superimposable except for the peak at 206 c.p.s.[5] due to the methyl protons in cyclopropyl-*o*-tolylmethane. A strong band at 755 cm.$^{-1}$ in the infrared spectrum of cyclopropyl-*o*-tolylmethane indicates that the methyl group is *ortho* to the cyclopropyl methyl substituent.



(2)

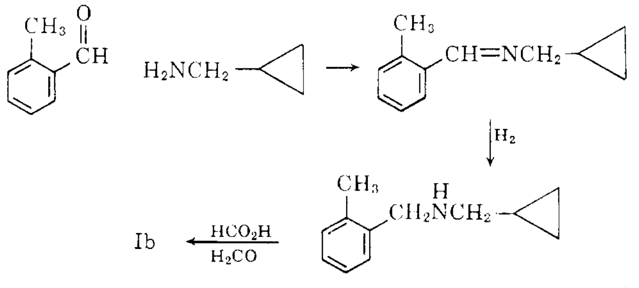
The remaining isomers produced by rearrangement of bromide Ia are assigned structure Ib (cyclopropylcarbinylmethyl-*o*-xylylamine) and structure IV (benzylcyclopropylcarbinyldimethylamine) which represent, respectively, approximately 18% and 9% of the amine mixture.



IV

Isomer Ib has resonances in its n.m.r. spectrum at −13 c.p.s.[5] (phenyl), 135 c.p.s. (methylene), 177 and 187 c.p.s. (methyls) and 251 c.p.s. (cyclopropyl). A strong band at 741 cm.$^{-1}$ in the infrared indicates an *o*-disubstituted benzene derivative. Direct comparison with an authenic specimen, independently prepared as shown in Chart 1, verified the assignment.

CHART 1



The Schiff base formed by condensation of cyclopropylcarbinylamine with *o*-tolualdehyde was hydrogenated catalytically and the resulting secondary amine was then methylated to yield amine Ib.

The identity of amine IV was also established by an independent synthesis. Application of the Leuckart reaction to benzyl cyclopropyl ketone gave benzylcyclopropylcarbinylamine which was methylated with formic acid and formaldehyde. The starting ketone was prepared from cyclopropyl cyanide and benzyl Grignard reagent (see Experimental).

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(3) J. D. Roberts and R. M. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(4) C. L. Bumgardner, *ibid.*, **83**, 4420 (1961).

(5) Referred to external benzene; negative values indicate resonance at lower field than the standard. Neat liquids at 25° were analyzed using a 40-mc. probe.

(6) W. H. Hartung and R. Simonoff, "Organic Reactions," Vol. VII, ed. by R. Adams, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 263.

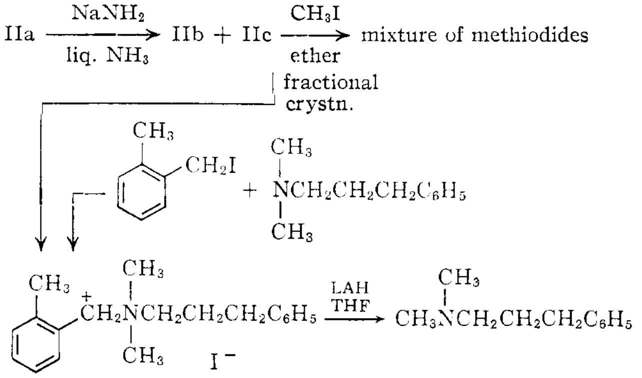
(7) M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 1886 (1960).

Treatment of bromide IIa with sodium amide in liquid ammonia gave in 35% yield[8] the mixture of amines shown in eq. 3.

$$\text{IIc, } 26\% \longleftarrow \text{IIa} \longrightarrow \text{IIb, } 74\% \qquad (3)$$

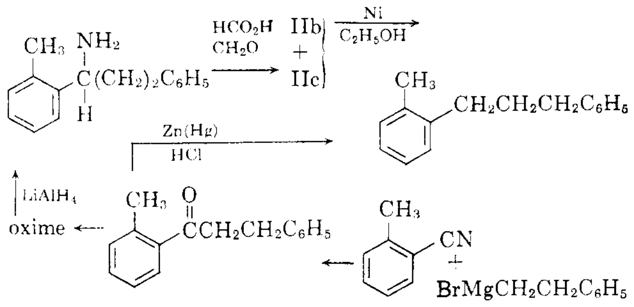
The mixture consists of 74% of 3-phenylpropyl-*o*-xylylmethylamine (IIb) and 26% of β-phenylethyl-*o*-tolylcarbinyldimethylamine (IIc) according to gas phase chromatographic analysis.[9] The structures IIb and IIc were inferred from evidence presented in Charts 2 and 3.

CHART 2



Methylation with methyl iodide of the amine mixture (Chart 2) gave a mixture of methiodides from which a pure isomer was obtained by fractional crystallization from alcohol. Cleavage of this methiodide with lithium aluminum hydride in tetrahydrofuran yielded 3-phenylpropyldimethylamine, the product expected from hydride attack at the reactive benzyl position.[10] An independent synthesis involving alkylation of 3-phenylpropyldimethylamine with *o*-xylyl iodide confirmed the structure of the methiodide and established the presence of amine IIb, its precursor, in the mixture.

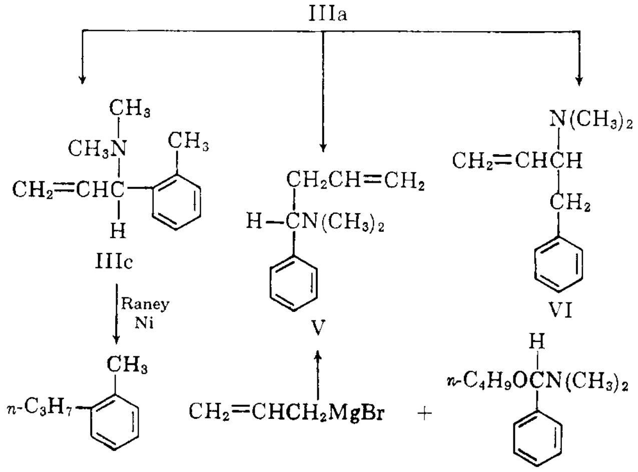
CHART 3



In Chart 3 are outlined the steps by which the structure of the remaining isomer was determined. The amine mixture was treated with Raney nickel in refluxing ethanol and yielded 1-*o*-tolyl-3-phenylpropane. Isolation of this hydrocarbon suggested that IIc was present in the amine mixture since the dimethylamino group should undergo facile cleavage from the benzyl position.[6] This inference was confirmed by the independent synthesis shown. Reaction of the Grignard reagent from β-phenylethyl bromide with *o*-methylbenzonitrile gave β-phenylethyl *o*-tolyl ketone. A sample of this ketone was reduced by the Clemmensen method to 1-*o*-tolyl-3-phenylpropane, the same hydrocarbon isolated from the hydrogenolysis experiment. Another sample of β-phenylethyl *o*-tolyl ketone was converted to its oxime which was reduced with lithium aluminum hydride. The primary amine which resulted was methylated with formic acid and formaldehyde to give the tertiary amine IIc. Retention times (gas phase chromatography) and comparison of infrared spectra indicate that this synthetic sample and the minor component of the amine mixture are identical.

When bromide IIIa was allowed to react with sodium amide in liquid ammonia, a mixture of isomers was isolated in 20% yield. Gas phase chromatography resolved the mixture into three components (Chart 4), *o*-tolylvinylcarbinyldimethylamine (IIIc), allylphenylcarbinyldimethylamine (V) and benzylvinylcarbinyldimethylamine (VI). Amine IIIc accounted for 32% of the mixture, amine V, 18%, and amine VI, 50%. In addition, 4-phenylbutyraldehyde was isolated by distillation of the acid-insoluble fraction.[11]

CHART 4



The n.m.r. spectrum of amine IIIc has resonances centered at −4 c.p.s.[5] (phenyl), 67 c.p.s. (vinyl), 127 and 135 c.p.s. (methynyl) and at 187 and 192 c.p.s. (C–methyl and N–methyl). The infrared spectrum shows strong bands at 918 cm.$^{-1}$ (terminal methylene) and at 757 cm.$^{-1}$ (*o*-disubstituted benzene). Treatment of IIIc with Raney nickel in refluxing ethanol yielded *n*-propyl-2-methylbenzene. Amine V was identified by hydrogenolysis to *n*-butylbenzene and by comparison with an authenic sample prepared by the general method described by Stewart and Hauser[12] for synthesis of α-substituted benzylamines. Signals in the n.m.r. spectrum of amine VI are observed at −10 c.p.s.[5] (phenyl), 71 c.p.s. (vinyl), 161 and 164 c.p.s. (methynyl and methylene), and 187 c.p.s. (methyl). Strong bands in the infrared spectrum are present at 922 cm.$^{-1}$ (terminal methylene) and at 700 cm.$^{-1}$ (monosubstituted benzene). Identification of VI was completed by synthesizing an authenic sample according to the directions of Thomson and Stevens[13] and comparing infrared spectra.

Discussion

The results are reviewed in Table I. For purposes of comparison, results of the Sommelet rearrangement of dibenzyldimethylammonium chloride (VII), previously reported by Kantor and Hauser,[2c] are included.

Table I and eq. 3 show that in the case of bromide IIa rearrangement by route 1 is favored by a factor of about 2.8. Since this value is close to the ratio of α-methyl hydrogen atoms to non-benzylic α-methylene

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[8] A competing elimination reaction accounts for the low yield. The elimination products are considered in ref. 4.

[9] These results are comparable to those recently reported by Jones and Hauser[2f] for rearrangement of *n*-propylbenzyldimethylammonium bromide.

[10] A. C. Cope, E. Ciganek, L. J. Fleckenstein and M. A. P. Meisinger, *J. Am. Chem. Soc.*, **82**, 4651 (1960).

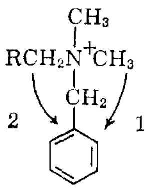
[11] Jenny and Druey, ref. 22, recently mentioned obtaining amine VI and 4-phenylbutyraldehyde from rearrangement of bromide IIIa.

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

[13] T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 1932 (1932).

Table I

Sommelet Rearrangement of



	Compound, R =	Preferred reaction route
Ia	Cyclopropyl	2
IIa	β-Phenylethyl	1
IIIa	Vinyl	2
VII	Phenyl[a]	2

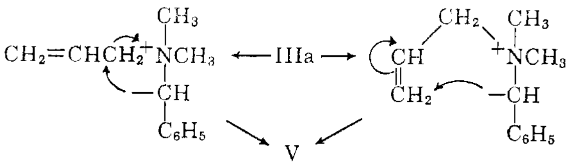
[a] Ref. 2c.

hydrogen atoms in bromide IIa, the rearrangement appears to be virtually indiscriminate.[14]

With bromide IIIa and with dibenzyldimethylammonium chloride, the situation is reversed, and an overriding preference for route 2 is shown. These two quaternary compounds, with base, can produce carbanions which are stabilized by delocalization into the unsaturated systems. Table I places bromide Ia in the unsaturated category with bromide IIIa and dibenzyldimethylammonium chloride. This similarity in reactivity suggests that the carbanion derived from the cyclopropylcarbinyl group is stabilized by the small ring.[15]

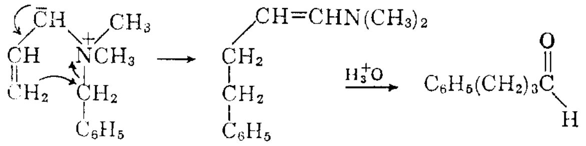
Some electron delocalization has been invoked to account for the dipole moment of cyclopropyl chloride,[16] the pK_a of cyclopropylamine[17] and the course of hydrogenation of certain unsaturated cyclopropane derivatives.[18,19]

Although amine IIIc results from Sommelet rearrangement of bromide IIIa, amine V may arise from either an allylic rearrangement or from a 1,2-shift (eq. 4).[13,20] Phenylbutyraldehyde probably comes

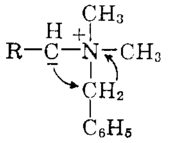


(4)

from hydrolysis of the vinylamine resulting from the allylic rearrangement given in eq. 5.[21] The 1,2-rearrangement shown below can account for amines VI and



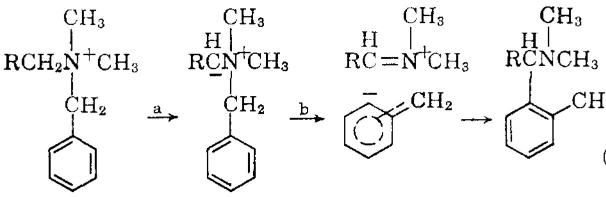
(5)



R = vinyl and cyclopropyl

IV. These conversions, involving stabilized carbanions, afford additional examples of rearrangements other than *o*-substitution occurring in the sodium amide–liquid ammonia system.[2]

An alternate pathway for rearrangement of bromides Ia–IIIa is pictured in eq. 6.[22] If this equation accurately describes the *o*-substitution rearrangement, step a appears to be rate-determining.[23] In such a case the greater reactivity of the cyclopropylcarbinyl group relative to methyl in bromide Ia would still depend on the ability of the cyclopropane ring to stabilize the adjacent developing negative charge. We conclude, therefore, that regardless of the exact mechanism, our results can best be interpreted in terms of carbanion stabilization by the cyclopropane ring.



(6)

Experimental[24]

Cyclopropylcarbinylbenzyldimethylammonium Bromide (Ia).—Cyclopropylcarbinyldimethylamine was prepared by treating

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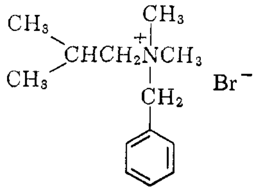
[14] In the case of bromide i (see ref. 2f), rearrangement by route 1 is favored even more strongly than in compound IIa. This rules out the possibility that a steric effect, due to branching at the β-carbon atom, is re-



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sponsible for compound Ia's preference for route 2.

[15] Analogous interactions involving a cyclopropane ring and other atoms may be important in certain reactions of cyclopropanols [C. H. DePuy, Abstracts of Papers, Meeting of the American Chemical Society, Washington, D. C., March 26–29, 1962], cyclopropylamines [C. Kaiser, A. Burger, L. Zirngibl, C. S. Davis and Charles L. Zirkle, *J. Org. Chem.*, **27**, 768 (1962)], cyclopropylcarbinyl halides [M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Ruchardt and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 2647 (1960)], ethyl 2-vinylcyclopropane-1,1-dicarboxylate [R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *J. Chem. Soc.*, 3616 (1952)] and methyl 2-carbomethoxycyclopropaneacetate [E. F. Ullman and W. J. Fanshawe, *J. Am. Chem. Soc.*, **83**,2379 (1961)].

[16] M. T. Rogers and J. D. Roberts, *ibid.*, **68**, 843 (1946).

[17] J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5030 (1951).

[18] E. F. Ullman, *ibid.*, **81**, 5386 (1959).

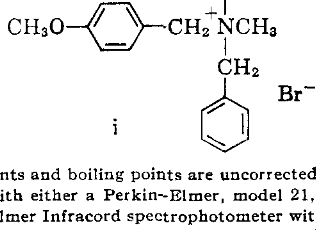
[19] Trachtenberg and Odian [*ibid.*, **80**, 4018 (1958)] and Cannon, Santilli and Shenian [*ibid.*, **81**, 4264 (1959)] have concluded that transmission of conjugation by the cyclopropane ring does not occur. The latter workers found that compounds such as diethyl 2-methylcyclopropane-1,2-dicarboxylate fail to undergo base-catalyzed deuterium exchange or alkylation reactions typical of active hydrogen compounds. A comparison of the Hammett ρ-value for dissociation of *trans*-2-phenylcyclopropanecarboxylic acid with those of *trans*-cinnamic acid and β-phenylpropionic acid led Trachtenberg and Odian to the conclusion that the cyclopropane ring is unable to transmit conjugation in the ground state. These findings, though, are not inconsistent with the cyclopropane ring functioning as an electron sink in the reactions reported in this paper.

[20] This type of reaction is generally known as the Stevens rearrangement which is discussed in refs. 2 and 22.

[21] H. Hellmann and G. M. Scheytt, *Ann.*, **654**, 39 (1962), have isolated valeraldehyde from rearrangement of allyltrialkylammonium salts.

[22] E. F. Jenny and J. Druey [*Angew. Chem. internat. Edit.*, **I**, 155 (1962)] recently have proposed that the Stevens(1,2) rearrangement proceeds by a mechanism which involves elimination and recombination rather than internal nucleophilic displacement.

[23] See results of rearrangement of salt i, ref. 2e.



i

[24] Melting points and boiling points are uncorrected. Infrared spectra were determined with either a Perkin-Elmer, model 21, spectrophotometer or with a Perkin-Elmer Infracord spectrophotometer with a sodium chloride prism. Nuclear magnetic resonance spectra were obtained with a Varian

cyclopropylcarbinylamine[3] with formic acid and formaldehyde using the procedure described[25] for converting β-phenylethylamine to β-phenylethyldimethylamine. For example, from 14.2 g. of cyclopropylcarbinylamine, 17.2 g. (87%) of **cyclopropylcarbinyldimethylamine**, b.p. 96–100°, was obtained. Redistillation through a 30 × 0.5-cm. spinning band column yielded an analytical sample having b.p. 98°, n^{20}D 1.4185. The n.m.r. spectrum showed signals at 179 c.p.s. (methyl), 188 c.p.s. (methylene) and 249 and 267 c.p.s. (cyclopropyl) in the proper ratios for cyclopropylcarbinyldimethylamine.

Anal. Calcd. for $C_6H_{13}N$: C, 72.66; H, 13.21; N, 14.12. Found: C, 72.45; H, 13.36; N, 13.91.

Bromide Ia was obtained by allowing 13.3 g. of cyclopropylcarbinyldimethylamine to react with 22.9 g. of benzyl bromide in 200 ml. of benzene. After the mixture was refluxed for 12 hr., the two layers which resulted were allowed to stand for several days. The hygroscopic solid which formed was removed by filtration, washed with benzene, and pulverized under ligroin. The mixture was filtered and the separated white solid was dried in a vacuum desiccator. Bromide Ia (13.5 g.), m.p. 96–97°, was obtained in 37% yield.

Anal. Calcd. for $C_{13}H_{20}NBr$: C, 57.78; H, 7.46; N, 5.18. Found: C, 57.40; H, 7.73; N, 5.21.

Rearrangement of Cyclopropylcarbinylbenzyldimethylammonium Bromide (Ia).—To 100 ml. of liquid ammonia containing 0.07 mole of sodium amide was added, during 15 min., 13.0 g. of bromide Ia. Because bromide Ia is hygroscopic, it was distributed under nitrogen among twelve vials which were then tightly closed and placed in a desiccator. These vials were removed, one at a time, from the desiccator, and their contents quickly discharged into the liquid ammonia mixture. A light green color was observed immediately after each portion of the bromide was added. The mixture was stirred for 100 min.; then 5 g. of ammonium chloride was added. Ether (100 ml.) was introduced dropwise, the Dry Ice condenser was replaced by a water condenser, and the ammonia was allowed to evaporate overnight. Water was then added and the resulting layers separated. The ether solution was extracted with two 50-ml. portions of 10% hydrochloric acid solution. The combined acid extracts were made strongly alkaline with 10% sodium hydroxide solution and the oil which separated was extracted with ether. The ether extract was washed with water and dried over magnesium sulfate. Distillation through a small Vigreux column yielded 8.0 g. (88%) of a colorless oil, b.p. 96–98° (5 mm.).

Anal. Calcd. for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.67; H, 10.29; N, 7.58.

Gas phase chromatography indicated that the oil consisted of three components; the major one, accounting for 73% of the mixture, was shown (see below) to be **cyclopropyl-*o*-tolylcarbinyldimethylamine (Ic)**. Chromatography was performed at 167° using a 10 ft. × 0.25-in. column packed with Carbowax 20 M on 35/80 mesh Chromosorb in the ratio 1:3, respectively. Helium was employed as carrier, a thermal conductivity cell as detector. The salient features of the n.m.r. and infrared spectra of the isolated components are given in the Results section.

Raney Nickel Cleavage of Cyclopropyl-*o*-tolylcarbinyldimethylamine (Ic).—A mixture of 43 g. of wet No. 28 Raney active nickel catalyst (Raney Catalyst Co., Chattanooga, Tenn.), 115 ml. of absolute ethanol and 2.69 g. of amine Ic (described above) was stirred and refluxed for 24 hr. The mixture was filtered and the filtrate was poured into 1 l. of water. The oil which resulted was extracted with four 100-ml. portions of ether. The ether solution was washed with 10% hydrochloric acid solution, water, 5% sodium bicarbonate solution, water, and dried over magnesium sulfate. Distillation through a semi-micro column gave 1.05 g. (64%, based on amine consumed, see below) of **cyclopropyl *o*-tolylmethane**, b.p. 99–102° (18 mm). An analytical sample had n^{28}D 1.5151. The n.m.r. spectrum of cyclopropyl-*o*-tolylmethane appears in Fig. 1.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.14; H, 9.91.

From the aqueous hydrochloric acid solution mentioned above, 0.55 g. of amine Ic, identified by its infrared spectrum, was recovered by adding an excess of alkali, extracting the liberated amine with ether, and distilling.

Cyclopropylcarbinylmethyl-*o*-xylylamine (Ib).—Condensation of 3.68 g. of cyclopropylcarbinylamine[3] with 6.2 g. of *o*-tolualdehyde (K & K Laboratories, Jamaica 33, N. Y.) according to the general directions of Campbell, *et al.*,[26] gave *o*-xylylidenecyclopropylcarbinylamine, b.p. 115–116° (4 mm.), n^{20}D 1.5494, in 67% yield.

Anal. Calcd. for $C_{12}H_{15}N$: C, 83.19; H, 8.73. Found: C, 83.00; H, 8.75.

This Schiff base (3.04 g.) took up 99% of one molar equivalent of hydrogen on catalytic hydrogenation (PtO_2–ethanol) and **cyclopropylcarbinyl-*o*-xylylamine**, b.p. 83–84° (0.5 mm.), was isolated in 77% yield.

Anal. Calcd. for $C_{12}H_{17}N$: C, 82.16; H, 9.78. Found: C, 80.77; H, 9.51.

Methylation of this secondary amine (2.09 g.) with formic acid and formaldehyde[25] gave **cyclopropylcarbinylmethyl-*o*-xylylamine** (Ib), b.p. 72–74° (0.4 mm.), in 69% yield. The n.m.r. and infrared spectra showed this compound to be the same as the amine which constituted 18% of the mixture from rearrangement of bromide Ia (see above).

Anal. Calcd. for $C_{13}H_{19}N$: C, 82.48; H, 10.12. Found: C, 82.46; H, 10.46.

Benzylcyclopropylcarbinyldimethylamine (IV).—Reaction of cyclopropyl cyanide and benzyl Grignard reagent gave, after acid hydrolysis, cyclopropyl benzyl ketone (65% yield), b.p. 90–96° (0.75–1 mm.), n^{20}D 1.5325, $\nu_{C=O}$ 1700 cm.$^{-1}$ (neat).

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 81.74; H, 7.64.

This ketone was treated with ammonium formate according to the directions given by Ingersoll[27] for preparation of α-phenylethylamine from acetophenone. Benzylcyclopropylcarbinylamine, b.p. 90–92° (0.3 mm.), was isolated in 44% yield.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38. Found: C, 81.59; H, 9.22.

Methylation of the primary amine with formic acid and formaldehyde[25] produced **benzylcyclopropylcarbinyldimethylamine** (IV) (40% yield),[28] b.p. 94–96° (0.4 mm.). The infrared and n.m.r. spectra showed this material to be the same as the component which accounted for 9% of the amine mixture isolated from rearrangement of bromide Ia (see above).

Anal. Calcd. for $C_{13}H_{19}N$: C, 82.33; H, 10.28. Found: C, 82.29; H, 10.01.

Rearrangement of 3-Phenylpropylbenzyldimethylammonium Bromide (IIa).—To 400 ml. of liquid ammonia containing 0.3 mole of sodium amide, 66.8 g. of bromide IIa[4] was added during 50 min. The color of the mixture changed during this addition from a light green to a dark bronze shade. After the mixture was stirred for 4 hr., 10 g. of ammonium chloride was added and the amine products were isolated by steps similar to those described above for isolating amine Ic.

Distillation through a short, glass helices packed column separated 9.6 g. (36%) of 3-phenylpropyldimethylamine,[29] b.p. 87–90° (35 mm.), identified by its infrared spectrum,[4] from a higher boiling residue. This residue gave, upon distillation through a Claisen head, 17.6 g. (35%) of a mixture of amines, b.p. 137–142° (1.5 mm.), n^{28}D 1.5465–1.5460.

Anal. Calcd. for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.53. Found: C, 85.56; H, 9.43; N, 5.56.

Gas phase chromatography at 232° using a 6 ft. × 0.5 cm. column packed with Dow Corning silicone oil 710 on 80/100 mesh Chromosorb in the ratio of 1:4 indicated that the mixture consisted of approximately **74% of 3-phenylpropyl-*o*-xylylmethylamine (IIb) and 26% of β-phenylethyl-*o*-tolylcarbinyldimethylamine (IIc).**

3-Phenylpropyl-*o*-xylyldimethylammonium Iodide (IIb Methiodide). (a).—Methyl iodide (6 ml.) was added to 40 ml. of anhydrous ether containing 5.00 g. of the amine mixture obtained from rearrangement of bromide IIa (described above). The mixture was stored in a dark cabinet for 5 days, after which time white crystals were observed suspended in the solvent above an amorphous yellow residue. Filtration separated 2.64 g. (34%) of the white solid, m.p. 135–138°, from the yellow residue (no definite m.p.) which adhered to the bottom of the flask. An analytical sample of the white solid, shown below to be the methiodide of IIb, was recrystallized from alcohol.

Anal. Calcd. for $C_{19}H_{26}NI$: N, 3.54. Found: N, 3.26.

The yellow residue, upon recrystallization from alcohol–ether, gave an additional 1.69 g. of IIb methiodide as white crystals, m.p. 133–136°. The total yield of methiodide IIb was 57%.

(b).—A solution of 3.9 g. of 3-phenylpropyldimethylamine[4] in anhydrous ether was treated with 5.6 g. of *o*-xylyl iodide prepared from the reaction of sodium iodide in acetone with *o*-xylyl bromide (K & K Laboratories, Jamaica 33, N. Y.). The mixture

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Associates, model V-3000-B, high resolution spectrometer using a 40-mc. probe.

(25) R. N. Icke, B. B. Wisegarver and G. A. Allis, "Organic Syntheses," Coll. Vol. III, ed. by E. C. Horning, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 723.

(26) K. N. Campbell, A. H. Sommers and B. K. Campbell, *J. Am. Chem. Soc.*, **66**, 82 (1944).

(27) A. W. Ingersoll, "Organic Syntheses," Coll. Vol. II, ed. by A. H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 503.

(28) Another product, whose structure will be discussed in a subsequent publication, was also obtained.

(29) This amine is a product of the elimination reaction which bromide IIa undergoes, see ref. 4.

was allowed to stand overnight and filtered, giving 8.7 g. (92%) of crude IIb methiodide. An analytical sample which was recrystallized from absolute ethanol melted at 135–137° and did not depress the melting point of the methiodide described above in (a).

Anal. Calcd. for $C_{19}H_{26}NI$: C, 57.72; H, 6.63; N, 3.54. Found: C, 57.57; H, 6.86; N, 3.31.

Lithium Aluminum Hydride Cleavage of IIb Methiodide.—A mixture of 2.64 g. of IIb methiodide, obtained as described above in (a), 2.12 g. of lithium aluminum hydride and 63 ml. of dry tetrahydrofuran was treated in a manner similar to that described[30] for lithium aluminum hydride cleavage of *cis*-2-phenylcyclohexyltrimethylammonium iodide. 3-Phenylpropyldimethylamine, identified by its infrared spectrum,[4] was isolated in 26% yield.

Raney Nickel Cleavage of Amine Mixture from Bromide IIa.—A solution of 6.9 g. of the amine mixture resulting from rearrangement of bromide IIa (described above) in 200 ml. of absolute ethanol was stirred and refluxed with 75 g. of wet No. 28 Raney active nickel catalyst (Raney Catalyst Co., Chattanooga, Tenn.) for 24 hr. **1-*o*-Tolyl-3-phenylpropane**, b.p. 120–121° (0.5 mm.), n^{27}D 1.5511, was isolated in 31% yield by steps similar to those described above for isolating cyclopropyl-*o*-tolylmethane.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.55; H, 8.83.

The n.m.r. spectrum of 1-*o*-tolyl-3-phenylpropane had signals at −3 c.p.s.[5] (phenyl), 181 c.p.s. (methylene) and 193 c.p.s. (methyl). This same hydrocarbon, according to a comparison of infrared and n.m.r. spectra, was obtained by reducing β-phenylethyl *o*-tolyl ketone (described below) with zinc and hydrochloric acid by a procedure similar to that described for reducing *o*-heptanoylphenol.[31]

β-Phenylethyl-*o*-tolylcarbinyldimethylamine (IIc).—Reaction of the Grignard reagent derived from β-phenylethyl bromide with *o*-methylbenzonitrile by a procedure similar to that given for preparation of methyl 9-phenanthryl ketone[32] produced β-phenylethyl *o*-tolyl ketone, b.p. 115° (0.1 mm.), n^{20}D 1.5741, $\nu_{C=O}$ 1680 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.67; H, 7.21.

The oxime was prepared in 95% yield by treating the above ketone with hydroxylamine hydrochloride in pyridine and absolute ethanol in a manner similar to that used to oximate phenyl *o*-tolyl ketone.[33]

The crude oxime was reduced directly with lithium aluminum hydride in ether by a procedure patterned after that employed for reduction of methyl *p*-chlorophenylketoxime.[34] β-Phenylethyl-*o*-tolylcarbinylamine, b.p. 149–152° (0.27 mm.), ν_{N-H} 3330 cm.$^{-1}$, was obtained in 65% yield. An analytical sample had b.p. 152° (0.27 mm.), n^{21}D 1.5762.

Anal. Calcd. for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.26; H, 8.53; N, 6.08.

Methylation of this amine with formic acid and formaldehyde by a procedure similar to that described[25] for methylation of β-phenylethylamine gave **β-phenylethyl-*o*-tolylcarbinyldimethylamine** in 75% yield. An analytical sample had b.p. 138° (0.35 mm.), n^{20}D 1.5549.

Anal. Calcd. for $C_{18}H_{23}N$: C, 85.32; H, 9.15; N, 5.53. Found: C, 85.48; H, 9.41; N, 5.34.

Amine IIc prepared by this route showed the same infrared spectrum and retention time on chromatography (see above) as the minor component isolated from the amine mixture from bromide IIa (described above).

Allylbenzyldimethylammonium Bromide (IIIa).—A mixture of 12.1 g. of allyl bromide and 13.5 g. of benzyldimethylamine in 200 ml. of benzene was stirred and refluxed for 22 hr. The mixture consisting of a layer of sirup beneath the solvent, was allowed to stand at room temperature for 3 days; then the solvent was removed under reduced pressure. The white, hygroscopic solid which remained was dried under reduced pressure and yielded 22.5 g. (88%) of bromide IIIa, m.p. 98–100°.[13]

Anal. Calcd. for $C_{12}H_{18}NBr$: C, 56.26; H, 7.08; N, 5.47. Found: C, 56.35; H, 7.11; N, 5.66.

Rearrangement of Allylbenzyldimethylammonium Bromide (IIIa).—Bromide IIIa (20 g.) was treated with 0.12 mole of sodium amide in 200 ml. of liquid ammonia by the procedure given above for reaction of bromide Ia. The infrared spectrum of the crude basic fraction indicated the presence of a carbonyl-bearing compound (band at 1730 cm.$^{-1}$), which was removed by dissolving the mixture in 10% hydrochloric acid solution, washing with ether, adding an excess of 10% sodium hydroxide solution to the acid solution, extracting the liberated amines, and distilling. A total of 2.56 g. (19%), b.p. 98–104° (14 mm.), n^{20}D 1.5105–1.5133, of the amine mixture discussed below was obtained.[35] Distillation of the acid-insoluble fraction gave in 4% yield 4-phenylbutyraldehyde (*cf.* ref. 22).

Chromatography carried out at 165° on a 10 ft. × 0.25-in. column packed with Carbowax 20M separated the amine mixture into three components. Evidence presented below and discussed in the Results section indicates that the components are **_o_-tolylvinylcarbinyldimethylamine** (IIIc), **allylphenylcarbinyldimethylamine** (V), and **benzylvinylcarbinyldimethylamine** (VI).

Raney Nickel Cleavage of Amine IIIc.—A mixture of 27 g. of wet No. 28 active Raney nickel catalyst (Raney Catalyst Co., Chattanooga, Tenn.), 70 ml. of absolute ethanol and 1.20 g. of amine IIIc (separated by chromatography as described above) was stirred and refluxed for 28.5 hr. A colorless oil (0.44 g., 48%), b.p. 68–70° (11 mm.), was isolated by steps similar to those described above for isolating cyclopropyl-*o*-tolymethane, and was identified as **1-*n*-propyl-2-methylbenzene** by its infrared spectrum.[36]

Anal. Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.17; H, 10.37.

Allylphenylcarbinyldimethylamine (IV).—The general procedure described by Stewart and Hauser[12] for preparing amines similar to IV was followed. The Grignard reagent prepared from 4.8 g. of magnesium and 18.2 g. of allyl bromide was treated with 19.5 g. of dimethylaminobenzyl butyl ether.[12] **Allylphenylcarbinyldimethylamine** (IV), b.p. 87–88° (5.5 mm.), n^{20}D 1.5128, was isolated in 72% yield. An analytical sample which was redistilled through a semi-micro column had b.p. 72° (3.5 mm.), n^{20}D 1.5130. The infrared spectrum showed that this amine corresponded to one of the isomers isolated from rearrangement of bromide IIIa described above.

Anal. Calcd. for $C_{12}H_{17}N$: C, 82.23; H, 9.78. Found: C, 82.07; H, 9.61.

Benzylvinylcarbinyldimethylamine (VI) was prepared according to the directions in ref. 13. The infrared spectrum identified the remaining isomer from bromide IIIa (described above) as amine VI.

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(32) J. E. Callen, C. A. Darnfeld and G. H. Coleman, *ibid.*, p. 26.

(33) W. E. Bachmann and M. X. Barton, *J. Org. Chem.*, **3**, 300 (1938).

(34) C. R. Walter, Jr., *J. Am. Chem. Soc.*, **74**, 5185 (1952).

(35) A mixture having a slightly different composition was obtained in higher yield when commercial sodium amide (Farchan) was employed. These and other differences between freshly prepared sodium amide and the commercial product will be discussed in a future publication.

(36) Am. Pet. Inst. Spectrogram No. 1963.