128–138° at 13 mm., lit.[21] 130–131° at 12 mm. This experiment was repeated at room temperature for 118 hr. to give 17% of *n*-butyl benzylketone, 5% of regenerated nitrile, and some high boiling residue. In Exp. 23, 2,4,6-trimethylbenzyl *n*-butyl ketone was obtained, b.p. 142–147° at 7 mm.; 2,4-dinitrophenylhydrazone (yellow needles), m.p. 99° (recrystallized from ethanol).

Anal. Calcd. for $C_{12}H_{26}O_4N_4.C_2H_5OH$: N, 14.17. Found: N, 14.03.

Addition of reagents to benzalacetophenone. (Table II). These reactions were carried out as described in Exp. 1 by addition of benzalacetophenone in an appropriate solvent to the stirred reagent; the reaction mixtures were carbonated and worked up essentially as described for the α-hydrogen compounds.

In the experiment with phenylpotassium, no 1,4-addition product was isolated. A 67% yield of crude diphenylstyryl carbinol was obtained. After recrystallization from ligroin, the product melted at 109–111° (lit.[9] m.p. 108–111°). Some unidentified residue was obtained.

In the experiment with phenylsodium, β,β-diphenylpropiophenone, m.p. 94–95° (lit.[10] m.p. 96°) was obtained on acidifying the aqueous solution and decarboxylating the product. Diphenylstyrylcarbinol was isolated from the organic solution.

Reaction of phenylsodium with benzaldehyde. This reaction was carried out with 0.3 mole of phenylsodium and 0.21 mole of benzaldehyde in heptane (2 hr. at room temperature, 1 hr. at 50°). There was obtained 28 g. (72%) of benzhydrol, b.p. 175–180° at 17 mm. The product solidified; after recrystallization from ligroin (b.p. 90–120°), it melted at 66–67°. A mixed melting point with an authentic sample showed no depression.

DURHAM, N. C.

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(21) D. Ivanov, *Bull. Soc. Chem.*, [5], **4**, 682 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

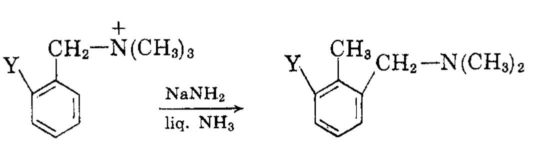
Ortho Substitution Rearrangement of Certain 3-Substituted and 3,5-Disubstituted Benzyltrimethylammonium Ions by Sodium Amide[1]

WILLIAM Q. BEARD, JR., DONALD N. VAN EENAM, AND CHARLES R. HAUSER

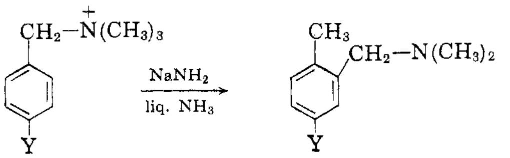
Received August 5, 1960

The 3-methoxy-, 3-methyl-, and 3-chloro-benzyltrimethylammonium ions underwent the ortho substitution rearrangement with sodium amide in liquid ammonia to form mixtures of the two possible types of isomeric amines in yields of 92, 90, and 16%, respectively. With the first two quaternary ions, rearrangement into the *ortho* position versus the *para* position occurred in the ratio of 2:1 and 1.2:1, respectively. The 3-bromo and 3-trifluoromethyl quaternary ions failed to yield isolable amounts of rearrangement products. The 3,5-dimethoxy- and 3,5-dimethyl-benzyltrimethylammonium ions underwent the rearrangement in 93% yield.

Previous papers[2–4] have described the *ortho* substitution rearrangements of several 2- and 4-substituted benzyltrimethylammonium ions (Equations 1 and 2, respectively) in which the substituents Y were such groups as alkyl, methoxy and chlorine.

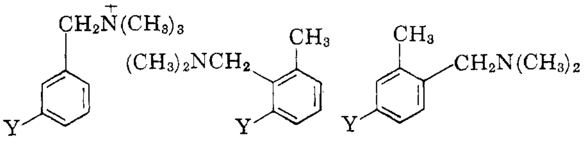


(1)



(2)

The present paper describes a similar study of certain 3-substituted and 3,5-disubstituted benzyltrimethylammonium ions with sodium amide in liquid ammonia. Whereas the rearrangement of a 2- or a 4- substituted benzyltrimethylammonium ion can form but a single amine (Equation 1 or 2), that of a 3-substituted quaternary ion of Type I (such as Ia) may afford a mixture of isomeric rearranged amines of Types II and III (such as IIa and IIIa). These isomers would arise through rearrangements into the *ortho*- and *para*- positions, respectively, relative to the 3-substituent.



Ia. Y = OCH_3
Ib. Y = CH_3
Ic. Y = Cl
Id. Y = Br
Ie. Y = CF_3

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

IIIa. Y = OCH_3
IIIb. Y = CH_3
IIIc. Y = Cl

Actually each of the three quaternary ions Ia–c produced a mixture of the possible isomeric amines of Types II and III. In Table I are summarized the yields of the amine mixtures and the relative proportions of the two isomers.

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(1) Supported by the National Science Foundation.

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

(3) C. R. Hauser and A. J. Weinheimer, *J. Am. Chem. Soc.*, **76**, 1264 (1954).

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

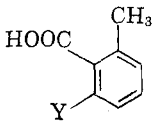
TABLE I

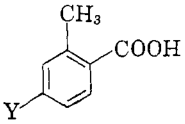
REARRANGEMENT OF 3-SUBSTITUTED BENZYLTRIMETHYLAMMONIUM IONS BY SODIUM AMIDE IN LIQUID AMMONIA

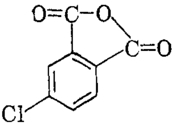
Quat. Ion	3-Substituent, Y	Amine Mixture, Yield %	Proportions of Isomers[a] Type II %	Type III %
Ia	OCH_3	92[b]	67 (IIa)	33 (IIIa)
Ib	CH_3	90	54 (IIb)	46 (IIIb)
Ic	Cl	16[c]	—	—

[a] These proportions of isomers were estimated from comparisons of infrared data (see Experimental). [b] An 86% yield was obtained on stopping the reaction after five minutes. [c] A 5% yield was obtained on stopping the reaction after five minutes.

It can be seen from this table that the quaternary ions Ia–c produced mixtures of the corresponding isomeric amines IIa–c and IIIa–c in yields of 92, 90, and 16%, respectively. These isomers were not separated; they were oxidized with permanganate to form the known acids IVa–c and Va–c, respectively. These acids were readily separated, since those of type IV were considerably more soluble in water than those of type V. Acid Vc was further oxidized and dehydrated to give anhydride VI.







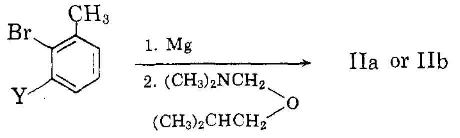
IVa. Y = OCH_3
IVb. Y = CH_3
IVc. Y = Cl

Va. Y = OCH_3
Vb. Y = CH_3
Vc. Y = Cl

The amine mixture from quaternary ion Ia was also converted to a mixture of the corresponding picrates, which were separated and identified as the picrates of amines IIa and IIIa.

The infrared spectra of each of the three amine mixtures from quaternary ions Ia–c showed bands characteristic of the two isomeric amines of types II and III. Thus, the three adjacent aromatic hydrogens of amines of type II were indicated in each case by a strong band in the region 810–770 cm.$^{-1}$, and the two adjacent aromatic hydrogens and one isolated aromatic hydrogen of amines of type III were indicated in each case by a strong band in 860–800 cm.$^{-1}$ region and a weak band in the 900–860 cm.$^{-1}$ region, respectively.[5] Moreover, the spectra of the amine mixtures from quaternary ions Ia and Ib showed all of the bands (and no others) exhibited by samples of pure amines which were independently synthesized as described below. By adjusting the relative proportions of pairs of isomers it was found that mixtures of pure amines IIa and IIIa in the ratio of about 2:1 and of pure amines IIb and IIIb in the ratio of about 1.2:1 gave infrared spectra that were practically identical with the mixtures obtained from the rearrangements of Ia and Ib, respectively. The relative proportions of the two amine mixtures given in Table I were determined in this manner (see Experimental).

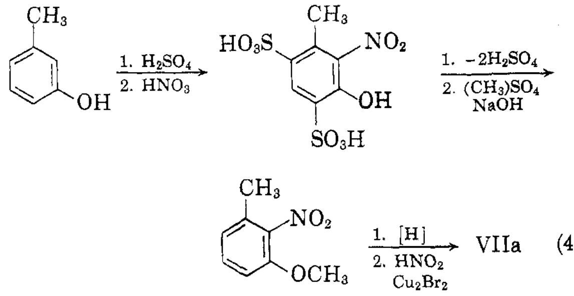
Rearranged amines IIa and IIb were independently synthesized by the condensations of dimethylaminomethyl isobutyl ether with the Grignard reagents of compounds VIIa and VIIb, respectively (Equation 3).



(3)

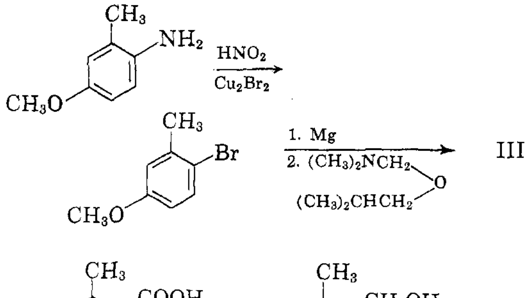
VIIa. Y = OCH_3
VIIb. Y = CH_3

Compound VIIa was prepared from *m*-cresol by a modification of the method of Gibson,[6] and compound VIIb from commercially available 2,6-dimethylaniline. Although the former method involved several steps (Equation 4), the structures in all steps had been established by earlier workers.



(4)

Rearranged amines IIIa and IIIb were independently synthesized from commercially available compounds as represented by equations 5 and 6, respectively.



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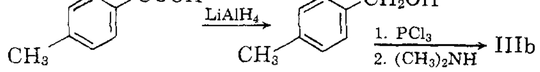

(6)

The fact that the yield of rearrangement product from the chloro quaternary ion Ic was much lower than those from the methoxy and methyl quaternary ions Ia and Ib under similar conditions (see Table I) may have been due partly to the occurrence of a

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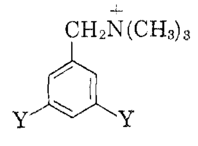
[5] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley & Sons, Inc., New York, N. Y., 1958, p. 78–79.

[6] G. P. Gibson, *J. Chem. Soc.*, 123, 1269 (1923).

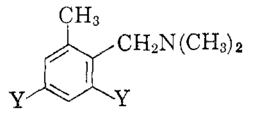
side-reaction involving the formation of a benzyne[7] (see Experimental). However, since some of the starting quaternary salt was recovered, the ion Ic evidently underwent the rearrangement more slowly than ions Ia and Ib.

Unsuccessful attempts were made to obtain the rearrangement products from the 3-bromo- and 3-trifluoromethyl quaternary ions, Id and Ie, respectively. The former ion evidently underwent mainly the benzyne reaction,[7] while the latter ion produced much tarry material although some of the starting quaternary salt Ie was recovered.

Next, consideration will be given to the 3,5-disubstituted benzyltrimethylammonium ions VIIIa and VIIIb, which, in contrast to the 3-substituted quaternary ions presented above, may undergo the ortho substitution rearrangement without forming isomeric mixtures. These quaternary ions both rearranged in 93% yield to form amines IXa and IXb, respectively.

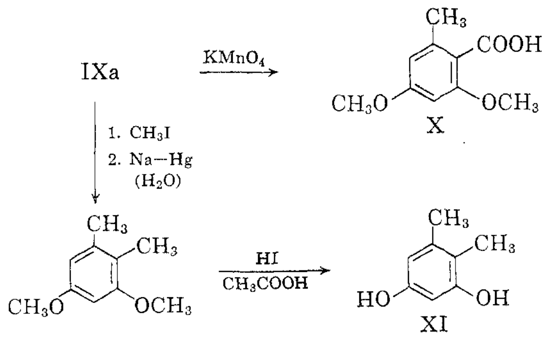


VIIIa. Y = OCH_3
VIIIb. Y = CH_3

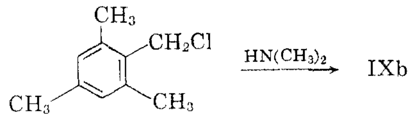


IXa. Y = OCH_3
IXb. Y = CH_3

The structure of the product from the rearrangement of VIIIa was established as IXa by oxidation to the known benzoic acid derivative X and by the Emde reduction of the methiodide of IXa followed by cleavage of the two methyl ether groups to form the known dihydroxy compound XI (Scheme A).



The structure of the product from the rearrangement of VIIIb was established as IXb by an independent synthesis from α^2-chloroisodurene (Equation 7).

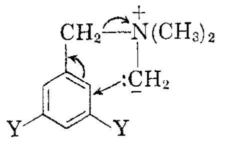


(7)

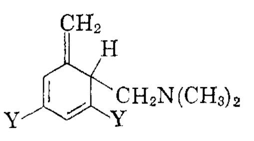
DISCUSSION

The predominant rearrangement of Ia and Ib into the 2-position relative to the 3-methoxy or 3-methyl substituent rather than into the 4-position is of interest. Apparently steric factors are not important, a conclusion supported by a consideration of molecular models.

The mechanism of the rearrangement has been considered[2] to involve the SNi′ type of displacement indicated in XII to form *exo*-methyleneamine (XIII), which undergoes a prototropic change to regenerate the aromatic ring. Actually the rearrangement of the 2,4,6-trimethylbenzyltrimethylammonium ion produces an isolable *exo*-methyleneamine that cannot undergo such a prototropic change.[8]



XII (Y = hydrogen of a substituent)



XIII

This mechanism suggests that the rearrangement would be retarded appreciably when Y in XII is methoxy or methyl, since such a group should increase the electron density at the position where the methyl carbanion attacks the ring. However, the rearrangement appears to be retarded just slightly. Thus the yields of rearranged amines from the unsubstituted benzyltrimethylammonium ion and the 3-methoxy substituted quaternary ion Ia were 90% and 86% within one minute and five minutes, respectively. Moreover, when an equimolar mixture of the unsubstituted and the 3,5-dimethylsubstituted salts was added to excess of the reagent and the reaction stopped in thirty seconds, the yield of rearranged amine from the former was 59% and that from the latter 49%. Even this slight retardation may not be real, since the quaternary salts were not entirely in solution.

Mechanism XII might also suggest that the rearrangement would be facilitated by a 3-chloro substituent as in Ic, but this is apparently not the case (see above).

These results may be reconciled with mechanism XII if it is assumed that substituents which increase the electron density at the point of attack also lower the energy of the transition state leading to the *exo*-methyleneamine XIII.

EXPERIMENTAL[9]

3-Methoxybenzyltrimethylammonium bromide (Ia). 3-Methoxybenzoic acid (110 g., 0.725 mole) was reduced with 38 g.

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

(8) C. R. Hauser and D. N. Van Eenam, *J. Am. Chem. Soc.*, **76**, 1264 (1954).

(0.95 mole) of 95% pure lithium aluminum hydride[10] to give 89.7 g. (90%) of 3-methoxybenzyl alcohol, b.p. 129–131: at 9 mm., lit.[11] b.p. 129° at 9 mm.

This alcohol (89.3 g., 0.647 mole) was treated with 95 g. (0.35 mole) of phosphorus tribromide in 1500 ml. of absolute ether overnight. The mixture was hydrolyzed with ice water, and the layers separated. The ether layer was washed with sodium bicarbonate solution, dried, and distilled to give 116.8 g. (90%) of 3-methoxybenzyl bromide, b.p. 123–124° at 13 mm., lit.[11] b.p. 123.5° at 13 mm.

A solution of 116.8 g. (0.58 mole) of this bromide in 500 ml. of acetonitrile was cooled in an ice bath and treated with 51 g. (0.87 mole) of liquid trimethylamine. After stirring for several hours, 1500 ml. of dry ether was added to precipitate 147 g. (98%) of 3-methoxybenzyltrimethylammonium bromide (Ia), m.p. 171–171.5°. One recrystallization from acetonitrile raised the melting point to 172.5–173°.

Anal. Calcd. for $C_{11}H_{18}BrNO$: C, 50.75; H, 6.97; N, 5.38. Found: C, 50.65; H, 7.02; N, 5.35.

Rearrangement of bromide Ia. To a stirred suspension of 0.22 mole of sodium amide[12] in 600 ml. of liquid ammonia was added over a period of 10 min. 52.0 g. (0.2 mole) of 3-methoxybenzyltrimethylammonium bromide (Ia). The initial green color changed rapidly to brownish-red. After 30 min., 11.8 g. (0.22 mole) of ammonium chloride was added, and the ammonia was replaced by ether. Inorganic salts were removed by filtration, and the ether was evaporated. The residue was distilled to give 33.08 g. (92%) of a mixture of amines IIa and IIIa, b.p. 108.5–116° at 10.5 mm., n_D^{25} 1.5135.

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 74.01; H, 9.42; N, 8.08.

Treatment of a sample of the amine mixture with excess picric acid in 95% ethanol solution gave a picrate mixture which was recrystallized slowly from 95% ethanol. The resulting two types of crystals were separated mechanically and recrystallized to give the picrates of amines IIa and IIIa, m.p. 139–140° and 114–115°, respectively. Admixture with independently synthesized samples of these picrates (see below) did not depress the melting points.

Oxidation of a 2.0-g. sample of the amine mixture was effected by stirring with 3.0 g. of potassium permanganate and 2.0 g. of sodium hydroxide in 100 ml. of water at room temperature. When the purple color had disappeared, three 1.0-g. portions of permanganate were added, each after the color of the preceding portion had faded. After removing the precipitated manganese dioxide by filtration through a Super-cell mat, the colorless alkaline solution was acidified with concentrated hydrochloric acid to liberate 6-methoxy-2-methylbenzoic and 4-methoxy-2-methylbenzoic acids, IVa and Va, respectively. The latter acid, which precipitated, was collected on a funnel and recrystallized from ethanol-water; yield, 0.42 g. (23%), m.p. 175–175.5°, lit.[13] m.p. 176°. The m.p. was not depressed on admixture with acid Va obtained from the oxidation of independently synthesized amine IIIa (see below).

Acid IVa, which remained in solution, was isolated by saturating the hydrochloric acid filtrate with sodium sulfate and extracting with ether. The extract was dried, filtered, and evaporated. The residue was recrystallized from hexane-ethanol to give 0.49 g. (26%) of 6-methoxy-2-methylbenzoic acid (IVa), m.p. 137–138°, lit.[14] m.p. 139°. The melting point was not depressed on admixture with acid IVa obtained from the oxidation of independently synthesized amine IIa (see below).

Estimation of the composition of the rearrangement product of Ia. The infrared spectrum of a 5% solution of the rearrangement product of Ia in cyclohexane was compared with the spectra of two cyclohexane solutions containing a total of 5% of independently synthesized amines IIa and IIIa. One of these solutions contained a mixture of IIa and IIIa in a ratio of 7:3 and the other contained a mixture of IIa and IIIa in a ratio of 6:4. The relative intensities of the moderate bands at 710 cm.$^{-1}$ (IIIa) and 700 cm.$^{-1}$ (IIa) led to a composition estimate for the rearrangement product of 67% 6-methoxy-2-methylbenzyldimethylamine (IIa) and 33% 4-methoxy-2-methylbenzyldimethylamine (IIIa).

Independent synthesis of amine IIa. *2-Nitro-m-cresol*, b.p. 106–108° at 9.5 mm., was prepared in 42% yield from 69 ml. of *m*-cresol, 304 ml. of 20% fuming sulfuric acid, and 28 ml. of fuming nitric acid (sp. gr. 1.5) according to the modification of Hodgson and Beard[15] of the method of Gibson.[6]

2-Nitro-3-methylanisole, m.p. 48–49°, lit.[14] m.p 49°, was obtained in 93% yield by the treatment of 37.5 g. of 2-nitro-*m*-cresol with a sevenfold excess of dimethyl sulfate and sodium hydroxide.

2-Amino-3-methylanisole, b.p. 114.5–116.5° at 15 mm., lit.,[6] b.p. 124–126° at 15 mm., was obtained in 75% yield by the reduction of 37.9 g. of 2-nitro-3-methylanisole with iron powder in glacial acetic acid.

2-Bromo-3-methylanisole, m.p. 34–36°, lit.[15] m.p. 35.5–36.5°, was obtained in 86% yield by the Sandmeyer reaction on 23.4 g. of 2-amino-3-methylanisole using the sulfuric acid procedure.[16]

6-Methoxy-2-methylbenzyldimethylamine (IIa) was prepared in 61% yield from 9.2 g. (0.0458 mole) of 2-bromo-3-methylanisole, 1.22 g. (0.05 g.-atom) of magnesium turnings, and 6.65 g. (0.0458 mole) of α-dimethylaminomethyl isobutyl ether.[17,18] The product boiled at 106–108° at 10.5 mm., nn^{24} 1.5140.

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.51; H, 9.54; N, 7.91.

The picrate (recrystallized from 95% ethanol) melted at 139–140°.

Anal. Calcd. for $C_{17}H_{20}N_4O_8$: C, 50.00; H, 4.94; N, 13.72. Found: C, 50.26; H, 4.73; N, 13.59.

The methiodide, m.p. 153–154°, was prepared from the amine and excess methyl iodide in acetonitrile, precipitated with ether, and recrystallized from acetonitrile and ether.

Anal. Calcd. for $C_{12}H_{20}INO$: C, 44.73; H, 6.25; N, 4.35. Found: C, 44.66; H, 6.37; N, 4.33.

Oxidation of 2.0 g. of the pure amine IIa was effected as described for the rearrangement product of Ia to give the water-soluble 2-methyl-6-methoxybenzoic acid (IVa), m.p. 138° (recrystallized from hexane-ethanol), lit.[14] m.p. 139°; yield 38%.

Independent synthesis of amine IIIa. 4-Methoxy-2-methylaniline (0.5 mole) in 175 ml. of 48% hydrobromic acid and 125 ml. of water was diazotized at 0° with a solution of 35 g. of sodium nitrite in 100 ml. of water. The solution was poured onto 0.30 mole of freshly prepared cuprous bromide[19] in 120 ml. of 48% hydrobromic acid and 60 ml. of water to

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(9) Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn. All melting points and boiling points are uncorrected.

(10) See W. G. Brown, *Org. Reactions*, VI, 491–492 (1951).

(11) E. Späth, *Monatsh.*, **34**, 1998 (1913).

(12) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, VIII, 122 (1954).

(13) C. Schall, *Ber.*, **12**, 824 (1879).

(14) P. Chuit and F. Bolsing, *Bull. Soc. chim. France* [3], **35**, 143 (1906).

(15) H. H. Hodgson and H. G. Beard, *J. Chem. Soc.*, **127**, 498 (1925).

(16) A. I. Vogel, *Textbook of Practical Organic Chemistry*, 3rd ed., Longmans, Green and Co., New York, N. Y., 1956, p. 602.

(17) G. M. Robinson and R. Robinson, *J. Chem. Soc.*, 532 (1923).

(18) See A. T. Stewart and C. R. Hauser, *J. Am. Chem. Soc.*, **77**, 1098 (1955).

(19) J. L. Hartwell, *Org. Syntheses*, **Coll. Vol. III**, 186 (1955).

give (steam distilled) 69.75 g. (69%) of 5-methoxy-2-methylbromobenzene, b.p. 106–108.5° at 11 mm., lit.[20] b.p. 108.5° at 12 mm.

This halide (0.12 mole) was converted to its Grignard reagent, which was treated with 0.78 mole of dimethylaminomethyl isobutyl ether to give amine IIIa (49%), b.p. 113.5–115° at 9.5 mm., $n^{25}_{\rm D}$ 1.5136.

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.52; H, 9.63; N, 7.92.

The picrate (recrystallized from 95% ethanol) melted at 115–115.5°.

Anal. Calcd. for $C_{17}H_{20}N_4O_8$: C, 50.00; H, 4.94; N, 13.72. Found: C, 50.10; H, 4.99; N, 13.60.

The methiodide, m.p. 202.5–203°, was prepared from the amine and excess methyl iodide in acetonitrile, precipitated with ether, and recrystallized twice from acetonitrile-ether.

Anal. Calcd. for $C_{12}H_{20}INO$: C, 44.73; H, 6.25; N, 4.35. Found: C, 44.62; H, 6.02; N, 4.38.

Oxidation of 2.0 g. of pure amine IIIa was effected as described for the rearrangement product of Ia to give the water-insoluble 4-methoxy-2-methylbenzoic acid (Va), m.p. 174–175° (recrystallized from ethanol-water), lit.[13] m.p. 176°; yield 73%.

3-Methylbenzyltrimethylammonium bromide (Ib). This salt, m.p. 217–219°, prepared in 90% yield from 0.2 mole of α-bromo-*m*-xylene and excess trimethylamine as described for Ia. Recrystallization from acetonitrile raised the m.p. to 222–223°.

Anal. Calcd. for $C_{11}H_{18}BrN$: C, 54.10; H, 7.43. N, 5.73. Found: C, 54.04; H, 7.57; N, 5.76.

Rearrangement of bromide Ib. This rearrangement was carried out with 36.6 g. (0.15 mole) of 3-methylbenzyltrimethylammonium bromide (Ib) in a suspension of 0.30 mole of sodium amide in 500 ml. of liquid ammonia as described for the rearrangement of Ia. The initial bright green color faded in 45–60 seconds, indicating a rapid reaction. There was obtained a mixture of 21.86 g. (90%) of amines IIb and IIIb, b.p. 91.8–93.2° at 12 mm., $n^{25}_{\rm D}$ 1.5077.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.87; H, 10.52; N, 8.70.

Oxidation of 2.0 g. of the amine mixture was effected as described for the rearrangement product of Ia to give the water-insoluble 2,4-dimethylbenzoic acid (Vb) (28%), m.p. 127.5–128.5°, lit.[21] m.p. 128°, mixed m.p. with authentic sample, 128–128.5°, and the water-soluble 2,6-dimethylbenzoic acid (IVb) (3% impure). After five recrystallizations from hexane, the latter acid melted at 113.5–114.5°, lit.[22] m.p. 116°. The melting point was not depressed on admixture with the acid obtained from the oxidation of independently synthesized amine IIb (see below).

Estimation of the composition of the rearrangement product of Ib. The infrared spectrum of a 4% solution of the rearrangement product of Ib in cyclohexane was compared with the spectra of two cyclohexane solutions containing a total of 4% of independently synthesized amines IIb and III. One of these solutions contained a mixture of IIb and IIIb. in a ratio of 55:45 and the other contained a mixture of IIb and IIIb in a ratio of 50:50. The relative intensities of the moderate bands at 689 cm.$^{-1}$ (IIb) and 713 cm.$^{-1}$ (IIIb) led to a composition estimate for the rearrangement product of 54% 2,6-dimethylbenzyldimethylamine (IIb) and 46% 2,4-dimethylbenzyldimethylamine (IIIb).

Independent synthesis of amine IIb. 2,6-Dimethylbromobenzene, b.p. 91–93.5^4° at 20 mm., $n^{25}_{\rm D}$ 1.5549, lit., 23 b.p. 98–99° at 20 mm., $n^{25}_{\rm D}$ 1.5552, was prepared from 2,6-dimethylaniline as described by Brown and Grayson.[23]

2,6-Dimethylbenzyldimethylamine (IIb) was prepared from 6.55 g. (0.05 mole) of dimethylaminomethyl isobutyl ether,[17] 11.59 g. (0.0625 mole) of 2,6-dimethylbromobenzene, and 3.04 g. (0.125 g.-atoms) of magnesium turnings[18] employing 9.4 g. (0.045 mole) of 1,2-dibromoethane to activate Grignard formation. Distillation of the product gave 5.87 g. (72%) of amine IIb, b.p. 91–92° at 10.3 mm., $n^{25}_{\rm D}$ 1.5100.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.70; H, 10.41; N, 8.56.

The methiodide, prepared as described for that of IIa, melted at 192–193° dec.

Anal. Calcd. for $C_{12}H_{20}IN$: C, 47.25; H, 6.56; N, 4.59. Found: C, 47.07; H, 6.47; N, 4.54.

Oxidation of 1.0 g. of amine IIb was effected with 3.0 g. of potassium permanganate to give 0.13 g. (14%) of 2,6-dimethylbenzoic acid (IVb), m.p. 111–113° and at 114–114.5° after another recrystallization from hexane, lit.[22] m.p. 116°.

Independent synthesis of amine IIIb. 2,4-Dimethylbenzoic acid (0.086 mole) was reduced with lithium aluminum hydride[10] to give 2,4-dimethylbenzyl alcohol (52%), m.p. 27–28° (recrystallized from petroleum ether (b.p. 30–60°), cooled in Dry Ice), lit.[24] m.p. 22°.

A solution of 0.45 mole of this alcohol in 50 ml. of dry ether was treated 3 hr with 0.023 mole of phosphorus trichloride in 10 ml. of dry ether. Water was added, and the ethereal layer was washed with sodium bicarbonate solution and water. After drying the ethereal solution was evaporated and the residue taken up in benzene. The benzene solution was added to 4.5 g. (0.10 mole) of dimethylamine in 50 ml. of benzene, 3 g. more of the amine being bubbled through the mixture. After 2 hr., the solution was extracted with 2*M* hydrochloric acid (total 200 ml.) and the extract made basic with solid sodium hydroxide. The liberated amine was extracted with ether, dried, and distilled to give 2.07 g. (29%) of 2,4-dimethylbenzyldimethylamine (IIIb), b.p. 91–92° at 10.3 mm., $n^{25}_{\rm D}$ 1.5040, was obtained.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.73; H, 10.42; N, 8.56.

The methiodide, prepared as described for that of Ia, melted at 215–216° dec.

Anal. Calcd. for $C_{12}H_{20}IN$: C, 47.25; H, 6.56; N, 4.59. Found: C, 47.38; H, 6.51; N, 4.72.

3-Chlorobenzyltrimethylammonium bromide (Ic). This salt was prepared in 96% yield from 24.7 g. (0.12 mole) of 3-chlorobenzyl bromide and excess trimethylamine by the procedure described for Ia. After one recrystallization from a mixture of ethanol, acetonitrile, and ether it melted at 224–225°.

Anal. Calcd. for $C_{10}H_{15}BrClN$: C, 45.39; H, 5.71; N, 5.29. Found: C, 45.25; H, 5.70; N, 5.24.

Rearrangement of bromide Ic. This rearrangement was carried out essentially as described for the rearrangement of Ia. The quaternary salt was added as rapidly as possible; the reaction period was 1 hr. There was obtained 2.98 g. (16%) of a mixture of rearranged amines IIc and IIIc, b.p. 100–106° at 12 mm., $n^{25}_{\rm D}$ 1.5233.

Anal. Calcd. for $C_{10}H_{14}ClN$: C, 65.82; H, 7.68; N, 7.63; Cl, 19.30. Found: C, 65.59; H, 7.49; N, 7.72; Cl, 19.14.

Much of the original quaternary salt Ic was recovered contaminated with a salt containing an aromatic primary amine group as indicated by a positive test on diazotization and coupling with α-naphthol. This was supported by an infrared spectrum which showed bands for the N-H bond.

In another experiment using inverse addition and a reaction period of only 5 min., the mixture of rearranged amines was obtained in 5% yield. The recovered salts gave a weak positive test for an aromatic primary amine.

Treatment of a small sample of the amine mixture with excess picric acid in ethanol produced two types of crystals, which were separated mechanically and recrystallized

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(20) R. Pschorr, *Ann.*, **391**, 50 (1912).

(21) E. V. Meyer and F. Nabe, *J. Prakt. Chem.* [2], **82**, 537 (1910).

(22) W. A. Noyes, *Am. Chem. J.*, **20**, 813 (1898).

(23) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 20–24 (1953).

(24) W. Hindrichsen, *Ber.*, **21**, 3085 (1888).

separately from 95% ethanol. The main picrate melted at 165.5–166.5°.

Anal. Calcd. for $C_{16}H_{17}ClN_4O_7$: C, 46.56; H, 4.14; N, 13.56. Found: C, 46.50; H, 4.28; N, 13.50.

The other picrate, obtained in very small amount, melted at 152°.

Oxidation of 0.97 g. of the amine mixture with 2.9 g. of potassium permanganate gave the water-insoluble 4-chloro-2-methylbenzoic acid (Vc) (21%), m.p. 169–171° (recrystallized from ethanol-water), lit.[25] m.p. 171–172°, and much less of the water-soluble 6-chloro-2-methylbenzoic acid (IVc), m.p. 100–101° after three recrystallizations from hexane, lit.[26] m.p. 102°.

Further oxidation of acid Vc (0.2 g.) was effected with 0.37 g. of potassium permanganate in 10 ml. of water and enough 20% sodium hydroxide solution to dissolve the acid. After heating on the steam bath until the purple color faded, the precipitated manganese dioxide was removed by filtration through a Supercell mat. The filtrate was acidified with concentrated hydrochloric acid, and the small amount (0.03 g.) of unchanged acid Vc was removed by filtration. After saturating with sodium sulfate, the filtrate was extracted with several portions of ether. The ethereal solution was dried and evaporated to leave 0.19 g. (85%) of 4-chlorophthalic acid, m.p. 152–153°, lit.[27] m.p. 150–150.5°. A small sample of this acid was boiled in a test tube and allowed to resolidify. The 4-chlorophthalic anhydride (VI) produced melted at 97.5–98.5°, lit.[27] m.p. 98.5°.

3-Bromobenzyltrimethylammonium iodide (Id). To 49.6 g. (0.21 mole) of *m*-dibromobenzene in 100 ml. of dry ether was added gradually 5.34 g. (0.22 g.-atom) of magnesium turnings. One hour after refluxing had ceased, 25.8 g. (0.197 mole) of dimethylaminomethyl isobutyl ether[17] in an equal volume of dry ether was added. After 20 hr. the solution was poured onto 200 g. of ice and 40 ml. of concd. hydrochloric acid. The aqueous acid layer was separated and made strongly basic with solid sodium hydroxide. The resulting mixture was steam distilled, and the distillate was extracted with several portions of ether. The combined extract was dried and distilled to give 27.85 g. (66%) of 3-bromobenzyldimethylamine, b.p. 105–108° at 9.8 mm., n_{D}^{25} 1.5388.

Anal. Calcd. for $C_9H_{12}BrN$: C, 50.49; H, 5.65; N, 6.54. Found[28]: C, 52.56; H, 6.20; N, 7.04.

This amine (27.42 g., 0.128 mole) was treated 3 hr. with 35 g. (0.25 mole) of methyl iodide in 125 ml. of acetonitrile. Ether was added to precipitate 3-bromobenzyltrimethylammonium iodide (Id), m.p. 189–191° after recrystallization from acetonitrile-ether; yield 45.5 g. (98%). Two more recrystallizations from acetonitrile-ether raised the melting point to 191.5–192°.

Anal. Calcd. for $C_{10}H_{15}BrIN$: C, 33.77; H, 4.25; N, 3.94. Found: C, 33.60; H, 4.41; N, 3.74.

Treatment of bromide Id *with sodium amide.* To 35.5 g. (0.1 mole) of 3-bromobenzyltrimethylammonium bromide (Id) in 200 ml. of liquid ammonia was added during 15 min. a suspension of 0.101 mole of sodium amide in 300 ml. of liquid ammonia to produce yellow, orange, and finally dark red-brown colors. After 15 min., 5.40 g. (0.101 mole) of ammonium chloride was added and the ammonia replaced by ether. No ether-soluble amine was obtained. The ether-insoluble material (resinous salts) was diazotized and coupled with α-naphthol to give a brilliant water-soluble red dye indicating a considerable amount of primary amino quaternary salt.

3-Trifluoromethylbenzyltrimethylammonium iodide (Ie). 3-Trifluoromethylbenzyldimethylamine was obtained from 45.0 g. (0.20 mole) of *m*-bromobenzotrifluoride, 4.86 g. (0.20 g.-atom) of magnesium turnings, and 18.92 g. (0.148 mole) of dimethylaminomethyl isobutyl ether[17,18]; yield 20.4 g. (68%), b.p. 104–107° at 60 mm., n_{D}^{25} 1.4453.

Anal. Calcd. for $C_{10}H_{12}F_3N$: C, 59.09; H, 5.95; N, 6.89. Found: C, 58.93; H, 5.73; N, 6.82.

This amine (20.1 g., 0.099 mole) was treated with excess methyl iodide as described in the preparation of Id to give 33.2 g. (97%) of 3-trifluoromethylbenzyltrimethylammonium iodide (Ie), m.p. 163–164° and at 163.5–164° after recrystallization from acetone-ether.

Anal. Calcd. for $C_{11}H_{15}F_3IN$: C, 38.28; H, 4.35; N, 4.06. Found: C, 38.48; H, 4.51; N, 3.87.

Treatment of iodide Ie *with sodium amide.* This reaction was carried out with 13.8 g. (0.04 mole) of Ie and 0.041 mole of sodium amide as described for Id. The ether-soluble fraction was evaporated leaving a viscous black basic tar from which no pure compound was isolated. The ether-insoluble salts were triturated in acetonitrile and the mixture filtered. Ether was added to the filtrate to precipitate 6.4 g. (46%) of recovered quaternary salt Ie, m.p. 159–160°, mixed m.p. 161–162°.

3,5-Dimethoxybenzyltrimethylammonium chloride (VIIIa). This salt, m.p. 191–192°, was prepared in 93% yield from 67.5 g. (0.362 mole) of 3,5-dimethoxybenzyl chloride[29] (m.p. 46°) (obtained from 3,5-dimethoxybenzyl alcohol)[10] and excess trimethylamine as described for Ia. The picrate of this hygroscopic quaternary salt was prepared for analysis. After three recrystallizations it melted at 159–160°.

Anal. Calcd. for $C_{18}H_{22}N_4O_9$: C, 49.31; H, 5.06; N, 12.78. Found: C, 49.31; H, 4.92; N, 12.76.

Rearrangement of chloride VIIIa. This reaction was carried out with 24.6 g. (0.10 mole) of quaternary salt VIIIa and 0.20 mole of sodium amide as described for the rearrangement of Ia to give 19.6 g. (93%) of 2,4-dimethoxy-6-methylbenzyldimethylamine (IXa), b.p. 100–101° at 1.0 mm.

Anal. Calcd. for $C_{12}H_{19}NO_2$: C, 68.86; H, 9.15; N, 6.69. Found: C, 69.05; H, 9.04; N, 6.63.

The picrate, recrystallized three times from ethanol, melted at 142–143°.

Anal. Calcd. for $C_{18}H_{22}N_4O_9$; C, 49.31; H, 5.06; N, 12.78. Found: C, 49.38; H, 5.16; N, 12.85.

Oxidation of 0.5 g. of amine IXa was effected as indicated for amine IIIa to give 0.2 g. (45%) of crude 2,4-dimethoxy-6-methylbenzoic acid (X) which, after one recrystallization from aqueous ethanol, melted at 140–141° dec., lit.,[30] m.p. 140 dec.

The methiodide of IXa was prepared from 43.8 g. (0.209 mole) of the amine and excess methyl iodide as described for Id. Recrystallization from ethanol gave 73 g. (99%) of 2,4-dimethoxy-6-methylbenzyltrimethylammonium iodide, m.p. p. 169–170° (shrinking and darkening, did not actually melt even at 250°). The quaternary picrate, recrystallized three times from water, melted at 172.5–173.5°.

Anal. Calcd. for $C_{19}H_{24}N_4O_9$: C, 50.44; N, 5.35; N, 12.39. Found: C, 50.69; H, 5.31; N, 12.31.

Emde reduction of the methiodide of IXa was effected with 17.55 g. (0.05 mole) of the salt and 210 g. of 5% sodium amalgam in water by the *Org. Syntheses* procedure for the preparation of hemimellitene[31] to give 2.86 g. (35%) of 3.5-dimethoxy-*o*-xylene, b.p. 117.5–120° at 13 mm., n_{D}^{25} 1.5263.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26;; H, 8.49. Found: C, 72.07; H, 8.48.

Ether cleavage of 3,5-dimethoxy-*o*-xylene was effected with 2.0 g. of the compound in 10 ml. of glacial acetic acid

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(25) K. von Auwers and L. Harres, *Z. physik. Chem.* [A], **143,** 16 (1929).

(26) J. Kenner and E. Witham, *J. Chem. Soc.,* **119,** 1458 (1921).

(27) W. Miersch, *Ber.,* **25,** 2116 (1892).

(28) This analysis checks closely for an impurity of about 8.6% of *m*-bis(dimethylaminomethyl)benzene, which would arise from the formation of the di-Grignard reagent.

(29) R. Adams, S. MacKenzie, Jr., and S. Leowe, *J. Am. Chem. Soc.,* **70,** 664 (1948).

(30) J. Herzig and F. Wenzel, *Monatsh.,* **24,** 901 (1904).

(31) W. R. Brasen and C. R. Hauser, *Org. Syntheses,* **34,** 56 (1954).

and 10 ml. of 47% hydriodic acid refluxing under an air condenser for 2 hr. The solvents were removed under reduced pressure leaving orange crystals which were recrystallized from water (Norite) to give 3,5-dihydroxy-*o*-xylene (XI), m.p. 136°, lit.[32] m.p. 136–137° (from water).

3,5-Dimethylbenzyltrimethylammonium bromide (VIIIb). 3,5-Dimethylbenzoic acid (30.0 g., 0.2 mole) was added slowly to a slurry of 10.0 g. (0.25 mole) of 95% pure lithium aluminum hydride in 500 ml. of anhydrous ether. The addition required about 1.5 hr. because of the unusually vigorous reaction. After 3 hr. of mechanical stirring the reaction was worked up by the usual procedure[10] to give 24 g. (88%) of 3,5-dimethylbenzyl alcohol, b.p. 115–117.5° at 10 mm., lit.,[33] b.p. 218–221.°

This alcohol, 26.7 g. (0.16 mole), was treated with 27.1 g. (0.10 mole) of phosphorus tribromide in 500 ml. of ether. After the usual work-up the product was recrystallized once from methanol at −70° to give 31.2 g. (80%) of 3,5-dimethylbenzyl bromide, m.p. 37.5–38°, lit.,[33] m.p. 37.5–38°.

Quaternary salt VIIIb, m.p. 238.5–239°, was prepared in 84% yield from 31.2 g. (0.157 mole) of this bromide and excess trimethylamine as described for Ia.

Anal. Calcd. for $C_{12}H_{20}BrN \cdot 1/2\ H_2O$[34]: C, 54.01; H, 7.92; N, 5.25. Found: C, 54.17, 54.05; H, 8.13, 7.98; N, 5.17, 5.14.

Rearrangement of bromide VIIIb. This rearrangement was carried out with 30.5 g. (0.114 mole) of quaternary salt VIIIb and 0.24 mole of sodium amide as described for the rearrangement of Ia to give 19.6 g. (97%) of 2,4,6-trimethylbenzyldimethylamine (IXb), b.p. 108–109° at 10.5 mm., n_D^{25} 1.5109, lit.[2] b.p. 112–113° at 13 mm. The picrate melted at 148–149°, lit.[2] m.p. 149–150°. The methiodide melted at 195–196°, lit.[2] m.p. 196–197° dec.

Independent synthesis of amine IXb. To a solution of 9.0 g. (0.2 mole) of dimethylamine in 50 ml. of benzene was added 9.3 g. (0.0436 mole) of 2,4,6-trimethylbenzyl bromide in 25 ml. of benzene. After 1 hr., the mixture was shaken with 300 ml. of $2M$ hydrochloric acid and the layers separated. The aqueous phase was made strongly basic with solid sodium hydroxide, cooled, and extracted with ether. The ethereal solution was dried, filtered, and evaporated. Vacuum distillation yielded 5.68 g. (74%) of 2,4,6-trimethylbenzyldimethylamine (IXb), b.p. 107–108° at 10 mm., n_D^{25} 1.5109 (identical with that of the rearrangement product). The melting points of its picrate and methiodide were the same as those of the rearranged amine and mixed melting points were not depressed. In addition the infrared spectra of the two samples of amine were identical.

Rearrangement of a mixture of benzyltrimethylammonium iodide and 3,5-dimethylbenzyltrimethylammonium bromide (VIIIb). To a stirred suspension of 0.30 mole of sodium amide in 300 ml. of liquid ammonia was added during 1 min. a mixture of 25.8 g. (0.10 mole) of 3,5-dimethylbenzyltrimethylammonium bromide and 27.7 g. (0.10 mole) of benzyltrimethylammonium iodide in 1000 ml. of liquid ammonia. Most of the solid salts had dissolved in the ammonia before the addition. After 30 sec., 16 g. (0.3 mole) of ammonium chloride dissolved in liquid ammonia was added rapidly. The ammonia was replaced by ether and the mixture was filtered. The filtrate was distilled to give 8.72 g. (59%) of 2-methylbenzyldimethylamine, b.p. 80–85° at 14 mm. and 8.73 g. (49%) of 2,4,6-trimethyldimethylamine (IXb), b.p. 113–115° at 14 mm. Also a middle cut (2.16 g.), b.p. 85–113° at 14 mm., was obtained. These two amines were identified by comparison of their infrared spectra with those of authentic samples.

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(32) O. Simon, *Ann.*, **329**, 305 (1903).

(33) P. Wispek, *Ber.*, **16**, 1577 (1883).

(34) The yields of rearranged amine from salt VIIIb are nevertheless based on the anhydrous salt. The yields based on the hydrated form would be about 4% higher.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF FLORIDA]

Tetraphenylbutatriene from the Reaction of 1,1-Diphenyl-2-nitroethylene with Potassium *t*-Butoxide[1]

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Treatment of 1,1-diphenyl-2-nitroethylene with potassium *t*-butoxide gives, in addition to products resulting from *beta*-addition of base, small amounts (up to 10%) of tetraphenylbutatriene II. Employing spectrophotometric techniques, it was shown that this reaction does not involve an intermediate carbene. A mechanism for this reaction involving *alpha*-addition of a vinyl carbanion to the nitroolefin is suggested.

In the course of some examinations of the scope and mechanism of *alpha*-eliminations from vinyl systems (the Fritsch-Buttenberg-Wiechell rearrangement)[3,4] we felt that it would be interesting to investigate the reactions of 1,1-diphenyl-2-nitroethylene with strong base under typical *alpha*-elimination conditions. It was recognized from the outset that *beta*-addition of base to the nitroolefin[5,6] would certainly compete with *alpha*-elimination. We therefore selected the rather bulky base,

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[1] Taken in part from the dissertation submitted by Charles D. Broaddus to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1960.

[2] Du Pont Teaching Fellow, 1959–60.

(3) P. Fritsch, *Ann.*, **279**, 319 (1894); W. P. Buttenberg, *Ann.*, **279**, 327 (1894); H. Wiechell, *Ann.*, **279**, 337 (1894). For a review of this type of reaction see T. L. Jacobs, *Org. Reactions*, V, 1 (1949). More recent references can be found in A. A. Bothner-By, *J. Am. Chem. Soc.*, **77**, 3293 (1955) and reference 4.

(4) J. F. Pritchard and A. A. Brothner-By, *J. Phys. Chem.*, **64**, 1271 (1960); D. Y. Curtin and E. W. Flynn, *J. Am. Chem. Soc.*, **81**, 4714 (1959).

(5) The addition of basic reagents to 1,1-diphenyl-2-nitroethylene is a well known reaction. *E.g.* see P. Lipp, W. Ludicke, N. Kalinkoff, and A. P. Pethoff, *Ann.*, **449**, 15 (1926); M. Konowalow and G. Jatzewitsch, *J. Russ. Phys. Chem. Ges.*, **37**, 542 in *Chem. Zent.*, **76**, II, 824 (1905).

(6) R. Anschutz and E. Romig, *Ann.*, **233**, 327 (1886).