initial brief period of vigorous refluxing, the mixture was diluted with 50 cc. of ether and 50 cc. of toluene and then heated at reflux for one hour. After hydrolysis by pouring on iced ammonium chloride, part of the product was recovered by filtration and the remainder by evaporation of the ether–toluene layer. The total yield of (*o*-anisyl)-triphenyllead was 22.1 g. (81% yield). A portion crystallized from absolute alcohol melted at 128–129°.

Anal. Calcd. for $C_{25}H_{22}OPb$: Pb, 37.98. Found: Pb, 38.01.

(*p*-Anisyl)-triphenyllead.—This compound was prepared like the *o*-anisyl compound, with substitution of *p*-bromoanisole for *o*-bromoanisole. The original reaction product was insoluble in ether–toluene; therefore, hydrolysis was effected by addition of ice and ammonium chloride solution to the reaction mixture. The crude product (86% yield) was recrystallized from alcohol and then melted at 150–151° with slight decomposition. Towne[16] reported a melting point of 152° with some decomposition.

Summary

1. Five (hydroxyalkylphenyl)-triphenyllead compounds have been prepared by the reaction of triphenyllead chloride with the organolithium compounds formed by halogen-metal interconversion between bromophenylalkanols and *n*-butyllithium.

2. (*p* - Hydroxymethylphenyl) - triphenyllead has been oxidized by permanganate in acetone to (*p*-carboxyphenyl)-triphenyllead, and (*o*-hydroxymethylphenyl)-triphenyllead has been similarly oxidized to (*o*-carboxyphenyl)-diphenyllead hydroxide.

3. (β-Diethylaminoethyl)-triethyllead and (γ-diethylaminopropyl)-triethyllead have been prepared by reaction of triethyllead-sodium with the appropriate dialkylaminoalkyl chloride.

4. (*p*-Bromophenyl)-triethyllead, prepared from *p*-bromophenylmagnesium bromide and triethyllead chloride, reacted with activated copper–magnesium alloy but the product could not be converted to an acid by carbonation.

AMES, IOWA RECEIVED NOVEMBER 7, 1949

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quaternary Intermediates in the Alkylation of Certain Esters by Tertiary Amines

BY H. R. SNYDER, ERNEST L. ELIEL AND ROBERT E. CARNAHAN*

In a previous report it was noted that 1-methylgramine reacts with cyanoacetic ester and with other esters containing active methylene or methinyl groups. The product, after hydrolysis and decarboxylation, was 1-methylindole-3(β)-propionic acid or a derivative of it. In an attempt to elucidate the mechanism of such alkylations the investigation has been continued and extended to reactions of benzyldimethylamine.

Benzyldimethylamine was found to react with tricarbethoxymethane at a temperature (180–200°) somewhat above that (160–170°) required with 1-methylgramine. Hydrolysis and decarboxylation of the products converted them to hydrocinnamic acid and dibenzylacetic acid. During the course of the alkylation gases were evolved; carbon dioxide and the tertiary amine dimethylethylamine were identified as components of the gaseous mixture. The secondary amine dimethylamine was not found. Similarly, the basic gas evolved during the alkylation of methyl cyanoacetate with 1-methylgramine, described earlier,[1] has been shown to be the tertiary amine trimethylamine. Finally, the alkylation of methyl cyanoacetate by benzyldimethylamine was found to occur with the evolution of the tertiary amine trimethylamine.

The formation of a tertiary amine in each of these reactions indicates that the first step in the alkylation is the reaction of the ester[2] with the amine to give the quaternary ammonium salt of an acid (equation 1), and the quaternary ammonium cation is the active alkylating agent. The anion of the acid or another molecule

$$C_6H_5CH_2N(CH_3)_2 + NCCH_2CO_2CH_3 \longrightarrow C_6H_5CH_2\overset{+}{N}(CH_3)_3 + NCCH_2CO_2^- \quad (1)$$

of the original ester may be alkylated by the cation. Decarboxylation of one or more of the anionic species at the high temperature employed and some dialkylation lead to the formation of the mixture of hydrocinnamonitrile and dibenzylacetonitrile. Support for this interpretation of the reaction was found in the fact that the thermal decomposition of benzyltrimethylammonium cyanoacetate occurred in the expected fashion, yielding a mixture of the same nitriles. The participation of esters in this reaction is, of course, not excluded, inasmuch as it is known[3] that quaternary ammonium salts of acids generate esters on thermal decomposition.

A free radical mechanism recently has been suggested for thermal alkylations with benzyl bromide.[4] Although it seemed unlikely that such a mechanism was operative in the present alkylations, because of the presence of amines, a test was made by carrying out parallel experiments

---

* Minnesota Mining and Manufactoring Co. Fellow, 1950-1951.

(1) For the preceding paper in this series see Snyder and Eliel, THIS JOURNAL, **71**, 663 (1949).

(2) (a) Willstätter and Kahn, *Ber.*, **35**, 2757 (1902); (b) Hammett and Pfluger, THIS JOURNAL, **55**, 4079 (1933).

(3) (a) Prelog and Piantanida, *Z. physiol. Chem.*, **244**, 56 (1936); (b) Lawson and Collie, *J. Chem. Soc.*, **53**, 624 (1888).

(4) McElvain and Schroeder, THIS JOURNAL, **71**, 47 (1949).

with and without the addition of hydroquinone. The amounts of carbon dioxide (weighed as barium carbonate) produced in the two experiments were nearly identical, and the presence of hydroquinone did not result in an induction period. The effect of hydroquinone was tested similarly on a thermal alkylation with benzyl bromide; it proved to be an excellent inhibitor, confirming the proposed free radical mechanism for this reaction.

The reaction of benzyldimethylamine with methyl cyanoacetate gave considerable amounts of dibenzylmethylamine, in addition to the products mentioned above. This substance results from the disproportionation of benzyldimethylamine through a cyclic process involving the benzyltrimethylammonium ion (equations 2 and 3).

$$C_6H_5CH_2\overset{+}{N}(CH_3)_3 + C_6H_5CH_2N(CH_3)_2 \longrightarrow (C_6H_5CH_2)_2\overset{+}{N}(CH_3)_2 + (CH_3)_3N \quad (2)$$

$$(C_6H_5CH_2)_2\overset{+}{N}(CH_3)_2 + C_6H_5CH_2N(CH_3)_2 \longrightarrow (C_6H_5CH_2)_2NCH_3 + C_6H_5CH_2\overset{+}{N}(CH_3)_3 \quad (3)$$

This interpretation of the reaction was confirmed by heating benzyldimethylamine alone and in the presence of varying amounts of the methochloride. Excellent yields of dibenzylmethylamine were obtained when the quaternary salt was present, and in the range of 5–50 mole per cent. of the salt in the original reaction mixture the yield was independent of the concentration of the salt. The addition of a little hydrochloric acid or boron fluoride etherate to benzyldimethylamine also promoted the disproportionation.

A similar disproportionation must have occurred in the experiment in which benzyltrimethylammonium cyanoacetate was heated. The amine isolated was α,β-diphenylethyldimethylamine, undoubtedly formed by Stevens[5] rearrangement of the dibenzyldimethylammonium ion. The occurrence of the rearrangement product suggests that dibenzyldimethylammonium cyanoacetate will yield α,β-diphenylethyldimethylamine on heating; this prediction was verified by experiment. The Stevens rearrangement was not observed in the experiments in which benzyldimethylamine and methyl cyanoacetate were heated together. Presumably, the reason is that in such reactions the benzyltrimethylammonium cyanoacetate decomposes about as rapidly as it is formed, so that there is never a high concentration of the cyanoacetate anion, the base which effects the rearrangement.

Experimental[6,7]

Reaction of Benzyldimethylamine with Tricarbethoxymethane.—A solution of 13.6 g. (0.1 mole) of commercial benzyldimethylamine (Rohm and Haas) in 21.6 g. (0.1 mole) of tricarbethoxymethane[8] was heated at 180–190° for nineteen hours. The exit gases were passed through a Dry Ice–alcohol trap, then through a barium hydroxide solution, and then through 3 *N* hydrochloric acid. There was a vigorous evolution of carbon dioxide. At the end of the heating period the reaction mixture was refluxed overnight with a solution of 40 g. of potassium hydroxide in 40 ml. of water and 320 ml. of 95% alcohol. The alcohol was distilled and 150 ml. of water was added. The aqueous solution was extracted twice with about 100 ml. of ether and was then evaporated almost to dryness on the steam-bath. Sixty-five milliliters of concentrated hydrochloric acid was added cautiously to the residue with cooling and the oil which separated together with the aqueous layer was decanted from the precipitated salts. The decanted liquor was twice extracted with ether. The aqueous layer was recombined with the salts and evaporated to dryness *in vacuo*. The dry residue was extracted repeatedly with warm chloroform and the chloroform solution was combined with the ether extract containing the acid portions and dried over sodium sulfate. After distillation of the solvents the residue was heated at 180–200° in order to complete decarboxylation. When gas evolution had ceased, the product was distilled *in vacuo* from a modified Claisen flask. After a small forerun, the main fraction was collected at 96–104° (0.25 mm.). It weighed 5.85 g. (39%) and solidified on standing; the solid melted at 44–47.5° and gave no depression in melting point on admixture with an authentic sample of hydrocinnamic acid (m. p. 48–49°). The *p*-bromophenacyl ester melted at 104–105° (lit.[9] 104°).

When the distillation residue was heated to about 200°, a second fraction of b. p. 152–158° (0.35 mm.) passed over. It weighed 2.25 g. (19%) and crystallized on standing. It was collected in ether and extracted with 5% aqueous sodium hydroxide. The alkaline solution was treated with solid carbon dioxide (which did not liberate any organic material) and then acidified with concentrated hydrochloric acid. An oil separated and crystallized after a short time. The suspension was chilled and the crystals were collected, washed and dried; m. p. 73–85°. Recrystallization from aqueous alcohol yielded 1.15 g. of dibenzylacetic acid; m. p. 85–88°. A second recrystallization from the same mixture of solvents raised the melting point to 88–89°[10]; the mixed melting point with an authentic sample of dibenzylacetic acid of m. p. 87.5–89° was 87.5–89°. The amide melted at 129.5–131° (lit.[10] 128–129°).

The liquid condensed in the Dry Ice–alcohol trap did not give a test with the nickel chloride–carbon disulfide–ammonia reagent (Duke[11]), and, therefore, must have contained no secondary amine. A picrate, prepared from it in benzene, melted at 201–204°. Two recrystallizations from absolute ethyl alcohol raised the melting point to 204–206°. This value agrees with that of dimethylethylamine picrate.[12]

Anal. Calcd. for $C_{10}H_{14}N_4O_7$: N, 18.54. Found: N, 18.70.

Reaction of Benzyldimethylamine with Methyl Cyanoacetate.—Benzyldimethylamine, 40.8 g. (0.3 mole), and methyl cyanoacetate, 29.7 g. (0.3 mole), (both reagents redistilled) were heated at 200–210° for sixteen hours. The trap arrangement was as described in the preceding experiment. Carbon dioxide evolution was vigorous and after a few minutes the barium hydroxide solution was drained and the corresponding trap left empty as a safety device. The Dry Ice trap clogged after one hour and was removed from the system. It was flushed out with 95%

---

[5] Thompson and Stevens, *J. Chem. Soc.*, 1936 (1932).

[6] All melting points are corrected.

[7] Microanalyses by Miss Emily Davis, Miss Rachel Kopel, Mrs. Jane Wood and Mr. Howard Clark.

[8] Lund and Voight, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 594.

[9] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 157, 223.

[10] Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 140.

[11] Duke, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 196 (1945).

[12] Hanhart and Ingold, *J. Chem. Soc.*, 1005 (1927).

alcohol and the resulting saturated solution of trimethylamine, which contained no secondary amine as shown by the Duke[11] test, was used in the preparation of a picrate; m. p. 216.5–218.5° dec. Recrystallization from absolute ethanol raised the melting point to 217.5–220.5° dec. A mixed melting point with an authentic specimen gave no depression, and infrared spectra of the two samples were identical.

The reaction mixture was fractionated *in vacuo* through a 7-inch Fenske column. The following fractions were collected.

Fraction	Boiling point		Weight,	
	°C.	Mm.	g.	n^{20}_{D}
1	31–34	1	0.80	1.5020
2	103–104	3	1.24	1.5180
3	106–111	3	4.61	1.5196
4	111–120	3	1.14	1.5228
5	131–138	3	1.00	1.5409
6	142–146	3	6.16	1.5566
7	148	3	1.04	1.5557
8	165–175	1	0.64	1.5589
9	172–177	1.2	6.33	

Fractions 2 and 3 were hydrocinnamonitrile, 5.85 g. (14.8%). Fraction 3 was fractionally distilled to obtain an analytical sample; b. p. 142° (25 mm.), n^{20}_{D} 1.5179.

Anal. Calcd. for C_9H_9N: C, 82.40; H, 6.91. Found: C, 82.40; H, 7.32.

A small portion of Fraction 3, 0.6 g., was hydrolyzed overnight with 1 g. of potassium hydroxide in 5 ml. of water and 5 ml. of 95% alcohol. The resulting acid was converted to its *p*-bromophenacyl ester[9]; m. p. 104–105°.

Fractions 6 and 7 were dibenzylmethylamine; 7.20 g. (22.7%). Fraction 6 was redistilled for analysis.

Anal. Calcd. for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.39; H, 8.27; N, 6.81.

Several drops of the amine were used to prepare the hydrochloride, which after recrystallization from acetone melted at 199.5°. The mixed melting point with an authentic sample[13] (m. p. 202.5–203°) was 202°. A picrate was prepared in 95% alcohol and recrystallized from an alcohol-water mixture; it melted at 106.5–108°. A mixed melting point with an authentic sample (m. p. 106.5–107.5°) was 106.5–107.5°.

Fraction 9, which proved to be dibenzylacetonitrile, was a yellow oil which crystallized on standing; recrystallized from 95% alcohol, it melted at 89.5° (lit.[14] 89.7–90.4°). A sample was submitted for analysis.

Anal. Calcd. for $C_{16}H_{15}N$: C, 86.83; H, 6.84. Found: C, 86.69; H, 7.03.

A portion of this fraction, 1 g., was hydrolyzed by refluxing overnight with 0.5 g. of sodium hydroxide in a mixture of 5 ml. of ethylene glycol and 5 ml. of water. The resulting acid was converted to the anilide, which after recrystallization from 95% alcohol melted at 155.5–157.5° (lit.[15] 155°).

Reaction of 1-Methylgramine with Cyanoacetic Ester (in the Absence of Sodium).—The reaction was carried out as previously described.[1] The gas given off was collected in alcohol. This solution, which gave a negative Duke[11] test for secondary amines, was used in the preparation of a picrate, recrystallized from alcohol, m. p. 217–219.5° dec.; mixed melting point with an authentic specimen of trimethylamine picrate, 216.5–218° dec. The infrared absorption curves were identical.

Pyrolysis of Benzyltrimethylammonium Cyanoacetate.—The salt was prepared by the neutralization of cyanoacetic acid with benzyltrimethylammonium hydroxide (obtained from the iodide and silver oxide) and evaporation of the resulting aqueous solution *in vacuo* at 30–40°. Near the end of the evaporation benzene was added and evaporated to assist in the removal of water. The residual crystalline mass was recrystallized from pure, dry acetone and dried to constant weight *in vacuo*. The extreme hygroscopicity of the salt rendered the melting point determination and microanalysis inaccurate. In the melting-point tube the substance appeared to liquefy partially at about 115°, to begin to generate trimethylamine at about 165°, and to decompose violently at 185°.

Anal. Calcd. for $C_{13}H_{18}O_2N_2$: C, 66.64; H, 7.74. Found: C, 65.77; H, 7.74 (and, when the sample was redried and reanalyzed, C, 64.59, H, 8.22).

The decomposition was carried out as previously described for the amine and ester. In an experiment with 30.23 g. of the salt decomposition was vigorous at 200° and the salt liquefied completely after two and one-quarter hours at this temperature; heating was continued for a total of ten and three-quarters hours, at the end of which time the evolution of gases (trimethylamine and carbon dioxide) had become very feeble. The cooled reaction mixture was separated into neutral and basic components by dilution with ether and extraction with dilute hydrochloric acid. The low-boiling portion of the neutral fraction contained benzyl alcohol[16] (identified as the α-naphthylurethan) which interfered with the separation of hydrocinnamonitrile. However, the presence of this nitrile was established by hydrolysis with hydrobromic acid and conversion of the hydrocinnamic acid to the *p*-bromophenacyl ester,[9] m. p. 99.2–101.2°; a mixed m. p. with an authentic sample of m. p. 103.6–104.8° was 102–103.5°. The higher-boiling neutral fraction (4.00 g., 35.6%) solidified on standing and after recrystallizations from 95% ethanol and from low-boiling petroleum ether melted at 92.5–93.5°. This melting point was not lowered by admixture of known dibenzylacetonitrile.

The basic fraction was distilled; b. p. 98° (0.3 mm.), n^{21}_{D} 1.5581; weight 0.75 g. A picrate was prepared and recrystallized from 95% alcohol, m. p. 155.8–156.8°. The hydrochloride was also prepared and recrystallized from isopropyl alcohol, m. p. 188.5–189.5°. These values agree with those reported for the picrate and hydrochloride of α,β-diphenylethyldimethylamine.[17] When the hydrochloride was recrystallized from ethyl alcohol, the above melting point was observed. However, recrystallization of the sample from isopropyl alcohol generally yielded material of m. p. 212.5–213°. The melting point of one such sample fell to that recorded above after standing for a few days. Admixture of these two derivatives with the corresponding ones prepared from a sample of α,β-diphenylethyldimethylamine obtained from the thermal decomposition of dibenzyldimethylammonium cyanoacetate gave no depression in melting point. The infrared absorption spectra were identical (the hydrochlorides were dissolved in chloroform; the picrates were suspended in Nujol).

Pyrolysis of Dibenzyldimethylammonium Cyanoacetate.—The salt was prepared by shaking overnight a suspension of equivalent amounts of silver cyanoacetate and dibenzyldimethylammonium chloride in methanol, filtering and evaporating the solution *in vacuo* at room temperature. The residual salt from 0.0319 mole of each reagent was heated at 200° for twenty-eight hours. Trimethylamine and carbon dioxide, evolved during the reaction, were identified as before. Only the basic components of the residual reaction mixture were examined; fractionation of the bases gave two products: (1) b. p. 51–59° (16 mm.), n^{20}_{D} 1.5016, weight 0.85 g. and (2) b. p. 165–174° (16 mm.), n^{20}_{D} 1.5298, weight 1.18 g. Fraction (1)

---

[13] Holmes and Ingold, *J. Chem Soc.*, **127**, 1816 (1925).

[14] Bergstrom and Agostinho, THIS JOURNAL, **67**, 2152 (1945).

[15] Heilbron and Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1943, Vol. I, p. 668.

[16] Any water present in the salt is alkylated during the thermal decomposition. In a preliminary experiment in which the apparatus and the benzyltrimethylammonium cyanoacetate were not rigorously dried benzyl alcohol and benzyl ether were the only neutral products isolated.

[17] Stevens, Kowan and MacKinnon, *J. Chem. Soc.*, 2571 (1931); α,β-diphenylethyldimethylamine picrate m. p. 156–157°; hydrochloride m. p. 187–188°.

was shown to be benzyldimethylamine by the preparation of the picrate, m. p. and mixed m. p. 91–92.5°. Fraction (2) was identified as α,β-diphenylethyldimethylamine[17] by conversion to the hydrochloride (m. p. 186–187.5°) and the picrate (m. p. 156–157°).

Experiments Involving a Free Radical Inhibitor.—(1) Reaction of benzyldimethylamine with methyl cyanoacetate: Two experiments were carried out simultaneously. Flask A contained 1.35 g. (0.01 mole) of benzyldimethylamine and 0.99 g. (0.01 mole) of methyl cyanoacetate. Flask B contained the same quantities of benzyldimethylamine and methyl cyanoacetate and 0.2 g. (0.0018 mole) of hydroquinone. The flasks were maintained at 200° for seventeen hours and the exit gases which were protected from the atmosphere by soda-lime tubes were bubbled through saturated solutions of barium hydroxide. A continuous stream of nitrogen was maintained over the reaction mixtures during the first hour. Copious evolution of carbon dioxide commenced from both flasks as soon as they reached reaction temperature. At the completion of the period of heating, both reaction mixtures had the same tarry appearance. The precipitated barium carbonate was collected on tared sintered glass funnels, which were then dried at 60° for 20 minutes and weighed. The weights of barium carbonate from experiments A and B were 0.272 g. and 0.266 g., respectively.

(2) Reaction of benzyl bromide with methyl benzylcyanoacetate[18]: Parallel experiments were carried out in the manner described above. Flask A contained 2.0 g. (0.0106 mole) of methyl benzylcyanoacetate and 3.64 g. (0.0212 mole) of benzyl bromide. Flask B contained the same quantities of these reagents and 0.2 g. (0.0018 mole) of hydroquinone. Heating was maintained at 160° for seventeen hours, the current of nitrogen being maintained throughout. The precipitated barium carbonate from experiment A weighed 0.039 g., that from B, 0.001 g. The appearance of the two reaction mixtures was quite different at the conclusion of heating. Mixture A (no hydroquinone present) was charred while mixture B remained clear and apparently unchanged.

Disproportionation of Benzyldimethylamine.—(1) In the presence of an equimolar amount of benzyltrimethylammonium chloride: Two flasks equipped with air condensers and the trap arrangement already described were heated in an oil-bath at 200° for seventeen hours. Flask A contained 18.6 g. (0.1 mole) of benzyltrimethylammonium chloride. Flask B contained the same quantity of benzyltrimethylammonium chloride and 13.5 g. (0.1 mole) of benzyldimethylamine. When the reaction was complete, the Dry Ice–acetone trap from reaction A was practically dry. The trap from reaction B contained 3–4 ml. of liquid which was identified as trimethylamine by the method used above.

Reaction mixture A was rinsed with ether. The ether was dried over sodium sulfate and removed by distillation. Only a few drops of a liquid, having an odor similar to that of benzyl chloride,[19] remained. Attempts to prepare a derivative of this material failed.

Reaction mixture B was thoroughly rinsed with ether. The ether solution was dried over sodium sulfate and distilled. The remaining liquid was distilled *in vacuo* from a modified Claisen flask and separated into the following fractions: (1) b. p. 58–62° (15 mm.); $n^{20}D$ 1.5049; wt. 1.34 g.; (2) b. p. 69° (15 mm.); $n^{20}D$ 1.5105; wt. 1.20 g.; (3) b. p. 161–165° (14 mm.); $n^{20}D$ 1.5602; wt. 8.28 g. A picrate was prepared from a few drops of fraction 2; after recrystallization from 95% alcohol it melted at 91.5–92.5°, and this melting point was not depressed by admixture of authentic benzyldimethylamine picrate (m. p. 92.5–94°). Fraction 1 was assumed, on the basis of solubility in dilute acid, to consist principally of benzyldimethylamine, the recovery of which was therefore 2.54 g. (18.8%). Fraction 3 was identified as dibenzylmethylamine (yield 78%, based on benzyldimethylamine) by the picrate, which melted at 105–105.5° alone or mixed with the authentic salt.

(2) In the presence of one-tenth the molar amount of benzyltrimethylammonium chloride: Benzyldimethylamine, 13.5 g. (0.1 mole), and 1.86 g. (0.01 mole) of benzyltrimethylammonium chloride were placed in a flask and heated as described in the preceding experiment. The exit gas was identified as trimethylamine. After extraction of the reaction mixture with ether, drying, and distillation of the solvent, fractionation of the residue yielded 7.73 g. (73%) of dibenzylmethylamine identified as above in addition to 1.90 g. (14.1%) of unchanged benzyldimethylamine.

(3) In the presence of concentrated hydrochloric acid: Benzyldimethylamine, 13.5 g. (0.1 mole), to which was added two drops of concentrated hydrochloric acid was treated as described above. Treatment of the mixture resulted in the recovery of 10.50 g. (78%) of unchanged benzyldimethylamine and 0.85 g. (8.1%) of dibenzylmethylamine, identified as before.

(4) In the presence of boron trifluoride: This reaction was carried out in exactly the same way as that with concentrated hydrochloric acid, except that two drops of boron trifluoride etherate were substituted for the hydrochloric acid. The experiment resulted in the production of 1.58 g. (15.0%) of dibenzylmethylamine and the recovery of 9.65 g. (71.5%) of unchanged benzyldimethylamine.

Summary

Benzyldimethylamine has been shown to alkylate tricarbethoxymethane and methyl cyanoacetate. These two reactions in addition to the previously reported alkylation of methyl cyanoacetate with 1-methylgramine proceed under similar experimental conditions with the evolution of trimethylamine or dimethylethylamine in the case of tricarbethoxymethane. A substitution mechanism for these reactions is proposed which involves the formation of a quaternary salt as the first step. A free radical mechanism is untenable.

Benzyldimethylamine disproportionates to yield dibenzylmethylamine and trimethylamine in the presence of traces of the benzyltrimethylammonium ion. A cyclic process in which the benzyltrimethylammonium ion is regenerated is proposed. Traces of acids which form substituted ammonium ions with the amine cause the disproportionation to a lesser extent.

The dibenzyldimethylammonium ion has been observed to undergo the Stevens rearrangement to α,β-diphenylethyldimethylamine when heated in the presence of the cyanoacetate ion.

URBANA, ILLINOIS RECEIVED OCTOBER 10, 1949

---

(18) The ester was prepared by the method of Alexander and Cope, [THIS JOURNAL, **66**, 886 (1944)] for the ethyl ester. The material had a melting point of 35–36° which could not be raised by recrystallization from petroleum ether (30–60°). *Anal.* Calcd. for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86. Found: C, 69.93; H, 5.87.

(19) Collie and Schryver [*J. Chem. Soc.*, **57**, 767 (1890)] found that benzyltrimethylammonium chloride decomposes at temperatures slightly above 300° to give benzyl chloride, benzyldimethylamine, trimethylamine and methyl chloride.