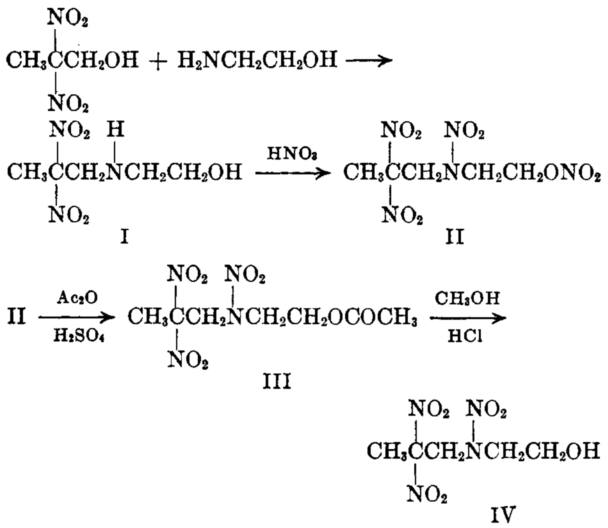
CHART I



scribed by Wolfrom *et al.*,[5] the nitrate ester was readily converted with acetic anhydride and sulfuric acid to the corresponding acetate (III), which was hydrolyzed to *N*-(2,2-dinitropropyl)-*N*-nitroethanolamine (IV).

EXPERIMENTAL[7,8]

N-(2,2-Dinitropropyl)-N-nitroethanolamine nitrate (II). A mixture of 30.0 g. (0.5 mole) of ethanolamine, 80 ml. of methanol, 31.0 g. (0.5 mole) of glacial acetic acid, and 75.0 g. (0.45 mole) of 90% 2,2-dinitropropanol was refluxed for 3 hr. The methanol was removed by concentration *in vacuo* and the residual brown oil was diluted with water. The aqueous solution was extracted twice with methylene chloride. The combined extracts were washed with water and saturated sodium chloride solution, dried, and concentrated, leaving 46.0 g. of brown oil.

A mixture of 220 ml. of absolute nitric acid and 195 ml. of concd. sulfuric acid was heated to 40–45° and the above oil was added in 10 min. The yellow solution was heated at 54–57° for 35 min., cooled, and poured onto ice. The beige colored solid was collected, washed well with water, and recrystallized from methanol to give 27.0 g. (21.2%) of almost colorless plates, m.p. 108–111°.

Anal. Calcd. for $C_5H_9N_5O_9$: C, 21.21; H, 3.20. Found: C, 21.89; H, 3.33.

N-(2,2-Dinitropropyl)-N-nitroethanolamine acetate (III). A solution of 1.0 g. (0.0035 mole) of *N*-(2,2-dinitropropyl)-*N*-nitroethanolamine nitrate in 8 ml. of acetic anhydride was cooled in an ice bath and 1 ml. of concd. sulfuric acid was added. On warming, an exothermic reaction with gas evolution took place. After 5–10 min. at 80°, the solution was cooled and poured onto ice. The solid was collected and recrystallized from methanol to give 0.54 g. (54.2%) of colorless plates, m.p. 56–57°.

Anal. Calcd. for $C_7H_{12}N_4O_8$: C, 30.00; H, 4.32; N, 20.00. Found: C, 30.44; H, 4.55; N, 20.01.

N-(2,2-Dinitropropyl)-N-nitroethanolamine (IV). A solution of 0.4 g. of *N*-(2,2-dinitropropyl)-*N*-nitroethanolamine acetate, 12 ml. of methanol, and 1 ml. of concd. hydrochloric acid was refluxed for 3.5 hr. and concentrated, leaving a solid, m.p. 53–55°. Recrystallization of the product from chloroform yielded colorless needles, m.p. 59–60°.

Anal. Calcd. for $C_5H_{10}N_4O_7$: C, 25.21; H, 4.23; N, 23.53. Found: C, 25.48; H, 4.06; N, 23.78.

2,2-Dinitrobutyl acrylate. This preparation is typical of the synthesis of the *gem*-dinitroalkyl acrylates. A mixture of 164 g. (1.0 mole) of 2,2-dinitrobutanol, 108 g. (1.5 moles) of glacial acrylic acid stabilized with methylene blue, 500 ml. of benzene, and 2 ml. of concd. sulfuric acid was refluxed under a Dean-Stark trap until the theoretical amount of water was collected. The solution was diluted with 250 ml. of benzene and washed with five 250-ml. portions of water, three 250-ml. portions of 5% sodium bicarbonate, and two 250-ml. portions of water. The solution was dried over sodium sulfate, concentrated, and the residue distilled to give 148 g. (67.8%) of 2,2-dinitrobutyl acrylate, b.p. 74/2 μ, n_D^{25} 1.4579.

Acknowledgment. We are indebted to the Office of Naval Research for the financial support of this work.

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[5] M. I. Wolfrom, R. S. Bower, and G. G. Maher, *J. Am. Chem. Soc.*, **73**, 874 (1951).

[6] In this preparation acrylic acid and trifluoroacetic anhydride were used according to the procedure of A. H. Ahlbrech and D. W. Codding, *J. Am. Chem. Soc.*, **75**, 984 (1953).

[7] All melting points and boiling points are uncorrected.

[8] Microanalyses by Elek Microanalytical Laboratories, Los Angeles, Calif.

Di- and Tetracarboxydiphenylmethanes and Derivatives

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The condensation of aromatic compounds with carbonyl compounds to form diphenylmethanes has been known for many years. There are many references to the condensation of "activated" aromatics such as phenols, anilines, toluene, and naphthalene with acetone, formaldehyde, etc. However, there are few references to the condensation of negatively substituted benzenes such as benzoic acid, nitrobenzene and x-chloronitrobenzenes with formaldehyde. Prior to this publication, the condensation of the phthalic acids (*o*, *m*, or *p*) with formaldehyde to form diphenylmethanes had not been reported.

In 1894, Schopff[2] and Weil[3] in separate communications reported the condensation of benzoic acid with formaldehyde to give a product which they stated was the *meta*-substituted diphenylmethane. It was reasoned that since the product had a lower melting point than the known *para* isomer and did not form anthrone-1-carboxylic acid on heating with sulfuric acid, it must have been the *meta* isomer.

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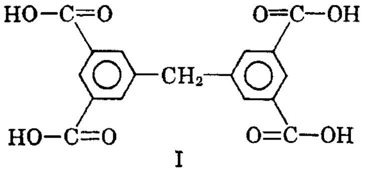
[2] M. Schopff, *Ber.*, **27**, 2321, 2324 (1894).

[3] H. Weil, *Ber.*, **27**, 3315 (1894).

Schopff[2] also showed that nitrobenzene condensed with formaldehyde in sulfuric acid in unreported yield and conversion. Nastjukow[4] also investigated this reaction in concentrated sulfuric acid at higher temperature.

Matsukawa[5] showed that benzoic acid derivatives and nitrobenzenes could be chloromethylated in concentrated sulfuric acid and that the corresponding diphenylmethanes were byproducts in the reaction.

The present studies continued the investigation of the condensation of negatively substituted aromatics with formaldehyde to form diphenylmethanes. Additional evidence that 3,3′-dicarboxydiphenylmethane is the product of the condensation of benzoic acid with formaldehyde was obtained. It was also found that sulfuric acid containing 20% sulfur trioxide permits condensation of a highly "deactivated" aromatic such as isophthalic acid with formaldehyde to form the corresponding diphenylmethane (I).



I

It was discovered that zinc chloride (or boron trifluoride) phosphoric acid catalyst "complex" enables condensation of benzoic acid with formaldehyde to give 3,3′-dicarboxydiphenylmethane. This product was characterized as the dimethyl ester. It was compared with the dimethyl ester of the bisacid obtained by Schopff and Weil and shown to be identical.

Reduction of 3,3′-dicarbomethoxydiphenylmethane with lithium aluminum hydride gave 3,3′-dihydroxymethyldiphenylmethane. While the infrared spectrum of 3,3′-dicarboxydiphenylmethane gives no indication of the aromatic substitution due to interference in the substitution region, the infrared spectrum of the 3,3′-dihydroxymethyldiphenylmethane clearly shows *meta* substitution.

Reduction of the tetramethyl ester of the condensation product of isophthalic acid and formaldehyde gave 3,3′,5,5′-tetrahydroxymethyldiphenylmethane. The structure of this compound was confirmed by elemental and NMR analyses and by infrared analysis which showed the 1,3,5-substitution.

EXPERIMENTAL

3,3′,5,5′-Tetracarbomethoxydiphenylmethane. Isophthalic acid (33 g., 0.20 mole) was dissolved in 100 ml. of 20% oleum. To the solution, 95% paraformaldehyde (3.1 g., 0.10 mole) was added. The mixture was maintained at 111–119° for 6 hr. The mixture was cooled, poured onto ice water, filtered and dried in a vacuum oven at 50°. The solid products were dissolved in 100 ml. of methanol, saturated with hydrochloric acid and refluxed for 30 min. The mixture was cooled to 10° and the solid product which appeared was filtered, washed with cold methanol, and dried to give 13.0 g. of product, m.p. 196–198°. Recrystallization from benzene gave 9.7 g. (14.8% yield) of purified 3,3′,5,5′-tetracarbomethoxydiphenylmethane, m.p. 199–201°. In addition a 40% yield of dimethyl isophthalate was obtained.

Anal. Calcd. for $C_{21}H_{20}O_8$: C, 63.00; H, 5.00; sapon. equiv., 100. Found: C, 63.17; H, 5.34; sapon. equiv., 100.

3,3′,5,5′-Tetracarboxydiphenylmethane. The tetramethyl ester (1.5 g.) was dissolved in 5 ml. of concd. sulfuric acid, warmed on the steam bath for 30 min., diluted with water, cooled, and filtered. The product was washed with water, redissolved in 20% sodium hydroxide solution, and refluxed for 30 min. The mixture was cooled to room temperature and acidified with sulfuric acid. After filtration, washing and drying, 1.1 g. (85%) of 3,3′,5,5′-tetracarboxydiphenylmethane, m.p. 346–350°, was obtained.

Anal. Calcd. for $C_{17}H_{12}O_8$: C, 59.30; H, 3.49; neut. equiv., 86.0. Found: C, 59.3; H, 3.65; neut. equiv., 86.6.

3,3′,5,5′-Tetrahydroxymethyldiphenylmethane. Tetracarbomethoxydiphenylmethane (10 g., 0.025 mole) was dissolved in 400 ml. of dry tetrahydrofuran. The solution was added over a 1-hr. period to a stirred mixture of 200 ml. of tetrahydrofuran and 3 g. (0.079 mole) of lithium aluminum hydride. The mixture was heated to reflux and then cooled to 10°. Water, 50 ml., was then added slowly with ice cooling and the mixture was acidified with 10% sulfuric acid. After removal of the solvent, the solid residue was recrystallized from acetone giving 3,3′,5,5′-tetrahydroxymethyldiphenylmethane, 3 g. (48.6%), m.p. 106–107° and 1.5 g. (24.3%), m.p. 103–105°.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.83; H, 6.95; OH, 23.6. Found: C, 70.8; H, 6.92; OH, 23.2.

The structure proposed was consistent with NMR data obtained in the melt. Infrared data clearly showed the absence of carbonyl and the presence of predominantly 1,3,5-substitution.

3,3′-Dicarbomethoxydiphenylmethane. To a stirred solution of 180 g. of zinc chloride (or equimolar quantities of boron trifluoride) in 100 g. of phosphoric acid (85%) was charged 61 g. (0.50 mole) of benzoic acid and 15 g. (0.50 mole) of paraformaldehyde. The mixture was stirred at 115–124° for 2.5 hr. and after cooling, poured cautiously onto ice water. The solid product was filtered and then extracted overnight with hot water in a Soxhlet apparatus to remove unchanged benzoic acid. The residue was dried and then esterified by treatment with methanolic hydrochloric acid in the conventional manner. Distillation gave 12 g. of crude 3,3′-dicarbomethoxydiphenylmethane, b.p. 200–220°/1–2 mm., which solidified on seeding. This was further purified by three recrystallizations from methanol giving 7.2 g. (10.1%), m.p. 61.0–62.0°. Mixed melting point with a sample of 3,3′-dicarbomethoxydiphenylmethane derived from 3,3′-dicarboxydiphenylmethane prepared in sulfuric acid showed no depression. The infrared spectra of both dimethyl ester samples taken as 20% solutions in carbon tetrachloride and in carbon disulfide were identical.

3,3′-Dihydroxymethyldiphenylmethane. To a stirred mixture of 200 ml. of dry ether and 3.0 g. (0.079 mole) of lithium aluminum hydride was added in 1 hr. 14.2 g. (0.05 mole) of 3,3′-dicarbomethoxydiphenylmethane dissolved in 150 ml. of ether. The mixture was refluxed for 1 hr., cooled, cautiously hydrolyzed with water, and then poured over 10% sulfuric acid. The ether layer was separated, washed neutral, and then the ether was distilled. The product, which solidified on standing was recrystallized from benzene giving 8.0 g. (77%) of 3,3′-dihydroxymethyldiphenylmethane, m.p. 42–43°.

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(4) A. Nastjukow, *J. Russ. Phys.-Chem. Soc.*, **40**, 1376 (1909).

(5) T. Matsukawa and K. Sirakawa, *J. Pharm. Soc. Japan*, **70**, 25–28 (1950).

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 79.0; H, 7.03; OH, 14.9. Found: C, 78.8; H, 7.02; OH, 15.3.

Infrared data were consistent with the proposed structure and showed a predominance of *meta* substitution.

Acknowledgment. The authors are indebted to Mr. L. Boros and Mr. R. B. Smith for infrared interpretations and to Mr. J. V. Pustinger for NMR interpretations.

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Synthesis of N-Substituted Aminophosphonium Halides by Alkylation Reactions

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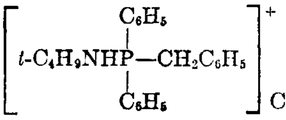
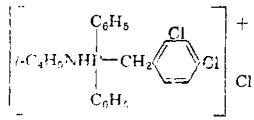
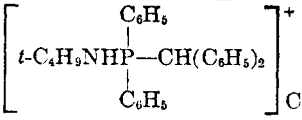
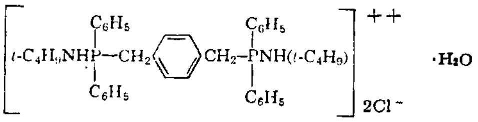
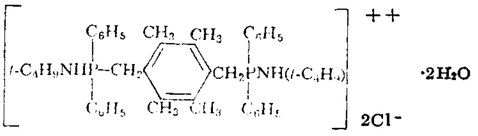
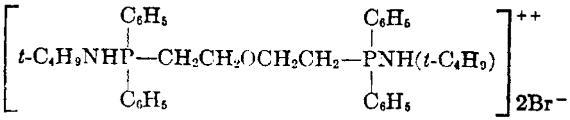
The preparation of trisubstituted aminophosphonium chlorides by the reaction of chloramine with tertiary phosphines, first established in our laboratory,[1] has been extended to additional compounds with alkyl,[2,3] alkenyl,[3] and aralkyl[3] substitutions on the phosphorus atom. The variety of *N*-substitutions in aminophosphonium chlorides by this mode of synthesis is, however, limited at present by the availability of only a few *N*-substituted chloramines.

A promising alternative approach to the *N*-substituted aminophosphonium halides was suggested by the relatively simple quaternization of tertiary phosphines by organic halides.[4] By the use of this method we have been able to synthesize easily mono- and diquaternary aminophosphonium halides with *N*-substitutions by the interaction of *N*-substituted aminophosphines with alkyl halides and dihalides. Solvents of the polar type such as dimethylformamide are useful in promoting this reaction.

The following *t*-butylaminodiphenylphosphonium chlorides were prepared by this method: *P*-benzyl-, *P*-(2,4-dichlorobenzyl)-, *P*-benzhydryl-, *P*-(*p*-xylylene)bis-, and *P*-(*p*-tetramethylxylylene)bis-(*t*-butylaminodiphenylphosphonium) chloride. Using a similar reaction with *β,β'*-dibromodiethyl ether,

TABLE I

SOME MONO- AND DIQUATERNARY AMINOPHOSPHONIUM HALIDES

Formula	Yield, %	M.P.	C, % Calcd. Found	H, % Calcd. Found	Cl, % Calcd. Found
 $\left[t\text{-}C_4H_9NHP(C_6H_5)_2\text{—}CH_2C_6H_5\right]^+ Cl^-$	48	247° dec.	71.95 71.72	7.09 6.98	9.23 9.15
	46	271° dec.	61.01 60.96	5.57 5.58	23.49 23.64
 $\left[t\text{-}C_4H_9NHP(C_6H_5)_2\text{—}CH(C_6H_5)_2\right]^+ Cl^-$	50	247° dec.	75.72 75.68	6.79 6.92	7.71 7.95
	80	269° dec.	67.69 67.60	7.10 7.13	9.99 9.70
	52	295° dec.	67.42 67.46	7.97 7.86	9.05 9.19
 $\left[t\text{-}C_4H_9NHP(C_6H_5)_2\text{—}CH_2CH_2OCH_2CH_2\text{—}P(C_6H_5)_2NH(t\text{-}C_4H_9)\right]^{++} 2Br^-$	50	278° dec.	57.92 57.86	6.48 6.39	(Br)21.41 (N)3.75 (P)8.30 21.69 3.98 8.50

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[1] H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Am. Chem. Soc.*, **81**, 2982 (1959).

[2] R. Appel and A. Hauss, *Ber.*, **93**, 405 (1960).

[3] H. H. Sisler, H. S. Ahuja, and N. L. Smith, *J. Org. Chem.*, *in press*.

[4] R. N. McDonald and T. W. Campbell, *J. Am. Chem. Soc.*, **82**, 4669 (1960).