removed by vacuum distillation. The resulting solid, m.p. 105–106°, was identified as 3-*n*-butyl-4-hydroxy-4-methyl-5,5-pentamethylene-2-oxazolidinone.

The infrared spectrum showed characteristic peaks at 3.00 and 5.77 μ for the −OH and cyclic urethane carbonyl.

Anal. Calcd. for $C_{13}H_{23}NO_3$: C, 64.70; H, 9.61; N, 5.80. Found: C, 64.54; H, 9.48; N, 5.54.

The hydroxy compound was dehydrated by refluxing a benzene solution under a Dean–Stark trap. Vacuum removal of the solvent yielded an oil, b.p. 165° at 2 mm., yield 4.0 g. (72%).

Anal. Calcd. for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 69.85; H, 9.46; N, 6.25.

Method B.—Equal quantities (25 g.) of 1-acetylcyclohexanol and *n*-butyl isocyanate were dissolved in ether. The mixture was cooled in ice due to spontaneous exothermic reaction. Vacuum removal of the solvents yielded the hydroxymethyl oxazolidinone, m.p. 105–106°, identical with that obtained from the dioxolanone.

Treatment of 2-Imino-4,4-pentamethylene-5-methylenedioxolane with Aqueous Sodium Hydroxide.—A sample of the crude 2-iminodioxolane (IX) was dissolved in 10% sodium hydroxide solution. The resulting mixture was extracted with ether. The ether was removed at reduced pressure and the 1-acetyl-1-cyclohexanol distilled, b.p. 105–107° (26 mm.), $n^{25}D$ 1.4660.[6]

Acknowledgment.—The microanalyses were performed by Messrs. William Brown, Howard Hunter, George Maciak, David Cline, and Alfred Brown. Many of the starting materials were prepared in this laboratory by Mr. Lawrence White. The infrared and n.m.r. spectra were obtained by Mr. John Klemm, Mrs. Doris Stephens, and Miss Martha Hofmann. The authors wish to thank especially Dr. Harold Boaz and Messrs. Paul Landis and Donald Woolf, Jr., for their assistance in interpreting the infrared and n.m.r. data.

[6] G. F. Hennion and E. J. Watson, *J. Org. Chem.*, **23**, 656 (1958).

Cannizzaro Reactions Involving Aromatic Dialdehydes[1]

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An example of a Cannizzaro reaction of an aromatic dialdehyde is on record; Löw[2] found that the reaction of terephthalaldehyde with sodium hydroxide solution yields terephthalic acid, *p*-hydroxymethylbenzoic acid, and α,α′-*p*-xylenediol.

Bromoterephthalaldehyde has now been subjected to Cannizzaro reaction conditions and rather similar results have been observed. The products formed are: the diacid (15% yield), 3-bromo-4-hydroxymethylbenzoic acid (63% yield), and the diol (19% yield); total yield, 97%. The results indicate that the aldehyde function in bromoterephthalaldehyde which is *ortho* to halogen is more easily reduced and that the other aldehyde function is more easily oxidized.

The behavior of mixtures of terephthalaldehyde and formaldehyde and of bromoterephthalaldehyde and formaldehyde in strong sodium hydroxide solution has been studied also. It was found that the extent of reduction of the aromatic dialdehyde to diol increased as the relative amount of formaldehyde was increased. Two examples of these reactions are reported in the Experimental section: (1) a 1:8 terephthalaldehyde to formaldehyde mixture gave 68% yield of α,α′-*p*-xylenediol and 9% yield of *p*-hydroxymethylbenzoic acid; (2) a 1:12 bromoterephthalaldehyde to formaldehyde mixture gave 76% yield of bromo-α,α′-*p*-xylenediol and 22% yield of 3-bromo-4-hydroxymethylbenzoic acid.

Some of the compounds required for use or comparison were prepared by methods which have been described previously (terephthalaldehyde,[2] *p*-hydroxymethylbenzoic acid,[2] and α,α′-*p*-xylenediol[3]) or were available (terephthalic acid, Eastman White Label). Others have now been synthesized, and methods and related data are reported in the Experimental section; derivatives of a number of these compounds have been prepared by standard procedures.

Experimental

Bromoterephthalaldehyde.—Crude α,α,α′,α′-tetrabromobromo-*p*-xylene (100 g., 0.2 mole, from *p*-xylene → bromo-*p*-xylene[4] → α,α,α′,α′-tetrabromobromo-*p*-xylene[5]) and 200 ml. of concentrated sulfuric acid were placed in a flask fitted with a stirrer and attached to a glass aspirator to remove hydrogen bromide and bromine fumes; this was maintained at 140° until no more fumes were evolved (*ca.* 45 min.). The reaction mixture was poured onto crushed ice; after the ice had melted, the mixture was steam distilled. The product weighed 21 g. (49% yield), m.p. 67–68°; further purification by steam distillation or by crystallization from water increased the melting point to 75°.

Anal. Calcd. for $C_8H_5BrO_2$: C, 45.07; H, 2.35; Br, 37.56. Found: C, 44.97; H, 2.54; Br, 37.73.

From the aldehyde, the following compounds were prepared: (a) the **dioxime**, (b) the **tetraacetate**, and (c) **bromoterephthalic acid**.

The dioxime melted at 218° (from ethanol).

Anal. Calcd. for $C_8H_7BrN_2O_2$: Br, 32.92; N, 11.52. Found: Br, 33.25; N, 11.39.

The tetraacetate melted at 132° (from ethanol).

Anal. Calcd. for $C_{16}H_{17}BrO_8$: C, 46.04; H, 4.08; Br, 19.18. Found: C, 46.00; H, 4.27; Br, 18.99.

Bromoterephthalic acid melted at 299° (from water, sublimes), lit.[6] m.p. 299°, neut. equiv. 124.

α,α′-Dibromobromo-*p*-xylene.—To bromo-*p*-xylene[4] (92.5 g., 0.5 mole) bromine (160 g., 1 mole) was added slowly (quartz apparatus; ultraviolet irradiation; oil bath temperature, 130°; reaction time, 2 hr.). Cooling the reaction mixture caused the major portion of it to solidify; recrystallization from ligroin (b.p. 90–120°) gave colorless crystals, 60 g. (35% yield), m.p. 91–92°.

Anal. Calcd. for $C_8H_7Br_3$: Br, 69.97. Found: Br, 69.94.

Bromo-α,α′-*p*-xylenediol.—The above tribromo compound (25 g., 0.0729 mole) was refluxed with 10% potassium carbonate solution. The hot reaction mixture was filtered, and the cooled filtrate was saturated with potassium carbonate. The precipitated diol weighed 5.5 g. (35% yield), m.p. 110–111° (from water).

Anal. Calcd. for $C_8H_9BrO_2$: C, 44.24; H, 4.15; Br, 36.87. Found: C, 44.52; H, 4.43; Br, 36.80.

From the diol, the following compounds were prepared: (a) the **diacetate**, (b) the **dibenzoate**, and (c) the **di-*p*-nitrobenzoate**.

The diacetate melted at 66–67° (from ethanol).

Anal. Calcd. for $C_{12}H_{13}BrO_4$: Br, 26.58. Found: Br, 26.64.

The dibenzoate had a melting point of 98–99° (from ethanol).

Anal. Calcd. for $C_{22}H_{17}BrO_4$: Br, 18.82. Found: Br, 18.82.

The di-*p*-nitrobenzoate melted at 164.5–165.5° (from benzene).

Anal. Calcd. for $C_{22}H_{15}BrN_2O_8$: Br, 15.53; N, 5.44. Found: Br, 15.57; N, 5.24.

α-Bromo-2-bromo-*p*-tolunitrile.—2-Bromo-*p*-tolunitrile (42.5

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[1] This investigation was supported in part by the Office of Naval Research.

[2] W. Löw, *Ann.*, **231**, 373 (1885).

[3] E. Grimaux, *ibid.*, **155**, 338 (1870).

[4] G. T. Morgan and E. A. Coulson, *J. Chem. Soc.*, 2211 (1929).

[5] By a method analogous to that used by J. M. Snell and A. Weissberger [*Org. Syn.*, **20**, 92 (1940)] for the preparation of α,α,α′,α′-tetrabromo-*p*-xylene.

[6] F. C. Whitmore and L. L. Isenhour, *J. Am. Chem. Soc.*, **51**, 2787 (1929).

g., 0.199 mole, from 2-bromo-*p*-toluidine[7] → 2-bromo-*p*-tolunitrile[8,9]) was brominated (34 g., 0.213 mole of bromine) under ultraviolet irradiation in a quartz flask; the system was heated in an oil bath (bath temperature, 175–180°). The reaction was continued until the gain in weight was *ca.* 17 g. When purification was attempted by warming the product with 200 ml. of ethanol, 4.5 g. of material did not dissolve, and it was discarded. The purified crystalline product weighed 24 g. (41% yield), m.p. 92° (from methanol).

Anal. Calcd. for $C_8H_5Br_2N$: Br, 58.18; N, 5.09. Found: Br, 58.31; N, 4.95.

2-Bromo-4-hydroxymethylbenzonitrile.—The α-bromo compound (10 g., 0.0341 mole) was refluxed with 1.5 l. of water in the presence of infusorial earth for 2.5 hr. The hot mixture was filtered, and the filtrate on cooling gave 6.2 g. (86% yield) of product, m.p. 101–102° (from water).

Anal. Calcd. for C_8H_6BrNO: Br, 37.74; N, 6.60. Found: Br, 37.56; N, 6.65.

2-Bromo-4-hydroxymethylbenzoic Acid.—The above nitrile (6.2 g., 0.0292 mole) was refluxed for 3 hr. with 80 ml. of 10% sodium hydroxide solution. Acidification of the reaction mixture with concentrated hydrochloric acid precipitated the product, 2.5 g. (37% yield), m.p. 147–148° (from water).

Anal. Calcd. for $C_8H_7BrO_3$: C, 41.56; H, 3.03; Br, 34.64; neut. equiv., 231. Found: C, 41.83; H, 3.12; Br, 34.74; neut. equiv., 232.2.

The **acetate** was prepared, m.p. 113–114° (from ethanol).

Anal. Calcd. for $C_{10}H_9BrO_4$: Br, 29.30; neut. equiv., 273. Found: Br, 29.18; neut. equiv., 272.9.

2-Bromoterephthalaldehydonitrile. A.—2-Bromo-4-hydroxymethylbenzonitrile (5 g., 0.0236 mole) was dissolved in concentrated nitric acid (25 ml.) at 15°. In a few minutes, evolution of oxides of nitrogen was observed; after *ca.* 5 min., when the reaction had subsided, the mixture was diluted with 125 ml. of water. The colorless product which separated was extracted with ether. Shaking the ether solution with saturated sodium bisulfite solution resulted in the formation of an addition compound; this was collected by filtration and washed with ethanol and with ether. In turn, the addition compound was dissolved in a minimum amount of water and decomposed by the addition of potassium carbonate solution and gentle warming. The yield of aldehyde was 4 g. (83%), m.p. 123° (from water).

Anal. Calcd. for C_8H_4BrNO: Br, 38.10; N, 6.67. Found: Br, 38.16; N, 6.64.

B.—2-Bromoterephthalaldehydonitrile, m.p. 123°, was obtained also in low yield by refluxing α-bromo-2-bromo-*p*-tolunitrile with cupric nitrate and nitric acid; the product was isolated first as the bisulfite addition compound, which was decomposed by warming it in potassium carbonate solution.

The melting point of a mixture of approximately equal parts of the isomeric 2- and 3-bromoterephthalaldehydonitriles (see below for the 3-bromo compound) was *ca.* 95°.

The **oxime** was prepared, m.p. 170° (from dilute ethanol).

Anal. Calcd. for $C_8H_5BrN_2O$: Br, 35.56; N, 12.44. Found: Br, 35.43; N, 12.53.

2-Bromoterephthalaldehydamide.—The aldehydonitrile (2 g., 0.00952 mole) was dissolved in 15 ml. of concentrated sulfuric acid, and the solution was warmed on a steam bath for 1 hr. The reaction mixture was cooled and diluted with 100 ml. of cold water; cooling the solution in a refrigerator for 12 hr. gave 1 g. of crystals (46% yield), m.p. 175° (from water).

Anal. Calcd. for $C_8H_6BrNO_2$: Br, 35.09; N, 6.14. Found: Br, 34.74; N, 6.38.

2-Bromoterephthalaldehydic Acid.—A 4-g. sample (0.0175 mole) of the amide was dissolved in 15 ml. of concentrated sulfuric acid, and a saturated solution of sodium nitrite (containing 1.2 g.) was added slowly below the surface of the liquid.[11] During the addition of the nitrite solution, the temperature of the reaction mixture was maintained at *ca.* 15°. After dilution with two volumes of water and cooling, the acid was collected by filtration. The product was dissolved in a slight excess of 10% potassium carbonate solution, and this was filtered to remove a trace of unchanged amide. The filtrate was acidified, and the product was recrystallized from a small volume of water; drying was accomplished in an atmosphere of nitrogen in a desiccator yielding 3 g. (75%), m.p. 172°.

Anal. Calcd. for $C_8H_5BrO_3$: C, 41.92; H, 2.18; Br, 34.93; neut. equiv., 229. Found: C, 41.96; H, 2.32; Br, 34.73; neut. equiv., 226.

From the aldehydic acid, the following compounds were prepared: (a) the **methyl ester** and (b) the **oxime**.

The methyl ester (with diazomethane) melted at 44° (from methanol).

Anal. Calcd. for $C_9H_7BrO_3$: C, 44.44; H, 2.88; Br, 32.92. Found: C, 44.51; H, 3.07; Br, 32.85.

The oxime melted at 120° (from dilute ethanol).

Anal. Calcd. for $C_9H_8BrNO_3$: Br, 31.01; N, 5.43. Found: Br, 30.92; N, 5.16.

α-Bromo-3-bromo-*p*-tolunitrile.—3-Bromo-*p*-tolunitrile (50 g., 0.255 mole, from *p*-nitrotoluene → 2-bromo-4-nitrotoluene → 3-bromo-*p*-toluidine → 3-bromo-*p*-tolunitrile[8,12]) was placed in a quartz flask fitted with a stirrer, a dropping funnel, and a reflux condenser. The system was heated in an oil bath (bath temperature, 175–180°) and irradiated with ultraviolet light. Bromine (40 g., 0.25 mole) was added slowly; the gain in weight was 17 g. The reaction mixture was poured into water, and the product which crystallized was collected by filtration and pressed free of oil. Crystallization from methanol gave 35 g. (50% yield) of product, m.p. 81°.

Anal. Calcd. for $C_8H_5Br_2N$: Br, 58.18; N, 5.09. Found: Br, 58.09; N, 5.14.

3-Bromo-4-hydroxymethylbenzonitrile.—α-Bromo-3-bromo-*p*-tolunitrile (25 g., 0.0909 mole) was refluxed with 2 l. of water until nearly complete solution was effected, and then the reaction mixture was subjected to steam distillation. The hot residue was filtered, the filtrate was allowed to cool, and crystals formed; the yield was 11 g. (57%), m.p. 134.5–135.5° (from water).

Anal. Calcd. for C_8H_6BrNO: Br, 37.74; N, 6.60. Found: Br, 37.61; N, 6.26.

3-Bromo-4-hydroxymethylbenzoic Acid. A. From 3-Bromo-4-hydroxymethylbenzonitrile.—The nitrile (10 g., 0.0472 mole) was warmed for 20 min. on a steam bath with 200 ml. of concentrated sulfuric acid; the reaction mixture was allowed to stand overnight at room temperature. It was then poured into 800 ml. of ice water, and the solution was evaporated to one-half volume. The crystals which formed when the aqueous solution was cooled were dissolved in potassium carbonate solution, and the acid was precipitated by acidifying the solution with dilute hydrochloric acid, giving 6.2 g. (57% yield), m.p. 174.5–176.5° (from water).

B. From α-Bromo-3-bromo-*p*-tolunitrile.—This nitrile (10 g., 0.0364 mole) was refluxed for 10 hr. with 125 ml. of 10% sodium hydroxide solution. The reaction mixture was cooled and acidified with concentrated hydrochloric acid, and the product which precipitated was recrystallized from water, giving 3.2 g. (38% yield), m.p. 175–176°.

Anal. Calcd. for $C_8H_7BrO_3$: C, 41.56; H, 3.03; neut. equiv., 231. Found: C, 41.47; H, 3.08; neut. equiv., 230.2.

From the alcohol acid, the following compounds were prepared: (a) the **acetate** and (b) the **methyl ester**.

The acetate melted at 145–146° (from 50% ethanol).

Anal. Calcd. for $C_{10}H_9BrO_4$: Br, 29.30; neut. equiv., 273. Found: Br, 29.36; neut. equiv., 274.5.

The methyl ester (with diazomethane) melted at 88–89° (from 50% methanol).

Anal. Calcd. for $C_9H_9BrO_3$: Br, 32.61. Found: Br, 32.59.

3-Bromoterephthalaldehydonitrile.—To a solution containing 20 g. of cupric nitrate, 30 ml. of concentrated nitric acid, and 250 ml. of water, 10 g. (0.0364 mole) of α-bromo-3-bromo-*p*-tolunitrile was added, and the mixture was refluxed for 12 hr. The reaction mixture was cooled and extracted with ether. The ether solution was concentrated to *ca.* 30 ml. and shaken with saturated sodium bisulfite solution. The bisulfite addition compound was collected and dissolved in a minimum amount of water, and the aldehyde was regenerated by saturating the aqueous solution with potassium carbonate and warming it. The aldehyde was recrystallized from 50% ethanol, yielding 3.1 g. (41%), m.p. 120.5°.

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(7) J. R. Johnson and T. L. Sandborn, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 111.

(8) A. Claus and H. Kunath, *J. prakt. Chem.*, [2]**39**, 485 (1889).

(9) This nitrile was converted to 2-bromo-*p*-toluamide by the action of concentrated sulfuric acid at 100° for 1 hr., m.p. 175° (from water), lit. m.p. 137°[8] and 175–176°.[10] A mixture of approximately equal amounts of this amide and the 3-bromo isomer (see ref. 12) melted at 142°.

(10) M. S. Gibson, *J. Chem. Soc.*, 776 (1956).

(11) J. J. Sudborough, *ibid.*, **67**, 602 (1895).

(12) This nitrile was converted to 3-bromo-*p*-toluamide by the method used for the 2-bromo isomer (see ref. 9), m.p. 174–175° (from water). *Anal.* Calcd. for C_8H_8BrNO: N, 6.54. Found: N, 6.38.

Anal. Calcd. for C_8H_4BrNO: Br, 38.10; N, 6.67. Found: Br, 38.20; N, 6.63.

The **oxime of 3-bromoterephthalaldehydonitrile** was prepared, m.p. 151° (from 50% ethanol).

Anal. Calcd. for $C_8H_5BrN_2O$: Br, 35.56; N, 12.44. Found: Br, 35.20; N, 12.53.

3-Bromoterephthalaldehydamide.—The nitrile (2 g., 0.00952 mole) was hydrolyzed by warming it with 20 ml. of concentrated sulfuric acid on a steam bath for 1 hr. The resulting solution was poured into 100 ml. of water, and the amide was purified by crystallization from water, yielding 2.1 g. (97%), m.p. 173°.

Anal. Calcd. for $C_8H_6BrNO_2$: Br, 35.09; N, 6.14. Found: Br, 34.99; N, 6.22.

3-Bromoterephthalaldehydic Acid.—The amide (2 g., 0.00877 mole) was dissolved in 20 ml. of concentrated sulfuric acid, and saturated sodium nitrite solution (containing 2.6 g.) was added slowly below the surface of the liquid.[11] The mixture was cooled and stirred; then it was warmed on a steam bath for a short time; finally it was poured into 100 ml. of water, yielding 1.93 g. (96%), m.p. 236° (from water).

Anal. Calcd. for $C_8H_5BrO_3$: C, 41.92; H, 2.18; neut. equiv., 229. Found: C, 41.83; H, 2.32; neut. equiv., 228.

The **methyl ester of 3-bromoterephthalaldehydic acid** was prepared (with diazomethane), m.p. 77° (from 25% ethanol).

Anal. Calcd. for $C_9H_7BrO_3$: C, 44.44; H, 2.88; Br, 32.92. Found: C, 44.85; H, 3.14; Br, 32.79.

The **oxime** of the methyl ester (above) was prepared, m.p. 131° (from 50% ethanol).

Anal. Calcd. for $C_9H_8BrNO_3$: Br, 31.01; N, 5.43. Found: Br, 30.78; N, 5.43.

Analysis of 3-Bromo-4-hydroxymethylbenzoic Acid–Bromoterephthalic Acid Mixtures.—By experiment it was shown that the volume of standard alkali solution required to neutralize mixtures of these acids was a linear function of weight–percentage composition. A graph[13] representing these data was constructed. Samples of the acid mixtures from the Cannizzaro reaction of bromoterephthalaldehyde (below) were titrated; from the graph, the compositions were determined.

Cannizzaro Reactions. A. Terephthalaldehyde and Formaldehyde.—A mixture of 45 g. (0.6 mole) of 40% formaldehyde solution and 10 g. (0.0746 mole) of terephthalaldehyde was placed in a flask fitted with a stirrer, a dropping funnel, and a thermometer. Methanol (50 ml.) was added, and the mixture was stirred until solution was effected. Sodium hydroxide solution (30 g. in 30 ml. of water) was added in small portions at such a rate that the temperature of the reaction mixture did not exceed 60°. In turn, the mixture was cooled to room temperature and poured into four volumes of water.

Crystals of α,α'-*p*-xylenediol formed and were collected by filtration. The filtrate was extracted with two 150-ml. portions of ether. From the ether solution, additional diol was obtained. The total yield was 7 g. (68%), m.p. 119° (from water).

The aqueous alkaline solution from which the diol had been extracted was acidified with 50% sulfuric acid, and two extractions with 150-ml. portions of ether were made. From the ether solution, *p*-hydroxymethylbenzoic acid was recovered. The yield was 1 g. (9%), m.p. 181° (from water).

B. Bromoterephthalaldehyde and Formaldehyde.—Bromoterephthalaldehyde (10.6 g., 0.05 mole) and formaldehyde (45 g. of 40% solution, 0.6 mole) were dissolved in methanol and treated with sodium hydroxide solution as in A immediately above.

Bromo-α,α'-*p*-xylenediol was isolated in a total yield of 8.25 g. (76%), m.p. 113° (from water).

The acidic product, which was recovered as in A above, was 3-bromo-4-hydroxymethylbenzoic acid, 2.5 g. (22% yield), m.p. 176° (from water).

C. Bromoterephthalaldehyde.—Bromoterephthalaldehyde (10.6 g., 0.05 mole) was dissolved in 100 ml. of methanol. This solution was cooled in an ice bath, and sodium hydroxide solution (40 g. in 60 ml. of water) was added in small portions at such a rate that the reaction temperature did not exceed 60°. After the alkali had been added, the ice bath was removed, and the reaction mixture was maintained at 60° for 1 hr.; then it was poured into three volumes of water, and this solution was warmed on a steam bath to remove methanol.

The aqueous alkaline solution was extracted with two 150-ml. portions of ether, and from the ether solution, 2 g. (19% yield) of bromo-α,α'-*p*-xylenediol was recovered, m.p. 113° (from water).

The aqueous alkaline solution was acidified with hydrochloric acid, and the acidic organic material (7 g.) which precipitated was collected by filtration. The filtrate was extracted with two 150-ml. portions of ether. From the ether solution, more acidic organic material (2 g.) was obtained. The total weight of acidic material was 9 g. Fractional crystallization of a portion of the acid mixture[14] from water resulted in the isolation of two components, bromoterephthalic acid which sublimes at 299° and 3-bromo-4-hydroxymethylbenzoic acid, m.p. 176°. Analysis of the acid mixture by the procedure described above gave bromoterephthalic acid (20%) and 3-bromo-4-hydroxymethylbenzoic acid (80%). This corresponds to 1.8 g. (15% yield) of the dibasic acid and 7.2 g. (63% yield) of the alcohol acid.

The total yield of products—diol and acids—corresponded to 97% of the aldehyde used in the reaction.

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(13) S. E. Hazlet and R. B. Callison, *J. Am. Chem. Soc.*, **66**, 1248 (1944).

(14) The melting behavior of this mixture was studied carefully. Melting started at 169°, and the major portion of the sample was converted to a clear liquid at *ca.* 175°; suspended in the liquid was a solid phase which persisted until the temperature was 235–240°; between 240 and 255° this last solid portion melted. Because melting was not observed below 169°, it was concluded that 2-bromo-4-hydroxymethylbenzoic acid (m.p. 147–148°) was not present in the mixture.

Mixtures were prepared [(a) 10:1, (b) 10:3, and (c) 10:10, respectively] from 3-bromo-4-hydroxymethylbenzoic and bromoterephthalic acids. Melting points were (a) major portion, 165–170°, suspended solid persisted to *ca.* 230°; (b) major portion, 161–170°, suspended solid remained to *ca.* 235°; (c) partial melting, 173°, second component melted at *ca.* 275°.

The Preparation of Organic Phosphorus Compounds by Ivanov Reactions. II

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It has been found, contrary to a statement in the literature,[1] that the Ivanov-like reagent diethyl α-chloromagnesiobenzylphosphonate (I), prepared by the action of isopropylmagnesium chloride on diethyl benzylphosphonate, does behave like a Grignard reagent.

Interaction of I with carbon dioxide yielded an oily acid, diethyl α-carboxybenzylphosphonate (II) which could not be purified; by the use of diazomethane the pure ester, diethyl α-carbomethoxybenzylphosphonate (III), was obtained.

Reagent I reacted with ethylene oxide and with diphenylchlorophosphine oxide to produce diethyl α-(β-hydroxyethyl)benzylphosphonate (IV) and diethyl α-(diphenylphosphinyl)benzylphosphonate (V), respectively.

It was shown that after reaction of I with formaldehyde, acidification of the reaction mixture, and distillation of the crude product (an oil), diethyl α-methylenebenzylphosphonate (VI) was formed; this product may have been formed by spontaneous loss of water from the α-hydroxymethyl derivative which had been produced after acidification of the reaction mixture or possibly during distillation.

The product isolated after the reaction of I with benzophenone was also an unsaturated phosphorus compound, diethyl α-(diphenylmethylene)benzylphosphonate (VIII), which may have been produced by

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(1) D. Ivanov and G. Borissoff, *Naturwissenschaften*, **46**, 171 (1959).