naphthyridine derivative and 0.54 g. (20%) of unchanged starting material was obtained.

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## *p*-*t*-Butylphenylphosphonic Acid

BY GENNADY M. KOSOLAPOFF

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The chemical literature does not record the preparation of alkylphenylphosphonic acids, which carry radicals higher than methyl, as pure individual substances. It was necessary to obtain some *p*-*t*-butylphenylphosphonic acid for some of our work on organophosphorus compounds. This afforded a comparison of the results of synthesis by two routes. The Friedel–Crafts synthesis, the technique of which was reported earlier,[1] gave a mixture of products from which the desired substance was isolated after considerable purification work. The diazonium fluoborate method yielded the desired substance in pure state in a 55% yield.

### Experimental Part

**The Friedel–Crafts Method.**—The reaction was run according to the previously described procedure,[1] with employment of 67 g. of *t*-butylbenzene, 270 g. of phosphorus trichloride, 45 g. of aluminum chloride, and 115 g. of absolute ethanol. Distillation afforded but 21.5 g. of product, which boiled at 165–180° at 2–3 mm., with considerable resinous residue. The distillate of diethyl *t*-butylphenylphosphonate was hydrolyzed with concentrated hydrochloric acid at reflux and yielded some 10 g. of the *p*-isomer of the free acid, m.p. 199–200°, after repeated crystallization from water. When the distillation residue was extracted with warm 1% sodium hydroxide and the extract was acidified, there was obtained a mixture of phosphonic and phosphinic acids which, after repeated crystallization from glacial acetic acid, gave 10.4 g. of bis-*p*-*t*-butylphosphinic acid, m.p. 211–212°. The residual material appeared to consist of a mixture.

**The Diazonium Fluoborate Method.**—Acetanilide was alkylated with isobutyl bromide, with aluminum chloride catalyst, in tetrachloroethane[2] yielding 45% *p*-*t*-butylacetanilide, m.p. 169° (from dilute alcohol). This was refluxed for six hours with concentrated hydrochloric acid (20 g. of amide was employed) and the solution was directly employed for diazotization with 6.9 g. of sodium nitrite. The solution of the diazonium salt was treated with sodium fluoborate, in the usual manner, yielding 16 g. of *p*-*t*-butylphenyldiazonium fluoborate. This, after thorough drying, was suspended in dry dioxane and treated with 10 ml. of phosphorus trichloride, followed by 2 g. of dry cuprous bromide. The usual treatment of the reaction mixture[3] resulted in isolation of 55% pure *p*-*t*-butylphenylphosphonic acid, which formed long needles, m.p. 199.5–200° (from water). A very small amount (0.15 g.) of the corresponding phosphinic acid, m.p. 211–212° (from acetic acid) was obtained from the water-insoluble material formed in the reaction. Mixed melting points with specimens obtained from the Friedel–Crafts synthesis, described above, showed no depressions.

*Anal.* Calcd. for $C_{10}H_{15}O_3P$: P, 14.5; equiv. wt., 107. Found: P, 14.3, 14.4; equiv. wt., 106, 107.5. Calcd. for $C_{20}H_{27}O_2P$: equiv. wt., 330. Found: equiv. wt., 328, 329.

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[1] G. M. Kosolapoff and W. F. Huber, THIS JOURNAL, **69**, 2020 (1947).

[2] G. S. Kolesnikov, "Syntezy Organicheskikh Soedinenii," Sbornik 1, 134, Acad. Sci. U.S.S.R., Moscow, **1950**.

[3] G. O. Doak and L. D. Freedman, THIS JOURNAL, **73**, 5658 (1951).

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## Bromomethylcyclobutane

BY ROBERT C. KRUG, LOUIS W. SMITH AND CHARLES E. FRY

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Bromomethylcyclobutane (I) was prepared in 59% yield by the addition of hydrogen bromide to methylenecyclobutane in the presence of benzoyl peroxide. The anilide from I was prepared and after repeated recrystallizations from petroleum ether was found to melt at 80.0–81.0°. For comparison the anilide from bromocyclopentane (II) was prepared and the melting point of the compound after recrystallization from carbon tetrachloride was found to be 160.1–161.2°. The lack of simple derivatives of II prompted the preparation of the corresponding α-naphthalide. A mixture of the two anilides melted over the range 80–136°. These data plus the data available on the melting points of the anilides derived from the simpler aliphatic halides show that the four carbon ring compound did not undergo ring enlargement or ring rupture during the peroxide-catalyzed addition of hydrogen bromide.

Thus, it is found that the addition of hydrogen bromide to methylenecyclobutane in the presence of benzoyl peroxide proceeds smoothly, and on the basis of the well-known peroxide effect the addition product is assigned the structure corresponding to I.

### Experimental[1]

**Methylenecyclobutane.**—Crude pentaerythrityl bromide[2] was converted to methylenecyclobutane by the procedure of Slabey[3] with the exception that sodium carbonate and sodium iodide were not present in the reaction mixture. The presence of these substances caused considerable frothing during the debromination.

**Bromomethylcyclobutane.**—Methylenecyclobutane (b.p. 38.5–39.5° at 707 mm., $n^{25}D$ 1.4120–1.4160) was dissolved in an equal volume of 30–60° petroleum ether to which benzoyl peroxide was added in a ratio of 0.03 mole of peroxide to one mole of olefin. Hydrogen bromide was generated by the dropwise addition of bromine to tetralin, and a second flask of tetralin was used to scrub the gas free of bromine. The gas was then passed into the petroleum ether solution of methylenecyclobutane in a glass vessel cooled to −6°. No hydrogen bromide was evolved at the exhaust until the addition had proceeded for 2.5 hours. Hydrogen bromide was passed into the solution for an additional 30 minutes to ensure maximum conversion. The solution from the reactor was washed with water to remove excess hydrogen bromide and with ferrous sulfate solution to remove the peroxide. The liquid, dried over calcium chloride, was distilled to give crude bromomethylcyclobutane in 59% yield. Redistillation gave a product having a boiling range of 121–123° at 710 mm. with a refractive index of $n^{25}D$ 1.4704.

*Anal.* Calcd. for $C_5H_9Br$: C, 40.29; H, 6.09; Br, 53.62. Found: C, 40.39; H, 6.13; Br, 53.79.

**Anilide from Bromomethylcyclobutane.**—The anilide was prepared by the conversion of 16.4 g. (0.11 mole) of bromomethylcyclobutane to the Grignard reagent and the subsequent reaction of this reagent with an ether solution containing 9.5 g. (0.08 mole) of phenyl isocyanate. Upon hydrolysis of this reaction mixture and the evaporation of the ether an oil was obtained. The oil was subjected to mild steam distillation for 5 minutes after which the residual oil was separated from the water. The oil solidified upon cooling, and the solid was crystallized from methanol followed by successive recrystallizations from petroleum ether to give a solid melting at 80.0–81.0° (cor.).

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[1] Analyses performed by Oakwold Laboratories, Alexandria, Virginia, and Micro-Tech Laboratories, Skokie, Illinois.

[2] H. B. Schurink, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 476.

[3] V. A. Slabey, THIS JOURNAL, **68**, 1335 (1946).

*Anal.* Calcd. for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.24; H, 8.04; N, 8.32.

**Anilide from Bromocyclopentane.**—The Grignard reagent was prepared by the action of 22.4 g. (0.15 mole) of bromocyclopentane on 3.6 g. (0.15 mole) of magnesium in a total of 225 ml. dry ether. To the solution was added 12.6 g. (0.12 mole) of phenyl isocyanate in 130 ml. of dry ether. The stirring of the reaction mixture was continued for 35 minutes after the addition was complete, and the product was then poured into an ice-water–hydrochloric acid mixture. A total of 18 g. of the anilide was isolated, representing a yield of 81%. The crude anilide was recrystallized once from methanol and subsequently from carbon tetrachloride to a constant melting point of 160.1–161.2° (cor.).

*Anal.* Calcd. for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.33; H, 7.99; N, 7.85.

**α-Naphthalide from Bromocyclopentane.**—The Grignard reagent was prepared as in the preparation of the anilide using 14.9 g. (0.10 mole) of bromocyclopentane and 1.9 g. (0.08 mole) of magnesium in 225 ml. of dry ether. To this reagent was added a solution of 19.1 g. (0.08 mole) of α-naphthyl isocyanate in 135 ml. of dry ether. Hydrolysis of the mixture was accomplished as in the previous experiment and a total of 13.5 g. of the naphthalide was isolated. The naphthalide was recrystallized once from ethanol and subsequently from carbon tetrachloride to a constant melting point of 174.2–175.0° (cor.).

*Anal.* Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16, N, 5.85. Found: C, 79.45; H, 6.89; N, 6.07.

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## Nitrate Esters of 2,2-Dimethylol-1-propanol Monoacetate and Diacetate[1]

BY N. S. MARANS AND R. F. PRECKEL

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In continuation of the investigation of nitrate esters of polyols[2] the mononitrate, dinitrate, acetate dinitrate and diacetate nitrate of 2,2-dimethylol-1-propanol, the alcohol commonly known as metriol, have been synthesized.

A mixture of metriol monoacetate and diacetate was prepared by equilibration of metriol and metriol triacetate in the presence of potassium carbonate.[3] Difficulty was encountered in the separation of the acetates but nitration of the reaction mixture gave the readily separable metriol acetate dinitrate. The metriol diacetate mononitrate was prepared by nitration of carefully fractionated metriol diacetate. Controlled saponification of metriol diacetate mononitrate and metriol acetate dinitrate gave metriol mononitrate and dinitrate, respectively. The preferential cleavage of the organic ester grouping in such compounds has been emphasized previously.[4]

### Experimental

**Materials.**—Metriol, m.p. 198–200°, and metriol triacetate were obtained from Trojan Powder Company and were used without further purification.

**Metriol Acetate Dinitrate.**—A mixture of 106 g. of metriol and 123 g. of metriol triacetate in the presence of 2 g. of potassium carbonate was heated at 175–180° for 16 hours in a 500-ml. round-bottom flask equipped with a reflux condenser. Distillation of the crude product at 5 mm. gave the following fractions: (1) 122–130°, 101.5 g.; (2) 130–136°, 91 g.; and (3) residue, 16 g., m.p. 160–170°. Treatment of all three fractions with ethylene chloride gave a recovery of 65 g. of metriol as an insoluble precipitate.

After removal of the ethylene chloride by reduced pressure evaporation, a portion of fraction 2, 17 g., was nitrated at 0° using 90% water-white nitric acid and air agitation. The nitration solution was added to water and the organic layer separated and washed several times with water. The metriol acetate dinitrate was isolated by solution in ethanol and fractional precipitation with water. The first two fractions consisting of 16.5 g. (65.4%) gave similar nitrogen analyses and were metriol acetate dinitrate, $d^{25}$ 1.302, $n^{25}\text{D}$ 1.4566.

*Anal.* Calcd. for $C_7H_{12}O_8N_2$: C, 33.33; H, 4.76; N, 11.11. Found: C, 34.24; H, 4.89; N, 10.78.

The ethanolic mother liquors contained a mixture of metriol acetate dinitrate and metriol diacetate nitrate. An 85–15 mixture of acetate and diacetate was obtained on nitration of fraction I.

**Metriol Dinitrate.**—A solution of 20 g. of metriol acetate dinitrate, 5.0 g. of sodium hydroxide and 150 ml. of 95% ethanol was allowed to stand for 20 minutes. The final solution was neutralized with 2.5 *N* HCl and then concentrated by evaporation under reduced pressure to remove the ethanol. Extraction of the mother liquors with ether and evaporation of the ethereal layer under reduced pressure gave 9.7 g. (57%) of metriol dinitrate, $n^{25}\text{D}$ 1.4692, $d^{25}$ 1.362.

*Anal.* Calcd. for $C_5H_{10}O_7N_2$: C, 28.57; H, 4.81; N, 13.33. Found: C, 28.65; H, 4.87; N, 13.15.

**Metriol Diacetate Nitrate.**—A mixture of 60 g. of metriol and 260 g. of metriol triacetate in the presence of 4 g. of potassium carbonate was heated at 140° for five hours, then distilled collecting four fractions of equal weight. Fractionation of the initial distillate gave 55 g. of metriol diacetate, b.p. 107–108° (3 mm.), $n^{25}\text{D}$ 1.4409, $d^{25}$ 1.109. The remaining distillates were mixtures of metriol acetate and diacetate.

*Anal.* Calcd. for $C_9H_{16}O_5$: C, 52.94; H, 7.84. Found: C, 52.39; H, 7.90.

Metriol diacetate, 18 g., was nitrated at 0° using water-white 90% nitric acid and air agitation. The nitration solution was added to ice and water and the solution ethereally extracted. The ethereal extracts were washed three times with water to remove residual nitric acid and then the ethereal layers concentrated by reduced pressure distillation at 2 mm. to give 16 g. (72.7%) of metriol diacetate nitrate, $n^{25}\text{D}$ 1.4455, $d^{25}$ 1.213.

*Anal.* Calcd. for $C_9H_{15}O_7N$: C, 43.37; H, 6.02; N, 5.62. Found: C, 43.39; H, 5.99; N, 5.27.

Material prepared by nitration of a crude mixture of metriol diacetate and monoacetate and separated by differential solubility gave in two runs 5.95 and 6.05%, N.

**Metriol Mononitrate.**—Metriol diacetate mononitrate, 8.0 g., was dissolved in a solution containing 5.0 g. of sodium hydroxide, 30 ml. of ethanol and 10 ml. of water. After 20 minutes at 25° the solution was neutralized with 3 *N* HCl and the major portion of the ethanol removed under reduced pressure. The aqueous solution was saturated with sodium chloride and then ethereally extracted three times. Evaporation of the ethereal extracts yielded a semi-solid which was recrystallized from benzene to give 4.0 g. (75%) of metriol mononitrate, m.p. 76–77°.

*Anal.* Calcd. for $C_5H_9O_4N$: C, 36.37; H, 6.67; N, 8.48. Found: C, 36.56; H, 6.84; N, 8.08.

Metriol mononitrate was acylated in a 75% yield to metriol diacetate mononitrate using acetic anhydride and pyridine at 25°.

**Acknowledgment.**—The authors wish to express their thanks to Dr. L. G. Bonner for his advice during the course of these investigations. Some of the initial investigations on this problem were conducted by Mr. Robert Feero of this Labora-

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[1] This work was performed at the Allegany Ballistics Laboratory, an establishment owned by the U. S. Navy and operated by Hercules Powder Company under Contract NOrd 10431.

[2] N. S. Marans, D. E. Elrick and R. F. Preckel, THIS JOURNAL, **76**, 1304 (1954).

[3] R. H. Barth and H. Burrell, U. S. Patent 2,356,745 (August 29, 1944). This patent described the preparation of pentaerythritol monoacetate and diacetate by this method.

[4] N. S. Marans and R. P. Zelinski, THIS JOURNAL, **73**, 5329 (1950).