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).

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).