Hydrolysis of Ethyl Trithioörthoglyoxylate Semicarbazone to Glyoxylic Acid Semicarbazone (V).—The above ethyl trithioörthoglyoxylate (400 mg.) was added to a mixture of 66 ml. of ethanol and 10 ml. of 12 *N* (concd.) hydrochloric acid. A stream of nitrogen gas was passed through the mixture while it was refluxed under a condenser containing water at 40°. The reaction was stopped when no more ethanethiol was evolved as detected by odor. Solvent removal under reduced pressure yielded a product that was obtained crystalline from 50% aqueous ethanol; m.p. 220–224° dec. An authentic sample of glyoxylic acid semicarbazone showed no melting point depression on admixture with the above product and the following X-ray powder diffraction measurements were identical when made on the two preparations: 6.48,[7] 1[8]; 4.53, 3; 4.25, 7; 3.58, 2; 3.13, 1; 2.81, 6; 2.46, 4; 2.26, 9; 1.89, 10.

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(7) Interplanar spacing in Å., CuKα radiation.

(8) Relative intensity; 1 = highest; estimated visually.

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Di-*t*-butyl Phosphonate

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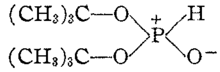
The reaction of *t*-butyl alcohol with phosphorus trichloride has been reported to give tri-*t*-butyl phosphite (I).[1] Previous to this publication, several attempts were made in this Laboratory to prepare I by analogous procedures, but instead di-*t*-butyl phosphonate (II) was obtained; b.p. 62–62.5° at 4 mm.,[2]


(II)

n^{25}_D 1.4168, d^{25} 0.975; *M*D calcd. 50.18,[3] found 50.03. This appears to be the first example of the preparation of a tertiary dialkyl phosphonate from an aliphatic tertiary alcohol.[4]

II is insoluble in water and 3 *N* sodium hydroxide, but it dissolves immediately in 3 *N* hydrochloric acid with the evolution of isobutylene. This gas is also evolved slowly when the compound is heated to 70° at atmospheric pressure. II is relatively stable at room temperature, although evidence of slight decomposition was noted after storage for several weeks. Upon redistillation, the original material was recovered with little loss.

The infrared spectrum exhibits the characteristic strong absorption for the $\overset{+}{P}$–$\overset{-}{O}$ stretching vibration[5] at 1270 cm.$^{-1}$ as well as another strong band at 2420 cm.$^{-1}$ corresponding to the P–H bond.[5,6] There is little or no absorption in the 750 cm.$^{-1}$ region where the aliphatic C–P stretching frequency usually appears,[6] an observation which rules out structures which are based on catalytic isomerization of the Arbusov type.[7]

Although repetition of the literature procedure[1] afforded a substance having the reported refractive index, it could not be redistilled without decomposition and concomitant lowering of the refractive index. The infrared spectra showed strong P–H and $\overset{+}{P}$–$\overset{-}{O}$ absorption and were not significantly different from the spectrum of pure II. Successive redistillations eventually yielded material having a refractive index and infrared spectrum identical to II. In view of these results, the purity of I is doubtful.

Experimental[8]

A solution of 82.4 g. (0.6 mole) of phosphorus trichloride in 500 cc. of petroleum ether (b.p. 30–60°) was cautiously dropped over a period of one hour into an ice–methanol chilled solution of 267 g. (3.6 moles) of *t*-butyl alcohol and 91.2 g. (1.8 moles) of triethylamine in 3 l. of petroleum ether. Stirring was continued for one hour without external cooling, after which time the suspension was filtered, the cake being washed well with an additional 1 l. of petroleum ether. The solvent was removed on the steam-bath at water aspirator pressure, the resultant yellow residue being rapidly distilled at 0.1 mm. without fractionation. The distillate was distilled slowly (considerable frothing), giving 60 g. (51%), b.p. 72–78° at 10–12 mm., n^{25}_D 1.4162. A final distillation gave a single fraction b.p. 70–72° at 10 mm., n^{25}_D 1.4168, d^{25} 0.975.

Anal. Calcd. for $C_8H_{19}O_3P$: C, 49.5; H, 9.86; P, 15.9. Found: C, 49.5; H, 9.60; P, 15.8.

A portion of this product was redistilled at 4 mm., b.p. 62–62.5°. In various other preparations, samples of higher refractive index were obtained, but repeated slow distillations at 10–12 mm. eventually produced II of constant refractive index. The high refractive indices observed in some cases are probably due to the presence of some I which is decomposed on successive distillations.

Acknowledgment.—We are indebted to Mrs. Martha M. Taylor for the determination of the infrared spectra.

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(1) G. M. Kosolapoff, THIS JOURNAL, **74**, 4953 (1952).

(2) Compare b.p. 65–66° at 4 mm. for I (ref. 1). This b.p. was obtained by rapid distillation without fractionation (G. M. Kosolapoff, private communication).

(3) The value of 4.44 for the atomic refraction of phosphorus in secondary phosphites was used; G. M. Kosolapoff, *ibid.*, **73**, 4989 (1951).

(4) T. Milobedzki and A. Sachnowski, (*Chem. Polski*, **15**, 34 (1917) [*C. A.*, **13**, 2865 (1919)], report both tri- and di-*t*-butyl phosphites. They did not isolate either compound or report any physical properties.

(5) N. B. Colthup, *J. Opt. Soc.*, **40**, 397 (1950).

(6) It is noteworthy that di-*n*-butyl phosphonate has two corresponding bands at 1265 and 2410 cm.$^{-1}$; L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(7) T. Milobedzki and K. Szulgin, *Chem. Polski*, **15**, 66 (1917), [*C. A.*, **13**, 2866 (1919)], and numerous references given by G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

(8) (a) The analysis was performed in these laboratories under the direction of Dr. J. A. Kuck. (b) All operations were performed under an atmosphere of dry nitrogen.