CHEMISTRY

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1961

SovietRxiv

Abstract

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CHEMISTRY

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A NEW METHOD FOR THE SYNTHESIS OF OXYARYLPHOSPHINIC ACIDS

(Presented by Academician S. I. Vol̆ fkovich, July 19, 1960)

Oxyarylphosphinic acids are obtained from aminoarylphosphinic acids via diazo compounds (^{1}), by hydrolysis of haloarylphosphinic acids (^{2}) and methoxyarylphosphinic acids (^{3}). All three methods are based on replacement of one of the substituents in the aromatic nucleus of the arylphosphinic acid by hydroxyl and are far from always applicable; therefore the number of known oxyarylphosphinic acids is small. Lecher et al. (^{4}) obtained arylphosphinic acids by phosphorylating hydrocarbons or alkylaryl ethers with phosphorus pentasulfide and subsequently hydrolyzing the resulting arylphosphine disulfides. This method is unsuitable for phosphorylating phenols, since with phosphorus pentasulfide they form aryl thiophosphates (^{5}). In the present work, oxyarylphosphinic acids were obtained by phosphorylation of the phenyl ester of silicic or boric acid with phosphorus pentasulfide, followed by hydrolysis, according to the scheme:

$$\mathrm{Si(OC_6H_5)_4 + P_4S_{10} \rightarrow Si(OC_6H_4PS_2)_4 + 2H_2S;}$$

$$\mathrm{Si(OC_6H_4PS_2)_4 + 15H_2O \rightarrow 4HOC_6H_4PO(OH)_2 + 8H_2S + H_2SiO_3.}$$

In practice, the phosphorylation reaction does not proceed to completion, or during hydrolysis phosphoric acid is partially split off and phenol is formed, as was also noted by earlier investigators (^{6}). Nitration of *p*-oxyphenylphosphinic acid gave picric acid; analogously, trinitro-m-cresol was obtained from *m*-cresylphosphinic acid.

Oxyphenyl- and oxy-*m*-cresylphosphinic acids readily form solid polycondensation products with formaldehyde. On the basis of this and of the nitration reaction, it is evident that from *m*-cresol we obtained 1-methyl-3-oxybenzene-6-phosphonic acid. Oxyarylphosphinic acids enter into azo-coupling reactions with the formation of azo dyes.

Experimental Part

Synthesis of oxyphenylphosphinic acid. In a round-bottom flask fitted with a stirrer, reflux condenser with a calcium chloride tube, and a thermometer, 133.2 g (0.3 gram-mole) of phosphorus pentasulfide (technical grade, m.p. 275–276°) was added to 500 g (1.2 gram-moles) of tetraphenoxysilane, prepared according to (7). The mixture was heated with stirring for 12 h at 155–170° until evolution of hydrogen sulfide ceased. After cooling, 500 ml of water was gradually added and the mixture was again heated for 20 h. After completion of hydrolysis (cessation of hydrogen sulfide evolution), silicic acid was filtered off. The phenolic layer was separated, and the aqueous solution was extracted several times with ether; the extracts were combined with the phenolic layer. The aqueous layer was evaporated to 1/4 of its volume; on cooling, oxyphenylphosphinic acid crystallized from it, 53.5 g (25.6% of theory, calculated on P_4S_{10}). After crystallization from 6 *N* HCl, the acid had m.p. 173–173.5°.

Found, %: *C* 41.27; 41.27; *H* 4.11; 4.21; *P* 17.89; 18.01
$C_6H_7O_4P$. Calculated, %: *C* 41.39; *H* 4.05; *P* 17.79

From an equimolecular amount of triphenyl borate, 20.8 g of *p*-oxyphenylphosphinic acid was obtained by an analogous method (7.5% of theory).

The salts of alkali metals of *p*-oxyphenylphosphinic acid are readily soluble, while the Ba, Ca, and Pb salts are poorly soluble in water.

Condensation with formaldehyde. 5.1 g (0.3 g-mole) of *p*-oxyphenylphosphinic acid, 5.3 g of 32% formalin, and 1.5 ml of 25% aqueous ammonia solution were heated on a bath for 1.5 hours, after which a resin precipitated. It was washed with water and dried for 3 hours at 150°. This gave 6.2 g of a solid orange resin, which contains P, C, H, is unchanged up to 300°, and is insoluble in water and in ordinary solvents.

Synthesis of *o*-cresylphosphinic acid. In a manner analogous to the preceding experiment, from 392 g (0.86 g-mole) of tetra-*o*-cresyl silicate, prepared according to (8), and 89 g (0.2 g-mole) of phosphorus pentasulfide, 53 g of oxycresylphosphinic acid was obtained. The acid is partially soluble in ether and *o*-cresol. To isolate it, the ethereal solution of *o*-cresol was extracted several times with 3% sodium carbonate solution, the alkaline extracts were acidified with hydrochloric acid, extracted with ether, and after distilling off the ether a further 7.2 g of *o*-cresylphosphinic acid was obtained, 60.2 g in all (40% based on P_4S_{10}). It was purified by crystallization from 6*N* HCl; m.p. 160°.

Found, %: C 44.33; 44.32; H 5.47; 5.04; P 15.28; 16.15
$C_7H_9O_4P$. Calculated, %: C 44.69; H 4.82; P 16.46

o-Oxycresylphosphinic acid is readily soluble in water, alcohol, and acetone, less readily in ether. It is insoluble in benzene and petroleum ether; the Li, Na, and K salts are readily soluble in water, while the Ca, Ba, and Pb salts dissolve poorly in water.

Synthesis of *p*-cresylphosphinic acid. The reaction was carried out analogously to the synthesis of *o*-cresylphosphinic acid. Yield 30 g, 20%, calculated on P_4S_{10}. Recrystallized from $6N$ HCl; m.p. 218°.

Found, %: C 45.22; 45.15; H 4.55; 4.51; P 16.18; 16.19
$C_7H_9O_4P$. Calculated, %: C 44.69; H 4.82; P 16.46

The acid is readily soluble in water, alcohol, and acetone, sparingly soluble in ether, and insoluble in benzene; the Li, Na, and K salts are readily soluble, while the Ba and Pb salts are insoluble in water.

Synthesis of *m*-cresylphosphinic acid. The reaction was carried out analogously to the preceding one. 11.5 g of syrupy *m*-cresylphosphinic acid was obtained, approximately 30%. On standing for 20 days in a desiccator, the product crystallized.

Synthesis of an azo dye with *p*-diazonitrobenzene. 1.5 g of *m*-cresylphosphinic acid was dissolved in 20 ml of 2% caustic soda, ice was added, and the solution was coupled with a diazo solution from 1.4 g of *p*-nitroaniline. Coupling proceeded for 6 hours. 1.75 g of an orange dye was obtained. It was recrystallized from alcohol.

Found, %: N 9.4; 9.45; P 12.2; 12.32
$C_{13}H_{12}O_6N_3P$. Calculated, %: N 12.5; P 9.22

Condensation with formaldehyde. From 4 g of *p*-cresylphosphinic acid, 6.3 g of resin was obtained, analogously to the synthesis from *p*-oxyphenylphosphinic acid.

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Received
16 VII 1960

REFERENCES

1. G. O. Doak, L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 753 (1952).
2. G. B. Arnold, C. S. Hamilton, *J. Am. Chem. Soc.*, **63**, 2637 (1946).
3. G. O. Doak, L. D. Freedman, *J. Am. Chem. Soc.*, **75**, 6307 (1953).
4. H. Z. Lecher, R. A. Greenwood, K. C. Whitehouse, T. H. Chao, *J. Am. Chem. Soc.*, **78**, 5018 (1956).
5. P. S. Pishchemuka, *ZhRFKhO*, **44**, 1406 (1912).
6. G. M. Kosolapoff, V. L. Nell, *J. Am. Chem. Soc.*, **75**, 4901 (1953).
7. K. A. Andrianov, *Silicon-Organic Compounds*, Moscow, 1955.

8. J. Hertkorn, *Ber.*, **18**, 1679 (1885).

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