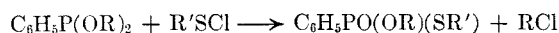


The Reaction of Benzenephosphonous Esters With Sulfenyl Chlorides¹

D. C. MORRISON

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A previous report² described the reaction of trialkyl phosphites with sulfenyl chlorides to form tertiary phosphorothioates, (RO)₂PO(SR').^{3,4} This reaction has now been extended to include the interaction of esters of benzenephosphonous acid with alkyl sulfenyl chlorides. The products are thiophosphonates, and the reaction may be represented as:



The thiophosphonates are colorless high-boiling liquids of unpleasant odors. The action of methane-

tions, the isolated phosphonous ester was employed and equimolar amounts of reactants were used.

A solution of 27.2 ml. (0.20 mole) of phenyl dichlorophosphine in 50 ml. of benzene was added dropwise, with stirring, to a solution of 28 ml. (0.42 mole) of ethylene chlorohydrin and 33.5 ml. (0.42 mole) of pyridine in 500 ml. of an equi-volume mixture of benzene and petroleum ether, cooled to 0° in an ice-bath. All reagents were anhydrous and freshly distilled. The mixture was left 2 hours in the bath and 6 hours at room temperature, and then was filtered. The filter cake was washed 3 times with the mixed solvent. The combined filtrates were cooled to 0° and then were treated dropwise with methanesulfenyl chloride solution which had been made one hour before. This was prepared from 9.7 ml. (0.11 mole) of dimethyl disulfide and 9 ml. (0.11 mole) of sulfonyl chloride in benzene-petroleum ether solution. The excess sulfenyl halide was employed to allow for the excess of reactants in the crude phosphonous ester. After 1/2 hour, the solution was washed with water, dilute sodium carbonate solution and twice by water. The solvents were removed at 70 mm. and the residue was fractionated under 2 mm. pressure. Thus 48 g. of an oil were obtained (95.8% yield). This was redistilled for analysis, b.p. 148–152° at 3 mm.

TABLE I

PROPERTIES OF THIOFOSPHONATES C₆H₅PO(OR)(SR')

R	R'	Yield, %	C, Calc'd	C, Found	H, Calc'd	H, Found	d ₄ ²⁰	B.P., °C.	MM.
Ethyl	Ethyl	88.7	52.17	52.22	6.52	6.58	1.1473	145–146	5
Ethyl	Methyl	71.3 ^a	50.00	50.16	6.02	5.98	1.1728	125–135	3
Ethyl	<i>beta</i> -Chloroethyl	76.8	45.37	45.02	5.29	5.21	1.2378	138–141	1–2
<i>beta</i> -Chloroethyl	Methyl	95.8	43.11	42.78	4.79	4.93	1.2940	148–152	3

^a Reaction carried out at 5–10°.

sulfenyl chloride,^{5,6} ethanesulfenyl chloride,⁷ and *beta*-chloroethanesulfenyl chloride⁸ on diethyl benzenephosphonite was examined and also the reaction of methanesulfenyl chloride with (unisolated) di(*beta*-chloroethyl) benzenephosphonite. The products were unsymmetrical esters if the alkyl groups of the reactants were different. They were employed in cancer chemotherapy studies.

EXPERIMENTAL

The sulfenyl halides were prepared in chloroform or in benzene-petroleum ether solution, and were kept below 0° (usually –30°) until used. They were added dropwise to the phosphonous ester solution at –30 to 0°, the orange color of the sulfenyl chloride being discharged.

As an example, the synthesis of *S*-methyl-*O*-(*beta*-chloroethyl) benzene-thiophosphonate is given. In other prepara-

The four esters which were prepared are listed in Table I, together with physical constants and analyses.

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY
UNIVERSITY OF CALIFORNIA SCHOOL OF MEDICINE
BERKELEY 4, CALIFORNIA

Basic Zinc Double Salts of *O,O*-Dialkyl Phosphorodithioic Acids

V. P. WYSTRACH, E. O. HOOK,¹ AND G. L. M. CHRISTOPHER

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In the course of preparing a series of zinc *O,O*-di-*n*-alkyl phosphorodithioates by metathesis between the corresponding sodium salts and zinc chloride in aqueous solution, a new and unusual type of basic zinc salt was isolated as a by-product from the preparation of zinc *O,O*-di-*n*-butyl phosphorodithioate. We should like to report some properties of two members of this new class of compounds.

Elemental analyses and non-aqueous acid-base titration data satisfied the requirements of a basic

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(1) Present address. Standard Oil Company, Cornell Road, Cleveland, Ohio.