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THE REACTIONS OF SULFUR-CONTAINING PHOSPHONIUM SALTS

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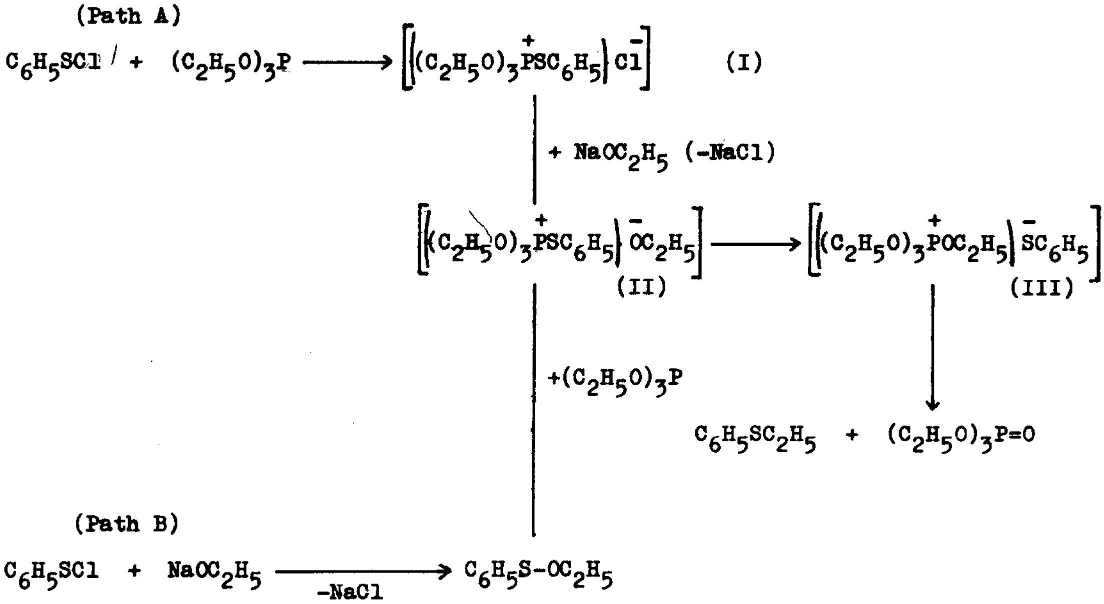
It is well known that sulfenyl chloride reacts with trialkyl phosphite (Michaelis-Arbuzov reaction) to yield alkyl halide and O,O,S-trisubstituted phosphorothioate ester.1) In the present study, it was found that the reaction of benzenesulfenyl chloride and trialkyl phosphite in the presence of sodium alkoxide resulted in the formation of alkyl phenyl sulfide and trialkyl phosphate. When benzenesulfenyl chloride (0.01 Mol) in acetonitrile was added drop by drop at 0°C to a sodium ethoxide (0.01 Mol) suspended solution of triethyl phosphite (0.01 Mol) in acetonitrile with vigorous stirring, the reaction smoothly occurred with quantitative separation of sodium chloride, and ethyl phenyl sulfide and triethyl phosphate were obtained both in 84% yields. Similarly, the reaction of benzenesulfenyl chloride and trialkyl phosphite (alkyl=methyl, n-butyl) in the presence of sodium alkoxide gave alkyl phenyl sulfide and trialkyl phosphate in good yields (TABLE 1).

TABLE 1

$$C_6H_5SCl + (RO)_3P + NaOR \longrightarrow C_6H_5SR + (RO)_3P{=}O + NaCl$$

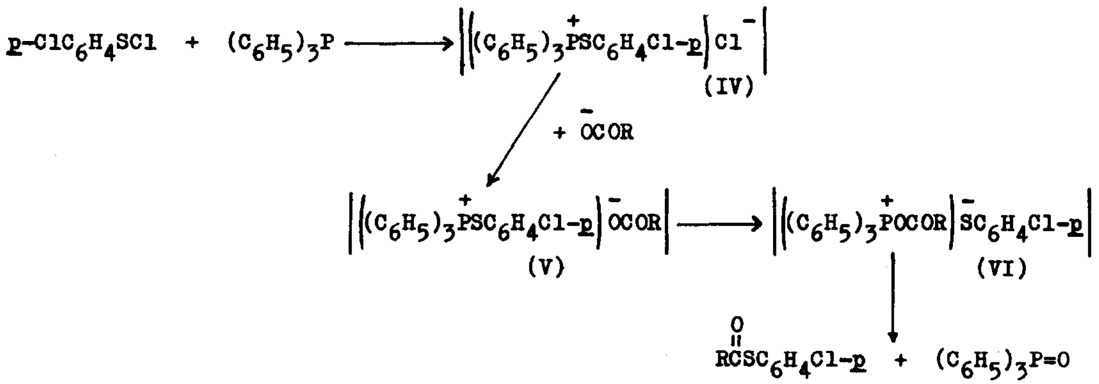
	C_6H_5SR			$(RO)_3P{=}O$		
R	Yield(%)	b.p.(°C/mm.)	$n_D^{t°C}$	Yield(%)	b.p.(°C/mm.)	$n_D^{t°C}$
CH_3	59	87/22	1.5887^{24}	69	87-89/17	1.4013^{23}
C_2H_5	84	98/22	1.5700^{20}	84	107-108/21	1.4102^{23}
n-C_4H_9	63	117/15	1.5472^{21}	71	105-106/0.16	1.4286^{21}

There are two possible alternative pathways for the reaction as represented in the following scheme. Namely, (path A) the quaternary-phosphonium salt I, arising from the reaction of sulfenyl chloride and phosphite, reacts with sodium ethoxide to form the second quaternary-phosphonium salt II. This



in turn decomposes to sulfide and phosphate through the salt III. (Path B) Sulfenate ester formed from sulfenyl chloride and sodium ethoxide reacts with phosphite to produce the same intermediate II. Indeed, methyl phenyl sulfide (72%), triethyl phosphate (71%) and O,O-diethyl S-phenyl phosphorothioate (20%) were obtained by the reaction of triethyl phosphite with methyl benzenesulfenate in methylene chloride at -78°C. But, path B is not probable because only a limited number of sulfenate esters has been synthesized by the reaction of sulfenyl chloride and sodium alkoxide. Further, it was established that treatment of benzenesulfenyl chloride and sodium ethoxide in acetonitrile and the successive treatment of the resulting reaction mixture with triethyl phosphite afforded only 35% yield of sulfide and 66% yield of triethyl phosphate along with small amounts of diphenyl disulfide and O,O-diethyl S-phenyl phosphorothioate. These results suggest that the reaction of benzenesulfenyl chloride, phosphite and sodium alkoxide would proceed via path A.

Next, p-chlorobenzenesulfenyl chloride was treated with triphenylphosphine in acetonitrile at room temperature and to the obtained colorless solution a suspension of anhydrous sodium benzoate in acetonitrile was added with vigorous stirring. After the mixture was stirred for 3hr., sodium chloride was separated quantitatively and S-p-chlorophenyl thiobenzoate, m.p. 75.5-76.5°, (lit.$^{2)}$m.p. 75-76°) and triphenylphosphine oxide were obtained in 83 and 93% yields, respectively. Similarly, when anhydrous sodium or triethylammonium acetate was treated with p-chlorobenzenesulfenyl chloride and triphenylphosphine, S-p-chlorophenyl thioacetate, b.p. 129°/13 mm, (lit.$^{2)}$ b.p. 153-154°/35 mm) was obtained in 66 or 81% yield, respectively. Thiol esters were identified by their infrared spectra and elemental analyses. The production of thiol ester may well be explained by the successive formation of quaternary phosphonium intermediates V and VI resulting from the reaction of chloride IV and sodium or triethylammonium carboxylate.



This reaction is expected to be a convenient method for the preparation of thiolcarboxylate esters; for the esters can be synthesized in high yields by one-step procedure starting from free carboxylic acid. Investigations of the applicability of this procedure to other sulfenyl parts are now in progress.

References

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