

in 25 ml of benzene. Stirring was continued for an additional 4 hr. The reaction mixture was poured over ice-water, extracted with 400 ml of ether and dried (MgSO_4). Evaporation of ether afforded a mixture of **13** and **14** which was separated by column chromatography over silica gel using the solvent mixture hexane-tetrahydrofuran-ethyl acetate (18:1:1). The first compound emerging from the column was identified as **13**, mp 123–124°, 0.8 g (7.3%).

Anal. Calcd for $\text{C}_8\text{HCl}_3\text{N}_2\text{S}$: N, 11.7; Cl, 44.5; S, 13.4. Found: N, 11.8; Cl, 44.4; S, 13.2.

The second fraction consisted of the N-oxide **14**: mp 144–147°; 0.4 g (3.4%); ir (KBr) 1370 cm^{-1} (N→O).

Anal. Calcd for $\text{C}_8\text{HCl}_3\text{N}_2\text{OS}$: N, 10.9; S, 12.5. Found: N, 10.5; S, 12.3.

Reaction of Diphenylglyoxime with Sulfur Monochloride. Preparation of 3,4-Diphenyl-1,2,5-thiadiazole (**16**) and 3,5-Diphenyl-1,2,5-thiadiazole N-Oxide (**17**).—Diphenylglyoxime, 30.0 g (0.125 mol), was added to a mixture of 32 ml (0.4 mol) of sulfur monochloride in 64 ml of dimethylformamide at 25°. The temperature of the reaction was maintained by external cooling with the aid of an ice bath. After 2 hr, the reaction mixture was poured onto 300 g of ice water and the precipitate was filtered and dried. Thin layer chromatography indicated the presence of three compounds in addition to large amounts of sulfur. The crude mixture was resolved by column chromatography on deactivated silica gel²⁸ using the solvent mixture hexane-tetrahydrofuran (9:1). Sulfur which emerged first from the column was discarded. After removal of the solvent, the second fraction was recrystallized from hexane to give 1.7 g (5.7%) of **16**: colorless, crystalline solid; mp 83–84°; nmr multiplet near 7.6 ppm (phenyl H).

Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{S}$: N, 11.75; S, 13.45. Found: N, 11.8; S, 13.1.

The third fraction was recrystallized from hexane and afforded 1.5 g (4.7%) of **17**: colorless crystalline solid; mp 124°; ir (KBr pellet): 1360 cm^{-1} (N→O).

Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{OS}$: N, 11.0; S, 12.9. Found: N, 10.8; S, 12.4.

A fourth compound, possibly the corresponding di-N-oxide, did not emerge from the column and therefore was not identified.

Preparation of Acenaphtho[1,2-c]-1,2,5-thiadiazole (18**) from Acenaphthoquinone Dioxime.** With Sulfur Dichloride.—Sulfur dichloride (20 ml, 32.4 g, 0.315 mol) was added dropwise with stirring at 25° to a solution of acenaphthoquinone dioxime (10.6 g, 0.05 mol) in dimethylformamide (150 ml). After 2.5 hr, the mixture was poured over ice-water and filtered. The solid was dissolved in methylene chloride, charcoaled, and dried (MgSO_4). Evaporation to dryness afforded a dark residual solid which was extracted with 500 ml of boiling hexane. This solution was concentrated to 150 ml and cooled to give 8.6 g (81.9%) of **18** as white solid melting at 132–133°. The nmr spectrum shows complex lines near 7.8 ppm (aromatic H).

Anal. Calcd for $\text{C}_{12}\text{H}_6\text{N}_2\text{S}$: N, 13.3; S, 15.3. Found: N, 13.2; S, 15.8.

With Sulfur Monochloride.—The reaction of acenaphthoquinone dioxime (10.6 g, 0.05 mol) with sulfur monochloride (25 ml, 42.5 g, 0.315 mol) which was carried out under the same reaction conditions (see above) afforded **18** in 23% yield with recovery of about 18% of acenaphthoquinone dioxime.

Registry No.—**3**, 23431-06-3; **5**, 273-13-2; **10**, 1143-73-3; **11**, 23431-09-6; **13**, 1982-55-4; **14**, 23431-11-0; **15**, 5728-20-1; **16**, 4057-61-8; **17**, 23431-14-3; **18**, 437-40-1; 3,4,6-trichloro-*o*-benzoquinone, 23431-16-5; acenaphthoquinone dioxime, 1932-08-7.

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Notes

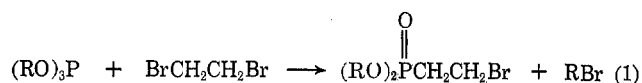
Reactions of Trihalopropionitriles with Trialkyl Phosphite. A Convenient Synthesis of 2-Haloacrylonitriles

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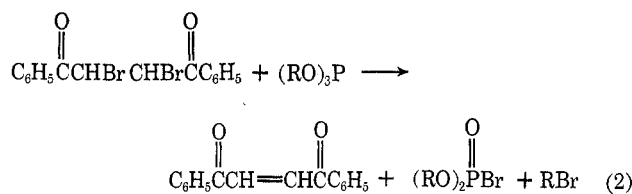
Vicinal dihalides react with trialkyl phosphites to yield either of two products, depending on the structure of the dihalide. In the absence of electron-withdrawing groups on the carbon atoms bearing the halogen atoms, phosphonate esters are formed (eq 1).¹



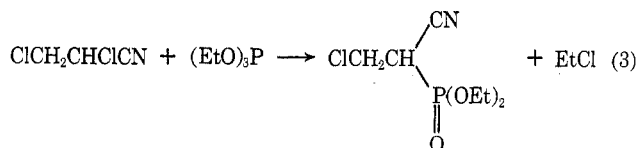
If, however, both halogen atoms are on carbon atoms bearing electron-withdrawing groups, dehalogenation occurs (eq 2), giving a high yield of olefin.²

(1) G. M. Kosolapoff, *J. Amer. Chem. Soc.*, **66**, 109 (1944).

(2) S. Dershowitz and S. Proskauer, *J. Org. Chem.*, **26**, 3595 (1961).



In the presence of an electron-withdrawing group on only one carbon atom, the usual course of reaction with trialkyl phosphites is formation of a phosphonate ester, as illustrated by the reaction of 2,3-dichloropropionitrile with triethyl phosphite (eq 3).³



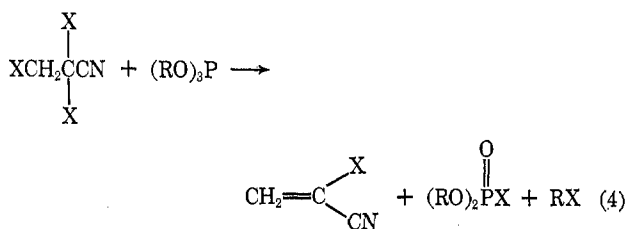
However, styrene dibromide has been found to undergo dehalogenation when allowed to react with triethyl phosphite to give styrene in 50% yield.⁴

(3) U. S. Abramov and N. A. Il'ina, *J. Gen. Chem. USSR*, **26**, 2014 (1956); *Chem. Abstr.*, **51**, 1822 (1957).

(4) B. A. Arbuzov and B. P. Lugovkin, *J. Gen. Chem. USSR*, **21**, 99 (1951); *Chem. Abstr.*, **45**, 7002 (1951).

We wish to report another reaction of preparative value, where dehalogenation has been shown to occur from a system containing vicinal halide groups.

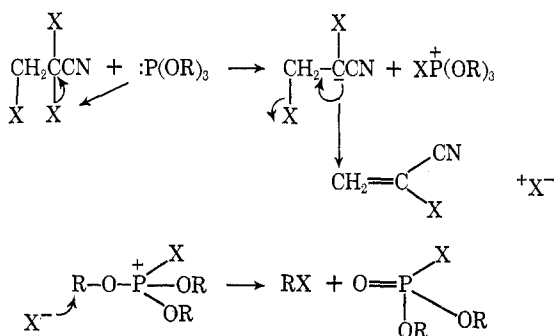
From the reaction of 2,2,3-trichloro- or tribromopropionitrile with triethyl or trimethyl phosphite below room temperature, almost quantitative yields of 2-haloacrylonitriles, halophosphates, and alkyl halides can be readily isolated, (eq 4).



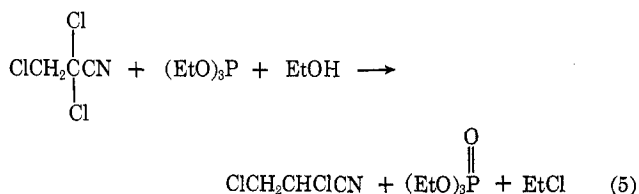
R = Et or Me, X = Cl or Br

The dialkyl chlorophosphates and 2-haloacrylonitriles were characterized by their boiling points, vpc retention times, and ir and nmr spectra. The dialkyl bromophosphates could not be distilled without decomposition. The identity of these compounds was verified by conversion into their anilino derivatives according to a known method.⁵

These results can be explained by nucleophilic attack of phosphorus on an α halogen, followed by elimination of β halogen from the resulting carbanion. Subsequent Arbuzov cleavage of the resultant phosphonium species by halide ion would explain the other products.



Attack by phosphorus on halogen is well established.⁶ The intermediacy of the carbanion in these dehalogenation reactions was confirmed by reacting 2,2,3-trichloropropionitrile and triethyl phosphite in ethanol. Ethanol served as a proton donor and the reaction took the following course (eq 5).



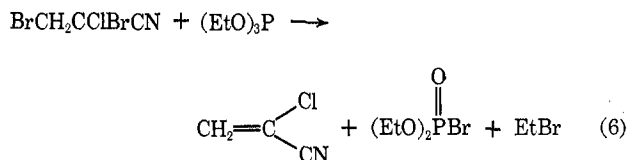
Comparing the reactions of trialkyl phosphites with those of 2,3-dichloropropionitrile and 2,2,3-trichloropropionitrile, it appears that the phosphite can attack the α carbon, giving the normal Arbuzov product (eq 3), or

(5) H. McCombie, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).

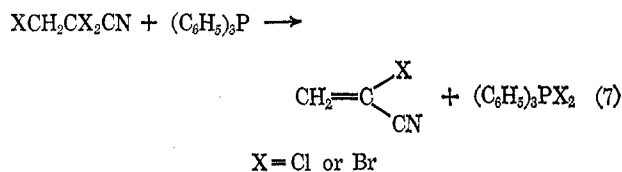
(6) M. Grayson and E. Griffith, "Topics in Phosphorus Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1965, pp 135-195.

the α chlorine, giving the dehalogenation product. Attack at the α carbon is apparently favored, but is prevented in the 2,2,3-trichloro derivative presumably by the bulky geminal chlorine atoms. Attack on chlorine is, therefore, favored in the latter case.

The reaction of 2-chloro-2,3-dibromopropionitrile and triethyl phosphite also gives high yields of 2-chloroacrylonitrile (eq 6), indicating that attack of trivalent phosphorus esters on bromine is favored over attack on chlorine.



Substituted phosphines such as triphenylphosphine have also been found to react with 2,2,3-trihalopropionitriles in ether solution to give 2-haloacrylonitriles in good to moderate yields (eq 7).



Experimental Section

General Comments.—All the reactions were carried out in a three-necked flask equipped with magnetic stirrer assembly, dropping funnel, and a condenser connected to a cold trap. Infrared spectra were recorded on a Beckman IR 7. Nmr spectra (CDCl_3) were obtained on a Varian A-60A instrument. Vpc analysis was carried out isothermally, using a Beckman Model 2 with a 10-ft column packed with silicon gum on Chromosorb W.

Reaction of 2,2,3-Trichloropropionitrile and Triethyl Phosphite.—Triethyl phosphite (33.0 g, 0.2 mol) was added dropwise to 2,2,3-trichloropropionitrile (32.0 g, 0.2 mol). The temperature of the reaction mixture was maintained at 5–10° by external cooling. After complete addition of the phosphite, the reaction mixture was fractionated to give ethyl chloride (12.0 g), 2-chloroacrylonitrile (16.0 g, 90%), bp 88–90°, and diethyl chlorophosphate, bp 55° (1.5 mm).

Reaction of 2,2,3-Tribromopropionitrile and Triethyl Phosphite.—The addition of triethyl phosphite (33.0 g, 0.2 mol) to 2,2,3-tribromopropionitrile (58.0 g, 0.2 mol) was carried out as described above and fractionated to give ethyl bromide (17.0 g, collected in the cold trap), 2-bromoacrylonitrile (20.0 g, 77%), bp 52–53° (85 mm), and a light yellow residue (ca. 50.0 g). This residue was identified as O,O'-diethyl bromophosphate by converting a portion of the residue into its anilino derivative as described in the literature to give diethyl anilinophosphonate, mp 93° (lit.⁵ mp 96.5°).

Reaction of 2,3-Dibromo-2-chloropropionitrile and Triethyl Phosphite.—The reaction was carried out by slow addition of triethyl phosphite (16.6 g, 0.1 mol) to 2,3-dibromo-2-chloropropionitrile (24.5 g, 0.1 mol) at 5–10°, followed by fractionation. The reaction yielded ethyl bromide (8.0 g) and 2-chloroacrylonitrile (7.5 g, 86%), bp 84–89°. The undistilled material was converted into its anilino derivative to give diethyl anilinophosphonate, mp 93°.

Reaction of 2,2,3-Trichloropropionitrile and Trimethyl Phosphite.—Trimethyl phosphite (24.8 g, 0.2 mol) was added to 2,2,3-trichloropropionitrile (32.0 g, 0.2 mol) at 5–10°. During the course of the exothermic reaction, methyl chloride (21.0 g) was collected in the cold trap. On fractionation, the reaction mixture gave 2-chloroacrylonitrile (14.5 g, 82%), bp 86–88°.

Reaction of 2,2,3-Trichloropropionitrile and Triethyl Phosphite in the Presence of Dry Ethanol.—To an ethanol (25.0 g) solution of 2,2,3-trichloropropionitrile (16.0 g, 0.1 mol) was added

