for a day, the product was precipitated by twofold dilution with water, filtered, and washed with 2 × 1.5 ml of ice-cold ethanol and 2 × 2 ml of water. In runs 8, 23, and 32 the crude products were strongly contaminated with high melting greenish materials and were not easy to purify. These by-products are obtainable alone from the mixture of aldehydes and ketones so that they are not self-condensation products.

Acknowledgments

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Reaction of dialkyl phosphorothioic acids with cyanogen bromide

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Dialkyl phosphorothioic acids (**1**) in benzene solution and in the presence of a tertiary amine react with cyanogen bromide to form the corresponding dialkyl phosphoroisothiocyanatidates (**2**). Under the reaction conditions these are partially decomposed to yield the alkylthiocyanates (**3**) and the alkylmetaphosphates (**4**).

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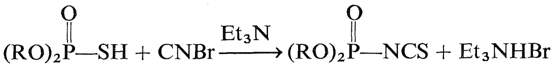
Several years ago Schrader obtained a German patent (1) for the preparation of thiophosphorylcarbimides by the action of cyanogen bromide on *O,O'*-dialkyl thionophosphoric acids. Although Schrader refers to the products as thiocarbimides and writes the structure as containing a P—N═C═S linkage, no evidence is presented which either supports the proposal, or excludes the presence of a P—S—C≡N type linkage. In the present work the reaction of cyanogen bromide with dialkyl phosphorothioic acids (**1**) has been studied under conditions similar to those used by Schrader with the resulting formation of the dialkyl phosphoroisothiocyanatidates (**2**).



$$\underset{(\mathbf{1})}{(RO)_2\overset{\overset{\displaystyle O}{\|}}{P}\text{—}SH} + CNBr \xrightarrow{Et_3N} \underset{(\mathbf{2})}{(RO)_2\overset{\overset{\displaystyle O}{\|}}{P}\text{—}NCS} + Et_3NHBr$$

a, R = Et
b, R = Bu

When diethyl phosphorothioic acid (**1***a*) in benzene solution and in the presence of triethylamine is treated with cyanogen bromide, a violent reaction occurs attended by a series of color changes (yellow→green→red→brown) and the formation of a precipitate. Upon removal of the precipitate (triethylamine hydrobromide) and the solvent, ethylthiocyanate (**3***a*), a nondistillable viscous liquid, presumably ethylmetaphosphate (**4***a*), (soluble in benzene and carbon tetrachloride) and diethyl phosphoroisothiocyanatidate (**2***a*) are isolated. Considering the decomposition material isolated, the primary reaction of diethyl phosphorothioic acid with cyanogen bromide proceeded to the extent of at least 60%.

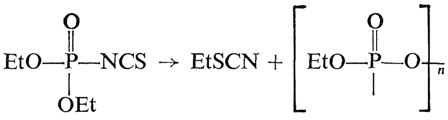
The formation of ethylthiocyanate was confirmed by comparison of infrared (i.r.) and nuclear magnetic resonance (n.m.r.) spectra with those of an authentic sample prepared by the action of potassium thiocyanate on ethyl iodide in acetone solution.

The structure of the viscous residue was deduced as ethylmetaphosphate (**4***a*) from its n.m.r. spectrum (symmetrical triplet at 1.42 δ,

$J = 7$ c.p.s., area of 3 protons; quintet centered at 4.23 δ, $J = 7$ c.p.s., area of 2 protons)[1] and its i.r. spectrum which exhibited a phosphoryl band at 1297 cm^{-1} (calculated position: 1308 cm^{-1}) (2). The diethyl phosphoroisothiocyanatidate structure (**2**a) was assigned to the remaining product after comparison of its spectral and chemical properties with those of an authentic sample prepared by a modification of the method of Kulka (3, 4) in which potassium thiocyanate in acetone solution was allowed to react with diethyl phosphorochloridate. Kulka (3) has shown the compound prepared under his experimental conditions to contain the P—N=C=S linkage by its formation of a thiourea in reaction with a secondary amine. Likewise, the material (**2**a) reacted violently with secondary amines even at 0°.

The i.r. spectrum of the compound prepared by both routes were identical exhibiting a broad band at 2005 cm^{-1} with a strong shoulder at 2065 cm^{-1}. This type of absorption has been noted (5) for —N=C=S linkages as opposed to the sharp bands for —S—C≡N systems. Also, both exhibited a phosphoryl band at 1290 cm^{-1} and had identical n.m.r. spectra (symmetrical triplet at 1.42 δ, $J = 7$ c.p.s., area of 3 protons; multiplet centered at 4.20 δ, area of 2 protons).

The diethyl phosphoroisothiocyanatidate is presumably the primary reaction product which undergoes subsequent decomposition under the reaction conditions to yield ethylthiocyanate (**3**a) and ethylmetaphosphate (**4**a). This decomposition route has previously been observed for the compound (3). Indeed, further heating of the compound (**2**a) isolated from the cyanogen bromide reaction yielded additional ethylthiocyanate and ethylmetaphosphate.



$$\mathrm{EtO{-}\overset{\overset{O}{\|}}{\underset{\underset{OEt}{|}}{P}}{-}NCS} \rightarrow \mathrm{EtSCN} + \left[\mathrm{EtO{-}\overset{\overset{O}{\|}}{\underset{|}{P}}{-}O}\right]_n$$

(**2**a) (**3**a) (**4**a)

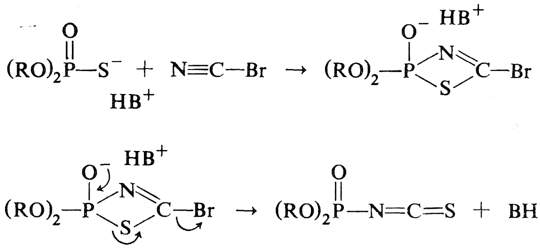
Similarly, upon treatment of dibutyl phosphorothioic acid (**1**b) with triethylamine and cyanogen bromide, butylthiocyanate (**3**b), butylmetaphosphate (**4**b), and the dibutyl phosphoroisothiocyanatidate (**2**b) were obtained.

Butylthiocyanate (**3**b) was identified by comparison of i.r. and n.m.r. spectra with those of an authentic sample prepared as above in the ethyl case.

The butylmetaphosphate (**4**b) was identified by its n.m.r. spectrum (triplet centered at 1.05 δ, $J = 6$ c.p.s., area of 3 protons; multiplet centered at 1.63 δ, area of 4 protons; multiplet centered at 4.13 δ, area of 2 protons) and the position of the phosphoryl band in its i.r. spectrum (1298 cm^{-1}).

As with the ethyl case, the dibutyl phosphoroisothiocyanatidate (**2**b) structure was assigned on the basis of its spectral and chemical properties compared with those of an authentic sample prepared by a modification of the method of Kulka (3, 4). Both materials in the i.r. spectrum exhibited a phosphoryl band at 1285 cm^{-1} and a broad band at 2002 cm^{-1} with a strong shoulder at 2065 cm^{-1}. The n.m.r. spectrum showed a triplet centered at 1.05 δ, $J = 6$ c.p.s., area of 3 protons; a multiplet centered at 1.57 δ, area of 4 protons; and a multiplet centered at 4.04 δ, area of 2 protons.

A mechanism analogous to that proposed by Douglas and Burditt (6) for the reaction of cyanogen bromide with salts of aliphatic acids is presumed to be operating here as shown in the following reaction:



Experimental

Reagents

The dialkyl phosphorothioic acids used were prepared according to the method described by Hoffmann *et al.* (7, 8). The cyanogen bromide was commercial material (Aldrich) and was used without further purification. Benzene solvent was dried by storage over sodium metal.

The Reaction of Cyanogen Bromide with Diethyl Phosphorothioic Acid

To a stirred solution of 4.60 g (0.037 mole) of diethyl phosphorothioic acid and 3.71 g (0.037 mole) of triethylamine in 30 ml of benzene cooled in an ice bath, was added dropwise, over a period of 1 h, 3.93 g (0.037 mole)

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[1] All positions given relative to tetramethylsilane observed on a Varian A-60A instrument purchased under NSF Grant GP6926.

of cyanogen bromide, dissolved in 30 ml of benzene. The reaction mixture was allowed to come to room temperature over a period of 1½ h, after completion of the addition of cyanogen bromide. After the precipitate of triethylamine hydrobromide had been removed by filtration, the solvent was removed using a rotary evaporator at room temperature and reduced pressure. Vacuum distillation of the liquid residue yielded 1.73 g (0.010 mole, 28%) of pure diethyl phosphoroisothiocyanatidate and 0.53 g (0.006 mole, 16%) of ethylthiocyanate. Also recovered was 1.22 g (0.011 mole, 31%) of ethylmetaphosphate.

The Reaction of Cyanogen Bromide with Dibutyl Phosphorothioic Acid

To a stirred solution of 10.0 g (0.042 mole) of dibutyl phosphorothioic acid and 4.3 g (0.042 mole) of triethylamine in 40 ml of benzene cooled in an ice bath, was added dropwise, over a period of 1 h, 4.5 g (0.042 mole) of cyanogen bromide, dissolved in 30 ml of benzene. The reaction mixture was allowed to come to room temperature over a period of 2 h, after completion of the addition of cyanogen bromide. After the removal of the triethylamine hydrobromide by filtration the solvent was removed using a rotary evaporator at room temperature and reduced pressure. Vacuum distillation of the residue yielded 2.13 g (0.0085 mole, 20%) of pure dibutyl phosphoroisothiocyanatidate and 0.63 g (0.0055 mole, 13%) of butylthiocyanate. Also recovered was 1.20 g (0.0088 mole, 21%) of butylmetaphosphate.

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Hexahalocyclopentadienes. I. A reinvestigation of the reaction of hexachlorocyclopentadiene with fluoro- and chlorosulfonic acids

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The reaction of hexachlorocyclopentadiene with chlorosulfonic acid has been reinvestigated and the product found by spectral methods to be the chlorosulfate ester of undecachloropentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decan-5-ol. With fluorosulfonic acid, the analogous fluorosulfate ester is formed and not octachloro-3*a*,4,7,7*a*-tetrahydro-4-7-methanoindene-1,8-dione as reported by McBee and Newcomer. A mechanism is proposed for the reaction.

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McBee and Newcomer (1, 2) have reported that hexachlorocyclopentadiene (**1**) when allowed to react with chlorosulfonic acid yielded a compound (m.p. 146–147°) of molecular formula "$C_{10}H_2OSCl_{12}$" whereas fluorosulfonic acid under similar conditions gave octachloro-3*a*,4,7,-7*a*-tetrahydro-4,7-methanoindene-1,8-dione (**2**). The formation (3) of pentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.-$0^{4,8}$] dodecan-5-one (**3**) on hydrolysis of "$C_{10}H_2O_3SCl_{12}$" suggests that the latter had the same pentacyclodecane carbon skeleton. In this note we report, firstly, spectral data which are in agreement[1] with the recently reported X-ray determination (7) of "$C_{10}H_2O_3SCl_{12}$" as the chlorosulfate ester of undecachloropentacyclo-[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$] decan-5-ol (**4***a*), and secondly, results which show that **1** and fluorosulfonic acid yield **4***b* and not compound **2** as reported by McBee and Newcomer.

The mass spectrum of **4***a* showed a parent peak *m*/*e* 620 and the presence of twelve chlorine atoms. Other ion peaks which support structure **4***a* were found at *m*/*e* 251 ($C_5Cl_5O^+$) and *m*/*e* 451 ($C_{10}Cl_9O^+$). In further support of **4***a* no hydrogens were discernible in the nuclear magnetic resonance (n.m.r.) spectrum and the ultraviolet spectrum of the compound was transparent above 215 mμ. In the infrared, the symmetric and antisymmetric stretching vibrations of the sulfonyl group were found at 1431 and 1209 cm^{-1} respectively.

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[1] X-Ray crystallographic studies are generally accepted as the ultimate in structural elucidations. The method, however, is not infallible. See for examples the work on triphenylene (4), β-selenium (5), and octaphenylcubane (6).