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REACTIONS OF COMPOUNDS OF TRIVALENT PHOSPHORUS WITH N-HALOAMIDES

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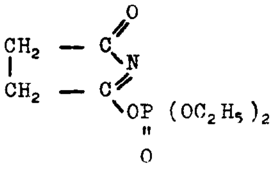
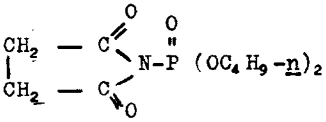
The reactions of compounds of trivalent phosphorus with N-haloamides have received but little attention up to the present time. Hettler, in a personal communication to Lichtenthaler (1), has claimed that the reaction of triethyl phosphite with N-chlorosuccinimide gave ethyl chloride and the phosphate ester (A). However, experimental details of this work have not been provided. We have now found that the reaction of N-chloro- and N-bromosuccinimide with tri-n-butyl phosphite in carbon disulfide or diethyl ether gives high yields of N-(di-n-butylphosphoro)succinimide (B), m.p. 45-47°, and the corresponding n-butyl halide.

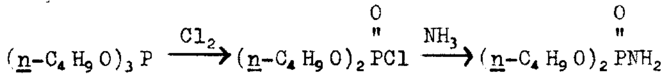


(A)



(B)

Hydrolysis of the product, m.p. 45-47°, in the presence of excess sodium borohydride in aqueous ethanol gave O,O-di-nbutylphosphoramidate (C), b.p. 117° (0.1 mm.), n_D^{30} 1.4345, succinic acid and other non-identified products of partial hydrolysis and/or reduction. An authentic sample of (C) was prepared by the following sequence of reactions, and its physical properties and infrared spectrum were identical with those of the sample cited above.

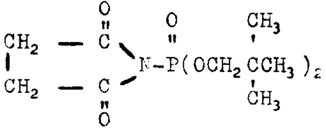


$$(\underline{n}\text{-}C_4H_9O)_3P \xrightarrow{Cl_2} (\underline{n}\text{-}C_4H_9O)_2\overset{O}{\overset{\|}{P}}Cl \xrightarrow{NH_3} (\underline{n}\text{-}C_4H_9O)_2\overset{O}{\overset{\|}{P}}NH_2$$

(C)

Additional evidence in support of structure (B) was derived from examination of its NMR spectrum, which exhibited a sextet centered about δ = 4.3 p.p.m. attributable to the α-methylene protons of the $\underline{n}$-butyl groups, a singlet at δ = 2.8 p.p.m. which showed no additional resolution when viewed with the aid of an oscilloscope and which is attributable to the four methylene protons of the succinimido ring, a group of unresolved signals centered about δ = 1.6 p.p.m. and assigned to the β- and γ- methylene protons of the butyl groups, and an intense signal at δ = 1.0 p.p.m. attributable to the methyl protons. The NMR spectrum, particularly the singlet at δ = 2.8 p.p.m., is inconsistent (2) with a structure analogous to (A).

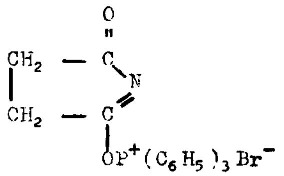
The reaction of tri-neopentyl phosphite, m.p. 64.5-66.5°, with N-bromosuccinimide gave N (di-neopentylphosphoro)-succinimide (D), m.p. 167-168°, and neopentyl bromide. The NMR spectrum of (D) exhibited a doublet centered about δ = 3.9 p.p.m. attributable to the methylene protons of the neopentyl groups, a singlet at δ = 2.8 p.p.m. which demonstrates that all four protons of the succinimido ring are equivalent, and a singlet at 1.0 p.p.m., the usual position for the methyl protons of the neopentyl groups.



(D)

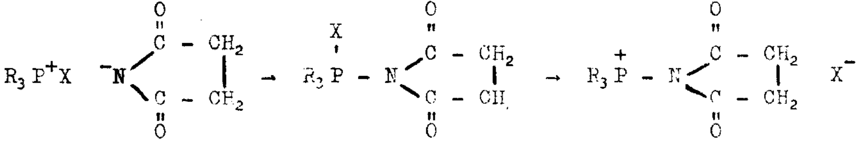
Trippett has reported (3) that triphenylphosphine undergoes vigorous reaction with N-bromosuccinimide in benzene to give a black syrup; when ethanol is added to the reaction mixture, triphenylphosphine oxide, succinimide and ethyl bromide are formed. On the basis of this information Trippett postulated formation of the enol phosphonium salt (E) as the initial product.

We have now carried out the reaction of triphenylphosphine with N-bromosuccinimide in anhydrous diethyl ether at -10^{c}. A colorless, crystalline product formed which underwent reaction with moist air to give hydrogen bromide. When the white solid was deliberately hydrolyzed, triphenylphosphine oxide, succinimide and hydrobromic acid were obtained. In an attempt to obtain additional evidence concerning the structure of the intermediate, the reaction was carried out in anhydrous chloroform solution contained in an NMR cell and under a nitrogen atmosphere. The spectrum was recorded immediately after the reagents were mixed. Whereas N-bromosuccinimide itself is but poorly soluble in anhydrous chloroform, it dissolves immediately on addition of one equivalent of triphenylphosphine; this fact constitutes evidence of a fast reaction to give a soluble product. The spectrum of the fresh solution consisted of a complex group of signals centered about $\delta = 7.3$ p.p.m. assigned to the solvent proton and phenyl protons and a sharp singlet at $\delta = 2.5$ p.p.m. attributable to the protons of the succinimido ring. The appearance of this singlet shows that all four ring protons are equivalent, and this fact excludes the presence of the enol phosphonium salt (E) in solution.



(E)

When the reaction of tri-*n*-butyl phosphite with N-bromosuccinimide was carried out in the presence of one equivalent of acetic acid, high yields of succinimide and n-butyl bromide were obtained. A control experiment showed that (B) is stable towards acetic acid. These results, together with the other data presented above, lead us to the conclusion that the first step in each of these reactions consists of a nucleophilic displacement of trivalent phosphorus on halogen to give the ion pair (F). This can give rise to the isomeric ion pair (H) possibly through the pentacovalent phosphorus intermediate (G). When R is an alkoxyl group, (H) can undergo further reaction, by nucleophilic attack of the halide ion on the α-carbon of the alkoxyl group, to give the N-(dialkylphosphoro)succinimide and the corresponding alkyl halide. However, when one equivalent of acetic acid is present, the succinimide anion accepts a proton from the acid and is replaced in the ion pair (F) by the acetate anion (4).



(F) (G) (H)

Acceptable elemental analyses have been obtained for all of the new compounds mentioned in this communication. The alkyl halides produced in the various reactions were identified by vapor phase chromatographic analysis and also by conversion to the anilide derivatives.

Other examples of apparent nucleophilic displacement on "positive" halogen of N-haloamides by trivalent phosphorus have been reported by Kenner, Todd and Weymouth (5) and by Speziale and Smith (6).

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