

Anal. Peroxide assay, 96–97%. Calcd. for $C_{15}H_{10}O_9N_2$: C, 49.73; H, 2.78; N, 7.73. Found: C, 50.34; H, 2.94; N, 7.91.

Kinetics.—Solutions of the peroxide were degassed, sealed in ampules and placed in a constant temperature bath. The decomposition was stopped by cooling the ampules in Dry Ice–acetone, and aliquots were analyzed by the method of Nozaki¹³ using a "dead-stop" end-point.¹⁴ It was found necessary to use carbonated water in order to get good results ($\pm 0.2\%$) with thiosulfate from 0.001 to 0.005 *N*.

Product Analysis.—With the exception of anisyl 3,5-dinitrobenzoate and the crude carboxy inversion product, no neutral products were formed in sufficient quantity for isolation, although various chromatographic adsorbents were tried. The acid mixtures were removed by extraction with sodium bicarbonate and analyzed for anisic and 3,5-dinitrobenzoic acid by means of infrared bands at 1612 and 1350 cm^{-1} . Control analyses indicate that the results are accurate to within 9% for the 3,5-dinitrobenzoic acid and 8% for the anisic acid. The mixture of acids is not readily separated by chromatography. Esters were estimated by sa-

ponification of the neutral fraction followed by infrared analysis of the resulting mixture of acids. Anisyl 3,5-dinitrobenzoate was identified by its melting point, mixed melting point and infrared spectrum.

The Carboxy-inversion Product III.—The neutral fraction of the decomposition products from the reaction in nitrobenzene gave a small amount of ethyl 3,5-dinitrobenzoate on treatment with ethanol, presumably because of the presence of III. The ester IV was isolated by crystallization of the decomposition products from the reaction in acetone and in benzene–picric acid, with the carboxy-inversion product as a likely precursor. The decomposition products from the reaction in thionyl chloride contained a substance of variable melting point (137–139 for one sample, 139–149 for another), evidently III in crude form. This crude product has an anhydride band at 1830 cm^{-1} , absent in the spectrum of the ester IV. All attempts at recrystallizing the crude product gave only the ester IV. Warming the crude III in methanol evolved 70% of the theoretical amount of carbon dioxide; saponification gave 94% of the theoretical amount of *p*-methoxyphenol. Attempts at synthesizing III from anisyl chloroformate and the sodium or silver salt of 3,5-dinitrobenzoic acid also gave the ester IV.

(13) K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).

(14) E. W. Abrahamson and V. H. Linshitz, *Anal. Chem.*, **24**, 1355 (1952).

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF WESTVACO CHLOR-ALKALI DIVISION OF FOOD MACHINERY AND CHEMICAL CORPORATION]

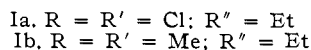
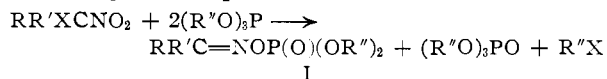
Phosphorus(V) Acid Esters of Oximes

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Alkyl esters of trivalent phosphorus acids react with α -halonitro compounds to form alkyl halide and oxime esters of the corresponding pentavalent phosphorus acids.

The similarity in the chemical behavior of the nitro and carbonyl groups in certain reactions suggested that α -halonitroparaffins should react with esters of trivalent phosphorus acids to form products which are analogous to the vinyl esters of pentavalent phosphorus acids which have recently been reported from this Laboratory² and by several other groups. The reaction of triethyl phosphite with several representative halonitroparaffins has been studied and the reaction shown to proceed according to the equation



Trimethyl phosphite and diethyl phenylphosphonite react in an analogous fashion, but triphenyl phosphite appears to react by a different mechanism. The ease with which the reaction takes place increases with the number of halogen atoms on the α -carbon atom and bromine compounds are more active than chlorine compounds. 1-Chloro-1-nitroethane and triethyl phosphite did not react at 50°, but 1,1-dichloro-1-nitroethane and triethyl phosphite reacted rapidly at 25°, and trichloronitromethane reacted violently with the phosphite at –40° producing smoke and flame unless carefully

controlled. 2-Bromo-2-nitropropane reacted rapidly with the phosphite at 50°.

Arbuzov and co-workers³ reported the reaction of triethyl phosphite with α -bromonitro compounds but were able to identify only triethyl phosphate and ethyl bromide. These investigators observed a two-stage reaction, the first occurring at or below ordinary temperatures and the second at about 90–100°. They found that nitromethane did not react with triethyl phosphite, indicating that the halogen atom plays an important role in the oxidation of the phosphite to the phosphate. The work reported in this paper indicates that the second reaction observed by the Russian workers was probably the Beckmann rearrangement of the primary reaction product I as reported recently by Kenner, Todd and Webb.⁴ Kamai⁵ treated trichloronitromethane with triethyl phosphite and tributyl phosphite and reported the corresponding dialkyl phosphorochloridates as the only identifiable products. The author has found that the reaction of two moles of triethyl phosphite with one mole of trichloronitromethane converts about 3 to 11% of the phosphite to the phosphorochloridate, about 50% to the phosphate and the remainder to Ia and other products. Ia has been obtained in yields of 32 to 63%. When

(3) A. E. Arbuzov, B. A. Arbuzov and B. P. Lugovkin, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 538 (1947).

(1) Food Machinery and Chemical Corporation, Chemical Divisions, Central Research Laboratory, Princeton, New Jersey.

(2) J. F. Allen and O. H. Johnson, *This Journal*, **77**, 2871 (1955).

(4) G. W. Kenner, A. R. Todd and R. F. Webb, *J. Chem. Soc.*, 1231 (1956).

(5) G. Kamai, *Doklady Akad. Nauk S.S.S.R.*, **79**, 795 (1951).

other halonitro compounds were treated with triethyl phosphite, the triethyl phosphate fraction was contaminated with a small amount of halogen compound, but this could not be identified as the phosphorochloridate. Since Ford-Moore and co-workers⁶ have reported the preparation of dialkyl phosphorochloridates from phosgene and trialkyl phosphites, it seemed possible that Ia, a phosgene derivative, might also convert phosphite to phosphorochloridate. However, when equimolar quantities of triethyl phosphite and Ia were heated at 75–150°, ethyl chloride (100%) was evolved slowly but the reaction mixture did not contain diethyl phosphorochloridate.

The assignment of structure I to the reaction products is based upon the following evidence: (a) elemental analysis and physical properties, including strong infrared absorption at 6.1–6.3 μ , characteristic of the carbon–nitrogen double bond; (b) the independent synthesis of Ib from acetone oxime, aqueous sodium hydroxide and diethyl phosphorochloridate; and (c) the hydrolysis of Ib to acetone.

It also should be noted that structure I is analogous to the vinyl phosphate structure, and it seems likely that both reactions proceed by the same mechanism. However, the reaction of the nitro compounds is complicated by the oxidation–reduction, and it is not apparent whether the nitro compound is first reduced to the nitroso compound which reacts with additional phosphite or whether the nitro compound forms an intermediate with the phosphite which is then reduced by additional phosphite. That the first route is possible was shown by the synthesis of Ib from 2-chloro-2-nitrosopropane and triethyl phosphite. But since the over-all reaction is usually very rapid, the initial stage must also be rapid, and it might be expected that the addition of phosphite to a large excess of nitro compound would result in the formation of nitroso compound which would be evident from its characteristic intense blue color. In no instance has more than a trace of color appeared, and in most reactions no color has been observed.

The presence of a hydrogen atom on the alpha carbon atom of the oxime moiety of I (R or R') lends instability to the molecule and no product of this type has been distilled. When heated to about 100° these products undergo a vigorous exothermic reaction as reported by Arbuzov and co-workers.³ The crude product of the reaction between trimethyl phosphite and 1-bromo-1-nitropropane at 30–40° showed strong infrared absorption at 6.3 μ which is assumed to indicate that the product had structure I (R = H, R' = Et, R'' = Me). The product of the reaction between triethyl phosphite and 2-bromo-2-nitropropane, Ib, when heated rapidly did not give the second-stage reaction below 175°. Although it is assumed that the second-stage reaction is a Beckmann rearrangement of the oxime ester, it is obvious that the reaction is accompanied by decomposition and most of the product is converted to a tar from which no pure product has been isolated.

(6) A. H. Ford-Moore, L. J. Lermitt and C. Stratford, *J. Chem. Soc.*, 1776 (1953).

Experimental

Preparation of Diethyl Isopropylideneamino Phosphate (Ib) (a) From 2-Bromo-2-nitropropane and Triethyl Phosphite.—One mole (166 g.) of triethyl phosphite was added dropwise with cooling and stirring to 0.5 mole (84.5 g.) of 2-bromo-2-nitropropane at 55–60°. The mixture was then heated to 75–85° for 30 minutes and the ethyl bromide (94%) removed at reduced pressure. Distillation of the reaction mixture through a 10-inch Vigreux column gave (a) 98 g., b.p. 57–85.5° (0.4 mm.), which is 108% of theory for triethyl phosphate, and (b) 66.5 g. (64%) of Ib, b.p. 101–110° (0.2 mm.). Redistillation gave an analytical sample, b.p. 95–98.5° (0.2 mm.), n_D^{25} 1.4359, and d_4^{25} 1.0949.

Anal. Calcd. for $C_7H_{16}NO_4P$: P, 14.8. Found: P, 15.2.

(b) From 2-Chloro-2-nitrosopropane and Triethyl Phosphite.—A solution of 0.5 mole (53.8 g.) of crude 2-chloro-2-nitrosopropane in 200 ml. of carbon tetrachloride was cooled to 0°, and 0.5 mole (83 g.) of triethyl phosphite was added with stirring. When addition of the phosphite was complete, the temperature was raised to 75°, and 21 g. of ethyl chloride containing a small amount of carbon tetrachloride was collected in a cold trap. The remainder of the volatile matter was removed *in vacuo* and the product fractionated to yield 53 g. (51%) of oxime ester, b.p. 88–96° (0.1 mm.), n_D^{25} 1.4360.

Anal. Calcd. for $C_7H_{16}NO_4P$: N, 6.7; P, 14.8. Found: N, 6.5; P, 14.9.

The nitroso compound used in this preparation was obtained by adding 1 mole of chlorine to 1 mole each of acetone oxime and sodium hydroxide dissolved in 400 ml. of water. The product was separated from the aqueous solution, dried with calcium sulfate and used without further purification.

(c) From Acetone Oxime and Diethyl Phosphorochloridate.—Two-tenths mole of diethyl phosphorochloridate was added gradually at 15–17° to 0.2 mole of acetone oxime and 0.3 mole of sodium hydroxide dissolved in 100 ml. of water. The mixture was shaken for 30 minutes, the 2 layers separated, and the aqueous layer extracted with ether. After drying the combined organic layers, the ether was evaporated and the product distilled to give 14 g. (33.5%) of oxime ester, b.p. 95–98° (0.2 mm.), n_D^{25} 1.4358, and d_4^{25} 1.0940. Infrared spectrograms of this product and the product of method (a) were essentially identical, both absorbing intensely at 6.1 μ .

Anal. Calcd. for $C_7H_{16}NO_4P$: P, 14.8. Found: P, 15.0.

Preparation of Diethyl (1-Chloroethylidene)-amino Phosphate.—With stirring and mild cooling 0.5 mole (83 g.) of triethyl phosphite was added gradually to 0.25 mole (36 g.) of 1,1-dichloro-1-nitroethane at 25–40°. Stirring was continued without cooling, and the temperature rose to 90° where it was held by mild cooling until the reaction began to subside (about 5 minutes). The temperature was then raised to 100° for 15 minutes to complete the reaction. The yield of ethyl chloride was 12 g. (74%). Fractionation of the product gave 42 g. (73%) of oxime ester, b.p. 103° (0.3 mm.), n_D^{25} 1.4408, and with intense infrared absorption at 6.1 μ .

Anal. Calcd. for $C_6H_{13}ClNO_4P$: Cl, 15.5; N, 6.1. Found: Cl, 15.2; N, 6.1.

Preparation of Diethyl (Dichloromethylene)-amino Phosphate.—One mole (166 g.) of triethyl phosphite was added gradually at 25° to 0.5 mole (82 g.) of chloropicrin dissolved in 300 ml. of carbon tetrachloride. The reaction was vigorous and appeared to be complete at the end of the mixing period. After removal of ethyl chloride and carbon tetrachloride by distillation, the resulting mixture was separated by fractionation (12 inch column Hastelloy B Heli-Pak) into 4 major fractions: (A) 14.3 g., b.p. 45–50° (0.7–0.3 mm.); (B) 46.4 g., b.p. 45–58° (0.3–0.2 mm.); (C) 26.0 g., b.p. 62.55° (1.4–1 mm.); and (D) 78.5 g. (63%) oxime ester, b.p. 80–85° (0.2 mm.), n_D^{25} 1.4518.

Anal. Calcd. for $C_6H_{10}Cl_2NO_4P$: Cl, 28.4; N, 5.6; P, 12.4. Found: Cl, 28.1; N, 5.4; P, 12.4.

Fractions A and B contained 6.6 and 0.54% chlorine, respectively, and if it is assumed that all the chlorine was in the form of diethyl phosphorochloridate, the yield of the latter was 5.8 g. which is equivalent to 3.4% of the phos-

phite used in the reaction. The chlorine-containing compound was identified as diethyl phosphorochloridate as follows. Thirteen grams of fraction A, containing 0.86 g. of chlorine, was treated with 4.5 g. of aniline (2 moles) and the mixture heated to 80° for 10 minutes. After adding 18 ml. of water, the solution was cooled to 5° and seeded with diethyl N-phenylphosphoramidate. The resulting solid after recrystallization from ethanol-water had m.p. 95.5–96° which was not depressed by mixing with an authentic sample of diethyl N-phenylphosphoramidate (lit.⁷ m.p. 95–96°).

When this preparation was repeated without solvent at –40°, the reaction was very vigorous and smoke and flame were occasionally observed when a drop of phosphite entered the chloropicrin. The yield of oxime ester was 32% and about 11% of the phosphite was converted to phosphorochloridate.

Preparation of Ethyl Isopropylideneamino Phenylphosphonate.—Sixty-five grams (0.31 mole) of diethyl phenylphosphonite was added dropwise with stirring and cooling at 15–28° to 26 g. (0.155 mole) of 2-bromo-2-nitropropane. When addition was complete, stirring was continued at 30° for 1 hour. Distillation gave 14.5 g. (86%) of ethyl bromide and fractionation of the remainder gave 28.5 g. (82%) of diethyl phenylphosphonate, b.p. 100° (0.5 mm.), and n_D^{25} 1.4897 (lit.⁸ b.p. 104–105° (0.5 mm.), n_D^{25} 1.4935), and 10 g. (27%) of oxime ester, b.p. 140° (0.5 mm.), and n_D^{25} 1.5082. There was a large tarry residue.

Anal. Calcd. for $C_{11}H_{16}NO_2P$: N, 5.8; P, 12.8. Found: N, 5.6; P, 12.5.

Preparation of Diethyl Benzylideneamino Phosphate.—To a mixture of 19.6 g. of benzaldehyde oxime (0.16 mole)

(7) F. R. Atherton, H. T. Howard and A. R. Todd, *J. Chem. Soc.*, 1106 (1948).

(8) G. M. Kosolapoff, "Organic Phosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 162.

and 12.6 g. of pyridine (0.16 mole) was gradually added at 0° 27.6 g. of diethyl phosphorochloridate (0.16 mole). The mixture was allowed to warm to room temperature where it was stirred for 1 hr. and then heated at 50–60° for 1 hr. After cooling, ether was added to the mixture and pyridine hydrochloride removed by filtration. Removal of volatile matter by heating *in vacuo* gave 36.5 g. (88%) of crude oxime ester which decomposed when distillation was attempted at 1 mm. pressure.

Anal. Calcd. for $C_{11}H_{16}NO_2P$: P, 12.1. Found: P, 11.9.

Pyrolysis of Diethyl Isopropylideneamino Phosphate.—Twenty grams of oxime ester was placed in a 50-ml. flask equipped with a thermometer dipping into the liquid and a water condenser. When heated to 175°, a vigorous exothermic reaction began which was controlled with difficulty by immersing the flask in a Dry Ice-bath. After the reaction subsided, heating was continued at 180–185° for 2 hr. Distillation at 0.6 mm. gave only 3 g., b.p. 53–55°, n_D^{25} 1.4060, the remainder being a viscous tar. Not only is the boiling point of the distillate considerably lower than would be expected for the Beckmann rearrangement product, but the phosphorus and nitrogen contents were low (12.4 and 4.45%, respectively).

Hydrolysis of Diethyl Isopropylideneamino Phosphate.—Ten grams of the oxime ester and 50 ml. of 5% hydrochloric acid were placed in a flask equipped with a distillation condenser. When heated to gentle boiling, a few drops of blue liquid distilled followed by 3.5 ml. of colorless distillate. This was identified as acetone by conversion to the 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 126° (lit.⁹ m.p. 126°).

(9) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 262.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM STANFORD RESEARCH INSTITUTE]

The Addition of Chloro- and Ethoxysilanes to Vinyl and Allyl Monomers^{1,2}

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The platinum-catalyzed addition of some chloro- and ethoxysilanes to a variety of vinyl and allyl monomers has been accomplished in good yield under mild conditions. Nuclear magnetic resonance spectra make it clear that the addition of methylchlorosilane to vinyl acetate gives the linear compound $CH_3SiCl_2CH_2CH_2COOCH_3$, while addition to methyl acrylate gives the branched compound $CH_3SiCl_2CH(CH_3)COOCH_3$. The latter compound represents the first reported example of a reversed addition orientation in additions of the elements of the Si-H bond to carbon-carbon double bonds.

The addition of the elements of the Si-H bond to a carbon-carbon double bond was first reported in 1947³ and has been the object of much study since that time. Peroxides and ultraviolet light were used as catalysts in the original study,³ and since that report the reaction has been carried out by employing high temperatures and pressures without catalyst⁴ and by using platinum and palladium as catalysts.⁵

We have utilized this platinum-catalyzed reaction for the synthesis of silicon monomers which

contain functional groups. The additions of trichlorosilane, methylchlorosilane and methyl-diethoxysilane to a variety of vinyl and allyl monomers were accomplished using mild conditions. These reactions are listed in Table I.

A 5% platinum-on-carbon catalyst was used in all these additions. It was demonstrated to be necessary in the trichlorosilane additions to vinyl acetate and to methyl acrylate, and we presume it to be necessary in all the reactions listed in Table I. The catalyst was used in the amount of about 0.25–0.50% by weight of the silane employed and, in most cases, that same weight of Ionol (2,6-di-*t*-butyl-4-methylphenol) was used as a polymerization inhibitor for the olefin.⁶

Two techniques were used in carrying out these reactions—use of a stainless steel sealed bomb

(6) The effectiveness of polymerization inhibition is shown by an experiment in which methyl acrylate, Ionol and a large excess of trichlorosilane were heated in a steel bomb at 150° for 20 hr. No polymerization of the acrylate was detectable, and there was no evidence of a silane-acrylate addition product.

(1) This work was supported by the Wright Air Development Command under Contract AF 33(616)-2998.

(2) (a) A preliminary communication appeared in *THIS JOURNAL*, **78**, 4493 (1956). (b) Presented in part at the 130th meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1956.

(3) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *THIS JOURNAL*, **69**, 188 (1947).

(4) A. J. Barry, L. DePree, J. W. Gilkey and D. F. Hook, *ibid.*, **69**, 2916 (1947).

(5) G. H. Wagner and C. O. Strother (to Union Carbide and Carbon), U. S. 2,632,013 (March 17, 1953).