of high stability may be formed through strong NHO hydrogen bonding[10] (VIa, R = OMe; VIb, R = Cl). Evidence for this chelation is found in the infrared spectrum of Ia, in which the single NH-stretching frequency is shifted from 3500–3310 to 3295 cm^{-1}. The shift in the N=O frequency[11] from 1340 to 1316 cm^{-1} confirms the chelation and the assigned structure.

Experimental Section

Melting points were determined in capillary tubes on an electrothermal apparatus and were corrected. Although not usually specified, infrared spectra were taken of all compounds using Perkin-Elmer Model 237 spectrophotometer. Unless specified, the spectra were taken in Nujol mulls and were used in conjunction with melting points and analyses to determine the structures of the products.

2-Aminothiazolo[5,4-*b*]pyridines.—These compounds were prepared as described in the literature[12] but with some modifications. During the addition of bromine in glacial acetic acid, the temperature was never allowed to exceed −20°. The orange residue on filtering was extracted with boiling acetone. The acetone extract was concentrated *in vacuo* leaving the acetic acid salt which was neutralized with dilute sodium hydroxide to give the desired product. More of this thiazolopyridine was obtained upon neutralizing the original filtrate with sodium carbonate (to pH 5.5) as reported. This technique led to increased yields (83–90.5%) compared with 50–60% yields if these compounds were prepared as reported.[12]

3-Amino-2-mercaptopyridines.—The compounds II were obtained from 2-aminothiazolo[5,4-*b*]pyridines as described in the literature[5a] except that the reflux time was increased from 1 to 3 hr to avoid partial hydrolysis which was observed with 2-amino-5-methoxythiazolo[5,4-*b*]pyridine.

3,5-Dinitro-4-hydroxypyridine.—The preparation of 3,5-dinitro-4-hydroxypyridine from 4-hydroxypyridine has been reported.[8a] Its preparation from 3-nitro-4-hydroxypyridine is therefore described. 4-Hydroxypyridine (mp 146–147°, lit.[13] mp 147–151°) was prepared from pyridine and converted to 3-nitro-4-hydroxypyridine (mp 278–279°, lit.[8b] mp 278–279°). To a cooled (0°) and well-stirred mixture of fuming nitric acid (225 ml) and 30% oleum (200 ml) was added 3-nitro-4-hydroxypyridine (140 g, 1.0 mole) at such a rate that the temperature never exceeded 50°. After the addition, the ice bath was removed and the mixture was stirred below 100° for 24 hr and at 140° for another 24-hr period. The mixture was cooled, poured into ice, and partially neutralized with concentrated ammonia solution. The product was collected and recrystallized from hot water giving light yellow platelets of 3,5-dinitro-4-hydroxypyridine (170.2 g, 92%): mp >300°; ν_{max} 1950, 1830, 1650, 1605, 1545, 1525, 1345, 1240, 1190, 1155, 1105, 1060, 980, 952, 920, 875, 827, 788, 758, and 703 cm^{-1}.

Anal. Calcd for $C_5H_3N_3O_5$: C, 32.44; H, 1.63; N, 22.70. Found: C, 32.31; H, 1.73; N, 22.61.

4-Chloro-3,5-dinitropyridine (III).—A mixture of 3,5-dinitro-4-hydroxypyridine (18.5 g, 0.1 mole), phosphorus pentachloride (38 g, 0.156 mole), and phosphoryl chloride (5.0 ml) was refluxed on an oil bath at 140–150° for 3 hr. The phosphorus halides were removed by distillation and the dark residue was extracted with five successive 100-ml portions of boiling light petroleum ether (bp 60–80°). The solvent was removed by distillation leaving a brown solid (16 g, 78.5%) which was used in the next stage of the synthesis without further purification, mp 236–239°.

1-Nitro-7-methoxy-3,6-diazaphenothiazine (Ia).—3,5-Dinitro-4-chloropyridine (III, 12.3 g, 0.06 mole) was added a little at a time to a stirred mixture of 6-methoxy-3-amino-2-mercaptopyridine (7.0 g, 0.045 mole) and 85% potassium hydroxide (6.6 g, 0.1 mole) in anhydrous methanol. The pH of the solution was measured from time to time and more methanolic potassium hydroxide was added to ensure that the solution remained basic (pH 8.5). The 4′-(3,5-dinitro)pyridyl-3-amino-6-methoxy-2-pyridyl sulfide (IVa, R = OMe) formed, rearranged to the diarylamine (Va, R = OMe), which, in the presence of excess base, cyclized to the desired product. The dark purple mixture was stirred for 3 hr at room temperature and filtered. The residue was washed with cold water to remove potassium salts. On filtering, a deep purple product was collected. The original dark purple filtrate was concentrated *in vacuo* to near dryness and, on mixing with water and filtering, another fraction of the product was collected. The combined product was recrystallized from acetone–ethanol mixture (1:1) after treatment with activated carbon giving 1-nitro-7-methoxy-3,6 diazaphenothiazine (Ia, 7.6 g, 61.3%) as deep, glistening, bluish purple platelets: mp 267–268° dec; ν_{max} 3295, 3025, 1605, 1570, 1510, 1440, 1425, 1395, 1316, 1300, 1275, 1250, 1225, 1195, 1175, 1150, 1130, 1100, 1025, 906, 880, 835, 820, 763, and 740 cm^{-1}.

Anal. Calcd for $C_{11}H_8N_4SO_3$: C, 47.82; H, 2.92; N, 20.28; S, 11.61. Found: C, 47.64; H, 3.00; N, 20.23; S, 11.70.

1-Nitro-7-chloro-3,6-diazaphenothiazine (Ib).—This compound was prepared from 3,5-dinitro-4-chloropyridine (III, 6.1 g, 0.03 mole), 3-amino-6-chloro-2-mercaptopyridine (IIb, 3.22 g, 0.02 mole), and 85% potassium hydroxide (3.3 g, 0.05 mole) in a manner similar to that described for 1-nitro-7-methoxy-3,6-diazaphenothiazine (Ia). A 2.9-g yield (52%) of the glistening platelets (Ib) was obtained: mp 294–295° dec; ν_{max} 3270, 3030, 1590, 1575, 1545, 1506, 1326, 1280, 1234, 1182, 1135, 1095, 920, 905, 860, and 766 cm^{-1}.

Anal. Calcd for $C_{10}H_5ClN_4O_2S$: C, 42.78; H, 1.78; Cl, 12.66; N, 19.96; S, 11.41. Found: C, 42.65; H, 1.82; Cl, 12.62; N, 19.86; S, 11.52.

Registry No.—Ia, 10425-68-0; Ib, 10425-69-1; III, 10425-70-4; 3,5-dinitro-4-hydroxypyridine, 10425-71-5.

Acknowledgment.—This project was sponsored by the Research Committee of the University of Nigeria whose financial support is gratefully acknowledged. The author is also grateful to Mr. F. I. Ozoh, now of this laboratory for the microanalyses, and to Mr. E. O. Ekechukwu of the Ministry of Commerce, Laboratory Section, Enugu, Eastern Nigeria, for the infrared spectra.

(10) (a) O. L. Brady and C. Waller, *J. Chem. Soc.*, 1218 (1930); (b) K. C. Roberts and H. B. Clark, *ibid.*, 1312 (1935); (c) see ref 7b.

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1964, p 254.

(12) (a) J. Bernstein, B. Stearns, E. Shaw, and W. A. Lott, *J. Am. Chem. Soc.*, **69**, 1151 (1947); (b) see ref 5b.

(13) (a) B. Bak and D. Christensen, *Acta Chem. Scand.*, **8**, 390 (1954); (b) E. Koenigs and H. Greiner, *Ber.*, **64**, 1049 (1931).

The Reaction of Trichloromethyl Aromatic Compounds with Triethyl Phosphite

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Recent publications[1,2] describing the synthesis and the polymerization of $\alpha,\alpha,\alpha',\alpha'$-tetrachloro-*p*-xylylene prompt us to record some observations made during an investigation into the chemistry of aromatic trichloromethyl compounds. When $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-hexachloro-*p*-xylene (I) is heated with triethyl phosphite (II) in homogeneous solution above 100°, an extremely exothermic reaction occurs with evolution of a gas and copious precipitation of a white solid. The gaseous product was collected in a cold trap and identified as ethyl chloride (IV) by its infrared spectrum[3] and by elemental analysis. The colorless, solid product is an intractable material, insoluble in all solvents including hot, concentrated sulfuric acid; this product believed to

(1) H. G. Gilch, *Angew. Chem. Intern. Ed. Engl.*, **4**, 598 (1965).

(2) H. G. Gilch, *J. Polymer Sci.*, **4A1**, 438 (1966).

(3) R. H. Pierson, A. N. Fletcher, and E. St. Clair Gantz, *Anal. Chem.*, **28**, 1218 (1965).

TABLE I

	Peaks					
	A	B	C	D	E	F
Triethyl Phosphite (II)						
Ppm shift referenced to 85% H_3PO_4	−137.1	−14.1	...	+1.2	+2.8	...
% of total P	87.2	4.2	...	4.8	3.8	...
Distillate from Reaction of Cl_3C–⟨⟩–CCl_3 with $P(OEt)_3$						
Ppm shift referenced to 85% H_3PO_4	−135.1	−14.4	−2.5	+1.5	+2.4	+13.6
% of total P	12.5	19.0	41.2	9.4	17.9	*Ca.* 1%
Assignment	$P(OEt)_3$	...	$(EtO)_2P(O)Cl$	$(EtO)_3PO$	...	$[(EtO)_2PO]_2O$
Ref shifts	−137 to −140[a,b]	...	−2.8 to −3.3[a,c-e]	+0.9 to +1.2[a,b,f,g]	...	+12.5 to +13.8

[a] N. Muller, P. C. Lauterbur, and J. Goldensen, *J. Am. Chem. Soc.*, **78**, 3557 (1956). [b] R. A. Y. Jones, A. R. Kabritzky, and J. Michalski, *Proc. Chem. Soc.*, 321 (1959). [c] H. Finegold, *Ann. N. Y. Acad. Sci.*, **70**, 875 (1958). [d] R. A. Y. Jones and A. R. Kabritzky, *Angew. Chem.*, **74**, 60 (1962). [e] K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. Eng. Data*, **7**, 307 (1962). [f] E. Schwarzman and J. R. Van Wazer, *J. Am. Chem. Soc.*, **83**, 365 (1961). [g] A. J. Speziale and R. C. Freeman, *J. Org. Chem.*, **23**, 1883 (1958).

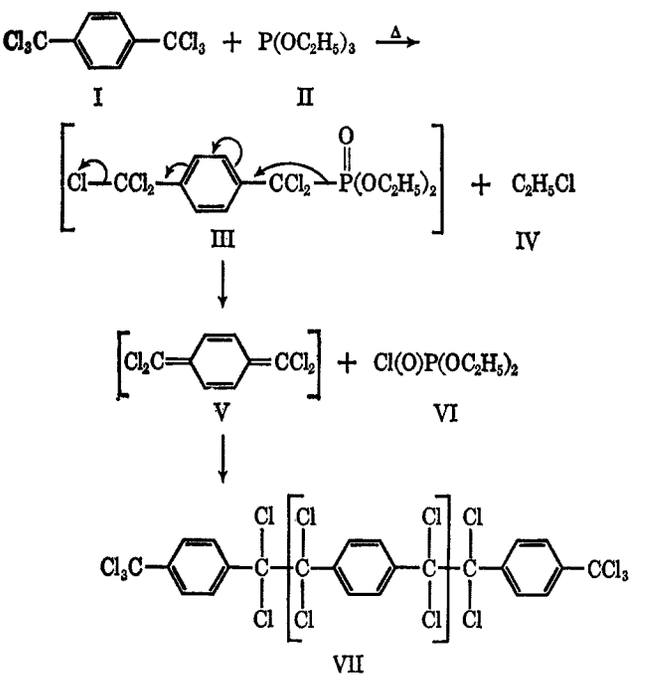
be poly($\alpha,\alpha,\alpha',\alpha'$-tetrachloro-*p*-xylylene) (VII) (*Anal.* Calcd for $C_8H_4Cl_4$: C, 39.71; H, 1.67; Cl, 58.62. Found: C, 39.88; H, 1.82; Cl, 58.52.) does not melt or soften up to 325°, and one sample was pyrolyzed without evidence of charring. Thermogravimetric analysis showed a 65% weight loss at 350–425°, followed by a decreasing rate loss at higher temperatures.

The evolution of ethyl chloride (moles of C_2H_5Cl/mole of I = ~1) suggests a Michaelis–Arbusov-type reaction[4,5] to yield the intermediate phosphonate (III). If it is assumed that an α,α-dihalobenzylphosphonate of this type would be intrinsically unstable,[6] then its decomposition, facilitated by the formation of a conjugated system, would yield the reactive monomer, $\alpha,\alpha,\alpha',\alpha'$-tetrachloro-*p*-xylylene (V), and chlorodiethyl phosphate (VI). The rapid polymerization of V accounts for the high thermal energy release during the reaction which can be moderated by use of a solvent.[7] (See Scheme I.)

Proof of the structure of VI as the major phosphorus-containing product produced in the reaction was obtained by fractional distillation to obtain a fraction corresponding to the reported[8] boiling point of chlorodiethylphosphate (VI) and phosphorus[31] nmr analysis of the composite distillate which indicated a major phosphorus environment at −2.5 ppm (peak C in Table I). Treatment of the composite distillate with water resulted in a pH change of 7 to 1 and subsequent nmr examination showed the loss of resonance at −2.5 ppm with appearance of a new peak corresponding to the known chemical shift of $(C_2H_5O)_2P(O)OH$ at +1.3 ppm. We have been unable to make definite structure assignments to components corresponding to peaks B and E (Table I) present in both reagent grade triethyl phosphite [bp 62–64° (24 min)] and the product.

This particular reaction appears to be specific for the *para* isomer (I). Reaction of the phosphite (II) with $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-hexachloro-*m*-xylene and with benzotrichloride proceeds only under forcing conditions with a catalyst and appears to proceed by a different mechanism.

SCHEME I

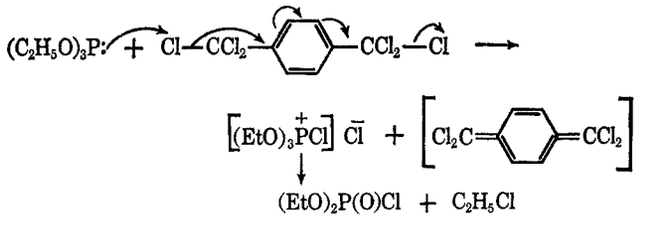


(4) A. Michaelis and R. Kaehne, *Chem. Ber.*, **31**, 1048 (1898).

(5) A. Arbusov, *J. Russ. Phys. Chem. Soc.*, **38**, 687 (1906).

(6) The literature is meager with respect to the reaction of geminal polyhalides with trialkyl phosphites. Such simple polyhaloaliphatic compounds as carbon tetrachloride and chloroform react with trialkyl phosphites only under abnormal, free-radical conditions: R. G. Harvey and E. R. De Sombre in "Topics in Phosphorus Chemistry," M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 68–71. Whereas the polyhalomethylaromatic compounds are generally more receptive to displacement reactions at the benzylic carbon atom, we have not succeeded in isolating the expected product, diethyl α,α-dichlorobenzylphosphonate, from reaction of triethyl phosphite with benzotrichloride nor has such a product been reported.

(7) We are grateful to one of the referees for his suggestion of a concerted mechanism for this reaction (see below). Some basis for such a direct nucleophilic attack by phosphorous on halogen is available in the reaction of trialkyl phosphites with vicinal dihalides, having adjacent negative substituents, to yield olefins (see Harvey and De Sombre[6]). In this instance the *p*-xylene hexachloride (I) can be considered reacting as a vinylogous dihalide.



(8) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, p 821.

Registry No.—I, 68-36-0; II, 122-52-1.

Acknowledgments.—The author is indebted to Mr. Claude H. Dungan for the nmr data and to Dr. Allen Kenyon for the thermogravimetric analysis.

Desulfurization of Thietanes by Triphenylphosphine and Triethyl Phosphite

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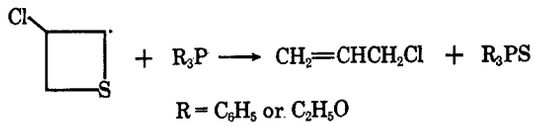
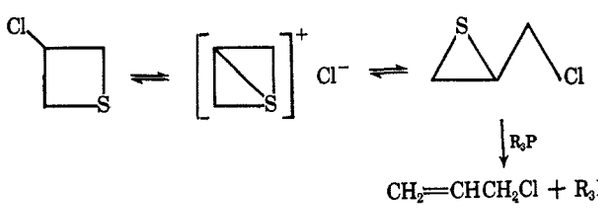
Trivalent phosphorus compounds such as triethyl phosphite or triphenylphosphine remove sulfur from episulfides (thiiranes) to give an olefin and the thionophosphate or phosphine sulfide.[2] We wish to report that certain four-membered ring sulfides (thietanes) also give up their sulfur to triphenylphosphine or triethyl phosphite, although less readily.

When 3-chlorothietane is treated with triphenylphosphine or triethyl phosphite, allyl chloride and triphenylphosphine sulfide or triethyl thionophosphate are produced. For example, in refluxing xylene (bp 137–140°) for 70 hr, a 93% yield of triphenylphosphine sulfide is obtained. 3-Hydroxythietane reacted much more slowly under the same conditions (34% of tri-



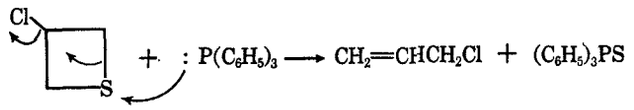
phenylphosphine sulfide after 115 hr in refluxing xylene), and thietane itself was desulfurized in low yield after a long reaction time (10% triphenylphosphine sulfide after 188 hr in refluxing xylene). Attempts to identify the organic products from the desulfurization of 3-hydroxythietane or thietane were not successful.

The desulfurization of 3-chlorothietane may proceed *via* chloromethylthiirane formed by rearrangement of 3-chlorothietane.[3] The desulfurization of chloromethylthiirane by triphenylphosphine in benzene was faster[4] than the desulfurization of 3-chlorothietane which indicates that, if the above scheme is correct, the slow



step is the rearrangement, which is not unreasonable considering the nonpolar nature of the solvent.

Alternatively, the reaction may be bimolecular.[5]



3-Hydroxythietane likewise may decompose to a cyclic ion which could rearrange to hydroxymethylthiirane which may be desulfurized to allyl alcohol. Both 3-hydroxythietane and thietane may undergo ring scission to mercaptans or mercapto radicals which can be desulfurized.[6] Possible three-carbon fragments from 3-hydroxythietane (allyl alcohol, *n*-propyl alcohol, isopropyl alcohol, acetone, propionaldehyde) were not detected by gas chromatography.

Experimental Section

3-Hydroxythietane was prepared by a modification of the method of Sjöberg.[7] 3-Chlorothietane was prepared by the procedure of Martin and Anderson by treatment of 3-hydroxythietane with thionyl chloride in chloroform.[8]

Reaction of Thietanes with Triphenylphosphine and Triethylphosphite.—3-Chlorothietane (2.0 g, 0.018 mole) and triphenylphosphine (4.7 g, 0.018 mole) were dissolved in 10 ml of xylene in a 50-ml, round-bottomed flask connected to a condenser and a Dean–Stark separator which was in turn connected to a Dry Ice–acetone condenser to condense volatile materials. Benzene also can be used as a solvent but yields are lower. The mixture was refluxed for 70 hr at the end of which *ca* 0.5 g of material was obtained in the Dean–Stark trap. This material gave an immediate precipitate when treated with alcoholic silver nitrate. The liquid collected in the trap was identified as allyl chloride by comparison of its infrared spectrum with an authentic sample.

The residue in the reaction flask solidified when it was cooled. It was chromatographed on an alumina (Fischer, 80–200 mesh, activated at 110°) column with cyclohexane and benzene as eluents. A 93.5% yield of triphenylphosphine sulfide (4.96 g) was obtained. The sulfide was identified by its melting point (160–162°; lit.[9] mp 161°) and its infrared spectrum which was identical with that of an authentic sample.

The reactions with triethyl phosphite were done in the same way except that the solvent was not removed. The reaction mixtures were analyzed either by gas chromatography or fractionated under reduced pressure. Triethyl thionophosphate was obtained in yields of 40–66%.

The reactions of 3-hydroxythietane and thietane with triphenylphosphine and triethyl phosphite were done in the same way as the reaction of 3-chlorothietane. 3-Hydroxythietane and triphenylphosphine in refluxing benzene for 110 hr gave 4% triphenylphosphine sulfide; in refluxing xylene for 115 hr a 34% yield of the phosphine sulfide was obtained. Yields of 11 and 13% of triethyl thionophosphate were obtained when 3-hydroxythietane was refluxed in xylene for 66 and 90 hr, respectively. No triphenylphosphine sulfide was obtained when the phosphine and thietane itself were refluxed in benzene for 110 hr. In refluxing xylene for 188 hr a 10% yield of triphenylphosphine

(1) To whom inquiries should be directed: Department of Chemistry, Syracuse University, Syracuse, N. Y. 13210.

(2) C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 282 (1949); R. E. Davis, *J. Org. Chem.*, **23**, 1767 (1958); N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **81**, 578 (1959); D. B. Denney and M. J. Boskin, *ibid.*, **82**, 4736 (1960); R. D. Schuetz and R. L. Jacobs, *J. Org. Chem.*, **26**, 3467 (1961).

(3) J. C. Martin and D. J. Anderson, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, Abstracts, p 31-O. The reverse rearrangement, probably through the bridged sulfonium ion, has been reported to occur in the alkaline hydrolysis of chloromethylthiirane to 3-hydroxythietane: E. P. Adams, K. N. Ayad, F. P. Doyle, D. O. Holland, W. H. Hunter, J. H. C. Nayler, and A. Queen, *J. Chem. Soc.*, 2665 (1960).

(4) After 9.5 hr a 77% yield of triphenylphosphine sulfide was obtained from chloromethylthiirane, whereas after 163.5 hr a 72% yield of the phosphine sulfide was obtained from 3-chlorothietane. Desulfurization of chloromethylthiirane by triethyl phosphite has been reported previously: R. D. Schuetz and R. L. Jacobs, *J. Org. Chem.*, **23**, 1799 (1958).

(5) We wish to thank the referee who suggested that the data in Table I are more in accord with second-order kinetics.

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(7) B. Sjöberg, *Svensk Kem. Tidskr.*, **50**, 250 (1938); B. Sjöberg, *Ber.*, **75**, 15 (1942); D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961).

(8) We are indebted to Professor J. C. Martin for communicating the details of this procedure to us. Further details may be found in M. E. Christy, Ph.D. Thesis, University of Pennsylvania, 1961; S. M. Kotin, Ph.D. Thesis, University of Pennsylvania, 1962.

(9) W. Strecker and C. Grossmann, *Ber.*, **49**, 74 (1916).