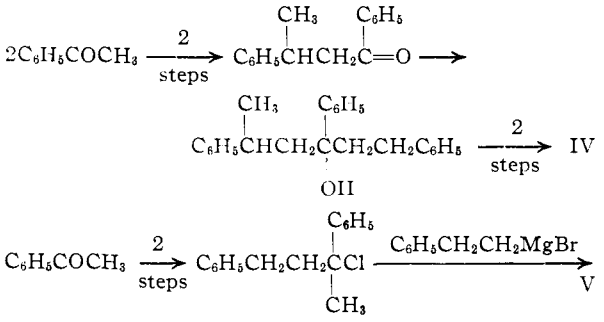
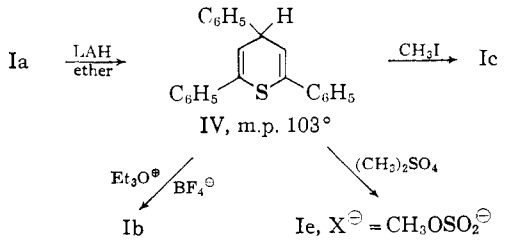


agree with the assigned structures, since the sulfur atom would be less sterically hindered in III than in II.

The factors affecting the ratio of 2-alkyl- to 4-alkylthiopyran are obscure. Under apparently similar conditions, ethylmagnesium bromide gave a mixture favoring the 2-isomer by 3:1, butylmagnesium bromide (or butyllithium) gave the 4-butyl compound while cyclopentadienyllithium gave the 2-isomer. The structure assignment for these compounds was made on the basis of the ultraviolet and infrared adsorption spectra. Only in the latter case did any complication occur; a shoulder at 239 mμ was assumed to be due to the cyclopentadienyl ring chromophore.

Reaction of the thiopyrylium salt I with lithium aluminum hydride produced a thiopyran which, on the basis of its spectrum, was assigned the structure of 4*H*-2,4,6-triphenylthiopyran. The major band at 235 mμ corresponds to this assignment. There is no band at 255–260 mμ.



The band at 348 mμ is only about one-quarter the intensity of the corresponding band in II.

We had hoped to alkylate the sulfur atom of VI and then proton abstraction by base might have produced the 1-alkylthiabenzene. Alkylation with methyl iodide, methyl sulfate and triethyloxonium fluoborate, however, led to the recovery of 2,4,6-triphenylthiopyrylium ion. The nature of the intermediates and the course of this "oxidation" of VI to I is not clear.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PA.]

Thiabenzene. III. 1,2,4,6-Tetraphenylthiabenzene, its Rearrangement and Oxidation[1]

BY GEORGE SULD[2] AND CHARLES C. PRICE

RECEIVED JANUARY 20, 1962

The reaction of phenyllithium with 2,4,6-triphenylthiopyrylium perchlorate gives an intensely purple colored amorphous solid. On the basis of its rapid decolorization by oxygen to a "peroxide" cleaved by acid to thiophenol and 2,4,6-triphenylpyryl-3-oxide (IC), this purple solid is assigned the structure of 1,2,4,6-tetraphenylthiabenzene (III). At room temperature, III rearranges to the isomeric colorless crystalline 2,4,4,6-tetraphenylthiopyran (II).

The observation that the intense color formed by reaction of phenyllithium with I in ether faded much more slowly than those colors from alkyl reagents[3] has encouraged us to undertake the isolation of the colored intermediate, which has been shown to be an etherate complex of 1,2,4,6-tetraphenylthiabenzene (III).

Experimental

2,4,4,6-Tetraphenylthiopyran (II).—To a finely powdered suspension of 2.5 g. (0.0059 mole) of 2,4,6-triphenylthiopyrylium perchlorate in 20 ml. of anhydrous ether was added 7.6 ml. (1 equiv.) of phenyllithium solution in ether and the reaction mixture was then shaken mechanically, in an atmosphere of nitrogen, for 7 days. The suspended thiopyrylium salt dissolved, forming initially a violet-red solution which lightened gradually to give a brownish-yellow ether solution. The ethereal solution was treated with aqueous ammonium chloride solution, the organic layer was washed with water and dried with anhydrous potassium carbonate. The solvent was removed under reduced pressure and the residual brown oil was dissolved in a small volume of ethanol. Since the oil showed no sign of crystallization, the solution was left standing for 3 months. After this period the oil had become a semi-solid mass (the solvent had evaporated). The oil was suspended in a small volume of ethanol and the suspension was shaken mechanically for 24 hr. A solid colorless crystalline product that was obtained was collected by filtration. It weighed 0.82 g. and melted, after two recrystallizations from ethanol, at 157–157.5°. The ultraviolet spectrum showed a single major peak at 235 mμ, log ε 4.29, and the principle infrared absorption bands were at 6.25, 6.70, 6.91, 9.25, 9.69, 10.90, 11.05, 11.25, 12.22, 12.98, 13.27, 14.25 and 14.47 μ (KBr disk).

Anal. Calcd. for $C_{29}H_{22}S$: C, 86.52; H, 5.51; Si, 7.97. Found: C, 86.34, 86.83; H, 6.03, 5.86; S, 8.25.

2,4,4,6-Tetraphenylthiopyran 1,1-Dioxide.—To a hot solution of 50 mg. of the tetraphenylthiopyran in 4 ml. of glacial acetic acid was added 6 drops of 30% hydrogen peroxide and the reaction mixture was heated on a steam-bath for 10 min. Upon dilution of the mixture with 10 ml. of ice-water, a colorless, crystalline solid separated. Twice recrystallized from ethanol, it melted at 192–193°. This sulfone had strong characteristic bands at 7.70 and 8.82 μ, and at 235 and 355 mμ, log ε 4.42 and 3.07.

Anal. Calcd. for $C_{29}H_{22}O_2S$: C, 80.15; H, 5.10. Found: C, 80.04; H, 5.18.

1,2,4,6-Tetraphenylthiabenzene (III).—Reaction of 35 ml. (3.5 equiv.) of phenyllithium in ether with a stirred suspension of 2.5 g. of I in 100 ml. of ether under nitrogen led to

(1) Presented in part at the 136th Meeting, Am. Chem. Soc., Atlantic City, N. J., September 15, 1959; see also G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961).

(2) Supported in part by National Science Foundation Grant No. G-6270.

(3) G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **84**, 2090 (1962).

rapid dissolution of the precipitate with the formation of a deep red-violet solution. After 5 min., this was washed with aqueous ammonium chloride and then water. The ether was dried over potassium carbonate and filtered into an erlenmeyer flask flushed with nitrogen and cooled in a Dry Ice–acetone-bath. After 30 min., it was centrifuged at −15° and decanted from a small amount of colorless solid. Then 50–75 ml. of cold petroleum ether (b.p. 30–60°, purified by percolation through alumina) was added, the solution again chilled and centrifuged at −15°. The deep violet solution was decanted from *ca.* 0.2 g. of pale solid and evaporated to dryness *in vacuo* at room temperature. The violet-red resin was again dissolved in 30 ml. of ether which was poured into 250 ml. of petroleum ether cooled in a Dry Ice–acetone-bath. The finely divided violet solid was collected by centrifugation at −15°; yield 0.7 g., m.p. 45–48°.

Anal. Calcd. for $C_{29}H_{22}S\cdot{}^1/_2C_4H_{10}O$[4]: C, 84.71; H, 6.19; S, 7.28; mol. wt., 439.5. Found: C, 85.26, 84.94; H, 5.80, 5.70; S, 7.06; mol. wt. (cryosc. benzene), 380.

This product showed no evidence of crystallinity by X-ray. It decomposed on exposure to light but samples in ethanol and isoöctane showed an absorption band at 525 mμ. Principal infrared absorption bands (CCl_4) were observed at 6.28, 6.70, 6.95, 7.05, 8.05 and 14.40 μ, very different from the isomeric thiopyran II.

A 200-mg. sample of III was sealed under nitrogen and kept at room temperature for 20 days. The powder resinified and the intense purple color faded to pale amber. The product was dissolved in hot methanol. On cooling, 50 mg. of colorless crystals separated, m.p. 151–154°. One recrystallization raised the melting point to 155–156°; mixture melting with II showed no depression. The mother liquors left a non-volatile yellow oil not further identified.

1,2,4,6-Tetraphenylthiabenzene Peroxide.—When oxygen was bubbled for 30 min. through a purple solution of III prepared from 1.25 g. of I the color faded to yellow. Evaporation left a colorless solid residue. The infrared spectrum had lost the strong bands of III at 7.05 and 8.05 μ, but had a new strong band at 8.20 μ (C–O stretch?). Because of the instability of this compound, due to its easy conversion to IV, it was not characterized further.

Conversion of III to IV.—An ethereal solution of III was prepared from 10 g. of I, washed with aqueous ammonium chloride and water, and dried over potassium carbonate. Oxygen was bubbled through the solution for 30 min., when the purple color had faded to yellow. No odor of thiophenol was detected at this stage. Gaseous hydrogen chloride was then bubbled into the "peroxide" solution for 2–3 min. A strong odor of thiophenol was immediately evident and an ocher precipitate separated. The solid was dissolved in 30 ml. of acetone, which was then poured into 2 l. of water precipitating 4.45 g. of dark red solid. Recrystallization from acetone gave 2.1 g. of IV as dark red needles with a bronze sheen, m.p. 193.5–195°. The compound gave a negative test for sulfur. Major infrared absorption bands (KBr disk) occurred at 6.52, 6.71, 7.27, 8.03, 12.70, 13.04, 13.62 and 14.70 μ. Ultraviolet absorption was sharply dependent on the solvent: in isoöctane, 275, 315, 519, 535 mμ; in ethanol, 230, 270, 308, 494 mμ (log ε 4.09, 4.02, 4.36, 4.19); in 0.1 *N* ethanolic perchloric acid; 220, 285, 355, 422 mμ (log ε 4.20, 4.23, 4.06, 4.19).

Anal. Calcd. for $C_{23}H_{16}O_2$: C, 85.20; H, 4.96. Found: C, 85.19; H, 5.09.

Further recrystallization of the residue from the acetone mother liquors above gave two isomeric colorless products, $C_{23}H_{16}O_3$, m.p. 280° (0.25 g.), and 180–181° (0.70 g.). The high melting material was insoluble in methanol but could be recrystallized from dimethylformamide; the latter produced colorless needles from methanol.

Anal. Calcd. for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74. Found (280°): C, 81.21; H, 5.02. (181°): C, 81.30; H, 4.92.

The lower melting isomer in acetone solution was converted to the higher by addition of a few drops of sulfuric acid.

The supernatant ether from which IV precipitated was extracted with alkali. An aliquot of the alkaline extract was acidified, extracted with ether and evaporated. The residue was dissolved in ethanolic potassium hydroxide and treated with 2,4-dinitrofluorobenzene to give 2,4-dinitrophenyl phenyl sulfide, m.p. 119–120° (lit.[5] 121°). The remaining alkali solution deposited a crystalline solid on standing. After recrystallization from methanol it melted at 59–60°, undepressed on mixture with authentic diphenyl disulfide.

The ether layer from the alkaline extraction was evaporated to dryness and the brown residual oil recrystallized twice from methanol to give 0.39 g. of II, m.p. 156–157.5°.

The perchlorate of IV was obtained by adding 25 ml. of 30% aqueous perchloric acid dropwise to 0.23 g. of IV in 25 ml. of acetone. The initially violet-red solution turned to yellow with a greenish fluorescence and yellow solid separated. After 1 hr., the solid was collected by filtration and recrystallized from glacial acetic acid containing a few drops of perchloric acid, yielding 0.21 g. of yellow crystals, m.p. 224° dec.

Anal. Calcd. for $C_{23}H_{17}ClO_6$: C, 65.02; H, 4.03. Found: C, 64.76; H, 4.31.

Solutions of the yellow salt in organic solvents were orange-red, suggesting dissociation to free IV may occur.

The picrate of IV was prepared from a hot solution of 1 g. of picric acid in 15 ml. of methanol and 400 mg. of IV in 20 ml. of methanol by concentrating to 15 ml. and cooling for 1 hr. to yield 570 mg. of orange platelets, m.p. 179–180°.

Anal. Calcd. for $C_{29}H_{19}N_3O_9$: C, 62.93; H, 3.46; N, 7.59. Found: C, 63.10; H, 3.48; N, 6.99.

Acetylation of IV.—To a solution of 0.40 g. (0.0012 mole) of IV in 15 ml. of acetic anhydride was added 6 drops of concentrated sulfuric acid and the reaction mixture was heated under reflux, in an atmosphere of nitrogen, for 4 hr. At the end of this period the color of the solution had changed from the original orange-red to deep yellow, with a greenish fluorescence. After cooling, the reaction mixture was poured into 150 ml. of ice-cold dilute perchloric acid (20%). A micro-crystalline, yellow solid that separated from the solution was collected by filtration and dried. It weighed 0.29 g. (59%). Recrystallization from glacial acetic acid afforded canary-yellow crystalline platelets, m.p. 230–231.5°. The ultraviolet spectrum showed absorption at 230, 240, 259, 318 mμ, log ε 4.21, 4.22, 4.19, 4.08. Major infrared absorption was observed at 5.61, 6.23, 6.28, 6.38, 6.72, 6.83, 6.97, 8.01, 8.58, 9.20, 11.26, 13.15, 13.63 and 14.70 μ.

Anal. Calcd. for $C_{25}H_{19}ClO_7$: C, 64.31; H, 4.10; Cl, 7.60. Found: C, 64.09; H, 4.16; Cl, 7.83.

3-Acetoxy-2,4,6-triphenylpyrylium Perchlorate.—To a solution of 1.78 g. (0.01 mole) of phenacyl acetate and 2.08 g. (0.01 mole) of benzalacetophenone in 20 ml. of acetic anhydride was added a solution of 5 ml. of perchloric acid (72%) in 5 ml. of glacial acetic acid and 5 ml. of acetic anhydride. The reaction mixture was heated on the steam-bath for 3–5 min. and then poured into 300 ml. of cold ether (cooled in a Dry Ice–acetone-bath). A grayish-yellow solid which was precipitated was collected by filtration and washed with several portions of ether; 2.10 g. After trituration with a small volume of acetic acid and several recrystallizations (the compound is quite difficult to purify) from the same solvent the yellow crystalline solid melted at 228.5–230°. A mixture melting point with the acetyl perchlorate derivative of IV obtained from the oxidative degradation of III showed no depression. The infrared spectra of the two compounds were found to be identical.

When the acetone solution of 3-acetoxy-2,4,6-triphenylpyrylium perchlorate was poured into a dilute sodium hydroxide solution, a red solid was obtained which was identical with IV.

2-(2-Acetoxyphenyl)-4,6-diphenylpyrylium Perchlorate.—To a stirred solution of 4.16 g. (0.020 mole) of benzalacetophenone and 2.5 g. (0.0185 mole) of *o*-hydroxyacetophenone in 25 ml. of acetic anhydride was added portionwise, over a period of 10 min., 8.0 g. of anhydrous ferric chloride. After the exothermic reaction had subsided, the dark reaction mixture was allowed to stand overnight and then diluted with 200 ml. of ether. Upon filtration, a dark, crystalline solid, weighing 2.9 g., was obtained. The chloroferrate salt was converted to the soluble phosphate salt by addition of an aqueous sodium dihydrogenphosphate solution to the acetone solution of the chloroferrate salt. The precipitate of the iron phosphate was removed by filtration through a Celite mat and the filtrate was poured into 300 ml. of perchloric acid (20%). The yellow perchlorate salt was collected by

(4) It has recently been found that ethers play an important role in stabilizing the thiabenzene structure (E. A. Blair).

(5) R. W. Bost, J. O. Turner and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932).

filtration. After several recrystallizations from methanol, it melted at 192–193°.

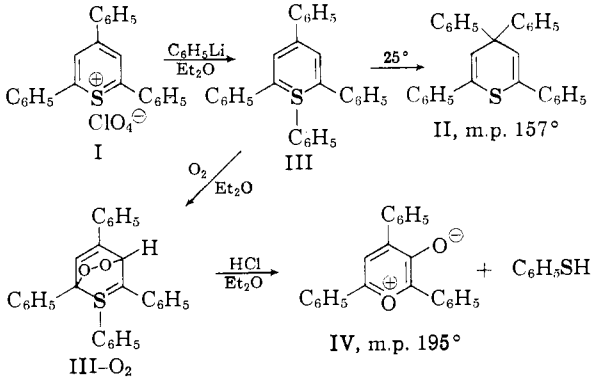
Anal. Calcd. for $C_{25}H_{19}ClO_7$: C, 64.31; H, 4.10. Found: C, 64.07; H, 4.36.

Maleic Anhydride Adduct of IV.—A solution of 0.46 g. (0.0041 mole) of maleic anhydride in 5 ml. of dry benzene was added to a solution of 0.30 g. (0.0008 mole) of IV in 15 ml. of benzene. An immediate color change from violet to orange-red was observed on the mixing of the two solutions. After heating under reflux for 20 min. the solvent was removed *in vacuo* and the semi-solid residue was dissolved in 30 ml. of ether. The ethereal solution was extracted ten times with small portions of water and the organic layer was dried with anhydrous magnesium sulfate. After removal of ether on the water-pump, the residue was recrystallized twice from ethanol. The colorless, crystalline solid weighed 0.035 g. and melted at 194–196°. Another recrystallization from ethanol raised the melting point to 195.5–196.5° (the compound turned pink above 170°, and formed a red melt at the melting point). Major infrared absorption was observed at 5.60, 5.86, 6.68, 6.88, 8.10, 9.23, 10.73, 13.35, 13.87 and 14.40 μ.

Anal. Calcd. for $C_{25}H_{18}O_5$: C, 76.77; H, 4.29. Found: C, 76.97; H, 4.63.

Discussion

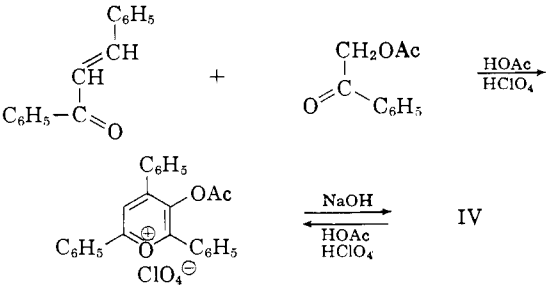
The reaction of phenyllithium with 2,4,6-triphenylpyrylium perchlorate (I) in ether gave an intensely purple solution which faded only slowly over a week. When the products from the aged solution were isolated, the only crystalline compound isolated in pure conditions was 2,4,4,6-tetraphenylthiopyran (II), assigned this structure on the basis of its ultraviolet spectrum (a single band at 235 mμ) and its ready oxidation to a sulfone (II-O_2).[3]



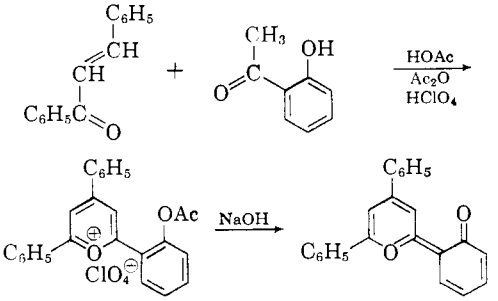
By working up ether solutions of III rapidly in the cold under nitrogen, III was obtained as a deep purple amorphous solid. It could be kept without apparent change for long periods in the refrigerator in the dark, but at 25°, particularly exposed to light, it lost its color in a few days, producing an amber resin from which a 25% yield of II was isolated.

When oxygen was bubbled through a fresh ether solution of III, the color rapidly discharged. Efforts to isolate the resulting "peroxide" in pure form were unsuccessful. However, the peroxide underwent rapid reaction when dry hydrogen chloride was passed into the ether, precipitating the compound IV and liberating phenyl mercaptan. The presence of the latter was readily detected qualitatively; it was confirmed by isolation and identification as the disulfide and the dinitro phenyl derivatives.

The structure of IV was established by its interconversion to the 3-acetoxy perchlorate derivative, which was synthesized by an independent route.

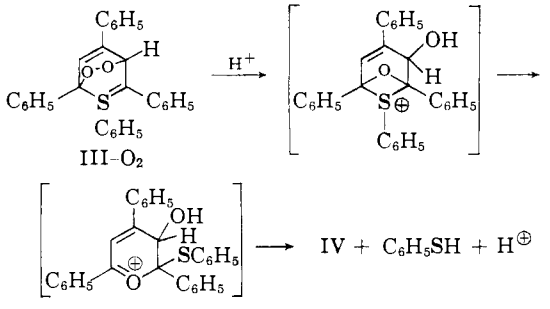


An alternate structure for IV and its acetate was eliminated by synthesis.



The isolation of phenyl mercaptan from acid cleavage of the peroxide is convincing evidence for the attachment of one phenyl group to the sulfur atom of III. There have been several proposals that organolithium compounds react with sulfonium salts to give transient tetravalent sulfur compounds, analogous to pentaphenylphosphorane.[6] Parham[7] has suggested them as intermediates in ring cleavage of dithiadiene sulfonium salts with phenyllithium, Bornstein and Supple[8] in the ring cleavage of the sulfonium salts from 1,3-dihydroisobenzothiophene and Franzen and Mertz[9] in the rapid exchange of alkyl or aryl groups between triarylsulfonium salts and organolithium compounds.

The location of the oxygen atoms in the peroxide from III is based on the proven structure of IV; this structure for III-O_2 attaches the peroxide oxygen atoms to two of the three carbons to which the oxygen atoms of IV are bonded.



(6) G. Wittig and M. Rieber, *Ann.*, **562**, 187 (1949).

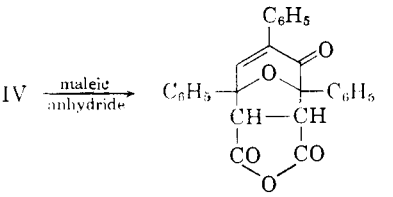
(7) W. E. Parham and P. L. Stright, *J. Am. Chem. Soc.*, **78**, 4785 (1956); W. E. Parham and M. T. Kneller, *J. Org. Chem.*, **23**, 1702 (1958).

(8) J. Bornstein and J. H. Supple, *Chemistry & Industry*, 1333 (1960).

(9) V. Franzen and Ch. Mertz, *Ann.*, **643**, 24 (1961).

From oxidation of fresh solutions of III, very small quantities (*ca.* 3%) of II were isolated. This could be taken as an upper limit of the amount of II formed directly in the phenylation of I, supporting the view that the attack of the organometallic compound on I proceeds with a strong preference on sulfur, and that II is produced only by a subsequent rearrangement of the thiabenzene III.

So far as we are aware, no earlier reports appear in the literature of 3-hydroxypyrylium salts and their anhydrobases IV, although one example of a flavylium analog has been reported.[10] We found compound IV to react readily with maleic anhydride to give a product whose infrared spectrum is in accord with structure V.



We are pursuing the further characterization of III as well as efforts to prepare additional examples of this new conjugated heterocyclic ring system.

(10) P. Karrer, R. Widmer, A. Halfenstein, W. Hurliman, O. Nievergelt and P. Monsarrat-Thomas, *Helv. Chim. Acta*, **10**, 729 (1927).

[CONTRIBUTION FROM THE EDGAR C. BRITTON RESEARCH LABORATORY, THE DOW CHEMICAL CO., MIDLAND, MICH.]

The Nucleophilicity of Phosphorohydrazidothionates[1]

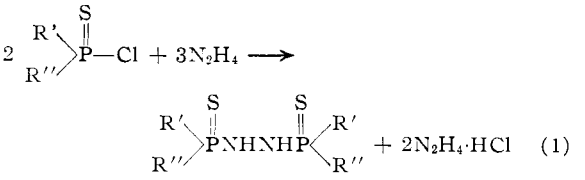
BY HENRY TOLKMITH

RECEIVED DECEMBER 8, 1961

The extent of formation of N^1,N^2-bis-(phosphorothioyl) hydrazides, a new type of compound produced by hydrazidation of phosphoromonochloridothionates, is predominantly controlled by the polar effects of the organic groups attached to phosphorus. The nucleophilic reactivity of phosphorohydrazidothionates is greater than is evident from their previously known chemistry. This is revealed by the formation of new types of compound, such as N^1-phosphorothioyl N^2-carbamoyl and thiocarbamoyl hydrazides, N^1-phosphorothioyl N^2-acyl hydrazides, N^1-phosphorothioyl N^1,N^2,N^2-tris-(acyl) hydrazides, and hexahydro-3,6-dioxo-*s*-tetrazine-1,4-ylene diphosphonothionates, all of which are readily produced from aliphatic phosphorohydrazidothionates and the appropriate substrates. N^1-Phosphorothioyl N^2-acyl hydrazides also possess some degree of nucleophilicity and yield 2-(O,O-dialkylphosphorothioyl)-3-acyl-1,4-phthalazinediones, the formation of which is favored by steric assistance, as rendered by the phthaloyl chloride substrate involved. Some theoretical aspects of these new reactions are discussed.

The reaction of the monochlorides of organic phosphorus acids, (R')(R'')P(X)Cl, with hydrazine has been consistently reported to yield but one type of structure, the primary hydrazides (R')(R'')P(X)NHNH$_2$, if R' and R'' represent various organic groups and X represents oxygen or sulfur.[2-8] This could imply that primary phosphoryl hydrazides lack sufficient nucleophilic strength to react with phosphoryl monochlorides under those conditions under which the strongly nucleophilic hydrazine does react with these substrates. However, the dihydrazide $C_6H_5OP(S)(NHNH_2)$, has been found to react readily with phenyl phosphorodichloridothionate to produce the heterocyclic compound $C_6H_5OP(S)(NHNH)_2P(S)OC_6H_5$ in high yield.[9] This evidence leads to the hypothesis that the nucleophilic reactivity of a hydrazide may rather markedly depend upon the structure of its acyl group and that certain phosphorohydrazides may possess greater nucleophilicity than is obvious from their previously described reactivity. The investigation to be described was aimed at testing this hypothesis and consisted of three phases, involving the extent of formation of N^1,N^2-bis-(phosphorothioyl) hydrazides, N^1-phosphorothioyl N^2-acyl hydrazides and N^1-phosphorothioyl N^1,N^2,N^2-tris-(acyl) hydrazides.

Formation of N^1,N^2-Bis-(phosphorothioyl) Hydrazides.—It was conceivable that the secondary hydrazides (R')(R'')P(S)NHNHP(S)(R')(R'') could be synthesized from phosphoromonochloridothionates by the new over-all reaction



Since we assumed that this reaction might be controlled by the polar effects of the groups R' and R'', a series of phosphorochloridothionates containing various types of R-group was investigated and found to react with hydrazine under various reaction conditions in the manner reported in Table I.

Aromatic ester monochlorides, such as $(C_6H_5O)_2P(S)Cl$ and (2-Cl-4-*t*-$C_4H_9C_6H_3O)(CH_3O)P(S)Cl$, always formed primary hydrazides (I and II, respectively) in high yields regardless of the mole ratio of reactants and the state of hydrazine hydration.

(1) Part of a lecture given at the Pesticide Research Institute of Canada at London (Ontario) on December 5, 1960, upon invitation by Dr. E. Y. Spencer, director.

(2) F. Ephraim and M. Sackheim, *Ber.*, **44**, 3416 (1911).

(3) W. Strecker and Ch. Grossmann, *ibid.*, **49**, 63 (1916).

(4) W. Autenrieth and W. Meyer, *ibid.*, **58**, 848 (1925).

(5) L. F. Audrieth, R. Gehr, Jr., and W. Ch. Smith, *J. Org. Chem.*, **20**, 1288 (1955).

(6) N. N. Melnikov and A. G. Zenkevich, *Zhur. Obshch. Khim.*, **25**, 828 (1955).

(7) E. H. Blair and H. Tolkmith, *J. Org. Chem.*, **25**, 1620 (1960).

(8) A. G. Zenkevich, P. G. Zaks, Y. A. Mandelbaum and N. N. Melnikov, *Zhur. Obshch. Khim.*, **30**, 2317 (1960).

(9) H. Tolkmith and E. C. Britton, *J. Org. Chem.*, **24**, 705 (1959).