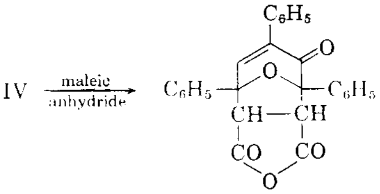
From oxidation of fresh solutions of III, very small quantities (*ca.* 3%) of II were isolated. This could be taken as an upper limit of the amount of II formed directly in the phenylation of I, supporting the view that the attack of the organometallic compound on I proceeds with a strong preference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

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[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]

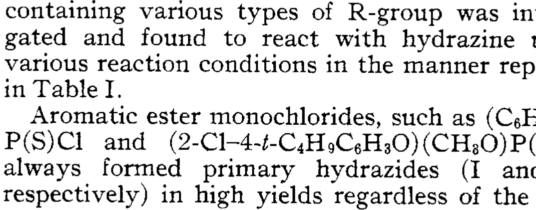
BY HENRY TOLKMITH

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 $C_6H_5OP(S)(NHNH_2)_2$ 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



$$2\,(R')(R'')P(S)\text{—}Cl + 3N_2H_4 \longrightarrow (R')(R'')P(S)NHNHP(S)(R')(R'') + 2N_2H_4\cdot HCl \quad (1)$$

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 $(2\text{-}Cl\text{-}4\text{-}t\text{-}C_4H_9C_6H_3O)(CH_3O)P(S)Cl$, always formed primary hydrazides (I and II, respectively) in high yields regardless of the mole ratio of reactants and the state of hydrazine hydration.

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[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).

TABLE I

REACTIONS OF PHOSPHOROMONOCHLORIDOTHIONATES WITH HYDRAZINE

		Types of main product (yields,[a] %)	
R′	R″	(R′)(R″)P(S)NHNH$_2$	(R′)(R″)P(S)NHNHP(S)(R′)(R″)
C$_6$H$_5$O	C$_6$H$_5$O	I (85.5)	.....
2-Cl-4-*t*-C$_4$H$_9$C$_6$H$_3$O	CH$_3$O	II (76.5)	.....
CH$_3$O	CH$_3$O	III (77)	VII (23)
C$_2$H$_5$O	C$_2$H$_5$O	IV (93)	VIII (43)
CH$_3$O	CH$_3$NH	V (54)	IX (10)
(CH$_3$)$_2$N	(CH$_3$)$_2$N	VI (80)	X (90)

[a] Yields given as found with separate reactions involving the mole ratios and reaction conditions described in the text.

Aliphatic ester monochlorides, *e.g.*, (CH$_3$O)$_2$P(S)Cl, (C$_2$H$_5$O)$_2$P(S)Cl and (CH$_3$O)(CH$_3$NH)P(S)Cl, proved to be capable of forming not only primary hydrazides but also secondary hydrazides. Maximum yields of N^1,N^2-bis-(phosphorothioyl) hydrazides, (R′)(R″)P(S)NHNHP(S)(R′)(R″), were obtained when *anhydrous hydrazine* was added to the monochloride at a mole ratio of 3:2 (compounds VII–IX). Hydrazine monohydrate was found to limit the extent of reaction to the formation of primary hydrazide (compounds III–V). The addition of four moles of hydrazine hydrate to two moles of monochloride represented the most suitable method of preparation of O,O-dialkyl phosphorohydrazidothioates (III and IV) and of O-methyl N-methyl phosphorohydrazidothioate (V).

Addition of aliphatic ester monochloride to an excess of hydrazine hydrate produced the primary hydrazides III and V in inferior purity, probably owing to a side reaction involving nucleophilic attack of hydrazine on the carbon atom linked to oxygen in the primary aliphatic hydrazide (alkylO)(R′)P(S)NHNH$_2$. This assumption was supported by results obtained from an investigation of the thermal stability of O,O-dialkyl phosphorohydrazidothioates (*cf.* Experimental).

The diamidomonochloride [(CH$_3$)$_2$N]$_2$P(S)Cl showed by far the strongest tendency to form secondary hydrazide. Addition of three moles of anhydrous hydrazine to two moles of this monochloride produced N^1,N^2-bis-(tetramethylphosphorodiamidothioyl) hydrazide in a yield of 90%. The reaction of two moles of hydrazine monohydrate per mole of phosphorus chloride also afforded the secondary hydrazide X in yields of 28 to 32%, regardless of the mode of addition of the reactants. According to this trend it was to be expected that the production of the primary hydrazide [(CH$_3$)$_2$N]$_2$P(S)NHNH$_2$ (VI) would require the presence of a substantial excess of hydrazine. It was found that this compound could be obtained in a yield of 80% by addition of one mole of diamidomonochloride to eight moles of hydrazine monohydrate.

According to the experimental results obtained, the extent of occurrence of reaction 1 increased with increasing electron-donating power of the substituents, R′ and R″. This reaction was not found to take place if the sum of the polar substituent constants ($\Sigma\sigma^*$)[10] of R′ and R″ was larger than +4, as in the case of compounds I and II. The tendency to produce reaction 1 became rather strong if $\Sigma\sigma^*$ had a value of approximately +1, as in the case of compound X. The formation of N^1,N^2-bis-(phosphorothioyl) hydrazides apparently involved a sequence of two bimolecular S$_N$-reactions. In the first of these reactions the phosphorus monochloride and hydrazine formed primary hydrazide. In the second one this intermediate was phosphorylated to yield secondary hydrazide. This assumption was supported by the experimental evidence described in Table II. The experimental findings referred to in the Tables I and II indicate that the formation of secondary hydrazides according to reaction 1 is predominantly controlled by the polar effects of the R-groups involved.

TABLE II

Reacn. 2: (R′)(R″)P(S)NHNH$_2$ +

$$\text{ClP(S)(OEt)}_2 \xrightarrow[-(\text{Et})_3\text{N}\cdot\text{HCl}]{+\ (\text{Et})_3\text{N}} (\text{R}')(\text{R}'')\text{P(S)NHNHP(S)(OEt)}_2$$

R′ and R″	Main product (yield, %)
CH$_3$O	XI (18)
C$_2$H$_5$O	VIII (80)
(CH$_3$)$_2$N	XII (56.5)

The critical influence of the state of hydrazine hydration on the extent of the reaction involving O,O-dialkyl phosphorochloridothionates could imply the formation of a hydrated primary hydrazide. The activation energy of this hypothetical intermediate would be greater, and its nucleophilic energy smaller, than the corresponding energies of the anhydrous, primary hydrazide. Such an assumption would be consistent with the fact that the energy of dehydration of hydrazine monohydrate at 298°K. equals 1.7 kcal.[11] In addition, the approach to the phosphorus atom of the substrate by the nitrogen atom of the NH$_2$-group of the nucleophile would presumably encounter more steric interference with a hydrated than with an anhydrous hydrazide intermediate. However, no hydrated hydrazides were isolated, evidently because water of hydration may have been azeotropically removed from their benzene solutions during the isolation of main product.

The assignment of structure to the secondary hydrazides VII–XII was based upon the following evidence. Data of combustion analysis and molecular weight determination proved that these compounds had the structure (R′)(R″)P(S)NHNHP(S)(R′)(R″) or [(R′)(R″)P(S)]$_2$NNH$_2$. These compounds did not show the presence of an NH$_2$-group in their infrared pattern and did not react with isocyanates or isothiocyanates. Thus, they were considered to be N^1,N^2-bis-(phosphorothioyl) hydrazides and not the N^1,N^1-isomers.

The O,O-dialkyl phosphorohydrazidothionates III and IV could not be satisfactorily purified by distillation owing to their thermal instability. To assure their structure they were converted to

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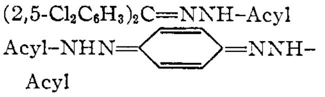
[10] *Cf.* R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, ed., J. Wiley and Sons, Inc., New York, N. Y., 1956, pp. 556–674.

[11] A. M. Hughes, R. J. Corruccini and E. C. Gilbert, *J. Am. Chem. Soc.*, **61**, 2639 (1939).

hydrazones. Previously, only one hydrazone derivative of a primary phosphorohydrazidothionate was known, $(C_6H_5O)_2P(S)NHN{=}CHC_6H_5$.[4] Of the new derivatives obtained (*cf.* Table III), those formed with acetone and with benzoquinone were of interest. The acetone derivatives were not obtained in pure, crystalline form probably because of the hydrolytic instability of the alkyl ester groups in basic media, as produced by the aliphatic hydrazone group. The formation of the dihydrazone from *p*-benzoquinone was noteworthy in view of the fact that phenylhydrazine was found to be oxidized by this reagent and certain acyl hydrazones, such as $(acyl)(C_6H_5)N{-}N{=}C_6H_4{=}O$, were reported to be unstable.[12] Reactions of the compounds III and IV with tetrachlorobenzoquinones produced tars only.

TABLE III

O,O-DIALKYL PHOSPHOROHYDRAZONOTHIONATES

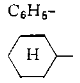
Structure $(CH_3)_2C{=}NNH$-Acyl	Acyl: $-P(S)(OCH_3)_2$ $n^{25}D$ 1.5215	Acyl: $-P(S)(OC_2H_5)_2$ $n^{25}D$ 1.4988
	Melting points, °C.	
$2\text{-}ClC_6H_4CH{=}NNH$-Acyl	51–52[a]	52–53[a]
$2,3,6\text{-}Cl_3C_6H_2CH{=}NNH$-Acyl	123–124[b]	122–123[b]
$2,3,4,5,6\text{-}Cl_5C_6CH{=}NNH$-Acyl	182–183[c]	158–159[c]
$(4\text{-}ClC_6H_4)(CH_3)C{=}NNH$-Acyl	69–71[a]	54–55[a]
$(C_6H_5)_2CNNH$-Acyl	86–87[a]	65–66[d]
$(2,5\text{-}Cl_2C_6H_3)_2C{=}NNH$-Acyl	123–124[a]	
 Acyl-NHN= =NNH- Acyl	138–139[e]	

[a] Recryst. from cyclohexane. [b] Recryst. from benzene. [c] Recryst. from monochlorobenzene. [d] Recryst. from ligroin (30–60°). [e] Recryst. from diethyl ether.

Formation of N¹-Phosphorothioyl N²-Acyl Hydrazides.—On the basis of the marked nucleophilic strength of primary, aliphatic phosphorohydrazidothionates, it was to be expected that they would react with various substrates known to be more sensitive to nucleophilic attack than aliphatic phosphorochloridothionates. Thus, it was of interest to study the reactivity of these hydrazides toward carboxylic chlorides, isocyanates and isothiocyanates. It was found that aliphatic phosphorohydrazidothionates reacted readily with isocyanates and isothiocyanates to produce N¹-phosphorothioyl N²-carbamoyl hydrazides and N¹-phosphorothioyl N²-thiocarbamoyl hydrazides (*cf.* Table IV).

TABLE IV

N¹-PHOSPHOROTHIOYL N²-CARBAMOYL AND THIOCARBAMOYL HYDRAZIDES, $RNHC(X)NHNHP(S)(R')(R'')$

R	X	R′ and R″ (yield, %): CH_3O	C_2H_5O	$(CH_3)_2N$
$CH_2{=}CHCH_2$-	S	XIII (67.5)	XVI (64.5)	
C_6H_5-		XIV (72.5)	XVII (63)	XX (71.5)
	O		XVIII (80.5)	
C_6H_5-		XV (61)	XIX (64.5)	

A different picture resulted from the reactions of primary, aliphatic phosphorohydrazidothionates with monofunctional and polyfunctional carboxylic chlorides. The reaction of $(R')(R'')P(S)NHNH_2$ with RCOCl was found to follow several courses, depending upon the mole ratio of reactants and the structure of the substituents, R, R′ and R″. Even at a mole ratio of 1:1 the following courses of reaction were found to occur, in contrast to the formally analogous reaction 2 involving the aliphatic ester monochlorides $(R')(R'')P(S)Cl$.

$$(R')(R'')P(S)NHNH_2 + RCOCl - HCl \longrightarrow \begin{cases} (R')(R'')P(S)NHNHC(O)R & (3) \\ \frac{1}{n}\,[(R')(R'')P('S)\overset{|}{N}{-}NH\overset{|}{C}(O)]_n + RH & (4) \\ \frac{1}{n}\,[-P(S)(R')NHNH-]_n + RC(O)R'' & (5) \end{cases}$$

The investigation of these reactions involved the three nucleophiles $(alkO)_2P(S)NHNH_2$, $(C_6H_5O)_2P(O)NHNH_2$ and $[(CH_3)_2N]_2P(S)NHNH_2$, and the three substrates CH_3COCl, C_6H_5COCl and C_2H_5OCOCl. It led to the results given in Table V. The aliphatic ester hydrazides reacted with acetyl chloride as well as with benzoyl chloride to form the N¹-phosphorothioyl N²-acyl hydrazides, XXII–XXV, in yields of 56–83% according to reaction 3. Their reaction with ethyl chloroformate, however, was found to produce ethanol and the phosphorus compounds XXVI and XXVII, the analytical data of which were consistent with the structure $[(alkylO)_2P(S)\overset{|}{N}NH\overset{|}{C}(O)]_2$, and which apparently represented phosphorothionylated *p*-urazines. Since these results indicated the occurrence of reaction 4 instead of reaction 3, the reaction of O,O-diphenyl phosphorohydrazidate with ethyl chloroformate was checked and found to give a high yield of the secondary hydrazide $(C_6H_5O)_2P(O)NHNHC(O)OC_2H_5$ (XXI)[13] according to reaction 3. The last of the nucleophiles studied, $[(CH_3)_2N]_2P(S)NHNH_2$, was found to react with acetyl chloride to produce N,N-dimethylacetamide and condensed phosphorus hydrazides, according to reaction 5. The structure assigned the compounds XIII–XXVII was based on the fact that they did not react with ketones and isothiocyanates and did not show the presence of an NH_2-group in their infrared spectrum.

TABLE V

REACTIONS OF THE HYDRAZIDES $(R')(R'')P(X)NHNH_2$ WITH CARBOXYLIC CHLORIDES RCOCl

R′ and R″	R	Actual reaction	Main product (yield, %)
C_6H_5O	C_2H_5O	3	$(C_6H_5O)_2P(O)NHNHC(O)OC_2H_5$ (XXI)
CH_3O	CH_3	3	$(CH_3O)_2P(S)NHNHC(O)CH_3$ (XXII, 60.8)
	C_6H_5	3	$(CH_3O)_2P(S)NHNHC(O)C_6H_5$ (XXIII, 56)
C_2H_5O	CH_3	3	$(C_2H_5O)_2P(S)NHNHC(O)CH_3$ (XXIV, 83)
	C_6H_5	3	$(C_2H_5O)_2P(S)NHNHC(O)C_6H_5$ (XXV, 75.5)
CH_3O	C_2H_5O	4	$[(CH_3O)_2P(S)\overset{|}{N}NH\overset{|}{C}(O)]_2$ (XXVI, 22)
C_2H_5O			$[(C_2H_5O)_2P(S)\overset{|}{N}NH\overset{|}{C}(O)]_2$ (XXVII, 31.5)
$(CH_3)_2N$	CH_3	5	$CH_3C(O)N(CH_3)_2$ + condensed hydrazides

These experimental findings reveal a consistent picture of the nucleophilicity of primary phosphorohydrazides if the inductive effects of the groups R, R′, R″ and X are taken into consideration.

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[12] (a) R. Willstätter and H. Veraguth, *Ber.*, **40**, 1432 (1907); (b) K. V. Auwers and E. Wolter, *Ann.*, **487**, 78 (1931).

[13] First reported by L. F. Audrieth, R. Gehr, Jr., and W. Ch. Smith, *J. Org. Chem.*, **20**, 1288 (1955).

The novel over-all reaction 4 apparently involves a sequence of two steps of SN-reaction which consist of the formation and the dealcoholation of the intermediate $(R')(R'')P(X)NHNHC(O)OC_2H_5$. The second reaction step presumably proceeds if two requirements are met: (i) the group at the carbonyl carbon must be easily removable, and (ii) the combined inductive effects of the groups R′, R″ and X must not cause strong electron withdrawal. The compounds XXII–XXV do not meet requirement i and compound XXI does not meet requirement ii; none of these compounds undergoes reaction 4. This reaction bears a certain resemblance to the dealcoholation of N-aminourethans, as reported by Diels.[14]

On the basis of the experimental evidence given in Tables II, IV and V, the nucleophile $[(CH_3)_2N]_2P(S)NHNH_2$ could be expected to react with carboxylic chlorides according to reaction 3, with formation of mixed, secondary hydrazides. However, the reaction of this compound with acetyl chloride was found to produce N,N-dimethylacetamide and unidentified reaction products.

The chemistry found to be involved in the acylation of primary phosphorohydrazides made it desirable to test their reactions with $POCl_3$ and $PSCl_3$. The results obtained were compared with the results from the reaction of $POCl_3$ and $PSCl_3$ with hydrazines (*cf.* Table VI). While the existence of phosphoryl trihydrazide (XXVIII) was proved by Klement and Knollmüller,[15] the synthesis of its thiono analog $(H_2NNH)_3PS$[16] was unsuccessful both in their and in our laboratory. Phenylhydrazine gave the expected, previously reported derivatives XXIX and XXX in satisfactory yield. Unsymmetrical dimethylhydrazine formed the thiono derivative XXXI in low yield. The reactions of the O,O-dialkyl phosphorohydrazidothionates III and IV with $POCl_3$ and $PSCl_3$ resulted in the formation of products, the structure of which could not be identified.

The various results obtained in the study of the formation of N¹-phosphorothioyl N²-acyl hydrazides led to some theoretical considerations, mentioned in the last section of this paper.

TABLE VI

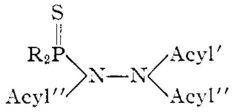
Reacn. 6: $Cl_3P(X) + 3H_2NN)(R')(R'') \longrightarrow [(R')(R'')NNH]_3P(X) + 3HCl$

X	R′	R″	Main product (yield, %)
O	H	H	$(H_2NNH)_3PO$ (XXVIII)[15]
	H	C_6H_5	$(C_6H_5NHNH)_3PO$ (XXIX, 73)
	H	$P(S)(Oalkyl)_2$	[a]
S	H	H	[a]
	H	C_6H_5	$(C_6H_5NHNH)_3PS$ (XXX, 62)
	H	$P(S)(Oalkyl)_2$	[a]
	CH_3	CH_3	$[(CH_3)_2NNH]_3PS$ (XXXI, 32)

[a] Not identified.

Formation of N¹-Phosphorothioyl N¹,N²N²-Tris-(acyl) Hydrazides.—From the results of the reactions of O,O-dialkyl phosphorohydrazidothionates with ethyl chloroformate, and $POCl_3$ as well as $PSCl_3$, it was apparent that certain N¹-phosphorothioyl N²-acyl hydrazides could be sufficiently reactive nucleophiles to undergo the new reaction 7. An investigation of the scope of this reaction involved eight nucleophiles (VII, VIII, X, XII, XXII–XXV) and the four substrates, acetyl chloride, benzoyl chloride, phthaloyl chloride and O,O-diethyl phosphorochloridothionate. The experiments were carried out by addition of theoretical amounts of substrate to the nucleophile, in the presence of triethylamine as an HCl-acceptor and of benzene as the reaction medium.

$$(R)_2P(S)NHNHAcyl' + 2Acyl''Cl \xrightarrow{-2HCl}$$

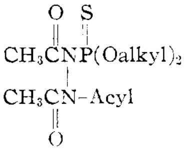
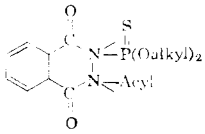


(7)

Acetyl chloride was found to give the following results. The two N¹-phosphorothioyl N²-acyl hydrazides XXII and XXIV formed the N¹-(O,O-dialkyl phosphorothioyl) N¹,N²,N²-tris-(acetyl) hydrazides XXXII and XXXIII (respectively) in rather low yields (*cf.* Table VII).

TABLE VII

N¹-PHOSPHOROTHIOYL N¹,N²,N²-TRIS(ACYL) HYDRAZIDES

Structure	Alkyl	Acyl	Compound (yield, %)
	CH_3	$C(O)CH_3$	XXXII (8.4)
	C_2H_5	$C(O)CH_3$	XXXIII (35)
	CH_3	$C(O)CH_3$	XXXIV (26)
	C_2H_5	$C(O)CH_3$	XXXV (60.1)
	CH_3	$P(S)(OCH_3)_2$	XXXVI (53.6)
	C_2H_5	$P(S)(OC_2H_5)_2$	XXXVII (43)

The reaction with the three N¹,N²-bis-(phosphorothioyl) hydrazides VII, X and XII produced triethylamine hydrochloride almost quantitatively, but the main products to be expected according to reaction 7 were not obtained. Compound VII reacted with formation of phosphorus compounds of unidentified structure, as probably caused by side reactions involving its methyl ester linkages. The nucleophiles X and XII produced mixtures of main products from which some N,N-dimethylacetamide could be isolated. This result was analogous to the one obtained from the reaction of compound VI with acetyl chloride and indicated that phosphorothioyl hydrazides of the structure $[(CH_3)_2N]_2P(S)NHNHX$ (X = H or acyl) generally caused amidation of carboxylic chlorides instead of hydrazidation according to the reactions 3 and 7, respectively.

The reaction of benzoyl chloride with compound XXV gave quantitative elimination of HCl and a viscous main product from which no N¹-phosphorothioyl N¹,N²,N²-tris-(benzoyl) hydrazide could be isolated. This result was not too unexpected in regard to the low yields of desired main products obtained from the reaction of

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[14] (a) O. Diels, *Ber.*, **36**, 736 (1903); (b) **47**, 2183 (1914).

[15] R. Klement and K. O. Knollmüller, *Chem. Ber.*, **93**, 834 (1960).

[16] R. Klement and K. O. Knollmüller, *Naturwiss.*, **46**, 227 (1959).

acetyl chloride with the compounds XXII and XXIV.

In connection with these findings the behavior of phthaloyl chloride in reaction 7 became of interest, and the reactions of this substrate with all eight nucleophiles were investigated. The compounds XXII and XXIV were found to produce the expected 2-(O,O-dialkyl phosphorothioyl)-3-acetyl-1,4-phthalazinediones XXXIV and XXXV in yields of 26 and 60.4%, respectively (*cf.* Table VII). These yields were markedly higher than the yields of the related compounds XXXII (8.4%) and XXXIII (35%). Thus, the phthaloylation of N^1-(O,O-dialkyl phosphorothioyl) N^2-acetyl hydrazides was more straightforward than their acetylation. This could have been caused by the higher susceptibility of phthaloyl chloride to nucleophilic attack as well as by steric assistance rendered by this substrate. In contrast to the behavior of XXII and XXIV, the compounds XXIII and XXV reacted with phthaloyl chloride with formation of viscous main products from which no N^1-phosphorothioyl N^1,N^2,N^2-tris-(acyl) hydrazide could be isolated. This result was analogous to the result from the reaction of compound XXV with benzoyl chloride and in contrast to the fact that tetrabenzoyl hydrazide was obtained previously.[17] The reaction of phthaloyl chloride with N^1,N^2-bis-(phosphorothioyl) hydrazides was found to give the following results. The secondary ester hydrazides VII and VIII yielded the 2,3-bis-(O,O - dialkyl phosphorothioyl) - 1,4 - phthalazinediones XXXVI and XXXVII. The secondary amido hydrazides X and XII produced side reactions of unidentified nature.

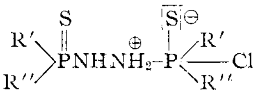
The substrate O,O-diethyl phosphorochloridothionate was not found to react with the nucleophiles VIII, X and XII; compound XII failed to react with phenyl isothiocyanate also. The lack of reaction shown by systems involving the monochloride $(C_2H_5O)_2P(S)Cl$ and the secondary hydrazides VIII, X and XII could have been caused by steric interference as well as by marginal reactivity of the nucleophiles involved. Thus, the hydrazidation of phosphoromonochloridothionates revealed the following over-all picture:

The extent of formation of the primary hydrazides $(R')(R'')P(S)NHNH_2$ apparently is not affected by the polar and steric effects caused by the groups R′ and R″. The extent of formation of the secondary hydrazides $(R')(R'')P(S)NH-NHP(S)(R')(R'')$ according to reaction 1 evidently is controlled by the polar effects of the R-groups involved. It is limited to monochloridothionates with R-groups of such a structure that their $\Sigma\sigma^*$-values are smaller than +3. Reaction 7 does not take place with phosphorothioyl groups in place of acyl′ and acyl″, presumably because of adverse effects that may be steric as well as inductive in nature. The limitations imposed by the structure of the R-groups may be overcome if hydrazine is replaced by a more basic diamine, such as a polymethylenediamine, as will be described elsewhere. Also, the limitations do not exist if the monochloridothionates $(R')(R'')P(S)Cl$ are replaced by carboxylic chlorides that are known to be more reactive and sterically less hindered substrates. This is evidenced by the existence of tetraacetyl and tetrabenzoyl hydrazide.[17,18]

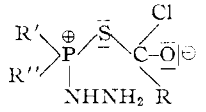
For the determination of the structure of the new compounds listed in Table VII it was of importance that their starting products were found to be N^1,N^2-diacyl hydrazides and not N^1,N^1-diacyl hydrazides.

Theoretical Aspects.—It appears reasonable to assume that the reactions 1, 2, 3, 4 and 5 involve nucleophilic displacements of chlorine on the P-atom or the carbonyl-carbon atom of the acyl chlorides by primary hydrazide $(R')(R'')P(S)NHNH_2$. The attacking atom involved in the initial step of these displacements is likely to be the one that possesses maximum polarizability of its outer electron shell. It has been shown that the refraction of the P=S group amounts to 11.9 cc. per mole for D-light.[19] The refraction of the phosphorus–hydrazine group, $PNHNH_2$, in $(C_2H_5O)_2P(S)NHNH_2$ and the molar refraction of hydrazine itself have been found to be 8.84 and 8.89 cc. per mole for D-light, respectively.[19,20]

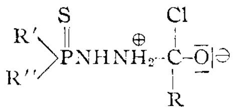
These data suggest that the nucleophiles $(R')(R'')P(S)NHNH_2$ tend to attack substrates through their sulfur atom. In the case of steric interference, as it exists possibly with phosphoromonochloridothionates, the attack on the substrate may come from the NH_2-group of the nucleophile. Thus, the reactions 1 and 2 may involve transition states corresponding to A. In the reactions 3, 4 and 5, however, the transition states may correspond to B$_1$. This state could undergo an intramolecular S$_N$-reaction to yield B$_2$ because such a reaction would decrease the polarizability and, therefore, decrease the free energy of the system.[19] Transition states like B$_1$ and B$_2$, instead of A, are even more likely to be involved in reaction 7.



A

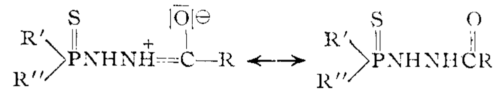


B$_1$



B$_2$

While dehydrochlorination of A would directly produce the compounds VII to XII the dehydrochlorinated state of B$_2$ would form the compounds XXII to XXV by a shift of electrons



B$_3$

Steps analogous to B$_1$, B$_2$ and B$_3$ may be involved in the formation of the compounds XXXII to

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(17) R. Stolle and R. Benrath, *J. prakt. Chem.*, **70**, 275 (1904).

(18) R. Stolle, *ibid.*, **69**, 145 (1904).

(19) H. Tolkmith, *Ann. N. Y. Acad. Sci.*, **79**, 203 (1959).

(20) L. D. Barrick, G. W. Drake and H. L. Lochte, *J. Am. Chem. Soc.*, **48**, 160 (1936).

XXXVIII. If R represents an easily removable group, such as ethoxyl, and if R′ and R″ do not exert a strongly electron-withdrawing influence, the nitrogen atom at phosphorus in B_3 may possess sufficient nucleophilicity to produce further transition states analogous to B_1, B_2 and B_3, and thus may cause the formation of the compounds XXVI and XXVII. If the R-group cannot be readily removed, as in the case of a methyl group, and if R′ and R″ are dimethylamido groups, their nitrogen atoms could be expected to have sufficient nucleophilic strength to convert B_3 to a reaction mixture containing dimethylacetamide.

Experimental

Starting Products.—The O,O-dialkyl phosphorochloridothionates $(CH_3O)_2P(S)Cl$ and $(C_2H_5O)_2P(S)Cl$ were obtained by vacuum fractionation of commercially available products and showed boiling points of 56° and 77°, respectively, at 10 mm. pressure. O,O-Diphenyl phosphorochloridothionate was prepared according to Autenrieth and Meyer.[4] O-Methyl O-2-chloro-4-*tert*-butylphenyl phosphorochloridothionate was prepared from the dichloridothionate[21] as described in the patent literature.[22]

Tetramethylphosphorochloridodiamidothionate, $[(CH_3)_2N]_2P(S)Cl$, was prepared by addition of gaseous dimethylamine (3 g.-moles) to an agitated solution of dimethylphosphoramidodichloridothionate (1 g.-mole) in benzene (1 l.) at +3°. Filtration of the reaction mixture and vacuum fractionation of the filtrate yielded the desired compound (144 g., 77%), m.p. 24–25°, b.p. 104–105° (10 mm.).

Anhydrous hydrazine and hydrazine monohydrate were used in their commercially available quality.

Reactions of Aromatic Phosphoromonochloridothionates.—Hydrazine, anhydrous or the monohydrate (1 g.-mole), was added dropwise to an agitated solution of phosphoromonochloridothionate (0.5 g.-mole) in benzene (900 ml.) over a period of 2 hours at room temperature. Several hours after completed hydrazine addition, water (250 ml.) was added with agitation. The benzene layer was separated and evaporated to leave the crude main product.

a.—Anhydrous hydrazine and O-methyl O-2-chloro-4-*tert*-butylphenyl phosphorochloridothionate produced the primary hydrazide II, m.p. 51–52°, 118 g. (76.5%), after recrystallization from ligroin (60–70°).

Anal. Calcd. for $C_{11}H_{18}ClN_2O_2PS$: N, 9.07; S, 10.39; mol. wt., 308.77. Found: N, 8.99; S, 10.45; mol. wt., 309.

b.—Hydrazine monohydrate and O,O-diphenyl phosphorochloridothionate gave 120 g. (85.5%) of the known hydrazide I, identified by infrared comparison with an authentic sample.

Addition of Hydrazine Monohydrate to Aliphatic Phosphoromonochloridothionates.—The reactions were carried out analogously to the reaction described with aromatic monochloridothionates. The addition time, however, was increased to about 15 hr. This slow rate of addition assured the absence of substantial quantities of unreacted hydrazine in the mixture. The presence of large amounts of base was found to be detrimental to the purity of those aliphatic main products which contained methyl ester linkages (compounds III, V, VII and IX). The crude main product, isolated from the reaction mixture as described before, was *shaken with cyclohexane (500 ml.) and again* evaporated. All evaporations were carried out in a water-bath at a pressure below 10 mm. and temperatures below 30° to assure complete removal of diluents without thermal rearrangement of the compounds formed.

a.—O,O-Dimethyl phosphorochloridothionate afforded 60 g. (77%) of the primary hydrazide III as a colorless oil (d^{25}_4 1.368, n^{25}_D 1.5428). *Anal.* Calcd. for $C_2H_9N_2O_2PS$: N, 17.94; S, 20.54; mol. wt., 156.15; R_D, 36.43.[19] Found: N, 18.5; S, 21.3; mol. wt., 165; R_D, 35.96.

b.—O,O-Diethyl phosphorochloridothionate yielded 85.6 g. (93%) of the primary hydrazide IV, isolated as a colorless oil (d^{25}_4 1.185, n^{25}_D 1.5010). *Anal.* Calcd. for $C_4H_{13}N_2O_2PS$: N, 15.21; S, 17.41; mol. wt., 184.19; R_D, 45.72.[19] Found: N, 15.2; S, 17.45; mol. wt., 189; R_D, 45.79.

c.—O-Methyl N-methyl phosphoramidochloridothionate gave the primary hydrazide V (42 g., 54%) as a colorless oil (d^{25}_4 1.308, n^{25}_D 1.5604). *Anal.* Calcd. for $C_2H_{10}N_3OPS$: N, 27.08; S, 20.66; mol. wt., 155.17; R_D, 38.41.[19] Found: N, 27.32; S, 21.65; mol. wt., 174; R_D, 38.38.

d. The reaction involving the monochloride $[(CH_3)_2N]_2P(S)Cl$ produced a well-crystallizing compound identified as the secondary hydrazide **N¹,N²-bis-(tetramethylphosphorodiamidothioyl) hydrazide (X)**, 23.5 g. (28%), m.p. 90–91° (cyclohexane). *Anal.* Calcd. for $C_8H_{26}N_6P_2S_2$: N, 25.28; S, 19.29; mol. wt., 332.42. Found: N, 25.41; S, 19.4; mol. wt., 325.

Addition of Anhydrous Hydrazine to Aliphatic Phosphoromonochloridothionates.—These reactions were carried out like those involving hydrazine monohydrate and aliphatic monochloridothionates, with the exception that quantities of 0.75 g.-mole of base and 0.5 g.-mole of acid chloride were used. The isolation of main product also was carried out as described in the preceding section.

a.—The chloridodiamidothionate $[(CH_3)_2N]_2PSCl$ gave a main product which according to infrared analysis was identical with compound X, as obtained in experiment d, but had a higher melting point (75 g., 90%; m.p. 92°).

b.—O-Methyl N-methyl phosphoramidochloridothionate yielded the secondary hydrazide **N¹,N²-bis-(O-methyl N-methyl phosphoramidothioyl) hydrazide (IX)**, 14 g. (10%), m.p. 99–100° (cyclohexane). *Anal.* Calcd. for $C_4H_{16}N_4O_2P_2S_2$: N, 20.14; S, 23.05; mol. wt., 278.28. Found: N, 20.54; S, 23.8; mol. wt., 260.

c.—O,O-Dimethyl phosphorochloridothionate afforded **N¹,N²-bis-(O,O-dimethyl phosphorothioyl) hydrazide (VII)**, m.p. 68° (cyclohexane), in a yield of 16 g. (23%). *Anal.* Calcd. for $C_4H_{14}N_2O_4P_2S_2$: N, 10.0; S, 22.88; mol. wt., 280.25. Found: N, 9.85; S, 22.7; mol. wt., 282.

d.—O,O-Diethyl phosphorodichloridothionate produced **N¹,N²-bis-(O,O-diethyl phosphorothioyl) hydrazide (VIII)**, m.p. 83–84° (cyclohexane), 30 g. (43%). *Anal.* Calcd. for $C_8H_{22}N_2O_4P_2S_2$: N, 8.33; S, 19.07; mol. wt., 336.35. Found: N, 8.64; S, 19.52; mol. wt., 324.

Addition of Aliphatic Phosphoromonochloridothionates to Hydrazine Hydrate. **a.**—A solution of O,O-dimethyl phosphorochloridothionate (1.0 g.-mole) in benzene (400 ml.) was added dropwise to an agitated mixture of hydrazine monohydrate (4 g.-moles) in benzene (400 ml.) over a period of 24 hr. at room temperature. The benzene layer was separated and the main product isolated from it as described with the experiments involving the reverse mode of addition. The primary hydrazide obtained (III, 60 g., 38.5%) showed inferior purity by infrared analysis and by chemical analysis (Found: S, 20.19; N, 15.73; mol. wt., 184).

b.—One g.-mole of *tetramethylphosphorochloridodiamidothionate* and 2 g.-moles of hydrazine were allowed to react as described in the preceding experiment. The addition of the chloridodiamidothionate (in 5 instead of 24 hr.) was followed by a brief period of reflux (20 minutes). Isolation of main product from the separated benzene layer produced a water-clear, viscous oil which was agitated with water (300 ml.) in order to remove the water-soluble, primary hydrazide $[(CH_3)_2N]_2P(S)NHNH_2$. This operation gave a white solid which was recrystallized from cyclohexane and identified by comparison of melting point (90–91°) and infrared pattern with an authentic sample of the secondary hydrazide X (obtained 54 g., 32.5%).

c.—A solution of the chloridodiamidothionate (0.5 g.-mole) in benzene (200 ml.) was added to an agitated mixture of hydrazine monohydrate (4 g.-moles) and benzene (100 ml.) within 1 hr. at about 30°. The benzene layer was separated and evaporated. The white, solid main product thus isolated was recrystallized from ether and identified as $[(CH_3)_2N]_2P(S)NHNH_2$ (VI), m.p. 41°, 73 g. (80%) of VI.

Anal. Calcd. for $C_4H_{15}N_4PS$: N, 30.71; S, 17.6; mol. wt., 182.23. Found: N, 30.44; S, 17.4; mol. wt., 190.

Reaction of Phosphorohydrazidothionates with O,O-Diethyl Phosphorochloridothionate.—A solution of O,O-diethyl phosphorochloridothionate (1.1 g.-mole) in benzene (900 ml.) was added dropwise over a period of 5 hr. at room temperature to an agitated solution of a primary hydrazide

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(21) H. Tolkmith, *J. Org. Chem.*, **23**, 1685 (1958).

(22) H. Tolkmith, E. H. Blair, K. C. Kauer and E. C. Britton, U. S. Patent 2,887,506 (May 19, 1959).

(1.0 g.-mole) and triethylamine (1.15 g.-mole) in benzene (700 ml.). Agitation was continued for 4 hr. at the same temperature and the reaction mixture then filtered. The amine salt isolated was washed with ether and the combined filtrates evaporated.

a.—O,O-Dimethyl phosphorohydrazidothionate (III) yielded **N^1-(O,O-dimethylphosphorothioyl) N^2-(O,O-diethylphosphorothioyl) hydrazide (XI)**, m.p. 52–53° (ether), 55.5 g. (18%). *Anal.* Calcd. for $C_6H_{18}N_2O_4P_2S_2$: N, 9.1; S, 20.75; mol. wt., 308.32. Found: N, 9.27; S, 20.46; mol. wt., 303.

b.—O,O-Diethyl phosphorohydrazidothionate (IV) produced the symmetrical derivative $(C_2H_5O)_2P(S)NHNHP(S)(OC_2H_5)_2$ (269 g., 80%); the melting point and infrared pattern were found to be identical to those of compound VIII.

c.—The primary diamidohydrazide $[(CH_3)_2N]_2P(S)NHNH_2$ (VI) afforded **N^1-(tetramethylphosphorodiamidothioyl) N^2-(O,O-diethylphosphorothioyl) hydrazide (XII)**, m.p. 101–102° (cyclohexane), in a yield of 190 g. (56.5%). *Anal.* Calcd. for $C_8H_{24}N_4O_2P_2S_2$: N, 16.76; S, 19.18; mol. wt., 334.38. Found: N, 16.81; S, 19.6; mol. wt., 344.

d.—A solution of this monochloride (0.2 g.-mole) in benzene (300 ml.) was added dropwise to an agitated solution of compound VIII, X or XII (0.1 g.-mole) and triethylamine (0.21 g.-mole) in benzene (300 ml.) at room temperature. No amine hydrochloride precipitate was formed, even after reflux of the reaction mixture for 3 hours. Evaporation of the mixture and extraction of the residue with cyclohexane produced the unreacted secondary hydrazide used as a starting product.

Hydrazonation of Phosphorohydrazidothionates.—These experiments were carried out to ascertain the presence of an unsubstituted NH_2-group in the primary hydrazides III–VI, and the absence of this group in the secondary hydrazides VII–XII. The experimental details related to the compounds of Table III have been reported elsewhere.[23]

Thermal Stability of O,O-Dialkyl Phosphorohydrazidothionates.—Solutions of the primary hydrazides III and IV (0.2 g.-mole) in chlorobenzene (200 ml.) were heated to reflux for a number of hours until a substantial quantity of precipitate was formed (after 5 hr. with III and after 25 hr. with IV). These precipitates were found to give the same combustion data as the starting products and to have melting point ranges (110–130° for the reaction product from III and 85–95° for the reaction product from IV) which were similar to the melting points reported elsewhere for $(CH_3O)_2P(S)NHNH_2$ and $(C_2H_5O)_2P(S)NHNH_2$, respectively.[6] Since trimethyl phosphorothionate and trimethylamine have been shown to react with formation of tetramethyl ammonium O,S-dimethyl phosphorothiolate at about 80°,[24] it was apparent that the thermal reaction of the primary hydrazides III and IV in refluxing chlorobenzene had caused their self-alkylation. This effect was most conspicuous with compound III.

Iso-(thio-)cyanate Derivatives.—The iso-(thio-)cyanates (0.4 g.-mole) were dissolved in benzene (400 ml.) and these solutions added dropwise at room temperature to agitated solutions of hydrazide (0.4 g.-mole) in benzene (400 ml.). The resulting reaction mixtures were worked up as subsequently described and yielded the **N^1-phosphorothioyl N^2-carbamoyl hydrazides, XV, XVIII and XIX, and the N^1-phosphorothioyl N^2-thiocarbamoyl hydrazides, XIII, XIV, XVI, XVII and XX.**

a.—The reaction of phenyl isocyanate with the O,O-dialkyl phosphorohydrazidothionates $(CH_3O)_2P(S)NHNH_2$ and $(C_2H_5O)_2P(S)NHNH_2$ produced benzene-insoluble precipitates which were filtered, washed with water and recrystallized from ether. Isolated was 67 g. (61%) of XV (m.p. 101.5–102°) and 78 g. (64.5%) of XIX (m.p. 145.5°).

Anal. Calcd. for $C_9H_{14}N_3O_3PS$ (XV): N, 15.27; P, 11.25; S, 11.65; mol. wt., 275.3. Found: N, 14.8; P, 11.8; S, 11.8; mol. wt., 272. Calcd. for $C_{11}H_{18}N_3O_3PS$ (XIX): N, 13.85; P, 10.02; S, 10.57; mol. wt., 303.3. Found: N, 13.2; P, 10.6; S, 10.9; mol. wt., 283.

b.—Cyclohexyl isocyanate reacted with $(C_2H_5O)_2P(S)NHNH_2$ to form a water-clear reaction mixture which was washed with water and evaporated. Recrystallization of the residue from cyclohexane produced 100 g. (80.5%) of compound XVIII (m.p. 83–84°).

Anal. Calcd. for $C_{11}H_{24}N_3O_3PS$: N, 13.58; P, 10.01; S, 10.37; mol. wt., 309.36. Found: N, 12.9; P, 10.3; S, 11.0; mol. wt., 279.

c.—Reactions of phenyl isothiocyanate with O,O-dialkyl phosphorohydrazidothionates gave clear solutions while its reaction with N',N',N'',N''-tetramethyl phosphorodiamidohydrazidothionate produced a benzene-insoluble precipitate. The solutions were worked up as described with experiment b and the precipitate as described with experiment a. These operations afforded the compounds XIV (84 g., 72.5%, m.p. 104–105°), XVII (80.5 g., 63%, m.p. 121–122°) and XX (90 g., 71.5%, m.p. 134–134.5°), respectively, after recrystallization from ether.

Anal. Calcd. for $C_9H_{14}N_3O_2PS_2$ (XIV): N, 14.42; P, 10.63; S, 22.01; mol. wt., 291.33. Found: N, 14.2, P, 10.7; S, 22.4; mol. wt., 267. Calcd. for $C_{11}H_{18}N_3O_2PS_2$ (XVII): N, 13.16; P, 9.70; S, 20.08; mol. wt., 319.39. Found: N, 13.1; P, 9.9; S, 20.8; mol. wt., 293. Calcd. for $C_{11}H_{20}N_5PS_2$ (XX): N, 22.07; P, 9.76; S, 20.2; mol. wt., 317.42. Found: N, 21.7; P, 9.9; S, 20.5; mol. wt., 322.

d.—Allyl isothiocyanate reacted with $(CH_3O)_2P(S)NHNH_2$ and $(C_2H_5O)_2P(S)NHNH_2$ in benzene to give a precipitate and a clear solution, respectively, which were worked up as described with the experiments a and b. Obtained were compounds XIII (69 g., 67.5%, m.p. 110.5–111°) and XVI (73 g., 64.5%, m.p. 114–115°), after recrystallization from diethyl ether.

Anal. Calcd. for $C_6H_{14}N_3O_2PS_2$ (XIII): N, 16.46; P, 12.13; S, 25.12; mol. wt., 255.3. Found: N, 16.6; P, 12.4; S, 25.1; mol. wt., 243. Calcd. for $C_8H_{18}N_3O_2PS_2$ (XVI): N, 14.83; P, 10.93; S, 22.63; mol. wt., 283.36. Found: N, 14.67; P, 11.0; S, 22.4; mol. wt., 286.

e.—A solution of phenyl isothiocyanate in benzene was added to a solution of compound XII in benzene; then the clear reaction mixture was refluxed for 0.5 hour. Evaporation of the reaction mixture and extraction of the residue with cyclohexane gave recovery of unreacted compound XII in a yield of 64%.

Acetyl Chloride Derivatives.—A solution of acetyl chloride (0.41 g.-mole) in benzene (300 ml.) was dropwise added to an agitated solution of the phosphorohydrazidothionate (0.4 g.-mole) and triethylamine (0.41 g.-mole) in benzene (500 ml.) at room temperature. The amine salt formed was filtered and washed with ether. The combined benzene and ether filtrates were evaporated, the residues obtained were recrystallized and the compounds identified as **N^1-phosphorothioyl N^2-acetyl hydrazides.**

a.—The reaction with $(CH_3O)_2P(S)NHNH_2$ and $(C_2H_5O)_2P(S)NHNH_2$ gave solid residues which were recrystallized from cyclohexane. Obtained was 48 g. (60.8%) of XXII (m.p. 96–97°) and 75 g. (83%) of XXIV (m.p. 75–76°).

Anal. Calcd. for $C_4H_{11}N_2O_3PS$ (XXII): N, 14.136; P, 15.63; S, 16.18; mol. wt., 198.19. Found: N, 13.65; P, 15.92; S, 16.48; mol. wt., 181. Calcd. for $C_6H_{15}N_2O_3PS$ (XXIV): N, 12.38; P, 13.69; S, 14.17; mol. wt., 226.37. Found: N, 11.88; P, 14.19; S, 14.51; mol. wt., 221.

b.—Acetyl chloride reacted with $[(CH_3)_2N]P(S)NHNH_2$ to give triethylamine hydrochloride (57 g., 104%). Evaporation of the filtrate and vacuum fractionation of the residue gave some N,N-dimethylacetamide (b.p. 74–76° (20 mm.)), as identified by infrared, and left condensed phosphorus hydrazides of unidentified structure in the still-pot.

c.—Solutions of acetyl chloride (0.6 g.-mole) in benzene (350 ml.) were added dropwise at room temperature over a period of 5 hours to agitated solutions of secondary hydrazide (0.3 g.-mole) and triethylamine (0.63 g.-mole) in benzene (350 ml.). The work-up of the reaction mixtures was the same as described with reactions involving phthaloyl chloride (*v.i.*). The compounds XXII and XXIV yielded the N^1-(O,O-dialkylphosphorothioyl) N^1,N^2,N^2-tris-(acetyl) hydrazides, XXXII and XXXIII, respectively. Isolated was 7 g. (8.4%) of XXXII (m.p. 82–84°) and 32.5 g. (35%) of XXXIII (m.p. 78–80°).

Anal. Calcd. for $C_8H_{15}N_2O_5PS$ (XXXII): N, 9.93; P, 10.97; S, 11.36; mol. wt., 282.3. Found: N, 9.91; P, 10.84; S, 11.37; mol. wt., 259. Calcd. for $C_{10}H_{19}N_2O_5PS$ (XXXIII): N, 9.03; P, 9.98; S, 10.34; mol. wt., 310.3. Found: N, 9.06; P, 10.41; S, 10.71; mol. wt., 284.

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(23) H. Tolkmith, U. S. Patent 2,965,667 (December 20, 1960).

(24) G. Hilgetag and H. Teichmann, *J. prakt. Chem.*, **280**, 90 (1959).

d.—Reactions of the secondary hydrazides VII, X and XII under the same conditions produced triethylamine hydrochloride in almost quantitative amounts. Vacuum distillation of the residues left from the filtrates of the reaction mixtures formed from X and XII gave some dimethylacetamide (identified by infrared analysis) and left condensed phosphorus hydrazides of unidentified structure in the still-pot. The run involving compound VII did not give identified compounds other than triethylamine hydrochloride.

Benzoyl Chloride Derivatives. a.—A solution of benzoyl chloride (0.41 g.-mole) in benzene (300 ml.) was added dropwise to an agitated solution of the O,O-dialkyl phosphorohydrazidothionate (0.4 g.-mole) and triethylamine (0.41 g.-mole) in benzene (500 ml.) at room temperature. The amine salt formed was filtered and washed with ether. The combined benzene and ether filtrates were evaporated; the residues obtained were recrystallized and identified as **N^1-phosphorothioyl N^2-benzoyl hydrazides**. The primary hydrazides $(CH_3O)_2P(S)NHNH_2$ and $(C_2H_5O)_2P(S)NHNH_2$ produced 58.5 g. (56%) of XXIII (m.p. 84–85°) and 87 g. (75.5%) of XXV (m.p. 102–103°), respectively, after recrystallization from ether.

Anal. Calcd. for $C_9H_{13}N_2O_3PS$ (XXIII): N, 10.77; P, 11.90; S, 12.32; mol. wt., 260.25. Found: N, 10.66; P, 11.97; S, 12.28; mol. wt., 275. Calcd. for $C_{11}H_{17}N_2O_3PS$ (XXV): N, 9.72; P, 10.74; S, 11.12; mol. wt., 288.3. Found: N, 9.97; P, 11.22; S, 11.44; mol. wt., 284.

b.—The reaction of benzoyl chloride (0.6 g.-mole) with compound XXV (0.3 g.-mole) in benzene (700 ml.) in the presence of triethylamine (0.63 g.-mole) at room temperature produced triethylamine hydrochloride quantitatively. Work-up of the filtrate gave recovery of some unreacted XXV, besides unidentified products.

Phthaloyl Chloride Derivatives.—Solutions of phthaloyl chloride (0.1 g.-mole) in benzene (170–230 ml.) were added dropwise at room temperature over a period of 3 hours to agitated solutions of secondary hydrazide (0.1 g.-mole of compound VII, VIII, X, XII, XXII–XXV) and triethylamine (0.205 g.-mole) in benzene (250 ml.). The reaction mixtures were filtered, the amine salts washed with ether and the combined filtrates evaporated. Crystallization of the crude main products from ether afforded the **2,3-bis-(O,O-dialkyl phosphorothioyl)-1,4-phthalazinediones XXXVI and XXXVII** (from the compounds VII and VIII, respectively), and the **2-(O,O-dialkyl phosphorothioyl)-3-acetyl-1,4-phthalazinediones XXXIV and XXXV** (from the compounds XXII and XXIV, respectively).

a.—N^1,N^2-Bis-(O,O-dimethylphosphorothioyl) hydrazide (VII) gave 22 g. (53.6%) of XXXVI (m.p. 113–114°). *Anal.* Calcd. for $C_{12}H_{16}N_2O_6P_2S_2$: N, 6.83; P, 15.1; S, 15.63; mol. wt., 410.35. Found: N, 6.76; P, 14.82; S, 15.29; mol. wt., 440.

b.—The reaction involving N^1,N^2-bis-(O,O-diethylphosphorothioyl) hydrazide (VIII) required heating of the reaction mixture for 6 hours at 60°, in order to complete reaction. Work-up of the mixture produced 20 g. (43%) of XXXVII (m.p. 106–107°).

Anal. Calcd. for $C_{16}H_{24}N_2O_6P_2S_2$: N, 6.0; P, 13.28; S, 13.75; mol. wt., 466.45. Found: N, 6.17; P, 13.1; S, 13.65.

c.—Reactions involving N^1-(O,O-dimethylphosphorothioyl) N^2-acetyl hydrazide (XXII) and N^1-(O,O-diethylphosphorothioyl) N^2-acetyl hydrazide (XXIV) went to completion at room temperature. Obtained was 8.5 g. (26%) of XXXIV (m.p. 112–113°) and 21.5 g. (60.4%) of XXXV (m.p. 97–98°).

Anal. Calcd. for $C_{12}H_{13}N_2O_5PS$ (XXXIV): N, 8.56; P, 9.46; S, 9.8; mol. wt., 327.28. Found: N, 8.58; P, 9.47; S, 10.08; mol. wt., 305. Calcd. for $C_{14}H_{17}N_2O_5PS$ (XXXV): N, 7.86; P, 8.69; S, 8.98; mol. wt., 356.33. Found: N, 7.8; P, 8.74; S, 8.91; mol. wt., 360.

d.—The secondary hydrazides X, XII, XXIII and XXV reacted with formation of triethylamine hydrochloride in quantities of 26–27 g. (0.19–0.195 g.-mole) and formation of unidentified phosphorus–hydrazine compounds.

Ethyl Chloroformate Derivatives.—A solution of ethyl chloroformate (0.8 g.-mole) in benzene (1 l.) was added dropwise at +5 to +25° to an agitated solution of O,O-dialkyl phosphorohydrazidothionate (0.8 g.-mole) and triethylamine (0.81 g.-mole) in benzene (800 ml.) at room temperature. The reaction mixture formed a precipitate which was removed by filtration. Fractionation of the filtrate gave a cut (b. 68–69°, 105 g.) which was identified by infrared as the benzene–ethanol azeotrope. Therefore, a total of 34 g. (0.74 g.-mole) of ethanol was formed during the reaction. The precipitate from the reaction mixture was dissolved in ethanol (1.8 l.) and reprecipitated by addition of water (1 l.) and partial evaporation of the liquid phase. The solid isolated was recrystallized from a methanol–ethanol mixture (1:1). The combustion data given below and the infrared pattern of the compounds thus isolated were consistent with the structure $(\text{alkylO})_2\text{P(S)}—\text{N}—\text{NH}—\text{C}{=}\text{O}$. Data from molecular weight determination indicated formation of dimer. On the basis of this evidence the compounds obtained were considered to be **O,O,O,O-tetralkyl hexahydro-3,6-dioxo-s-tetrazine-1,4-ylene diphosphonothionates (XXVI and XXVII)**. Obtained was 32 g. (22%) of XXVI (m.p. 201–202°) and 53 g. (31.5%) of XXVII (m.p. 154–155°).

Anal. Calcd. for $C_6H_{14}N_4O_6P_2S_2$ (XXVI): N, 15.38; P, 17.01; S, 17.64; mol. wt., 364.29. Found: N, 15.66; P, 17.25; S, 17.65; mol. wt., 391. Calcd. for $C_{10}H_{22}N_4O_6P_2S_2$ (XXVII): N, 13.33; P, 14.74; S, 15.26; mol. wt., 420.4. Found: N, 13.8; P, 14.57; S, 15.85; mol. wt., 448.

Phosphoryl Trichloride Derivatives. a.—The phosphoryl trichloride (0.1 g.-mole of $POCl_3$ or $PSCl_3$) was added dropwise at 0 ± 2° to an agitated solution of phenylhydrazine (0.7 g.-mole) in ether (900 ml.), over a period of 5 hr. The diluent was evaporated and the residue washed first with dilute HCl and then with water. The residue from the reaction of $POCl_3$ was recrystallized from absol. ethanol, and the residue from the $PSCl_3$ reaction was recrystallized from ethyl acetate. Obtained was 27 g. (73%, m.p. 188°) of XXIX and 24 g. of XXX (62%, m.p. 156°). The compounds were identified by comparison of their infrared pattern with the infrared spectra of authentic samples of XXIX and XXX.

b.—A solution of $PSCl_3$ (1.1 g.-moles) in ligroin (4 l., b.p. 60–70°) was added dropwise to N,N-dimethylhydrazine (8 g.-moles) with agitation at temperatures below 30°. The reaction mixture was refluxed and filtered. Evaporation of the filtrate left a white solid which was recrystallized from ether. Obtained was 85 g. of compound XXXI (32%, m.p. 79–80°), soluble in water.

Anal. Calcd. for $C_6H_{21}N_6PS$: N, 34.98; mol. wt., 240.32. Found: N, 34.4; mol. wt., 248.

Melting points were not corrected. Molecular weight determinations were carried out cryoscopically in benzene and ebullioscopically in methyl ethyl ketone.