

Under the same conditions, dibenzyl ketone gave 4,6-epidithio-1,3,5-triphenyl-3,5-hexadienone-2 (IVg), orange, m.p. 120–120.5° (hexane).

Anal. Calcd. for $C_{24}H_{18}OS_2$: C, 74.6; H, 4.7; S, 16.6. Found: C, 74.4; H, 4.9; S, 16.8.

Meribicyclo-3,5-epidithio-1,4-diphenyl-2,4-pentadienethione-1 (Va).—A mixture of 10.0 g. (0.034 mole) of 3,5-epidithio-1,4-diphenyl-2,4-pentadienone-1 (IVa) and 8.3 g. (0.037 mole) of phosphorus pentasulfide in 175 ml. of toluene was stirred and refluxed for 1 hr., cooled, filtered, and evaporated, giving a quantitative yield (10.5 g.) of crystalline red product, m.p. 123–128°. Crystallization from hexane (100 ml./g.) gave a 72% recovery of stubby purple needles, m.p. 129–131°.

Anal. Calcd. for $C_{17}H_{12}S_3$: C, 65.4; H, 3.8; S, 30.8. Found: C, 65.0; H, 3.9; S, 30.9.

Meribicyclo-3,5-epidithio-1,2,4-triphenyl-2,4-pentadienethione-1 (Vb), prepared similarly from 3,5-epidithio-1,2,4-triphenyl-2,4-pentadienone-1 (IVf), crystallized as black needles, m.p. 178–180°, from hexane.

Anal. Calcd. for $C_{23}H_{16}S_3$: C, 71.2; H, 4.1; S, 24.7. Found: C, 70.9; H, 4.0; S, 24.8.

Meribicyclo-1-*p*-dimethylaminophenyl-3,5-epidithio-4-phenyl-2,4-pentadienethione-1 (Vc), obtained similarly from IVd, crystallized from methylcyclohexane as purple plates, m.p. 174.5–176°.

Anal. Calcd. for $C_{19}H_{17}NS_3$: C, 64.3; H, 4.8; N, 3.9; S, 27.0. Found: C, 64.0; H, 4.9; N, 3.9; S, 26.7.

3,5-Epidithio-2,5-diphenyl-2,4-pentadienal (VI).—A solution of 3.2 g. (0.010 mole) of Va in 200 ml. of warm acetone was poured into a solution of 4.0 g. (0.013 mole) of mercuric acetate in 100 ml. of acetic acid. The resulting mixture was stirred overnight at room temperature and filtered. Dilution of the filtrate gave 3.0 g. (100%) of orange product, m.p. 119–120°. It crystallized as orange needles from hexane with unchanged melting point.

Anal. Calcd. for $C_{17}H_{12}OS_2$: C, 68.9; H, 4.1; S, 21.6. Found: C, 68.4; H, 4.0; S, 21.7.

It readily gave a 2,4-dinitrophenylhydrazone in methanol containing a little concentrated HCl; blue crystals from dimethylformamide, m.p. 250–253° dec.

Anal. Calcd. for $C_{23}H_{16}N_4O_4S_2$: C, 58.1; H, 3.2; N, 11.8; S, 13.5. Found: C, 57.8; H, 3.5; N, 12.2; S, 13.3.

Compound VI reacted rapidly with phosphorus pentasulfide in refluxing toluene to give a 93% yield of Va, identified by m.p., mixture m.p., and infrared comparison.

3,5-Epidithio-2,5-diphenyl-2,4-pentadienoic Acid (VII).—A solution of 1.50 g. of VI and 1.00 g. of 40% peracetic acid in 50 ml. of acetone was refluxed for 6 hr., cooled, diluted, and filtered. Starting material was removed by extraction with 150 ml. of boiling hexane. The residue (0.25 g.) was crystallized from

dilute acetic acid and then from propanol; brick-red needles, m.p. 147–151°.

Anal. Calcd. for $C_{17}H_{12}O_2S_2$: C, 65.4; H, 3.8; S, 20.5. Found: C, 65.3; H, 3.8; S, 20.9.

2-Cyano-3,5-epidithio-1,5-diphenyl-2,4-pentadienone-1 (XI).—A solution of 19.4 g. (0.100 mole) of 5-phenyl-1,2-dithiole-3-one⁴ (IX) and 10.0 g. (0.069 mole) of benzoylacetonitrile in 100 ml. of phosphorus oxychloride was warmed on the steam bath for 5 hr., left overnight at room temperature, and then poured carefully over ice. The solid was filtered, washed, dried, and freed of starting material by digestion with carbon disulfide. The crude product thus obtained (13.2 g.) was crystallized from 125 ml. of trichloroethylene, giving 10.0 g. (45%) of orange needles, m.p. 200–201°, unchanged on crystallization from methylcyclohexane.

Anal. Calcd. for $C_{18}H_{11}NOS_2$: C, 67.3; H, 3.4; N, 4.4; S, 19.9. Found: C, 66.9; H, 3.4; N, 4.3; S, 20.3.

From "Trithionium Salt."—Three grams (0.021 mole) of benzoylacetonitrile and 3.4 g. (0.010 mole) of the addition product²(X) of methyl sulfate with 5-phenyl-1,2-dithiole-3-thione were refluxed overnight in 30 ml. of acetic acid containing 3 drops of pyridine, cooled and filtered. The product was digested with water, filtered, dried, and crystallized from about 50 ml. of acetic acid, yielding 1.3 g. (41%) of slightly impure XI, m.p. 196–199°.

Meribicyclo-2-cyano-3,5-epidithio-1,5-diphenyl-2,4-pentadienethione-1 (XII).—A mixture of 1.50 g. (4.7 mmoles) of 2-cyano-3,5-epidithio-1,5-diphenyl-2,4-pentadienone-1 (XI) and 2.0 g. (9.0 mmoles) of phosphorus pentasulfide in 25 ml. of xylene was stirred and refluxed for 1 hr. and filtered hot. The orange product crystallized at once from the xylene; m.p. 203–205°, yield 1.55 g. (99%). Crystallization from 30 ml. of 2-methoxyethanol raised the m.p. to 216–217°, with a 73% recovery.

Anal. Calcd. for $C_{18}H_{11}NS_3$: C, 64.1; H, 3.3; N, 4.2; S, 28.5. Found: C, 64.0; H, 3.3; N, 4.3; S, 28.5.

Meribicyclo-3,5-epidithio-1,5-diphenyl-2,4-pentadienethione-1 (XIVb).—Meribicyclo-2-cyano-3,5-epidithio-1,5-diphenyl-2,4-pentadienethione-1 (XII, 3.37 g., 0.0100 mole) was stirred and refluxed in 250 ml. of acetic acid; 10 ml. of 48% HBr was added through the condenser. The addition of HBr was repeated after 24 and again after 48 hr. After 72 hr. the reaction mixture was diluted with 50 ml. of water, cooled, and filtered, yielding 2.25 g. (72%) of purple red product, m.p. 153–165°. Crystallization from methylcyclohexane (65–70 ml./g.) gave an 80% recovery of pure product, m.p. 166–168° (lit.¹² m.p. 162°), unchanged on admixture with a specimen obtained from dibenzoylacetone (XIIIb) and P_2S_5 in refluxing benzene.

Anal. Calcd. for $C_{17}H_{12}S_3$: C, 65.4; H, 3.8; S, 30.8. Found: C, 65.0; H, 3.9; S, 30.8.

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Nucleophilic Reactivity of Phosphoramidothionates. I. Halogen Displacements on Tetrahedral Carbon by Phosphorotriamidothionates¹

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The scope of novel reactions of phosphorotriamidothionates with alkyl halides in the absence of polar solvents to produce new types of onium compounds is strongly dependent upon the structure of the reactants. The parent anide $(H_2N)_3PS$ reacts with primary alkyl halides to form the onium derivatives to be expected. The hydrocarbon derivatives $(R'NH)_3PS$ undergo the same reaction and react also with isopropyl bromide, subject to the inductive effect of R' . Hydrocarbon analogs of the structure $[(R')(R'')N]_3PS$ react only with primary alkyl iodides, depending upon the steric effects of the R groups and alkyl groups involved. The steric limitations operative in the scope of formation of the onium compounds $\{[(R')(R'')N]_3PS \text{ alkyl}\}^+I^-$ apparently arise from a relatively narrow valence angle formed at the sulfur atom. Hydrocarbon derivatives of $(H_2N)_3PO$ and $(H_2N)_3PS$ do not react with *t*-butyl chloride but do react with *t*-butyl bromide without formation of onium compounds. New n.m.r. shift data as obtained for various compounds containing the N–P–S linkage are discussed. The findings described are compared with the extent of formation and the cation structure of isothiuronium halides.

In previous investigations on organic thionophosphorus compounds, relatively little attention was given to those reactions that involved nucleophiles containing the thionophosphorus group $P=S$. Our own previous

work had revealed that phosphorohydrazidothionates and N^1,N^2 -bis-(phosphorothionyl)-hydrazides showed greater nucleophilicity than was to be expected from the known reactivity of these hydrazides.² In regard to the nucleophilic reactivity of phosphoramidothionates very little was reported in the past.^{3–6} The phos-

(1) Presented in part at the XIXth IUPAC Congress (Section A4, Modern Aspects of Organometallic and Related Compounds), London, July, 1963, p. 183 of Abstracts.

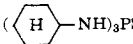
(2) H. Tolkmith, *J. Am. Chem. Soc.*, **84**, 2097 (1962).

phorotriamidothionates ($>N$)₃P(S) could be expected to show the same basic pattern of reactivity toward carbon as the thioureas for the following reason.

It is generally accepted that nucleophilic displacements of halogen on saturated carbon depend upon the nucleophilicity of the attacking reagent, *i.e.*, they depend upon the polarizability of the valence electron groups present in the nucleophile.⁷ In the amidothionates ($>N$)₃P(S) and ($>N$)₂C(S), the polarizability of the 3sp³ octet on sulfur amounts to 4.7 Å.³ and 4.4 Å.³, respectively, while the polarizability of the 2sp³ octet on the nitrogen atoms is less than half as large.⁸ These data are in agreement with the fact that pseudothiuronium halides have the structure [$>N^+=C(N<)-S$ -alkyl]Hal⁻,⁹ and suggest formation of the onium compounds [($>N$)₃P—S-alkyl]⁺Hal⁻. Concerning the formation of onium derivatives from the phosphorothionates R₃P(S) and methyl iodide, it is known that the reaction is positive if R is ethyl,¹⁰ diethylamino,⁵ or 2-pyridyl,¹¹ but negative if R is phenyl¹¹ or ethylamino.¹²

Because of this insufficient and apparently inconsistent evidence, the reactions of primary, secondary, and tertiary alkyl halides with a series of phosphorotriamidothionates, listed in Table I, were studied. For this purpose, mixtures consisting of the reactants at mole ratios of 5:1 to 10:1 were heated at reflux.

TABLE I

| NUCLEOPHILES INVESTIGATED | | | |
|--|------|--|------|
| Structure | Code | Structure | Code |
| (H ₂ N) ₃ PS | A | [(CH ₃) ₂ N] ₂ P(S)N(C ₂ H ₅) ₂ | J |
| (CH ₃ NH) ₃ PS | B | [(CH ₃) ₂ N] ₂ P(S)N(CH ₃) ₂ | K |
| (C ₂ H ₅ NH) ₃ PS | C | [(CH ₃) ₂ N] ₂ P(S)N(CH ₂ C ₆ H ₅) ₂ | L |
| () ₃ PS | D | [(C ₂ H ₅) ₂ N] ₂ PS | M |
| (C ₆ H ₅ CH ₂ NH) ₃ PS | E | [(CH ₃) ₂ N] ₂ PS | N |
| (4-CIC ₆ H ₄ NH) ₃ PS | F | [(CH ₃) ₂ NNH] ₂ PS ² | O |
| [(CH ₃) ₂ N] ₂ P(S)NHC ₂ H ₅ | G | (C ₆ H ₅ NHNH) ₂ PS | P |
| [(CH ₃) ₂ N] ₂ PS | H | [(CH ₃) ₂ N] ₂ P(S)NHNHP(S)[N(CH ₃) ₂] ₂ ² | Q |

Reactions with Primary Alkyl Halides.—The triamidophosphorothionate (H₂N)₃PS (A) reacted with methyl iodide, ethyl iodide, and allyl bromide at a mole ratio of 1:10 at reflux to give the onium compounds I, II, and III, respectively, in yields of more than 90%, while its reaction with benzyl chloride produced the derivative V in 70% yield (see Table II). These reactions of the phosphorothionate A were completely analogous to the reactions of thiourea with the same alkyl halides.^{13,14} As was to be expected, A and *n*-propyl bromide gave the onium derivative IV, in high yield.

N',N'',N'''-Trimethyl phosphorotriamidothionate, (CH₃NH)₃PS (B), also reacted with ethyl iodide, *n*-propyl bromide, allyl bromide, and benzyl chloride under the reaction conditions described and produced the onium compounds VI, VIII, VII, and IX, respectively, in yields of more than 85%. The nucleophile analogs (C₂H₅NH)₃PS (C) and (C₂H₅NH)₂CS reacted with refluxing ethyl iodide at a mole ratio of 1:10 to form [(C₂H₅NH)₃PSC₂H₅]⁺I⁻ (X) in 74% yield and [C₂H₅N⁺H]=C(NHC₂H₅)SC₂H₅I⁻ in 94% yield.

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

(b) E. H. Blair and H. Tolkmith, *ibid.*, **25**, 1620 (1960).

(4) Cf. G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 278-324.

(5) A. J. Burn and J. I. G. Cadogan, *J. Chem. Soc.*, 5532 (1961).

(6) H. Tolkmith, U. S. Patent 3,074,993 (January 22, 1963).

(7) Cf. J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 140.

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

(9) H. Lecher and Cl. Heuck, *Ann.*, **438**, 169 (1924).

(10) A. Hantzsch and H. Hibbert, *Ber.*, **40**, 1508 (1907).

(11) F. G. Mann and J. Watson, *J. Org. Chem.*, **13**, 502 (1948);

(12) A. Michaelis, *Ann.*, **326**, 207 (1903).

(13) A. Bernthsen and H. Klinger, *Ber.*, **11**, 492 (1878).

(14) E. Werner, *J. Chem. Soc.*, **57**, 283 (1890).

TABLE II

REACTIONS OF PHOSPHOROTRIAMIDOTHIONATES WITH PRIMARY ALKYL HALIDES

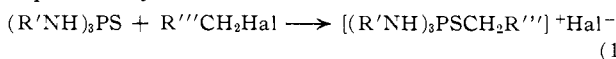
Main Products I-XX (yield, %)^a

| P com-pound | CH ₃ I | C ₂ H ₅ I | CH ₂ =CHCH ₂ Br | <i>n</i> -C ₃ H ₇ Br | C ₆ H ₅ -CH ₂ Cl |
|-------------|-------------------|---------------------------------|---------------------------------------|--|---|
| A | I (92.5) | II (94) | III (97) | IV (93) | V (70) |
| B | | VI (86) | VII (99) | VIII (94) | IX (87) |
| C | | X (74) | | | |
| D | | XI (92) | XII (96) | XIII (98) | |
| E | | XIV (84) | | XV (97) | |
| F | | n.r. | | n.r. | |
| H | XVI (80-94) | XVII (41) | n.r. | n.r. | |
| J | XVIII (38) | | | | |
| K | XIX (20) | | | | |
| M | XX (5) | n.r. | | | |
| N | n.r. | n.r. | n.r. | | n.r. |
| L | n.r. | | | | |

^a The abbreviation n.r. indicates that no reaction occurred under the conditions described.

The influence of sterically and inductively more effective R' groups in the nucleophiles (R'NH)₃P(S) became evident from the reactivity of the nucleophiles D, E, and F. The cyclohexyl compound D reacted with ethyl iodide, allyl bromide, and *n*-propyl bromide to produce the onium compounds XI-XIII, respectively, in nearly quantitative yields. The benzyl compound E formed the onium derivatives XIV and XV in yields of more than 80% when allowed to react with ethyl iodide and *n*-propyl bromide, respectively. In contrast, the nucleophile F did not react with these two substrates when heated to reflux at a mole ratio of 1:10 for long periods of time.

The experimental findings described thus far can be expressed by the reaction

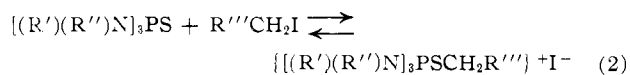


The data obtained, particularly those with ethyl iodide and *n*-propyl bromide, indicate that reaction 1 is predominantly controlled by the structure of R'. The reaction evidently is limited by the inductive effect but rather independent of the steric effect of this group. Since reaction 1 does not occur if R'NH₂ is weaker than aniline but still takes place if R'NH₂ is cyclohexylamine, it may be concluded that, in terms of Taft's constants, the reaction fails to occur if the σ*-value of R' is greater than +0.6 but still proceeds if R' has an E_S-value of -0.79.¹⁵

These criteria were not found to be valid for reactions of primary alkyl halides with the phosphorotriamidothionates, H through N, which had three secondary amido groups attached to the P=S group. N',N'',N'''-Hexamethyl phosphorotriamidothionate (H) and methyl iodide reacted readily at room temperature and at reflux temperature to give 80 and 94% yields, respectively, of the onium derivative expected (XVI), while the reaction with ethyl iodide produced the derivative XVII in 41% yield at a reaction temperature of 45-50° and in an even lower yield at the reflux temperature of 73°. These data indicated that the equilibrium of the reaction of ethyl iodide with the electron donor H was markedly more temperature-dependent than the equilibrium of the reaction of ethyl iodide with the isomeric electron donor C or with N',N''-diethylthiourea. It was also found that compound H did not react with allyl bromide and *n*-propyl bromide under those conditions under which the nucleophiles A, B, and D formed the corresponding onium derivatives in almost quantitative yields. The same lack of reactivity toward these

(15) Cf. R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 556-674.

bromide substrates was shown by the other phosphorotriamidothionates containing three secondary amido groups attached to the P=S group. However, some of these nucleophiles (J, K, and M) did react with methyl iodide according to the reaction



These results revealed that the scope of reaction of $(H_2N)_3PS$ with primary alkyl halides remained unchanged if not more than one hydrogen atom of each nitrogen atom was replaced by a hydrocarbon group of negligible electron-attracting power. A drastic reduction in reactivity occurred, however, if all six hydrogen atoms were replaced in this manner. This indicated that the reaction was strongly affected by the steric characteristics of the secondary amido groups present in the phosphorothionate nucleophile since the pK_a values of the parent amines were very similar.

The importance of steric effects became most obvious in the results obtained from the reactions of the electron donor N, N', N'', N''' -Tris-(pentamethylene) phosphorotriamidothionate (N) and its thiourea analog $[(CH_2)_5N]_2CS$ would appear to be strong nucleophiles if the steric effect of the puckered piperidine ring were disregarded. Compound N was heated with agitation at a mole ratio of 1:10 with methyl iodide and ethyl iodide at 45° and with allyl bromide at 75°, as well as with benzyl chloride at a mole ratio of 1:5 at 75°. In none of these four reactions, even after a reaction time of 150 hr., could an onium derivative be obtained. The same result was obtained when a reaction mixture containing compound N, methyl iodide, and nitromethane at the mole ratio of 1:10:10 was refluxed for 100 hr. In contrast, N', N'' -bis-(pentamethylene)-thiourea was found to produce the expected pseudothiuronium halides when refluxed with methyl iodide and allyl bromide at a mole ratio of 1:1 in ether and when heated at 75° with benzyl chloride at the same mole ratio in the presence of nitromethane.¹⁶ The yields of onium compound were found to be 45, 60, and 85%, respectively. This great difference in reactivity between $[(CH_2)_5N]_3PS$ and $[(CH_2)_5N]_2CS$ was undoubtedly caused by the steric effect produced by accumulation of three bulky piperidine groups at phosphorus. Thus the substitution of all six hydrogen atoms in $(H_2N)_3PS$ by aliphatic groups leads to a great reduction in nucleophilic reactivity from the large scope of reaction 1 to the narrow scope of the more temperature-sensitive reaction 2 and to complete lack of reactivity, depending upon the extent of steric hindrance caused by the secondary amido groups involved. Reaction 2 does not take place if the total number of carbon atoms in the substituents $R', R'',$ and R''' is larger than 12. Reaction 1, on the contrary, still proceeds with quantitative yield if this number is 23 (*cf.* onium compound XV).

These findings received additional support from a comparison of the nucleophilicity of compound H and its isomer $[(CH_3)_2N]_2(C_2H_5NH)PS$ (G). As was mentioned, the phosphorothionate H did not react with allyl bromide and *n*-propyl bromide but formed onium derivatives with methyl iodide and ethyl iodide. Although compound G should possess practically the same nucleophilic reactivity as H, its actual reactivity was greater. The nucleophiles G and H reacted with an excess of ethyl iodide to produce the derivatives $\{[(CH_3)_2N]_2(C_2H_5NH)PSC_2H_5\}^+I^-$ (XXI) and XVII in yields of 87 and 41%, respectively, under practically identical reaction conditions. In contrast to compound H, however, the thionate G did react with allyl bromide

and *n*-propyl bromide with formation of $\{[(CH_3)_2N]_2(C_2H_5NH)PSC_2CH=CH_2\}^+Br^-$ (XXII) and $\{[(CH_3)_2N]_2(C_2H_5NH)PSC_3H_7\}^+Br^-$ (XXIII) in yields of more than 80%.

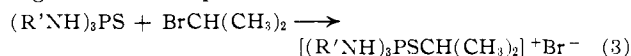
In connection with the results described so far it was of interest to investigate the reaction of ethyl iodide with the three phosphorohydrazidothionates O, P, and Q at a mole ratio of 5:1 at reflux. In all three cases extensive decomposition took place and no onium derivative could be isolated. Rather contrasting, the reaction of thiocarbohydrazide with methyl iodide in refluxing ethanol was reported to give the expected onium compound in 80% yield.¹⁷

Reactions with Isopropyl Bromide.—The remarkable difference in nucleophilic reactivity found to exist with phosphorotriamidothionates containing either primary or secondary amido groups prompted a study of the reaction of these phosphorus nucleophiles with isopropyl bromide as a representative secondary alkyl halide. The reactions were carried out with the primary amidothionates A, B, and D-F and the secondary amidothionates H and N under the same conditions as described with primary alkyl halides and gave the results presented in Table III.

TABLE III
REACTIONS OF PHOSPHOROTRIAMIDOTHIONATES WITH ISOPROPYL BROMIDE

| Nucleophile | Onium derivative (yield, %) |
|-------------|--|
| A | Not formed |
| B | $\{[(CH_3NH)_3PS-i-C_3H_7]\}^+Br^-$ (XXIV, 83) |
| D | $\{[(C_6H_{11}NH)_3PS-i-C_3H_7]\}^+Br^-$ (XXV, 87) |
| E | $\{[(C_6H_5CH_2NH)_3PS-i-C_3H_7]\}^+Br^-$ (XXVI, 75) |
| F | } Not formed |
| H | |
| N | |

Phosphorotriamidothionate (A) and isopropyl bromide did not react when their mixture (mole ratio 1:10) was refluxed for 150 hr. Similarly, the yield of S-isopropylpseudothiuronium bromide produced from thiourea under the same reaction conditions was found to be negligible. The nucleophiles B, D, and E, however, afforded the onium derivatives XXIV, XXV, and XXVI, respectively, in high yields after their mixtures with isopropyl bromide were refluxed at a mole ratio of 1:10 for 150 hr. The theoretically less reactive nucleophile F did not react with the bromide substrate under these conditions. The same negative result was found with the two electron donors containing secondary amido groups at phosphorus (H and N). While the results obtained with F, H, and N were altogether as to be expected from the previous findings, it was of interest to note that N', N'' -bis-(pentamethylene)-thiourea also did not react with isopropyl bromide under the conditions described. These results revealed the following about the scope of the reaction involved.



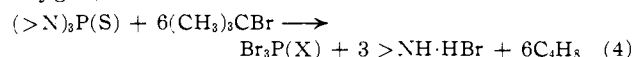
While both reactions 3 and 1 permit considerable variation in the steric characteristics of the R' groups, reaction 3 is more restricted by the polar effects of R' than is reaction 1. This follows from the following evidence. A proton in place of R' renders the electron donor sufficiently nucleophilic to permit formation of onium compound IV with *n*-propyl bromide but it does not leave sufficient reactivity with the sulfur atom to achieve the ejection of bromine from the less electrophilic carbon atom of isopropyl bromide. This situation is not caused by the steric characteristics of the iso-

(16) H. Tolkmith, U. S. Patent 3,087,931 (April 30, 1963).

(17) E. S. Scott and L. F. Audrieth, *J. Org. Chem.*, **19**, 1231 (1954).

propyl group since a cyclohexyl or benzyl group in place of R' does permit the formation of onium derivative in high yield (cf. XIII, XV, XXV, and XXVI). Consequently, the reaction of the triamidothionates (R'NH)₃PS with *i*-C₃H₇Br is limited to R' groups which, in terms of Taft's polar substituent constants, have σ^* -values that are negative or, if positive, are smaller than +0.3; the proton has a value of +0.49.¹⁵

Reactions with *t*-Butyl Halides.—Although the reaction of thiourea with *t*-butyl chloride and bromide was found to require the presence of a highly polar diluent,¹⁸⁻²⁰ the reaction of phosphorotriamidothionates with these halides was investigated under conditions comparable to those used for nontertiary alkyl halides. *t*-Butyl chloride failed to react with the thionates E, H, and N. With *t*-butyl bromide, however, the compounds E, F, H, and N reacted to give isobutylene in quantities of about six moles per mole of phosphorothionate. After removal of excess *t*-butyl bromide from the reaction mixture, extraction with ligroin afforded the amine hydrobromide as an insoluble component. Vacuum fractionation of the ligroin solution gave thiophosphoryl bromide. An analogous result was obtained with hexamethylphosphoramide. Therefore, the following reaction had taken place (X = sulfur or oxygen)



Reaction 4 represents the most interesting difference between phosphorotriamidothionates and thioureas in their reactivity toward alkyl halides. In regard to the differences in reactivity between the amidothionates (>N)₃P(S) and the amidates (>N)₃P(O) it is of interest that hexamethylphosphoramide does react with *t*-butyl bromide according to reaction 4 but does not react with methyl iodide according to reaction 2, in the absence of polar diluents.

Properties of the Onium Derivatives.—All of the onium compounds, I-XXVI, were soluble in dimethylformamide. The resulting solutions contained at least 15 g. of onium compound per 100 ml. of solvent at room temperature. The solubility in chloroform and acetone was clearly dependent upon the structure of the solute. Compounds containing at least one hydrocarbon group at each nitrogen atom (VI-XXVI) were much more soluble than those containing unsubstituted amido groups exclusively (I-V). The solubility of the compounds VI-XXVI in chloroform was about as good as their solubility in dimethylformamide, while their solubility in acetone was substantially smaller. The solubility of the onium compounds I-V in chloroform as well as in acetone was smaller than 2 g./100 ml. at room temperature, *i.e.*, the solubility was lower than the solubility of VI-XXVI in these solvents.

Addition of water to solutions of the compounds XVI and XVIII-XX in dimethylformamide was found to release methyl mercaptan. Aqueous solutions of various onium derivatives synthesized showed the presence of halide ion. These findings clearly indicated that phosphorotriamidothionates and alkyl halides underwent an S_N reaction involving the formation of a sulfur-carbon bond and cleavage of the carbon-halogen bond.

N.m.r. Studies (in cooperation with E. B. Baker).—Since no previous investigation of the n.m.r. spectra of organic compounds containing the grouping, -NHP(S)<, was reported in the literature, the spectra of several of the nucleophiles and their onium derivatives were studied in more detail (cf. Table IV).

(18) H. J. Backer and N. D. Dijkstra, *Rec. trav. chim.*, **51**, 289 (1932).

(19) H. J. Backer and P. L. Stedehouder, *ibid.*, **52**, 437 (1933).

(20) J. M. Sprague and T. B. Johnson, *J. Am. Chem. Soc.*, **69**, 1839 (1937).

TABLE IV

N.M.R. DATA OF SOME PHOSPHORUS-NITROGEN COMPOUNDS

| Compound | | P ³¹ shift (δ in p.p.m.) ^a | H ¹ shifts |
|---|------|---|-----------------------|
| [(CH ₃) ₂ N] ₃ P | | -122 ²³ | |
| [(CH ₃) ₂ N] ₃ PS | H | -81.7 | |
| {[(CH ₃) ₂ N] ₃ PSCH ₃ } + I ⁻ | XVI | -66.8 | |
| {[(CH ₃) ₂ N] ₃ PC ₄ H ₉ } + Br ⁻ | | -62 ²³ | |
| [(CH ₃) ₂ N] ₃ PO | | -27, ²³ -23.4 ²² | |
| (CH ₃ NH) ₃ PS | B | -68.8 | -2.5 ^b |
| (C ₆ H ₁₁ NH) ₃ PS | D | -58.4 | -3.13 ^b |
| [(CH ₃ NH) ₃ PSC ₃ H ₇] + Br ⁻ | VIII | -56.9 | -5.69 ^b |
| [(CH ₃ NH) ₃ PSC ₂ C ₆ H ₅] + Cl ⁻ | IX | -55.2 | -6.11 ^b |
| [(C ₆ H ₁₁ NH) ₃ PSC ₂ H ₅] + I ⁻ | XI | -44.4 | -6.08 ^b |
| [(C ₆ H ₅ CH ₂ NH) ₃ PSC ₂ H ₅] + I ⁻ | XIV | -52.2 | -6.0 ^b |
| (H ₂ N) ₃ PS | A | -59.4 | |
| [(H ₂ N) ₃ PSC ₃ H ₇] + Br ⁻ | IV | -51.8 | -5.80 ^c |
| [(H ₂ N) ₃ PSC ₃ H ₅] + Br ⁻ | III | -51.3 | -5.93 ^c |
| [(H ₂ N) ₃ PSC ₂ C ₆ H ₅] + Cl ⁻ | V | -50.9 | -6.22 ^c |
| [(H ₂ N) ₃ PSC ₃] + I ⁻ | I | -50.4 | -5.80 ^c |
| [(H ₂ N) ₃ PSC ₂ H ₅] + I ⁻ | II | -49.5 | -5.85 ^c |

^a Chemical shift in dimethylformamide (DMF) relative to 85% H₃PO₄. ^b Shift in p.p.m. of NH proton in chloroform relative to (CH₃)₄Si (TMS). ^c Shift in p.p.m. of NH₂ protons in DMF relative to (CH₃)₄Si; DMF is -2.85 p.p.m. relative to TMS.

The P³¹ spectra of compounds containing nonprotonated nitrogen gave the following picture. Compound H showed in its spectrum the presence of 13 or 15 lines of the 19 expected from its 18 equivalent protons and had a δ -value of -81.7 p.p.m. This value was 40.3 units higher than for [(CH₃)₂N]₃P and 58.3 units lower than the value for [(CH₃)₂N]₃PO. These differences were very close to the differences reported with homologous dialkylamido compounds.²¹⁻²³ The transformation of compound H and its sulfur-free analog to the alkyl halide derivatives {[(CH₃)₂N]₃PSCH₃} + I⁻ (XVI) and {[(CH₃)₂N]₃PC₄H₉} + Br⁻ produced δ -values of -66.8 and -62 p.p.m., respectively. Thus, the conversion of H to XVI increased the positive charge on phosphorus, corresponding to a shift of 14.9 p.p.m.

The behavior of compounds containing unprotonated nitrogen at phosphorus was studied with six compounds. The P³¹ splittings of both nucleophiles B and D were found to be unresolved because of different couplings of the NH protons and the methyl protons as well as the cyclohexyl protons nearest to phosphorus. The δ -values of the compounds H and B reflected the inductive effects caused by the groups attached to nitrogen. The value of -58.4 p.p.m. for compound D was almost identical with the δ -value of trimethylphosphine sulfide.²⁴ In the spectra of the onium derivatives VIII, IX, XI, and XIV, phosphorus appeared as a multiplet due to coupling to the nearest protons. This coupling could be removed by the spin decoupling technique, which produced sharper lines and increased the signal:noise ratio. The splitting obtained without proton irradiation appeared consistent with the structures involved. The conversion of the phosphorus nucleophiles B and D to onium compounds increased the δ -values by 11.9-14 p.p.m.

The spectrum of the inorganic parent compound (H₂N)₃PS (A) showed very little P-N-H coupling. From the behavior of the other compounds it would follow that this should be of the order of 10 c.p.s. with a seven-line pattern. Yet the signal was enhanced by H¹

(21) Cf. R. A. J. Jones and A. R. Katritzky, *Angew. Chem.*, **74**, 60 (1962).

(22) N. Muller, C. P. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956).

(23) J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *ibid.*, **78**, 5715 (1956).

(24) Cf. K. Moedritzer, L. Maier, and L. C. D. Groenweghe, *J. Chem. Eng. Data*, **7**, 307 (1962).

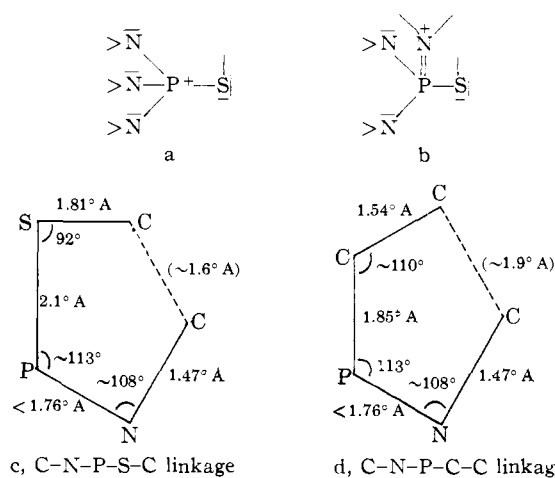
irradiation to just about the ratio of $H^1:P^{31}$ frequencies, *i.e.*, by a factor of 2.5. This was to be expected from the maximum Overhauser enhancement but implied that there was some P-H coupling. It could mean that there was a rapid exchange of the NH_2 protons in solution. Such an exchange could wash out the splitting (expected to give two lines) yet possibly still give the enhancement. This splitting also was not observed in the H^1 spectrum, but the NH_2 line was not sharp. The P^{31} splittings of the onium derivatives of the nucleophile A were as expected if only the NH_2 protons were decoupled but not resolved otherwise. The δ -values of compound A itself and the δ -shifts produced by N-methylation and S-alkylation were rather interesting. The δ -value of $(H_2N)_3PS$ was found to be practically identical with the δ -value of the well-known nucleophile $(CH_3)_3PS$. Monomethylation of the nitrogen atoms of compound A, to form compound B, caused a δ -shift of 9.4 p.p.m. while complete N-methylation (to form compound H) gave a δ -shift of 22.3 p.p.m. Thus, the substitution of a methyl group for a hydrogen atom in the amidothionate A decreased the positive charge on phosphorus by an amount approximately equivalent to 3.7 ± 0.6 p.p.m. Formation of the onium compounds I-V from compound A increased the positive charge on phosphorus by an approximately constant amount corresponding to a δ -shift of 8.7 ± 1.1 p.p.m. In general, however, the δ -shifts caused by onium formation varied between 7.6 and 14.9 p.p.m. This was of interest in regard to the previously reported finding that changes in P^{31} shifts, as produced by attachment of groups of different structure to quadruply connected phosphorus, were not found to be additive.²⁵

The H^1 spectra of the compounds containing amido protons showed the following picture. The NH group was more shielded in the nucleophile B than in nucleophile D; the amidoproton was found to be nearly coincident with the methyl protons. In pyridine solution it was removed from under the methyl group to a position corresponding to -4.4 p.p.m., which was nearly midway between its positions in the nonquaternized nucleophile (-2.5 p.p.m.) and the quaternized derivatives VIII and IX (-5.9 ± 0.21 p.p.m.). Quaternization of the phosphorotriamidothionates caused the amido protons to be shifted about 3 p.p.m. toward less electronic shielding. These shifts clearly indicated that the quaternization increased the positive charge not only on phosphorus but also on nitrogen. The position of the NH groups in the proton spectra was between their positions in amides and ammonium salts. According to this evidence, the location of the positive charge in the cations of the onium compounds discussed was distributed over both the phosphorus atom as well as the nitrogen atom. The proton spectra of the onium compounds I-V were as expected, with the exception of the spectrum of compound V. There was some evidence that could suggest the possibility of V consisting of stereoisomers. The work necessary to decide this was considered to be beyond the scope of this investigation.

Structure of the Onium Cations.—According to the chemical and spectroscopic evidence described, the structure of the cations of the onium compounds I-XXVI is a resonance hybrid of the two valence-bond structures, a and b predominantly. Contribution from a sulfonium form has not been apparent.

The structure of the onium cation formed is of importance in regard to the extent of steric interference presumed to occur in the reaction of the completely N-substituted nucleophiles H through N. The C-N-P-S-C linkage of the onium cation has the shape of an

(25) *Cf.* ref. 21, 22.



c, C-N-P-S-C linkage
d, C-N-P-C-C linkage
Bond lengths and valence angles of onium cations (approximate values).

open pentagon, as shown in c, if this linkage is projected into a plane. The three valence angles at P, N, and C have values of about $111 \pm 3^\circ$.^{26,27} The P-S-C angle, however, is likely to have a value of $91-92^\circ$.²⁷ This would give an approximate length of 1.6 Å. for the shortest possible distance between the two carbon atoms, if the P-N bond is not appreciably shortened by π -bond contribution.

In contrast to the lack of reactivity of $[(CH_2)_5N]_3P(S)$, the desulfurized nucleophile $[(CH_2)_5N]_3P$ reacts rapidly with alkyl halides.²⁸ The C-N-P-C-C linkage formed in this case has the shape of d when projected into a plane. The shortest possible distance between the terminal carbon atoms of this linkage is about 1.9 Å. long. Consequently, the steric limitations operative in the case of reaction 2 arise not only from the size and shape of the hydrocarbon groups involved but also from the size of the valence angle produced at the sulfur atom in the onium cation.

Experimental

The alkyl halides were obtained by redistillation of commercially available products.

N',N'' -Bis(pentamethylenethiourea) was prepared by addition of a solution of thiophosgene (0.575 g.-mole) in benzene (1 l.) at 5° to an agitated solution of piperidine (3 g.-moles) in benzene (0.4 l.) and keeping the reaction mixture for 0.5 hr. at 50° . The mixture was filtered and the benzene layer washed with water until the aqueous layer showed a neutral pH. Evaporation of benzene from the organic layer and repeated crystallization of the evaporation residue from ligroin ($30-60^\circ$) gave 85 g. (70%) of almost white crystals (m.p. $59-60^\circ$) of $[(CH_2)_5N]_2CS$.

Anal. Calcd. for $C_{11}H_{20}N_2S$: N, 13.2. Found: N, 13.0.

Phosphorotriamidothionates were prepared by the reaction of phosphorus pentasulfide and phosphorochloridothionates with amines.

Compound F was obtained by addition of a solution of *p*-chloroaniline (3.3 g.-moles) in benzene (1.5 l.) to an agitated suspension of phosphorus pentasulfide (0.5 g.-mole) in benzene (0.5 l.) at room temperature, followed by refluxing the reaction mixture for 3 hr. Benzene was removed by distillation at atmospheric pressure until the pot temperature was 175° . The hydrogen sulfide released during these operations was trapped in 5% aqueous sodium hydroxide solution. The crude main product was extracted three times with boiling toluene (1.5 l. each time) to remove unreacted amine and to leave a white solid which was crystallized from ethanol. This afforded 410 g. (93%) of $(4-ClC_6H_4NH_3)PS$, m.p. $221-222^\circ$ (lit.²⁹ $225-226^\circ$).

The nucleophiles A, D, E, and N were prepared by complete amidation of $PSCl_3$ involving addition of 1 g.-mole of this chloride

(26) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 38, 39, 292, 295, 306.

(27) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Engl. Translation, Butterworths Scientific Publications, London, 1950, pp. 72-75.

(28) First reported by A. Michaelis and K. Luxembourg, *Ber.*, **28**, 2205 (1895).

(29) A. C. Buck, J. D. Bartleson, and H. P. Lankelma, *J. Am. Chem. Soc.*, **70**, 744 (1948).

with agitation to liquid ammonia (20 g.-moles, at below -40°), cyclohexylamine (8 g.-moles, at $+6^\circ$), benzylamine (7 g.-moles diluted with 4 l. of ligroin, at room temperature), and piperidine (8 g.-moles, at $+6^\circ$). Run A was kept agitated for 10 hr. at below -40° and then slowly warmed to room temperature to remove excess of ammonia. Then chloroform (1.5 l.) and diethylamine (4 g.-moles) was added and the reaction mixture refluxed with agitation for 6 hr. to convert the ammonium chloride by-product to chloroform-soluble diethylamine hydrochloride.^{30a,b} The chloroform-insoluble triamidothiophosphate was isolated by filtration and crystallized from methanol to give 90 g. (81%) of white needles of $(\text{H}_2\text{N})_3\text{PS}$, m.p. $120-121^\circ$. The reaction mixtures of the runs D and N were agitated for 20 hr. at room temperature and for 20 hr. at about 100° . Then they were extracted with 1 l. of 2 N HCl to remove excess of unreacted amine and crystallized from ethanol to yield 306 g. (86%) of $(\text{C}_6\text{H}_{11}\text{NH})_3\text{PS}$, m.p. $142-143^\circ$ (lit.³¹ $143.5-144.5^\circ$), and 279 g. (88.5%) of $[(\text{CH}_3)_2\text{N}]_3\text{PS}$, m.p. 120° (lit.³¹ $120-122^\circ$), respectively. The reaction mixture of run E was refluxed for 6 hr., and the precipitate formed was isolated by filtration. Its weight (820 g.) indicated it to be a mixture of the main product E and benzylamine hydrochloride. The precipitate was dissolved in ethanol (2 l.) and water (3 l.) added to the solution. This produced precipitation of crude E which was isolated and crystallized from ethanol to give 350 g. (92%) of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH})_3\text{PS}$, m.p. $125-126^\circ$ (lit.²⁹ $125-126^\circ$).

Anal. Calcd. for $\text{H}_5\text{N}_3\text{PS}$ (A): N, 37.8. Found: N, 37.3. Calcd. for $\text{C}_{18}\text{H}_{36}\text{N}_3\text{PS}$ (D): N, 11.76. Found: N, 11.6. Calcd. for $\text{C}_{21}\text{H}_{24}\text{N}_3\text{PS}$ (E): N, 11.03. Found: N, 10.9. Calcd. for $\text{C}_{18}\text{H}_{15}\text{Cl}_3\text{N}_3\text{PS}$ (F): N, 9.54. Found: N, 9.4. Calcd. for $\text{C}_{15}\text{H}_{30}\text{N}_3\text{PS}$ (N): N, 13.31. Found: N, 13.1.

The phosphoramidodithionates B, C, G, L, and M were prepared by dropwise addition of the appropriate phosphoramidodichlorodithionates (1 g.-mole) to amides, which were refluxing at atmospheric pressure, at a mole ratio of 1:10 in the absence of inert diluents. The reaction mixture formed from N-methyl phosphoramidodichlorodithionate and methylamine was agitated for 10 hr. at -5° , diluted with ether (0.7 l.), allowed to warm to room temperature, and then filtered. The precipitate isolated was extracted with chloroform (1.5 l.). The combined ether and chloroform solutions were evaporated and the evaporation residue crystallized from benzene to give 113 g. (74%) of $(\text{CH}_3\text{NH})_3\text{PS}$, m.p. $107-108^\circ$. The reaction mixtures formed from N-ethyl phosphoramidodichlorodithionate with ethylamine (run C) and dimethylamine (run G) were agitated for 30 hr., allowed to warm to room temperature, and diluted with benzene (1.6 l.). Run C was evaporated to leave a solid residue which was extracted with chloroform and the chloroform extract evaporated. The residue was crystallized from cyclohexane to produce 163 g. (83.5%) of ether-soluble $(\text{C}_2\text{H}_5\text{NH})_3\text{PS}$, m.p. $66-67^\circ$ (lit.¹² 68°). Run G was filtered and the filtrate evaporated. The evaporation residue was dissolved in cyclohexane (1.5 l.), washed with water, and the organic layer again evaporated. This left 189 g. (97%) of $\text{C}_2\text{H}_5\text{NHP}(\text{S})[\text{N}(\text{CH}_3)_2]_2$ as an almost colorless oil. The reaction mixture formed from N,N-dibenzyl phosphoramidodichlorodithionate, $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{NPSCl}_2$ (m.p. $60-62^\circ$ from glacial acetic acid), and dimethylamine was found to contain 1 g.-mole of dimethylamine hydrochloride after a reaction time of 20 hr. The formation of 2 g.-moles of this salt, as necessary for completion of the reaction, required about 150 hr. This indicated steric interference during the replacement of the second chlorine by a dimethylamido group. Run L was worked up analogous to run G and the crude main product crystallized from isopropyl alcohol to give 69.5 g. (20%) of $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{NP}(\text{S})[\text{N}(\text{CH}_3)_2]_2$, m.p. $86-87^\circ$. The preparation of hexaethyl phosphorotriamidodithionate (M) from N,N-diethyl phosphoramidodichlorodithionate and diethylamine at a mole ratio of 1:10 at reflux in the absence of inert diluents was complicated by steric interference even more so than run L and did not give a product of satisfactory purity. Compound M was conveniently prepared, however, by sulfuration of $[(\text{C}_2\text{H}_5)_2\text{N}]_3\text{P}$ as described in the literature.³²

Anal. Calcd. for $\text{C}_3\text{H}_{12}\text{N}_3\text{PS}$ (B): N, 27.5. Found: N, 27.2. Calcd. for $\text{C}_6\text{H}_{18}\text{N}_3\text{PS}$ (C): N, 21.5. Found: N, 21.4. Calcd. for $\text{C}_9\text{H}_{24}\text{N}_3\text{PS}$ (G): N, 21.5. Found: N, 21.3. Calcd. for $\text{C}_{18}\text{H}_{26}\text{N}_3\text{PS}$ (L): N, 12.1. Found: N, 11.9. Calcd. for $\text{C}_{12}\text{H}_{30}\text{N}_3\text{PS}$ (M): N, 15.1. Found: N, 14.9.

The amidodithionate nucleophiles H, J, and K were obtained by dropwise addition of tetramethyl phosphorochlorodiamidodithionate, $[(\text{CH}_3)_2\text{N}]_2\text{P}(\text{S})\text{Cl}_2$ (1 g.-mole), to dimethylamine, diethylamine, and piperidine, respectively, at a mole ratio of 1:4 in the absence of inert diluents. The reaction temperature of run H was $+5^\circ$, and the reaction time after completed addition was 5 hr. The reaction mixture was diluted with ligroin ($60-70^\circ$, 2.8 l.) and filtered. The filtrate was evaporated and left 182 g.

(93.5%) of white crystals of $[(\text{CH}_3)_2\text{N}]_3\text{PS}$, m.p. 30° . Run J required a reaction time of 75 hr. to go to completion at the reaction temperature of $70-80^\circ$. The reaction mixture was diluted with ligroin ($60-70^\circ$) and washed with dilute acid and water to remove unreacted amine. After separation, drying, and evaporation of the organic layer there was obtained 163 g. (73%) of crude $(\text{C}_2\text{H}_5)_2\text{NP}(\text{S})[\text{N}(\text{CH}_3)_2]_2$ as a brownish oil which upon fractionation had a boiling range of $108-111^\circ$ at 1 mm. pressure. The addition of the monochloride to piperidine in run K was carried out at $25-30^\circ$ and the resulting reaction mixture kept agitated at 50° for 20 hr. After cooling to room temperature, the mixture was diluted with ligroin ($60-70^\circ$, 1.5 l.) and washed with dilute acid and water to remove piperidine hydrochloride. The organic layer was separated, dried, and evaporated to leave 195 g. (83%) of $(\text{CH}_2)_5\text{NP}(\text{S})[\text{N}(\text{CH}_3)_2]_2$ as a brown oil.

Anal. Calcd. for $\text{C}_8\text{H}_{18}\text{N}_3\text{PS}$ (H): N, 21.5. Found: N, 21.2. Calcd. for $\text{C}_9\text{H}_{22}\text{N}_3\text{PS}$ (J): N, 18.84. Found: N, 18.5. Calcd. for $\text{C}_9\text{H}_{22}\text{N}_3\text{PS}$ (K): N, 17.85. Found: N, 17.4.

Iodomethylmercaptotriaminophosphoranes, $([\text{>N}]_3\text{PSC}_2\text{H}_5)^+\text{I}^-$.—Mixtures of methyl iodide (1.5 g.-moles) and the nucleophiles A, H, J, K, and M (0.15 g.-mole each) were heated to reflux with agitation for 100, 2, 1, 60, and 24 hr., respectively. The reaction mixture were filtered and the precipitate dissolved in dimethylformamide (50–100 ml.). Addition of ether (0.5–1.0 l.) to these solutions caused precipitation of the iodophosphorane main products. By filtration the following compounds were isolated: $[(\text{H}_2\text{N})_3\text{PSC}_2\text{H}_5]^+\text{I}^-$ (I, 35 g., 92.5%, m.p. $159-160^\circ$), $\{[(\text{CH}_3)_2\text{N}]_3\text{PSC}_2\text{H}_5\}^+\text{I}^-$ (XVI, 47.5 g., 94%, m.p. $143-5^\circ$), $\{[(\text{CH}_3)_2\text{N}]_2[\text{C}_2\text{H}_5]_2\text{NPSC}_2\text{H}_5\}^+\text{I}^-$ (XVIII, 20.8 g., 38%, m.p. $103-105^\circ$), $\{[(\text{CH}_3)_2\text{N}]_2[\text{C}_2\text{H}_5\text{NH}]_2\text{PSC}_2\text{H}_5\}^+\text{I}^-$ (XIX, 11.3 g., 20%, m.p. $130-132^\circ$), and $\{[(\text{C}_2\text{H}_5)_2\text{N}]_3\text{PSC}_2\text{H}_5\}^+\text{I}^-$ (XX, 3.2 g., 5%, m.p. $82-83^\circ$), respectively.

Anal. Calcd. for $\text{CH}_5\text{IN}_3\text{PS}$ (I): I, 50.15; N, 16.61; P, 12.24; S, 12.67. Found: I, 49.4; N, 16.28; P, 11.9; S, 12.46. Calcd. for $\text{C}_7\text{H}_{21}\text{IN}_3\text{PS}$ (XVI): I, 37.65; N, 12.46; P, 9.21; S, 9.51. Found: I, 37.2; N, 11.94; P, 8.83; S, 10.16. Calcd. for $\text{C}_9\text{H}_{25}\text{IN}_3\text{PS}$ (XVIII): I, 34.75; N, 11.52; P, 8.51; S, 8.78. Found: I, 34.5; N, 11.75; P, 8.15; S, 8.61. Calcd. for $\text{C}_{10}\text{H}_{25}\text{IN}_3\text{PS}$ (XIX): I, 33.65; N, 11.13; P, 8.23; S, 8.5. Found: I, 33.67; N, 12.15; P, 7.90; S, 8.56. Calcd. for $\text{C}_{13}\text{H}_{33}\text{IN}_3\text{PS}$ (XX): I, 30.2; N, 9.98; P, 7.36; S, 7.6. Found: I, 29.5; N, 9.57; P, 7.03; S, 7.40.

Mixtures containing methyl iodide (1.5 g.-mole) and the amidodithionates L and N (0.15 g.-mole each) were refluxed with agitation for 100 hr. Since no precipitates were formed, the reaction mixtures were evaporated to dryness and gave solid residues which were identified as unreacted starting products by infrared analysis. Recrystallization of these residues gave 47.0 g. (90.5% recovery) of L (m.p. $85-87^\circ$ from *i*- $\text{C}_2\text{H}_5\text{OH}$) and 40.7 g. (86% recovery) of N (m.p. $119-120^\circ$ from $\text{C}_2\text{H}_5\text{OH}$). The same result was obtained after refluxing a reaction mixture of compound N (0.15 g.-mole), CH_3I (1.5 g.-moles), and nitromethane (1.5 g.-moles) for 100 hr.

Iodoethylmercaptotriaminophosphoranes, $([\text{>N}]_3\text{PSC}_2\text{H}_5)^+\text{I}^-$.—Mixtures of ethyl iodide (1.0 g.-mole) and the nucleophiles A, B, C, E, and G (0.1 g.-mole each) were heated to reflux with agitation for 100, 160, 110, 170, and 40 hr., respectively, while the mixture containing ethyl iodide (1.5 g.-moles) and the nucleophile D (0.1 g.-mole) was treated in the same manner for 110 hr. The mixture consisting of ethyl iodide (0.5 g.-mole) and compound H (0.1 g.-mole) was kept agitated for 40 hr. at a temperature of 50° . The solid reaction products formed in these reactions were thoroughly triturated in ether, filtered, and dried. Obtained were: $[(\text{H}_2\text{N})_3\text{PSC}_2\text{H}_5]^+\text{I}^-$ (II, 25 g., 94%, m.p. $162-163^\circ$), $\{[(\text{CH}_3\text{NH})_3\text{PSC}_2\text{H}_5]^+\text{I}^-$ (VI, 26.6 g. of yellow-colored crystals, 86%, m.p. $52-54^\circ$), $\{[(\text{C}_2\text{H}_5\text{NH})_3\text{PSC}_2\text{H}_5]^+\text{I}^-$ (X, 26.6 g. of yellow-colored crystals, 74%, m.p. $72-74^\circ$), $\{[(\text{C}_6\text{H}_5\text{CH}_2\text{NH})_3\text{PSC}_2\text{H}_5]^+\text{I}^-$ (XIV, 45 g., 84%, m.p. $104-106^\circ$), $\{[(\text{CH}_3)_2\text{N}]_2[\text{C}_2\text{H}_5\text{NH}]_2\text{PSC}_2\text{H}_5\}^+\text{I}^-$ (XXI, 30.5 g. of an oil, 87%), $\{[(\text{C}_6\text{H}_{11}\text{NH})_3\text{PSC}_2\text{H}_5]^+\text{I}^-$ (XI, 47 g., 92%, m.p. $144-145^\circ$), and $\{[(\text{CH}_3)_2\text{N}]_3\text{PSC}_2\text{H}_5\}^+\text{I}^-$ (XVII, 14.4 g., 41%, m.p. $131-133^\circ$), respectively.

Anal. Calcd. for $\text{C}_2\text{H}_{11}\text{IN}_3\text{PS}$ (II): I, 47.52; N, 15.73; P, 11.61; S, 12.01. Found: I, 47.6; N, 15.76; P, 11.52; S, 11.92. Calcd. for $\text{C}_5\text{H}_{17}\text{IN}_3\text{PS}$ (VI): I, 41.05; N, 13.58; P, 10.02; S, 10.36. Found: I, 41.1; N, 13.41; P, 9.68; S, 11.06. Calcd. for $\text{C}_9\text{H}_{23}\text{IN}_3\text{PS}$ (X): I, 36.15; N, 11.97; P, 8.83; S, 9.12. Found: I, 35.9; N, 11.46; P, 8.64; S, 9.63. Calcd. for $\text{C}_{20}\text{H}_{41}\text{IN}_3\text{PS}$ (XI): I, 24.75; N, 8.18; P, 6.05; S, 6.24. Found: I, 24.1; N, 7.89; P, 5.94; S, 6.65. Calcd. for $\text{C}_{23}\text{H}_{29}\text{IN}_3\text{PS}$ (XIV): I, 23.61; N, 7.82; P, 5.78; S, 5.97. Found: I, 23.0; N, 7.17; P, 5.66; S, 6.42. Calcd. for $\text{C}_9\text{H}_{23}\text{IN}_3\text{PS}$ (XXI): I, 36.15; N, 11.97; P, 8.83; S, 9.12. Found: I, 36.5; N, 10.73; P, 8.75; S, 9.15. Calcd. for $\text{C}_8\text{H}_{23}\text{IN}_3\text{PS}$ (XVII): I, 36.15; N, 11.97; P, 8.83; S, 9.12. Found: I, 35.4; N, 11.54; P, 8.53; S, 9.67.

Mixtures consisting of ethyl iodide (2.0 g.-mole) and the amidodithionates F, M, and N (0.2 g.-mole each) were agitated for 240,

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(31) L. F. Audrieth and A. D. F. Toy, *J. Am. Chem. Soc.*, **64**, 1553 (1942).

(32) C. Stuebe and H. P. Lankelma, *ibid.*, **78**, 976 (1956).

90, and 140 hr., respectively, at reflux temperature (in the case of F) and at 45° (in the case of M and N). The residues isolated after complete evaporation of ethyl iodide from the reaction mixture were by infrared analysis found to be the unreacted starting product, recovered in amounts of 91–94% by weight.

Bromoallylmercaptotriaminophosphoranes, $[(>N)_3PSC_3H_5]^+Br^-$.—Mixtures containing allyl bromide (1.5 g.-moles) and the nucleophiles A, B, D, and G (0.15 g.-mole each) were refluxed with agitation for 125, 170, 170, and 60 hr., respectively. The reaction mixtures were worked up like those obtained with ethyl iodide (*vide supra*). Obtained were: $[(H_2N)_3PSC_3H_5]^+Br^-$ (III, 33.7 g., 97%, m.p. 171–172°), $[(CH_3NH)_3PSC_3H_5]^+Br^-$ (VII, 40.7 g., 99%, m.p. 86–88°), $[(C_6H_{11}NH)_3PSC_3H_5]^+Br^-$ (XII, 69 g., 96%, m.p. 112–114°), and $\{[(CH_3)_2N]_2(C_2H_5NH)PSC_3H_5\}^+Br^-$ (XXII, 38 g., oil, 81%), respectively.

Anal. Calcd. for $C_3H_{11}BrN_3PS$ (III): Br, 34.43; N, 18.10; S, 13.82. Found: Br, 34.8; N, 18.35; S, 13.95. Calcd. for $C_6H_{17}BrN_3PS$ (VII): Br, 29.15; N, 15.33; S, 11.70. Found: Br, 30.0; N, 14.57; S, 10.99. Calcd. for $C_{21}H_{43}BrN_3PS$ (XII): Br, 16.70; N, 8.78; S, 6.70. Found: Br, 16.9; N, 8.91; S, 7.04. Calcd. for $C_9H_{23}BrN_3PS$ (XXII): Br, 25.43; N, 13.37; S, 10.20. Found: Br, 25.85; N, 13.76; S, 10.47.

Mixtures composed of allyl bromide (1.0 g.-mole) and the compounds H and N (0.15 g.-mole each) were heated to reflux with agitation for 50 and 200 hr., respectively. After complete evaporation of unreacted allyl bromide from the reaction mixtures the evaporation residues were by infrared analysis identified as unreacted starting products.

Bromo-*n*-propylmercaptotriaminophosphoranes, $[(>N)_3PSC_3H_7]^+Br^-$.—Mixtures consisting of *n*-propyl bromide (1.5 g.-moles) and the nucleophiles A, B, D, E, and G (0.15 g.-mole each) were refluxed for 100, 200, 170, 115, and 100 hr., respectively, with agitation and the resulting reaction mixture was worked up like those formed with ethyl iodide (*vide supra*). Obtained were: $[(H_2N)_3PSC_3H_7-n]^+Br^-$ (IV, 32.7 g., 93%, m.p. 163–164°), $[(CH_3NH)_3PSC_3H_7-n]^+Br^-$ (VIII, 38.8 g., 94%, m.p. 74–76°), $[(C_6H_{11}NH)_3PSC_3H_7-n]^+Br^-$ (XIII, 70.5 g., 98%, m.p. 128–130°), $[(C_6H_5-CH_2NH)_3PSC_3H_7-n]^+Br^-$ (XV, 73.5 g., 97%, m.p. 112–113°), and $\{[(CH_3)_2N]_2(C_2H_5NH)PSC_3H_7-n\}^+Br^-$ (XXIII, 46.5 g., oil, 98%), respectively.

Anal. Calcd. for $C_3H_{13}BrN_3PS$ (IV): Br, 34.14; N, 17.95; S, 13.70. Found: Br, 34.5; N, 17.78; S, 13.84. Calcd. for $C_6H_{19}BrN_3PS$ (VIII): Br, 28.94; N, 15.22; S, 11.61. Found: Br, 29.1; N, 15.26; S, 12.1. Calcd. for $C_{21}H_{43}BrN_3PS$ (XIII): Br, 16.63; N, 8.75; S, 6.67. Found: Br, 16.6; N, 9.52; S, 7.05. Calcd. for $C_{24}H_{51}BrN_3PS$ (XV): Br, 15.84; N, 8.33; S, 6.36. Found: Br, 16.1; N, 8.35; S, 6.74. Calcd. for $C_9H_{25}BrN_3PS$ (XXIII): Br, 25.27; N, 13.29; S, 10.14. Found: Br, 26.40; N, 13.52; S, 10.84.

Mixtures of *n*-propyl bromide (1.0 g.-mole) and the compounds F and H (0.1 g.-mole each) were heated at reflux temperature with agitation for 170 and 130 hr., respectively. The solids isolated from the reaction mixtures after complete removal of unreacted propyl bromide were found to consist of unreacted starting products, according to infrared analysis.

Bromoisopropylmercaptotriaminophosphoranes, $[(>N)_3PSC_3H_7-i]^+Br^-$.—Mixtures containing isopropyl bromide (1.0 g.-mole)

and the nucleophiles B, D, and E (0.1 g.-mole each) were heated with agitation to reflux for 160, 160, and 115 hr., respectively. The reaction mixtures produced were worked up as described with ethyl iodide (*vide supra*). Obtained were: $[(CH_3NH)_3PSC_3H_7-i]^+Br^-$ (XXIV, 23 g., 83%, m.p. 98–100°), $[(C_6H_{11}NH)_3PSC_3H_7-i]^+Br^-$ (XXV, 41.7 g., 87%, m.p. 120–122°), and $[(C_6H_5-CH_2NH)_3PSC_3H_7-i]^+Br^-$ (XXVI, 38 g., 75%, m.p. 122–124°), respectively.

Anal. Calcd. for $C_6H_{19}BrN_3PS$ (XXIV): Br, 28.94; N, 15.22; S, 11.61. Found: Br, 28.7; N, 14.98; S, 11.98. Calcd. for $C_{21}H_{43}BrN_3PS$ (XXV): Br, 16.63; N, 8.75; S, 6.67. Found: Br, 16.4; N, 9.34; S, 7.12. Calcd. for $C_{24}H_{51}BrN_3PS$ (XXVI): Br, 15.84; N, 8.33; S, 6.36. Found: Br, 15.9; N, 8.16; S, 6.71.

Mixtures of isopropyl bromide (1.0 g.-mole) and the compounds A, F, H, and N (0.1 g.-mole each) were heated at reflux temperature with agitation for 150 hr. The solid residues isolated by unreacted isopropyl bromide gave infrared spectra that were identical with the spectra of the phosphorothionates used as starting products.

Chlorobenzylmercaptotriaminophosphoranes, $[(>N)_3PSC_2C_6H_5]^+Cl^-$.—Mixtures composed of benzyl chloride (0.5 g.-mole) and the nucleophiles A and B (0.1 g.-mole each) were heated with agitation for 130 hr. at 95° and, respectively, for 170 hr. at 75°. After this treatment the mixtures were diluted with ligroin (0.5 l., b.p. 60–70°) and filtered. The solids thus isolated were dissolved in dimethylformamide (100 ml.) and the resulting solution diluted with ether (1 l.) to precipitate the onium derivatives. Obtained were: $[(H_2N)_3PSC_2C_6H_5]^+Cl^-$ (V, 16.6 g., 70%, m.p. 144–146°) and $[(CH_3NH)_3PSC_2C_6H_5]^+Cl^-$ (IX, 24.3 g., 87%, m.p. 156–158°).

Anal. Calcd. for $C_7H_{13}ClN_3PS$ (V): Cl, 14.92; N, 17.68; S, 13.49. Found: Cl, 14.7; N, 17.67; S, 13.67. Calcd. for $C_{10}H_{17}ClN_3PS$ (IX): Cl, 12.67; N, 15.02; S, 11.46. Found: Cl, 12.8; N, 14.67; S, 11.57.

A solution of compound N (0.1 g.-mole) in benzyl chloride (0.5 g.-mole) was heated with agitation at 75° for 170 hr. and then treated with ligroin as described with the compounds A and B. This caused formation of a precipitate which was identified as unreacted N (recovered in 20% yield).

Reaction with *t*-Butyl Bromide.—This bromide (1.3 g.-moles) was heated to reflux at atmospheric pressure with agitation in the presence of the compounds E, F, H, N, and $[(CH_3)_2N]_3PO$ (0.1 g.-mole each). It was noticed that the reaction caused a rather steady evolution of a gas which was collected in a Dry Ice trap connected with the reflux condenser. This gas was by infrared analysis found to be isobutylene and was recovered in quantities of 0.54–0.6 g.-mole, after a total reaction time of 200 hr. The reaction mixture formed by this reaction was diluted with the threefold volume of ligroin (b.p. 60–70°) and filtered. The salts thus isolated from the five experiments were identified as the hydrobromides of benzylamine, *p*-chloroaniline, diethylamine, piperidine, and dimethylamine, respectively. They were recovered in quantities of 0.25–0.3 g.-mole. The filtrate was fractionated under reduced pressure and gave $PSBr_3$ (b.p. 84° at 10 mm.) in quantities of 18–24 g. The run involving the compound $[(CH_3)_2N]_3PO$ gave 20 g. of phosphoryl bromide.

The melting points given were not corrected.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE STATE UNIVERSITY OF NEW YORK AT STONY BROOK, N. Y., AND THE ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO, ILL.]

Organic Compounds with Pentavalent Phosphorus. VIII.¹ Cyclic Unsaturated Oxyphosphoranes from the Reaction of Tertiary Phosphite Esters with *o*-Quinones and with α -Diketones

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Tertiary phosphite esters, $(RO)_3P$, react with *o*-quinones and with α -diketones, yielding 1:1 adducts. Six crystalline and three liquid adducts are described. The reactions are exothermic and the products are obtained in nearly quantitative yield. The adducts are stable, if protected against moisture and oxygen. The infrared, Raman, P^{31} n.m.r., and H^1 n.m.r. spectra suggest that the 1:1 adducts have a cyclic unsaturated oxyphosphorane structure, in which five oxygen atoms are covalently bound to phosphorus.

A phosphorus–oxygen bond is formed in the reaction of triphenylphosphine with the substituted *p*-quinone

chloranil; however, a phosphorus–carbon bond is established in the reaction of this phosphine with *p*-benzo-

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