

## Reactions of 4,5-Dicyano-1,3-dithiole-2-thione and -1,3-dithiol-2-one with Tervalent Phosphorus Compounds

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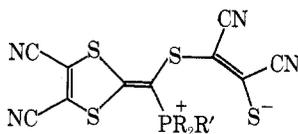
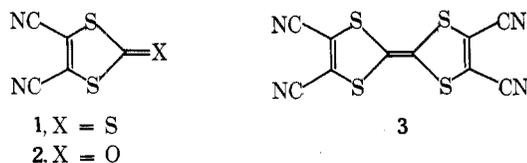
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In contrast to other reported reactions of 1,3-dithiol-2-ones and 1,3-dithiole-2-thiones with tervalent phosphorus compounds, which yield only tetrathiafulvalenes, the reaction of 4,5-dicyano-1,3-dithiole-2-thione (1) and -1,3-dithiol-2-one (2) with phosphines and phosphites is complex. Either tetracyanotetrathiafulvalene [ $\Delta^{2,2'}$ -bi(4,5-dicyano-1,3-dithiolidene)] (3), a betaine {(4,5-dicyano-1,3-dithiol-2-ylidene)methylene [tri(substituents)phosphonio](-2-thio-1-mercaptomaleonitrilate)} (4), or a dialkyl (4,5-dicyano-1,3-dithiol-2-yl)phosphonate may be formed, depending on the choice of reactant and conditions. In addition, Wittig-type products are formed on addition of aryl aldehydes to the reaction mixture. All of these products can be rationalized by means of a reaction scheme which assumes the ylide 4,5-dicyano-1,3-dithiolidenetri(substituent)phosphorane to be the key intermediate. Only tetracyanotetrathiafulvalene was isolated from the reaction of trimethyl phosphite with either 1 or 2 and tris(*p*-chlorophenyl)phosphine with 1, but reactions of other triarylphosphines and methyl diphenylphosphinite with 1 yielded varying amounts of fulvalene and betaine. Phosphorus trichloride, triphenyl phosphite, and triphenylarsine did not react with 1. The stoichiometric reaction of triphenylphosphine, 1, and terephthalaldehyde gave a near-quantitative yield of 2,2'-*p*-xylylidenebis(4,5-dicyano-1,3-dithiole) (8), which undergoes a reversible, electrochemical oxidation at  $E_p = 1.07$  V (vs. SCE) and an irreversible oxidation at  $E_p = 1.39$  V. With benzaldehyde under these conditions, however, both 4 and 2-benzylidene-4,5-dicyano-1,3-dithiole were isolated. The novel ester dimethyl (4,5-dicyano-1,3-dithiol-2-yl)phosphonate was isolated from a reaction of trimethyl phosphite plus 2 in the presence of benzoic acid.

Interest in the salts and charge-transfer compounds of tetrathiafulvalenes<sup>1</sup> prompted us to investigate the possibility of preparing cyano-substituted derivatives by means of desulfurization of 4,5-dicyano-1,3-dithiole-2-thione (1)



- 4a, R = C<sub>6</sub>H<sub>5</sub>; R' = CH<sub>3</sub>  
b, R = R' = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
c, R = R' = *m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
d, R = R' = C<sub>6</sub>H<sub>5</sub>  
e, R = C<sub>6</sub>H<sub>5</sub>; R' = CH<sub>3</sub>O

with phosphorus(III) compounds. Several reports have appeared in which clean, high-yield conversions of various

1,3-dithiole-2-thiones to  $\Delta^{2,2'}$ -bi(1,3-dithiolidenes)<sup>2</sup> and 1,3-diselenole-2-thiones to  $\Delta^{2,2'}$ -bi(1,3-diselenolidenes)<sup>3</sup> by the action of phosphines and phosphites have been described, and Corey and Märkl<sup>4</sup> have reported a Wittig-type reaction between trithiocarbonates, aldehydes, and trialkyl phosphites. We have found that the reactions of 1 under these conditions are more complex than those of other trithiocarbonates, and report our results here.

### Results

The thione 1 was allowed to react with 11 different phosphines and phosphites and triphenylarsine. The results appear in Table I. Three different products could be isolated from the reaction of triphenylphosphine with 1 at different temperatures: at 25°, an adduct of composition C<sub>6</sub>S<sub>4</sub>(CN)<sub>4</sub>(Ph<sub>3</sub>P)<sub>2</sub>S, 5, can be isolated in good yield; at 60–80°, a product identified as the betaine (4,5-dicyano-1,3-dithiol-2-ylidene)methylene (triphenylphosphonio)(2-thio-1-mercaptomaleonitrilate) (4d) is obtained (and, in fact, at that temperature 5 transforms quantitatively into 4); at 125°,  $\Delta^{2,2'}$ -bi(4,5-dicyano-1,3-dithiolidene) (3) is slowly formed. Tri-*n*-butylphosphine reacts with 1 at 0° in toluene to give a mixture of products including tri-*n*-butyl phosphine sulfide, identified by its <sup>31</sup>P NMR and mass

**Table I**  
**Reaction Products of 4,5-Dicyano-1,3-dithiole-2-thione with Phosphines and Phosphites**

Reactant, R <sub>2</sub> R'P		Registry no.	% Products, isolated yield		
R	R'		3	4	Other
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	1486-28-8		20	
C <sub>6</sub> H <sub>5</sub>	-CH <sub>2</sub> -	2071-20-7		49 <sup>a</sup>	
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	855-38-9		39	
<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	6224-63-1		45	
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	603-35-0	25 <sup>b</sup>	46-85 <sup>c</sup>	5, 70% <sup>d</sup>
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	1159-54-2	25		
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> O	4020-99-9		30	
CH <sub>3</sub> O	CH <sub>3</sub> O	121-45-9	25-30		
C <sub>6</sub> H <sub>5</sub> O	C <sub>6</sub> H <sub>5</sub> O	101-02-0			No reaction observed
Cl	Cl	7719-12-2			No reaction
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> <sup>e</sup>	603-32-7			No reaction

<sup>a</sup> Product Ph<sub>2</sub>PSCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>S-adduct. <sup>b</sup> Conditions: 2 hr at 125° in *o*-dichlorobenzene. <sup>c</sup> Higher yield, 2 hr at 60° in benzene; lower, 12 hr at 80° in cyclohexane (also 3% 3). <sup>d</sup> Conditions: 1 hr at 25° in benzene. <sup>e</sup> Triphenylarsine.

**Table II**  
**<sup>31</sup>P Chemical Shifts of Compounds 4**

R <sub>2</sub> R'PC <sub>6</sub> S <sub>4</sub> (CN) <sub>4</sub>	δ <sup>a</sup>	Δδ <sup>b</sup>
4a, R = C <sub>6</sub> H <sub>5</sub> ; R' = CH <sub>3</sub>	91.5 <sup>c</sup>	-48.5
4b, R = R' = <i>p</i> -CH <sub>3</sub> O <sub>6</sub> H <sub>4</sub>	96.3	-20.3 <sup>d</sup>
4c, R = R' = <i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	95.1	-22 <sup>e</sup>
4d, R = R' = C <sub>6</sub> H <sub>5</sub>	95.3	-23
4e, R = C <sub>6</sub> H <sub>5</sub> ; R' = CH <sub>3</sub> O	82.2	+86
Ph <sub>2</sub> PSCH <sub>2</sub> CH <sub>2</sub> P(Ph) <sub>2</sub> C <sub>6</sub> S <sub>4</sub> (CN) <sub>4</sub>	86.9, 67.4 <sup>f</sup>	

<sup>a</sup> Relative to external P<sub>4</sub>O<sub>6</sub>; CH<sub>2</sub>Cl<sub>2</sub> solvent except as otherwise indicated. <sup>b</sup> Change in chemical shift from free phosphine or phosphinite, parts per million. <sup>c</sup> Acetone solvent. <sup>d</sup> R. Pinnell, C. Megler, S. L. Manatt, and P. A. Kroon, *J. Am. Chem. Soc.*, **95**, 977 (1973). <sup>e</sup> This work. <sup>f</sup> AB quartet, J<sub>AB</sub> = 55 Hz.

spectra, and an unidentified phosphorus compound. The chemical shift of this latter species, +59 ppm from P<sub>4</sub>O<sub>6</sub> (-54.2 ppm from H<sub>3</sub>PO<sub>4</sub>), is considerably downfield from those of 4a-e; no structure can be assigned to this compound. With 1 and other phosphorus reactants either 3 or 4 was produced, or no reaction occurred. (However, it should be noted that in no cases other than the first two cited were the reactions carried out under conditions designed specifically to give products other than 3. In particular, since the original objective of the work was the preparation of 3, the reactions were generally carried out at higher temperatures and for longer times than would allow the isolation of analogs of 5.)

Heating 2 with triphenyl- or tributylphosphine at reflux in benzene gave no evidence for reaction, even after several days.

The preparation of 3 in high yield from the reaction of trimethyl phosphite with 2 has been described;<sup>5</sup> a description of this procedure and the characterization of 3 are given in the Experimental Section.

The conversion of 1 into 3, in 10% yield, can also be effected by triiron dodecacarbonyl.

The structure of 4 was assigned through the <sup>31</sup>P NMR chemical shifts of 4a-e, the proton spectrum of 4a, the ir spectrum of 4d, and analogy with the product formed from the reaction of triphenylphosphine with 2-dicyanomethylene-1,3-dithietane.<sup>6</sup>

(a) The <sup>31</sup>P chemical shifts of 4a-e and the reaction product of 1,2-bis(diphenylphosphino)ethane with 1 are compiled in Table II. The shifts of the phosphine adducts 4a-d are remarkably constant at 90-95 ppm upfield of

P<sub>4</sub>O<sub>6</sub> (-17 to -22 from H<sub>3</sub>PO<sub>4</sub>) and that of the phosphinite adduct appears only slightly to lower field. This chemical shift is appropriate for arylphosphonium salts or ylides, and not appropriate for five-coordinate phosphorus.<sup>7</sup>

(b) In the proton NMR spectrum of 4a, the methyl protons appear as a doublet at δ 3.05 ppm with J<sub>PCH</sub> = 14 Hz. For comparison, the methyl resonances in Ph<sub>2</sub>PMe and Ph<sub>3</sub>PMe<sup>+</sup>Br<sup>-</sup> appear at δ<sub>acetone</sub> = 1.58 and 3.16 ppm, respectively, with J<sub>PCH</sub> = 4 and 15 Hz. The close correspondence of δ and J<sub>PCH</sub> between 4a and Ph<sub>3</sub>PMe<sup>+</sup> suggests very strongly that the phosphorus in 4 is present as a phosphonium ion.

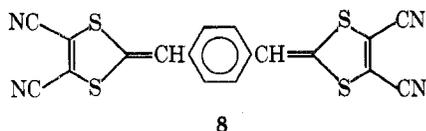
(c) The infrared spectrum of 4d contains, in addition to the band at 1540 cm<sup>-1</sup> assigned to the double bond conjugated to the cyano groups, a strong band at 1450 cm<sup>-1</sup> attributable to an unsymmetrically substituted C-C double bond. No comparable band is present in the symmetrical 3, but bands at similarly low frequencies have been reported by Blount et al.<sup>8</sup> for other multithiaethylenes.

(d) Finally, treatment of 4d with HBF<sub>4</sub> in acetone-dichloromethane at room temperature afforded a yellow, crystalline salt, whose composition corresponded to 4d + HBF<sub>4</sub>. The infrared spectrum of the salt retained the bands at 1540 and 1450 cm<sup>-1</sup>, and, in addition, exhibited bands at 3390 and 1060 cm<sup>-1</sup>, attributable to S-H and B-F stretches, respectively, and resulting from the protonation of thiolate and consequent formation of a normal fluoroborate salt.

Taken together, these results are compatible only with an open, betaine structure for 4.

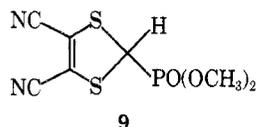
Bromine was found to react with 4d, giving a tetrabromide. The ir spectrum of this compound shows no band near 1540 cm<sup>-1</sup>, suggesting that the dicyanoethylene groups have become saturated, and the <sup>31</sup>P chemical shift, +93.5 ppm from P<sub>4</sub>O<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution, suggests that the phosphorous is still present as a phosphonium ion. The data available do not allow us satisfactorily to assign a structure to this product; however, one plausible structure would be that formed by addition of bromine across both dicyanoethylene groups.

**Reactions in the Presence of Aldehydes.** Addition of terephthaldehyde to a solution of trimethyl phosphite and 2 in benzene inhibits the coupling reaction, reducing the yield of 3 to about 40% without yielding any other easily isolable products. However, addition of terephthaldehyde to a solution of triphenylphosphine and 1 in benzene results in a quantitative yield of dark red needles, identified



as 8 by elemental analysis and mass spectrometry. In contrast, reaction of benzaldehyde, triphenylphosphine, and 1 in benzene gave both 4d and 2-benzylidene-4,5-dicyano-1,3-dithiole.

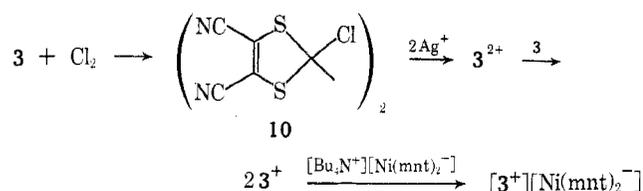
Addition of benzoic acid or an excess of impure benzaldehyde to a solution of 2 and trimethyl phosphite completely suppressed the coupling reaction, instead leading to a pale yellow compound, 9. On the basis of its mass spec-



trum [parent ion,  $m/e$  262; major fragments ions  $m/e$  153 ( $C_3HS_2(CN)_2$ ) and 109 ( $C_2H_5PO_3$ )] and  $^1H$  NMR spectrum [doublets at  $\delta$  4.0 ( $J = 10.84$  Hz) and 5.3 ( $J = 5.7$  Hz), area ratio 6:1], 9 is identified as 4,5-dicyano-1,3-dithiol-2-ylphosphonic acid dimethyl ester.<sup>9</sup>

**Redox Chemistry.** The electrochemical behavior of 3 has been described.<sup>4</sup> In an attempt to isolate the oxidation products of 3, a solution in dichloromethane was treated with chlorine. The deep wine color of 3 was slowly discharged and a new compound, 10, was isolated as pale straw-colored, moisture-sensitive crystals. The mass spectrum of 10 exhibits no apparent molecular ion; however,  $M^+ - Cl$  and other chlorine-containing fragments are observed, indicative of chlorine addition most probably across the central double bond. Thus the compound is assigned the structure 2,2'-bis(2-chloro-4,5-dicyano-1,3-dithioly)l. The chlorines can be removed quantitatively by reaction with 2 equiv of silver fluoroborate in acetonitrile. Addition of 1 equiv of 3 to a solution of 10 followed by reaction with silver ion gave a red solution of the monocation, which was isolated as its bis(maleonitriledithiolato)nickel,  $[Ni(mnt)_2^-]$ , salt (Scheme I).

Scheme I



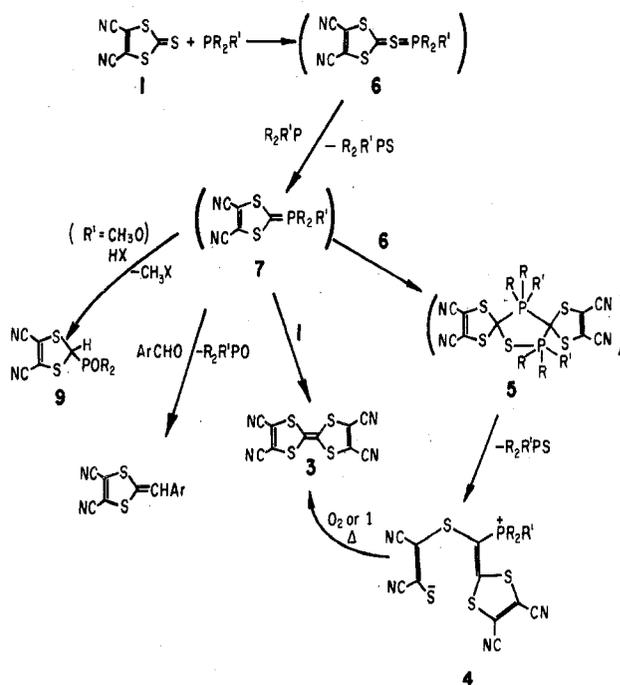
8 is reversibly oxidized in benzonitrile at  $E_p = 1.07$  V. It also undergoes an irreversible oxidation at  $E_p = 1.39$  V and an irreversible reduction at  $E_p = -1.18$  V. Chemical oxidation was not studied.

### Discussion

To allow the isolation of the spectrum of products found in this series of reactions there clearly must exist a much more delicate balance of electronic and other energetic effects than commonly obtains in other phosphine- or phosphite-thione reactions. We believe that the series of transformations outlined in Scheme II rationalizes the products observed; they also give us a basis for discussion of some of the factors involved.

Following Corey and Märkl,<sup>3</sup> we assert that the ylide 7 is a key intermediate in these reactions.<sup>10</sup> Whether it forms via displacement of  $R_2R'PS$  by  $R_2R'P$  from 6, or by dissociation of 6 into carbene and phosphine sulfide followed by

Scheme II



junction of phosphine and carbene, cannot be answered by the available data.

Formation of 5 requires the conjoining of 6 with 7. Both these species are strongly polarized, which suggests that they might react by a [3 + 2] dipolar addition. The initial product of such a reaction would have the structure given for 5 in Scheme II, but we have no evidence to support this structure assignment. A heterocycle of that structure could be expected readily to lose  $Ph_3PS$ ,<sup>12</sup> the remainder collapsing to an epiphosphorane. This, in turn, could easily transform into the observed betaine.

In like manner, the Wittig reactions with terephthalaldehyde and benzaldehyde presume the intermediacy of 7. The isolation of both 4d and the Wittig product in the benzaldehyde reaction, however, suggests that 6 competes strongly with aldehyde for the 7 available.

The formation of 9 presumably occurs via protonation of 7 at C-2, followed by displacement of a methyl group from methoxyl by the conjugate base (benzoate) of the protonating species, as in the Arbuzov reaction. One can invoke the existence of an adduct of benzaldehyde with 6, which is decomposed on protonation, to rationalize the high yield of 9, but its formation in the presence of benzoic acid, a very likely contaminant of the benzaldehyde used in that particular experiment, renders this unnecessary.

The bidithiolidene 3 can be formed either from the reaction of 1 plus 7 or from the dephosphinization of 4. In the case of the phosphines investigated in this work, it seems likely that the route via 4 predominates. In the reaction of 1 and 2 with phosphites, however, either route (or both!) may be followed; our results do not bear on this question.

The remaining observations to be rationalized can be summed up in the question of why 5 and 4 are observed in the reactions described here but not when other 1,3-dithiole-2-thiones are allowed to react with phosphines. It seems likely that the conjugated cyano groups must strongly stabilize both 6 and 7, compared to similar intermediates from other thiones, making their lifetimes in solution unusually long. Furthermore, 6 must be rather unreactive toward Brønsted acids, since no evidence was seen for products of the type reported very recently by Scherowsky and Weiland.<sup>11</sup>

Table III  
Data for the Characterization of Compounds 4

Compd	Mp, °C <sup>a</sup>	Yield, % <sup>b</sup>	% C		% H		% S	
			Calcd	Found	Calcd	Found	Calcd	Found
4a	142	20	54.76	54.41	2.58	2.36	25.40	25.54
4b	179	39	56.70	56.41	3.20	3.22	19.51	19.81
4c <sup>c</sup>	193–195	45	61.18	60.95	3.45	3.60	21.05	20.87
4d <sup>d</sup>	169	46	59.36	59.62	2.65	2.93	22.61	22.64
4e	237	30	53.08	53.15	2.50	2.71	24.62	25.24
(Ph <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> adduct <sup>e</sup>	164–166	49	56.39	56.04	3.13	2.82	25.06	25.24

<sup>a</sup> Usually with decomposition. <sup>b</sup> Conditions as in method A for 4d. <sup>c</sup> Molecular weight: calcd, 608; found (osmometric in dimethylformamide), 589. <sup>d</sup> Analysis for nitrogen: calcd, 9.89; found, 9.27. <sup>e</sup> (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(S)(CH<sub>2</sub>CH<sub>2</sub>P<sup>+</sup>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C[=C<sub>3</sub>S<sub>2</sub>(CN)<sub>2</sub>]SC(CN)=C(CN)S<sup>-</sup>).

It seems likely, too, that the  $\pi$ -donor properties of the phosphine must be important in stabilizing **6**, particularly. This follows from the highest yields of **4** being observed from those reactions involving the better  $\pi$ -donor phosphines, near the top of Table I, although the reactions involving tri(*p*-chlorophenyl)phosphine and methyl diphenylphosphonite are apparently anomalous if this is correct.

Conversely, in the reactions of **2** with phosphites, the intermediate corresponding to **6** should not be long lived, and no products comparable to **4** should be expected. However, the ylide **7** should be stable, and we observe the formation of products derived from it.

The relative stability of these intermediates, and the ease with which small variations in the stability can be effected by suitable choice of phosphine reagents, suggest that this system ought to be an interesting subject for a kinetic study. In particular, it may well be possible to resolve the questions of the intermediacy of any two-coordinate carbon species in the conversion of **6** to **7** and of the route by which **3** is formed. Studies such as these are outside the scope of our investigations, and we welcome any interest others may have in this subject.

The deep red-purple color of **3** is interesting inasmuch as tetrathiafulvalenes [including the tetrakis(trifluoromethyl) derivative] are normally yellow-orange. The absorption band at 495 nm (CH<sub>2</sub>Cl<sub>2</sub>) in the spectrum of **3** is not far from the corresponding long-wavelength band in tetrathiafulvalene itself (450 nm).<sup>13</sup> Its extinction coefficient ( $\epsilon_{495}$  2000) is an order of magnitude larger (TTF,  $\epsilon_{450}$  270), however, which suggests that a transition other than the  $b_{1u} \leftarrow a_g$  assigned to the long-wavelength band in TTF<sup>13</sup> is responsible for this band. The band exhibits a small solvent shift [ $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 495 nm,  $\lambda_{\max}$  (CH<sub>3</sub>CN) 501 nm] in the direction expected for an internal charge-transfer transition, and we suggest that in such a transition lies the origin of the band. Furthermore, the long-wavelength transition of tetrakis(trifluoromethyl)tetrathiafulvalene, which is unlikely to possess such a charge-transfer band, is shifted considerably to the blue from that of TTF ( $\lambda_{\max}$  412 nm).<sup>14</sup>

### Experimental Section

Cyclic voltammetry was conducted in either dry acetonitrile or benzonitrile, containing 0.1 *N* tetraethylammonium perchlorate, at a platinum button electrode in the manner previously described.<sup>15</sup>

X-Ray studies were performed with a conventional Nonius precession. Photographs were recorded using Ni-filtered Cu K $\alpha$  radiation. Infrared spectra were recorded using cesium iodide or potassium bromide disks. Proton NMR spectra were recorded at 60 MHz and are referenced to internal tetramethylsilane. Fourier transform <sup>31</sup>P spectra were recorded, with white noise <sup>1</sup>H decoupling, at 40.5 MHz and, except where otherwise noted, are referenced to external P<sub>4</sub>O<sub>6</sub>.<sup>16</sup> Melting points were obtained in capillaries and are uncorrected. Elemental analyses were performed by Galbraith Laboratories.

4,5-Dicyano-1,3-dithiole-2-thione (**1**) was prepared as described by Klingsberg<sup>17</sup> and 4,5-dicyano-1,3-dithiol-2-one (**2**) as reported by Ciganek and Krespan.<sup>18</sup> The phosphines were commercial materials and were used as received.

**$\Delta^{2,2}$ -Bis(4,5-dicyano-1,3-dithiolidene) (3).** A. Trimethyl phosphite (3.1 g, 0.025 mol) was added to a solution of **2** (4.2 g, 0.025 mol) in benzene (150 ml) and the resulting solution was heated under reflux in a nitrogen atmosphere for 3 hr. The solution slowly turned to a deep wine color and crystals started forming toward the end of the reaction. The reaction mixture was allowed to cool overnight. The product was collected and washed with benzene, yield 3.7 g (95%) of purple needles, mp 265–267°.

B. Trimethyl phosphite (0.27 g, 2.18 mmol), **1** (0.40 g, 2.18 mmol), and 25 ml of cyclohexane were refluxed and stirred for 15 min, then stirred overnight at room temperature. The cyclohexane phase was discarded and the residue was washed with 10 ml of cold benzene. The remaining solids were dissolved in a minimum amount of warm acetone. Benzene (5 ml) was added and the solution was concentrated on a hot plate until a solid phase appeared. On cooling, the product separated as purple needles. After an additional recrystallization, the yield was 0.1 g (30%), mp 263–265°. A thin layer chromatogram (silica, benzene) revealed only one component.

C. A suspension of **4d** (2 mmol) in *o*-dichlorobenzene (25 ml) containing **1** (3 mmol) was heated at 125°. After 1 hr the solid had dissolved and a deep red solution was obtained; heating was continued for 1 hr more. The solvent was removed under reduced pressure and the residue was recrystallized from dichloromethane-benzene, yield of 0.24 g (25%).

D. Triiron dodecacarbonyl (0.6 g, 1.43 mmol), **1** (0.65 g, 3.54 mmol), and 35 ml of dry, thiophene-free benzene were refluxed for 4 hr under nitrogen. The reaction mixture was filtered through Celite; slow evaporation of the filtrate with a nitrogen jet caused the separation of 0.055 g of **3** (10%), identified by its infrared spectrum and *R<sub>f</sub>*.

Anal. Calcd for C<sub>10</sub>N<sub>4</sub>S<sub>4</sub>: C, 39.47; N, 18.42; S, 42.11. Found: C, 39.31, 39.70; H, 0.02, 0.06; N, 18.20, 18.25; S, 41.88, 41.84. Spectral data: uv-visible  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 262 nm ( $\epsilon$  2 × 10<sup>4</sup>), 290 sh, 323 (1.4 × 10<sup>4</sup>), 495 (2 × 10<sup>3</sup>);  $\lambda_{\max}$  (CH<sub>3</sub>CN) 260 nm ( $\epsilon$  2.3 × 10<sup>4</sup>), 325 (1.4 × 10<sup>4</sup>), 501 (1.6 × 10<sup>3</sup>); ir 2242 (m), 2218 (m), 2212 (m), 1530 (s), 1135 (s), 1064 (s), 877 cm<sup>-1</sup> (w); mass spectrum (70 eV) *m/e* (rel intensity) 304 (100), 234 (48), 152 (64), 88 (0), 76 (57).

**(4,5-Dicyano-1,3-dithiol-2-ylidene)methylene (Triphenylphosphonio)(2-thio-1-mercaptomaleonitrilate) (4d).** A. A mixture of 0.34 g (2 mmol) of **1**, 0.52 g (2 mmol) of triphenyl phosphine, and 15 ml of cyclohexane was refluxed and stirred for 12 hr. Filtration of the reaction mixture gave an orange solid which was washed with benzene. The filtrate and washings were combined and evaporated to dryness. Crystallization from ethanol gave 0.01 g of **3** as the less soluble component and 0.32 g (54%) of triphenylphosphine sulfide, identified by its infrared spectrum. The orange solid was dissolved in 50 ml of warm dichloromethane and 10 ml of acetonitrile was added. Concentration of this solution on a rotary evaporator without heating gave 0.26 g (46%) of **4d** as small orange crystals, mp 169° dec.

B. A solution of **1** (0.184 g, 1 mmol) and triphenylphosphine (0.39 g, 1.5 mmol) in benzene (10 ml) was warmed at 60° for 1 hr. The reaction mixture was cooled and 0.24 g (85% yield) of orange crystals was collected.

Analytical data on this compound appear in Table III.

Spectral data: ir (KBr disk) 2200 (s), 2175 (s), 1585 (s), 1540 (s), 1480 (s), 1450 (sh), 1429 (s), 1183 (s), 1150 (s), 1105 (s), 995 (s), 844

(s), 743 (s), 719 (s), 683  $\text{cm}^{-1}$  (s);  $\text{uv } \lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 268 nm ( $\epsilon$  2.75  $\times$  10<sup>3</sup>), 362 (5.6  $\times$  10<sup>3</sup>).

The analogous compounds 4a-c and 4e were prepared by similar methods and purified by preparative thin layer chromatography or recrystallization. Their analytical data are collected in Table III.

The 1,2-bis(diphenylphosphino)ethane complex was purified by preparative scale thin layer chromatography (silica gel, dichloromethane) and recrystallized from acetone-2-propanol to give small orange needles of product. The <sup>31</sup>P NMR spectrum of the crude product disclosed an additional small peak at +68.4 ppm, but the product responsible for this signal could not be purified.

**Dichloromethane Solvate of 4d.** 5 (3 g, 3.3 mmol) was suspended in benzene (50 ml) and warmed at 60°. The crystals slowly dissolved, giving a purple-red solution with simultaneous formation of an orange, crystalline solid. The conversion was complete in 10 min. Recrystallization from dichloromethane gave 2 g (95%) of triclinic crystals, mp 187-189°.

Anal. Calcd for  $\text{C}_{28}\text{H}_{15}\text{N}_4\text{PS}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ : C, 56.20; H, 2.63; N, 9.20; P, 5.08; S, 21.05. Found: C, 56.73; H, 2.61; N, 9.26; P, 5.08; S, 21.20. Crystallographic data: reduced triclinic cell,  $a = 12.779$ ,  $b = 12.951$ ,  $c = 10.645$  Å,  $\alpha = 102.1$ ,  $\beta = 111.4$ ,  $\gamma = 110.0$ ; space group  $P1$  or  $P\bar{1}$ ; for  $Z = 2$  the calculated density for  $\text{C}_{28}\text{H}_{15}\text{N}_4\text{PS}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$  is 1.43  $\text{g cm}^{-3}$ ; density measured by flotation is 1.42  $\text{g cm}^{-3}$ . Ir (CsI disk) 3060, 3025, 2210, 2175, 1586, 1540, 1483, 1440, 1150, 1105, 748, 720, 687, 528, 511, 500  $\text{cm}^{-1}$ .

**HB<sub>4</sub>F<sub>4</sub> Adduct of 4d.** To a solution of 0.3 g (0.53 mmol) of 4d in 20 ml of 1:1 acetone-dichloromethane was added 1 ml of 48% aqueous fluoroboric acid. The mixture was stirred for 1.5 hr while the color changed from orange to yellow, then evaporated to ca. 5 ml under reduced pressure. The product was precipitated by addition of diethyl ether and recrystallized three times from acetone-ether to afford 0.3 g (88%) of 12 as yellow microcrystals. Anal. Calcd for  $\text{C}_{28}\text{H}_{16}\text{BF}_4\text{N}_4\text{PS}_4$ : C, 51.38; H, 2.45. Found: C, 51.35; H, 2.45. The infrared spectrum contained bands at 2.9 (SH) and 9.4  $\mu\text{m}$  ( $\text{BF}_4^-$ ).

**Bromination of 4d.** Compound 4d (0.8 g, 1.4 mmol) and 40 ml of dichloromethane were cooled in an ice bath. A solution of bromine (0.49 g, 3 mmol) in 10 ml of dichloromethane was added dropwise with stirring. The color changed from orange to yellow-orange. The reaction mixture was stirred for 2 hr at 0° after the addition was complete, then filtered to give 0.85 g (69%) of golden yellow microcrystals. Anal. Calcd for  $\text{C}_{28}\text{H}_{15}\text{Br}_4\text{N}_4\text{PS}_4$ : C, 37.92; H, 1.69. Found: C, 37.85; H, 1.87. Ir (KBr) 3030 (w), 2220 (w), 1590 (w), 1470 (m), 1450 (m), 1390 (s), 1176 (m), 1156 (s), 1100 (s), 995 (m), 746 (s), 719 (s), 687  $\text{cm}^{-1}$  (s).

**Adduct 5.** Triphenylphosphine (5.24 g, 0.02 mol) and 3 (3.68 g, 0.02 mol) were dissolved in benzene (100 ml) and stirred under nitrogen at room temperature. The solution turned deep red and after a period of 1 hr a red-brown solid slowly crystallized. This was collected (3 g, 70%), washed with benzene, and air dried, mp 94-95°. Anal. Calcd for  $\text{C}_{46}\text{H}_{30}\text{N}_4\text{S}_5\text{P}_2$ : C, 64.16; H, 3.51; N, 6.51; S, 18.62; P, 7.20. Found: C, 64.07; H, 3.47; N, 6.25; S, 18.49; P, 6.95.

**Reaction of 1 with Tri-*n*-butylphosphine.** A solution of 400 mg ( $2 \times 10^{-3}$  mol) of 1 in 50 ml of toluene was cooled in an ice-water bath; tri-*n*-butylphosphine (0.5 ml,  $2 \times 10^{-3}$  mol) was added dropwise. The solution quickly became dark red in color. It was allowed to stir at 0° for 30 min, and then to warm to room temperature over 18 hr. Evaporation of the toluene under vacuum left a dark red oil, evidently a mixture of compounds, one of which was identified as tri-*n*-butylphosphine sulfide by its mass (parent ion,  $m/e$  234) and <sup>31</sup>P NMR spectra (a sharp resonance, -46.7 ppm from  $\text{H}_3\text{PO}_4$ ).<sup>19</sup> A second phosphorus-containing component, which exhibited a broad peak at -54.2 ppm, apparently was not volatile in the mass spectrometer. No further attempt was made to identify it.

**2,2'-(*p*-Xylylene)bis(4,5-dicyano-1,3-dithiolidene) (8).** Triphenylphosphine (4 mmol), terephthalaldehyde (0.5 mmol), and 1 (1 mmol) were dissolved in benzene (10 ml) and the solution was left standing at ambient temperature overnight. The solution slowly turned red and dark red crystals formed. The crystals were filtered off, washed with benzene, and air dried. Recrystallization from benzonitrile gave a 95% yield of purple needles, mp >300° dec.

Anal. Calcd for  $\text{C}_{18}\text{H}_6\text{N}_4\text{S}_4$ : C, 53.18; H, 1.49; N, 13.78; S, 31.55. Found: C, 53.40; H, 1.55; N, 13.68; S, 31.38. Mass spectrum (70 eV)  $m/e$  406 (100), 298, 285, 266, 253, 221; ir (Nujol mull) 2210, 1690, 1575, 1550 (sh), 1410, 1280, 1180, 1070, 848, 785, 685  $\text{cm}^{-1}$ .

**2-Benzylidene-4,5-dicyano-1,3-dithiole.** Triphenylphosphine (5.24 g, 0.02 mol), 1 (1.84 g, 0.01 mol), and benzaldehyde (from a freshly opened commercial supply, 1.06 g, 0.01 mol) were dissolved

in benzene and allowed to stir under nitrogen for 24 hr at room temperature. At the end of this time the solution was dark red and an orange precipitate was present. The orange solid (0.55 g) was recovered by filtration and identified as 4d by its melting point (169°); the yield of 4d was 20%.

Evaporation of the filtrate left an oily, red residue which left an orange-brown solid upon treatment with 100 ml of absolute ethanol. Extraction of this solid with petroleum ether in a Soxhlet apparatus gave a mixture of red and colorless crystals, identified as 2-benzylidene-4,5-dicyano-1,3-dithiole (mp 142-145°) and triphenylphosphine sulfide, respectively, by their mass spectra. The mass spectrum of the former compound consists of a parent ion,  $m/e$  242 (100%), and major fragments at  $m/e$  (rel intensity) 166 [27,  $\text{M} - \text{C}_6\text{H}_4$  or  $\text{M} - \text{C}_2(\text{CN})_2$ ], 134 (37); 121 (27,  $\text{C}_6\text{H}_5\text{CS}$ ), 102 (30,  $\text{C}_3\text{H}_2\text{N}_2$ ), 90 (33), and 89 (43).

**Dimethyl (4,5-Dicyano-1,3-dithiol-2-yl)phosphonate (9). A.** Benzoic acid (0.59 g, 0.005 mol), 2 (0.84 g, 0.005 mol), and trimethyl phosphite (1.15 ml, 0.01 mol) were dissolved in 100 ml of methylcyclohexane. This solution was heated at reflux for 4 hr, during which time it became red. A brown solid separated on cooling; it was recovered by filtration. Recrystallization from benzene afforded 0.45 g (34%) of pale yellow plates, mp 142-143°.

**B.** Trimethyl phosphite (2 mmol), 2 (1 mmol), and aged benzaldehyde (4 mmol) were dissolved in hot methylcyclohexane (40 ml) and heated at 90° for 30 min. The solution slowly turned yellow. The reaction mixture was concentrated to 20 ml and set aside. The yellow crystals which slowly formed were collected, washed with methylcyclohexane, and air dried, yield 0.11 g (42%). Recrystallization from methylcyclohexane gave 90% recovery of pale yellow plates, mp 142-143°.

Anal. Calcd for  $\text{C}_7\text{H}_7\text{N}_2\text{S}_2\text{PO}_3$ : C, 32.06; H, 2.69; N, 10.68; S, 24.45; P, 11.81. Found: C, 32.26; H, 2.70; N, 10.63; S, 24.54; P, 11.64. Mass spectrum (70 eV)  $m/e$  262, 153 (100), 109; NMR ( $\text{CDCl}_3$ )  $\delta$  4.00 (d,  $J = 10.84$  Hz, 6 H), 5.28 (d,  $J = 5.7$  Hz, 1 H); <sup>31</sup>P NMR ( $\text{CDCl}_3$ ) -14.6 ppm (vs.  $\text{H}_3\text{PO}_4$ ).

**2,2'-Bis(2-chloro-4,5-dicyano-1,3-dithioly) (10).** 3 (1 mmol) was dissolved in warm dichloromethane (50 ml) and chlorine gas was bubbled through the solution. The deep wine color was slowly discharged and a pale yellow solution was obtained. The solution was concentrated to 20 ml, methylcyclohexane (20 ml) was added, and the solution was further concentrated to 20 ml. On cooling, a 90% yield of pale straw-colored crystals formed. These were collected, dried under vacuum, and stored under nitrogen, mp 170-172° dec.

Anal. Calcd for  $\text{C}_{10}\text{N}_4\text{S}_4\text{Cl}_2$ : C, 32.00; N, 14.93; Cl, 18.93. Found: C, 32.02; H, 0.10; N, 14.69; Cl, 18.77. Mass spectrum (70 eV)  $m/e$  339, 304 (100), 236, 234, 189, 187. Spectral data:  $\text{uv } \lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) 349 nm ( $\epsilon$  8080), 300 sh (6100), 282 (5730), 248 (11,500); ir (CsI disk), 2242, 2225, 1548, 1525, 1181, 1160, 1060, 694, 515, 490, 480  $\text{cm}^{-1}$ .

On treatment of a solution of 10 in acetonitrile with 2 equiv of silver hexafluoroantimonate a quantitative yield of silver chloride was obtained.

**$\Delta^{2,2'}$ -Bi(4,5-dicyano-1,3-dithiolidene)bis(maleonitriledithiolato)nickel.** 3 (0.5 mmol) was dissolved in dichloromethane (50 ml) and chlorine gas was bubbled through the solution. The resulting yellow solution was degassed and treated with 3 (0.5 mmol) followed by a solution of silver hexafluoroantimonate (1.0 mmol) in acetonitrile (40 ml). The precipitated silver chloride was filtered off and the resulting red solution was treated with a solution of tetra-*n*-butylammonium bis(maleonitriledithiolato)nickel (1 mmol) in acetonitrile (20 ml). The resulting solution was evaporated to dryness, treated with hot dichloromethane (50 ml), and filtered. The violet-black solid was washed with hot dichloromethane and dried under nitrogen. Recrystallization from acetonitrile gave 0.44 g (68%) of black crystals, mp >360°.

Anal. Calcd for  $\text{C}_{18}\text{N}_8\text{S}_8\text{Ni}$ : C, 33.60; N, 17.62; S, 39.87. Found: C, 33.74; H, 0.22; N, 17.32; S, 39.81.

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**Registry No.**—1, 1005-10-3; 2, 934-31-6; 3, 55052-32-9; 4a, 55758-94-6; 4b, 55758-95-7; 4c, 55758-96-8; 4d, 55758-97-9; 4d CH<sub>2</sub>Cl<sub>2</sub>, 55758-98-0; 4d tetrabromide, 55758-99-1; 4e, 55759-00-7; 5, 55759-01-8; 8, 55759-02-9; 9, 55759-03-0; 10, 55759-04-1; 12, 55822-52-1; Ph<sub>2</sub>PSCH<sub>2</sub>CH<sub>2</sub>P(Ph)<sub>2</sub>C<sub>6</sub>S<sub>4</sub>(CN)<sub>4</sub>, 55759-05-2; fluoroboric acid, 16872-11-0; tributylphosphine, 998-40-3; tributylphosphine sulfide, 3084-50-2; terephthaldehyde, 623-27-0; 2-benzylidene-4,5-dicyano-1,3-dithiole, 55759-06-3;  $\Delta^{2,2'}$ -bi(4,5-dicyano-1,3-dithiolidene)bis(maleonitriledithiolato)nickel, 55663-96-2.

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- (9) A referee correctly noted that a P-C-H coupling constant of 5.7 Hz is much smaller than expected for an ester of a methanephosphonic acid. In fact, the <sup>31</sup>P chemical shift (-14.6 ppm from H<sub>3</sub>PO<sub>4</sub>) is also smaller than would be expected for such a structure unless one takes into account the fact that substitution of second-row elements for hydrogen on the carbon  $\alpha$  to phosphorus in these structures reduces both the chemical shift and coupling constant. The values observed for **9** compare well with those quoted<sup>7</sup> for, e.g., ClCH<sub>2</sub>PO(OCH<sub>3</sub>)<sub>2</sub> (-18.5 ppm, 8.0 Hz) and Cl<sub>2</sub>CHPO(OEt)<sub>2</sub> (-9.3 ppm).
- (10) Very recently Scherowsky and Weiland published<sup>11</sup> results which call into question the intermediacy of ylides such as **7** in reactions of this sort. Under their conditions, however (they studied the reactions of benzo[d]-1,3-dithiole-2-thione with triethyl phosphite, alone and in the presence of sundry reagents), their intermediate **14** (which corresponds to our **6**) would be expected to be more reactive than **6**, especially toward electrophilic reagents. Conversion to an ylide, in their case, is being forestalled by other reactions.
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## Organophosphorus Compounds. XIII.<sup>1a</sup> Protonation, Cleavage, and Alkylation of Thiophosphates and Thiophosphites

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Protonation, cleavage, and alkylation reactions of phosphorothioic acids, H<sub>3</sub>PS<sub>n</sub>O<sub>4-n</sub> (*n* = 0-3), alkyl mono- and dithiophosphates, and systematically substituted phosphorothioites P(SC<sub>2</sub>H<sub>5</sub>)<sub>n</sub>(OCH<sub>3</sub>)<sub>3-n</sub>, phosphorothioates, OP(SC<sub>2</sub>H<sub>5</sub>)<sub>n</sub>(OCH<sub>3</sub>)<sub>3-n</sub>, and phosphorothionates, SP(SC<sub>2</sub>H<sub>5</sub>)<sub>n</sub>(OCH<sub>3</sub>)<sub>3-n</sub> (*n* = 0-3), were studied in fluorosulfuric acid solution by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy (primarily at -60 to -80°). Trivalent phosphorus compounds are protonated at phosphorus, phosphoryl compounds at the phosphoryl oxygen, and thiophosphoryl compounds at the thiono sulfur atom. In the last case, the two-bond coupling, <sup>2</sup>J<sub>PSH</sub>, is observed below -50°. In general, sulfur is less able than oxygen to donate nonbonded electron pairs to phosphorus in the stabilization of phosphonium ions. The change in the <sup>31</sup>P chemical shift of thiophosphates and thiophosphites upon protonation is a function of the site of protonation and the relative numbers of oxygen and sulfur atoms bonded to phosphorus. Isopropoxymercaptophosphonium ions undergo rearrangements by isopropyl group migration from oxygen to sulfur. All intermediates in these processes can be individually observed.

Since our report of nuclear magnetic resonance spectroscopic studies of protonated phosphates and phosphites (oxyphosphonium ions),<sup>1a</sup> we have extended our work to many thiophosphorus analogs. Considering that the most important influence on the structures of the oxyphosphonium ions, as particularly revealed by their <sup>31</sup>P chemical shifts, is electron donation by the oxygen atoms to phosphorus by means of p $\pi$ -d $\pi$  bond formation,<sup>1a</sup> our interest was in determining the relative ability of sulfur atoms bonded to phosphorus to similarly stabilize phosphonium ions. In general, phosphorus-sulfur  $\pi$ -bond formation is less favored geometrically than is phosphorus-oxygen  $\pi$ -bond formation.<sup>2</sup> Our expectation was that NMR spectroscopy would be a sensitive tool for determining the effects of sulfur substitution for oxygen in positively charged phosphorus intermediates.

We were particularly interested in whether the phosphorus lone electron pair (in the phosphites) is the site of pro-

tonation in strong acid solution, and otherwise whether the phosphoryl sulfur or oxygen atoms are protonated. These expectations, which were based on our work with phosphates and phosphites,<sup>1a</sup> would not necessarily arise from other earlier chemical observations. Trialkyl phosphorotriothioites undergo neither the Michaelis-Arbuzov reaction with alkyl or acyl halides nor the anti-Arbuzov reaction with polyhalocyclopentadienes<sup>28</sup> (nucleophilic attack by phosphorus). Rather, the sulfur atoms are the reactive sites, yielding, for example, dialkyl phosphorodithioic halides and dialkyl sulfides in the first case,<sup>3</sup> and halocyclopentadienyl alkyl sulfides and the phosphorodithioic halides in the second case.<sup>29</sup> Mixed phosphorothioites of the types (RO)<sub>2</sub>PSR and ROP(SR)<sub>2</sub> react in mixed fashion, giving products arising from both phosphorus and sulfur atom alkylation.<sup>4</sup> The nucleophilic reactivity of thiophosphoryl sulfur atoms has been interpreted in terms of the "hard-soft" acid-base concept,<sup>5</sup> with the "soft" sulfur