The Chemistry of Cyanodithioimidocarbonic Acid
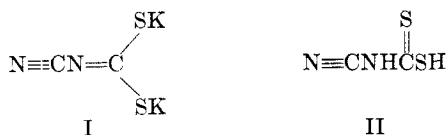
R. Jerome Timmons and Lawrence S. Wittenbrook

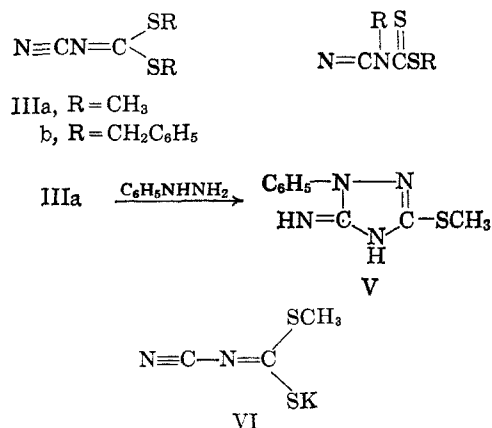*Chemical Research, O. M. Scott and Sons Company, Marysville, Ohio   43040*

The preparation of a large number of alkylation and acylation products of potassium methyl cyanodithioimidocarbonate (VI) was undertaken. Reaction of the dipotassium salt (I) of cyanodithioimidocarbonic acid with difunctional alkyl halides produces cyclic alkylene cyanodithioimidocarbonates. The chemistry of one of these, N-cyano-2-imino-1,3-dithiolane (XI), was investigated. Chlorinating agents effect the cyclization of VI to a new compound, 3-chloro-5-methylthio-1,2,4-thiadiazole (XXII).

The dipotassium salt of "dithiocyanic acid" was first obtained by Fleisher as an intermediate in the conversion of xanthan hydride with potassium hydroxide to perthiocyanic acid.[1] Its structure was later established by Hantzsch and Wolvekamp as dipotassium cyanodithioimidocarbonate (I) by an independent preparation from carbon disulfide, potassium hydroxide, and cyanamide.[2] The free acid (II), although unstable, can be isolated by careful acidification of a solution of I.[2]

$$N{\equiv}CN{=}C\underset{\displaystyle SK}{\overset{\displaystyle SK}{<}} \qquad\qquad N{\equiv}CNHC\overset{\displaystyle S}{\underset{}{\parallel}}SH$$

$$\text{I} \qquad\qquad\qquad \text{II}$$

Although the salts of II have attained importance in the control of slime-forming microorganisms,[3] its chemistry has received scant attention. This is surprising in view of the potential of its salts as low-cost chemical intermediates.

During the course of our investigation of the chemistry of I, we became particularly interested in the possibilities of S alkylation and S acylation. The dimethyl[2] and dibenzyl[4] esters have been reported from the silver and potassium (I) salts, respectively, of II. In accordance with the generally observed alkylation of sulfur in preference to nitrogen of dithiocarbamates, their structures were shown to correspond to III. For example, acid decomposition of IIIa at 200° gives rise to methyl mercaptan and ammonia, but no methylamine[2] (from N alkylation). Also, reaction of IIIa with phenylhydrazine produces the triazole (V)[4] which demands structure III rather than IV.

$$N{\equiv}CN{=}C\underset{\displaystyle SR}{\overset{\displaystyle SR}{<}} \qquad\qquad N{=}CN\overset{\displaystyle R}{\underset{}{\mid}}C\overset{\displaystyle S}{\underset{}{\parallel}}SR$$

IIIa, R = CH₃

b, R = CH₂C₆H₅

$$\text{IIIa} \xrightarrow{\text{C}_6\text{H}_5\text{NHNH}_2}$$

$$\begin{array}{c} \text{C}_6\text{H}_5{-}\text{N}{-}\!\!-\!\!\text{N} \\ \text{HN}{=}\text{C} \diagdown\ \diagup \text{C}{-}\text{SCH}_3 \\ \text{N} \\ \text{H} \end{array}$$

V

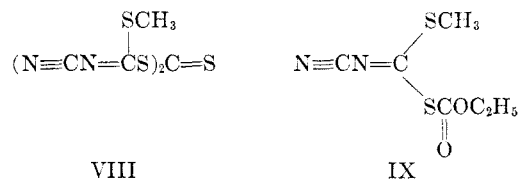$$N{\equiv}C{-}N{=}C\underset{\displaystyle SK}{\overset{\displaystyle SCH_3}{<}}$$

VI

We have found that reaction of the dipotassium salt (I) with methyl iodide procedes stepwise and that the monomethyl ester (VI) can be readily isolated. This compound, unlike I, is not hygroscopic. Reaction of I with a second mole of methyl iodide produces IIIa, identical with IIIa prepared by the method of Hantzsch and Wolvekamp.[2]

Alkylation of Potassium Methyl Cyanodithioimidocarbonate (VI).

—The monomethyl ester was successfully alkylated with a variety of alkyl halides. These are shown in Table I. In addition to the string nitrile band at 4.57–4.62 and the strong C=N band at 6.71–6.82 μ, these products all possessed characteristic bands at 7.05–7.12 (w), 9.78–9.90 (s), and 10.52–10.64 μ (s). The ester salt (VI) itself displayed its C=N band at 7.40, and the dipotassium salt (I) showed C=N absorption at 7.65 μ.

Attempts to alkylate VI with acrylonitrile or paraformaldehyde in the presence of hydrogen chloride gas were unsuccessful. Similarly, reaction with 4-chloro-3,5-dinitrotoluene in refluxing acetone produced an intractable gum.

Acylation of VI was not nearly so successful as alkylation. Reaction with thiophosgene did produce a refractory solid which gave an analysis close to the expected values for the trithiocarbonate (VIII). Furthermore, reaction of VI with ethyl chloroformate gave the expected product (IX). Attempted acylations of VI with ethyl isocyanate, dimethylcarbamoyl chloride, and acetyl chloride were all unsuccessful.

$$(N{\equiv}CN{=}C\overset{\displaystyle SCH_3}{\underset{}{\mid}}S)_2C{=}S \qquad\qquad N{\equiv}CN{=}C\underset{\displaystyle SCOC_2H_5}{\overset{\displaystyle SCH_3}{<}}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\overset{\displaystyle \parallel}{\displaystyle O}$$

$$\text{VIII} \qquad\qquad\qquad\qquad \text{IX}$$

Attempted arylation of dipotassium cyanodithioimidocarbonate (I) by reaction with bromobenzene in the presence of cuprous bromide in boiling lutidine[5] surprisingly gave a mixture of diphenyl sulfide and diphenyl disulfide indicating that the expected product (IIIc) may have formed but was unstable to the reaction conditions.[6]

(1) A. Fleischer, *Ann.*, **179**, 204 (1875).

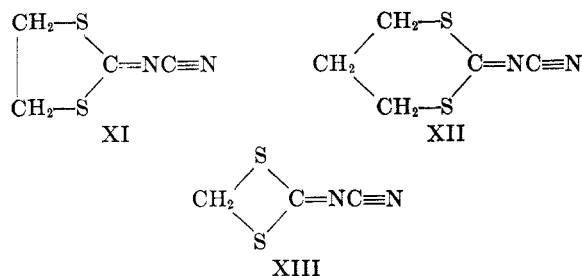(2) A. Hantzsch and M. Wolvekamp, *ibid.*, **331**, 265 (1904).

(3) (a) J. D. Pera (to Buckman Laboratories, Inc.), U. S. Patent 2,881,070 (April 7, 1959): *Chem. Abstr.*, **53**, 20678c (1959). (b) J. Buckman, J. D. Pera, and J. W. Appling (to Buckman Laboratories, Inc.), U. S. Patent 2,881,071 (April 7, 1959); *Chem. Abstr.*, **53**, 20678d (1959).

(4) E. Fromm and D. von Goncz, *Ann.*, **355**, 196 (1907).

(5) W. Reifschneider (to Dow Chemical Co.), U. S. Patent 3,124,619 (March 10, 1964).

(6) A referee has suggested that the formation of diphenyl sulfide and diphenyl disulfide might better be explained by the presence of water, which would form KSH from the starting material. Reaction with bromobenzene to form thiophenol in equilibrium with its potassium salt would lead the way for the continued formation of diphenyl sulfide (from H₂S released) and diphenyl disulfide (from traces of oxygen which would lead to water formation that would also promote the chain reaction). Both lutidine and the dipotassium salt are difficult to dry and sufficient water could be present to initiate the chain reaction which would be expected to be very fast at the temperature of boiling lutidine.

TABLE I

ALKYLATION PRODUCTS OF POTASSIUM METHYL CYANODITHIOIMIDOCARBONATE

$$N\equiv CN=C\overset{SCH_3}{\underset{SR}{}}$$

Compd	R	Halide	Mp, °C	Yield, %	Infrared bands, μ
IIIa	CH_3	CH_3I	51–52.5	58	4.61, 6.82, 7.10, 9.83, 10.60
Xa	CH_2OCH_3	$ClCH_2OCH_3$	Oil	19	4.58, 6.75, 7.05, 9.86, 10.64
Xb	$CH_2C(=O)N(CH_3)_2$	$ClCH_2C(=O)N(CH_3)_2$	102.5–103	45	4.59, 6.72, 7.10, 9.86, 10.55
Xc	$CH_2C(=O)NHC_2H_5$	$ClCH_2C(=O)NHC_2H_5$	125–126	46	4.57, 6.73, 7.05, 9.85, 10.60
Xd	$CH_2C(=O)NH_2$	$ClCH_2C(=O)NH_2$	152–154.5	40	4.62, 6.80, 7.12, 9.85, 10.56
Xe	$CH_2C(=O)OC_2H_5$	$ClCH_2C(=O)OC_2H_5$	34–36	36	4.61, 6.70, 7.05, 9.85, 10.52
Xf	$CH_2C\equiv N$	$ClCH_2C\equiv N$	59–60	58	4.58, 6.82, 7.06, 9.85, 10.57
Xg	$CH_2CH=CH_2$	$BrCH_2CH=CH_2$	Oil	76	4.60, 6.76, 7.05, 9.90, 10.62
Xh	$CH_2CCl=CH_2$	$ClCH_2CCl=CH_2$	Oil	56	4.61, 6.73, 7.06, 9.78, 10.54
Xi	CH_2CO_2H	$ClCH_2C(=O)ONa$	105–109	9	4.58, 6.71, 7.07, 9.85, 10.54

$$C_6H_5S\diagdown \atop C_6H_5S\diagup \!\!C=NC\equiv N$$

IIIc
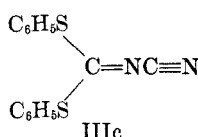
Preparation of Cyclic Alkylene Cyanodithioimidocarbonates.

—Reaction of I with ethylene dibromide and 1,3-propylene dibromide in aqueous acetone at room temperature produced the corresponding cyclic dithioimidocarbonates XI and XII, respectively. The cyclic

$$\begin{matrix}CH_2-S\\ |\quad\quad\diagdown\\ CH_2-S\diagup\end{matrix}\!\!C=NC\equiv N$$

XI

$$\begin{matrix}CH_2-S\\ \diagup\quad\quad\diagdown\\ CH_2\quad\quad C=NC\equiv N\\ \diagdown\quad\quad\diagup\\ CH_2-S\end{matrix}$$

XII

$$CH_2\diagdown \!\!\! \begin{matrix}S\\ \diagup\quad\diagdown\\ C=NC\equiv N\\ \diagdown\quad\diagup\\ S\end{matrix}$$

XIII

methylene ester could not be prepared from methylene iodide under these conditions. It was obtained, although in low yield along with much polymer, from I and methylene iodide in refluxing acetonitrile.

It is interesting to note the shift in the wavelength of the C=N band as the ring becomes more strained. The 6-ring compound (XII) absorbs at 6.86 μ in line with the absorption of the open-chain dithioimidocarbonates. As the ring decreases to five and then four atoms, the C=N bond tightens and absorbs at 6.66 and 6.43 μ, respectively. Apparently, the sulfurs in the strained rings interact less with the C=N group until, in the four-membered ring, this imino group absorbs nearer its normal range.

The cyclic ethylene ester (XI) was obtained in higher yield and purer form, and therefore it was chosen for an investigation of the physical and chemical properties of the cyclic alkylene dithioimidocarbonates.

The nmr spectrum of XI confirmed the assigned structure as opposed to the alternative formulation

$$\begin{matrix}CH_2-S\\ |\quad\quad\diagdown\\ \quad\quad\quad C=S\\ CH_2-N\diagup\\ \quad\quad\diagdown\\ \quad\quad\quad CN\end{matrix}$$

XIV
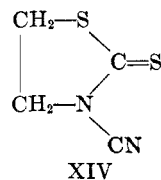
(XIV), for it showed only a sharp singlet at δ 3.85 (chloroform solution).

Conversions carried out on XI are summarized in Scheme I. The nitrile group of XI was readily hydrolyzed to a urea (XV) with concentrated hydrochloric acid.

SCHEME I
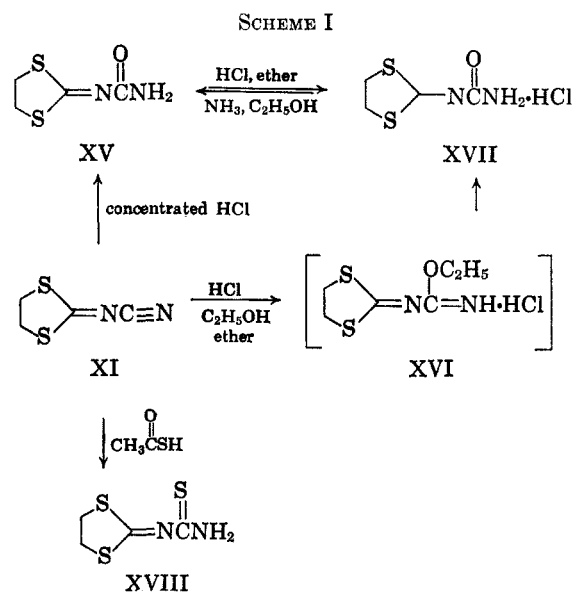
The imino ethyl ether[7a] derived from the nitrile (XI) could not be obtained pure and readily converted at room temperature to the urea hydrochloride (XVII).[7b] Evidence for the imino ether was obtained from its infrared spectrum which showed C—H stretching at 3.40 and a C=NH⁺ band at 6.00 μ.[8a] After standing for 48 hr in a desiccator, the intensity of the 6.00- and 3.40-μ peaks had greatly diminished with respect to bands at 3.85 ($NH_2\cdot HCl$),[8b] and 5.77 μ (C=O) owing to the urea hydrochloride (XVII). The urea hydrochloride was identified by conversion to the urea (XV) with ammonia and by the appearance of the same band at 5.75 μ in the infrared when a sample of XV was treated with ethereal hydrogen chloride.
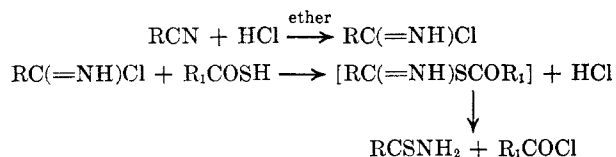
The stoichiometric conversion of XVI to XVII should lead to the free urea (XV). The source of the hy-

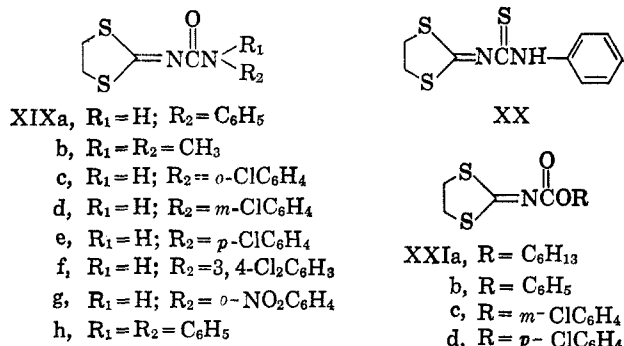(7) (a) R. Roger and D. G. Neilson, *Chem. Rev.*, **61**, 181 (1961); (b) *ibid.*, **61**, 188 (1961).
(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959; (a) p 269; (b) p 259.

drogen chloride in XVII may have been either excess hydrogen chloride absorbed on XVI or the formation of ethylene and hydrogen chloride rather than ethyl chloride as the second product in the rearrangement.[7b]

Several attempts were made to convert the nitrile (XI) to the thiourea (XVIII) with hydrogen sulfide in pyridine containing triethylamine,[9a] but only a trace of the desired product was obtained. The thiourea was successfully prepared by reaction of the nitrile with thiolacetic acid and hydrogen chloride at 0° in anhydrous ether.[9b] It has been postulated by Ishikawa[10] that this reaction proceeds through the imino chloride to the iminothiol ester which then decomposes to product as shown below.

$$RCN + HCl \xrightarrow{ether} RC(=NH)Cl$$

$$RC(=NH)Cl + R_1COSH \longrightarrow [RC(=NH)SCOR_1] + HCl$$
$$\downarrow$$
$$RCSNH_2 + R_1COCl$$

It was found possible to prepare derivatives (XIX) of the urea (XVII) in which the free NH_2 group of the urea was substituted by the reaction of 2-imino-1,3-dithiolane hydrochloride with isocyanates and carbamoyl chlorides in the presence of sodium bicarbonate. Similarly, reaction of the dithiolane hydrochloride with phenyl isothiocyanate and chloroformates produced XX and XXI, respectively.

XIXa, $R_1 = H$; $R_2 = C_6H_5$
  b, $R_1 = R_2 = CH_3$
  c, $R_1 = H$; $R_2 = o\text{-}ClC_6H_4$
  d, $R_1 = H$; $R_2 = m\text{-}ClC_6H_4$
  e, $R_1 = H$; $R_2 = p\text{-}ClC_6H_4$
  f, $R_1 = H$; $R_2 = 3,4\text{-}Cl_2C_6H_3$
  g, $R_1 = H$; $R_2 = o\text{-}NO_2C_6H_4$
  h, $R_1 = R_2 = C_6H_5$

XX

XXIa, $R = C_6H_{13}$
  b, $R = C_6H_5$
  c, $R = m\text{-}ClC_6H_4$
  d, $R = p\text{-}ClC_6H_4$

The 2-imino-1,3-dithiolane hydrochloride[11] was prepared by the method of Wheeler and Merriam[11] from thiolbenzoic acid and 2-chloroethyl thiocyanate. A new, more economical, preparation of this substance from cyanogen chloride and 1,2-ethanedithiol has been described by Addor.[12]

During this investigation we found that when VI was treated with perchloromethyl mercaptan the an-

VI
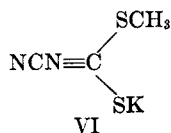
ticipated disulfide was not obtained. Instead, a solid which lacked the characteristic nitrile absorption in the infrared spectrum was isolated. This compound was subsequently characterized as 3-chloro-5-(methylthio)-1,2,4-thiadiazole (XXII) by elemental analysis, spectral data, and chemical means.

(9) (a) A. E. S. Fairfull, J. L. Lowe, and D. A. Peak, J. Chem. Soc., 742 (1952); (b) ibid., 51 (1952).
(10) S. Ishikawa, Sci. Papers Inst. Phys. Chem. Res. (Tokyo), 7, 293 (1928); Chem. Abstr., 22, 1343 (1928).
(11) H. L. Wheeler and H. F. Merriam, J. Am. Chem. Soc., 24, 439 (1902).
(12) R. W. Addor, J. Org. Chem., 29, 738 (1964).
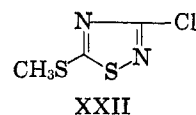
XXII

For example, the infrared spectrum was nearly superimposable on that of authentic 2,5-bis(methylthio)-1,2,4-thiadiazole.[13] Oxidation of XXII with an excess of 2 or more molar equiv of hydrogen peroxide gave only one sulfone product (XXIII) which is consistent with the assigned structure.
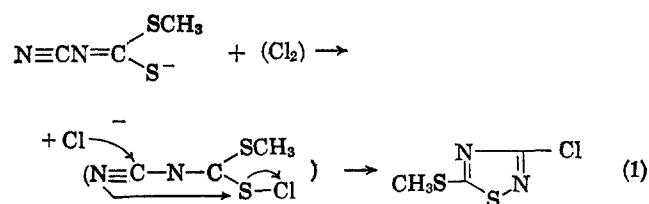
XXIII
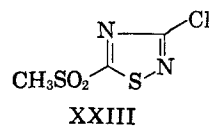
Goerdeler and co-workers[14] have prepared a series of 1,2,4-thiadiazoles by another route and among them was the isomeric 5-chloro-3-(methylthio)-1,2,4-thiadiazole (XXIV). Displacement of the chlorine in the 5
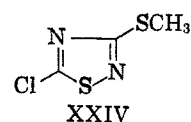
XXIV

position was readily affected in the case of XXIV. However, XXII was unreactive in comparable reactions. With boiling ammonium hydroxide or sodium methylmercaptide in refluxing methanol, only starting material was recovered. The sulfone (XXIII), with sodium methylmercaptide in boiling methanol, gave a crude product which exhibited a strong nitrile band in the infrared spectrum suggesting a ring-opening reaction with ejection of chloride ion. This possibility was not investigated further.

As the transformation of VI → XXII may also be carried out with sulfuryl chloride in refluxing chloroform, the first step undoubtedly involves a chlorination. A mechanistic interpretation of the transformation is presented in eq 1.

$$N\equiv CN=C\langle{}^{SCH_3}_{S^-} + (Cl_2) \longrightarrow$$

$$+Cl \langle (N\equiv C-N-C\langle{}^{SCH_3}_{S-Cl}) \rightarrow CH_3S-\overset{N}{\underset{S}{\|}}-Cl \quad (1)$$

An analogous scheme has recently been proposed by Hatchard[15] for the cyclization of di(sodiomercapto)-methylenemalonitrile to 3,5-dichloro-4-isothiazolecarbonitrile with excess chlorine in boiling carbon tetrachloride.

Experimental Section

(13) J. W. James, J. Prakt. Chem., 138, 352 (1879).
(14) J. Goerdler and K. H. Heller, Chem. Ber., 97, 225 (1964); J. Goerdler and H. W. Hammen, ibid., 1134 (1964).
(15) W. R. Hatchard, J. Org. Chem., 29, 660 (1964).

Potassium Methyl Cyanodithioimidocarbonate (VI).—A solution of 150.0 g (0.77 mole) of dipotassium cyanodithioimidocarbonate (I) in 615 ml of acetone and 690 ml of water was cooled below 0°, and 109.2 g (0.77 mole) of methyl iodide in 310 ml of acetone was added dropwise with rapid stirring below 0° under a nitrogen atmosphere. After completion of the addition, the reaction mixture was stirred for another 0.5 hr in the ice bath and for 3.5 hr at ambient temperature. The solution was evaporated and the product was dried at 50° to give 271.0 g of solid. This was stirred with 1625 ml of acetone and filtered. The filtrate was evaporated and the residue was washed with two 650-ml portions of ether to yield 124.5 g (95%) of crude product (mp 215.5–218.0°) which was sufficiently pure for use in further reactions.

Anal. Calcd for $C_3H_3KN_2S_2$: C, 21.15; H, 1.78; N, 16.45; S, 37.66. Found: C, 20.12; H, 1.60; N, 14.22; S, 31.15.

The product was further purified by dissolving in 2050 ml of ethyl acetate and reprecipitating with an equal volume of ligroin (bp 60–90°) to give 61.7 g (47%): mp 214–216°, infrared at 4.71 and 7.40 μ.

Anal. Found: 20.96; H, 1.88; S, 37.76.

Dimethyl Cyanodithioimidocarbonate (IIIa) from Potassium Methyl Cyanodithioimidocarbonate.—A solution of 12.8 g (0.075 mole) of VI in 64 ml of acetone was cooled below 10° in a nitrogen atmosphere and 12.8 g (0.090 mole) of methy iodide was added dropwise (mildly exothermic). The ice bath was removed, and the reaction mixture was stirred for 2.5 hr at room temperature. The acetone was removed in a rotary evaporator to leave a solid which was purified by twice dissolving in acetone and reprecipitating with water. The product weighed 6.4 g (58%), mp 51–52.5° (lit.[2] 57°).

Anal. Calcd for $C_4H_6N_2S_2$: C, 32.85; H, 4.14; S, 43.85. Found: C, 32.84; H, 4.15; S, 43.73.

An authentic sample of IIIa, prepared from disilver cyanodithioimidocarbonate and methyl iodide,[2] melted at 50.5–51.5°, with IIIa obtained above mmp 51.5–54°. The infrared spectra of the two samples were identical.

Alkylation of Potassium Methyl Cyanodithioimidocarbonate (VI).—Unless otherwise stated, the reactions were carried out by dropwise addition of 0.075 mole of alkyl halide in 20 ml of acetone solution to 12.8 g (0.075 mole) of VI in 65 ml of acetone under a nitrogen atmosphere. After stirring overnight (*ca.* 16 hr), the reaction mixture was refluxed for 1 hr. Inorganic salt produced was filtered off and the filtrate was evaporated with a rotary evaporator (*ca.* 50°, aspirator vacuum). The residue was taken up in 200 ml of chloroform. The chloroform solution was washed with two 100-ml portions of water, dried with magnesium sulfate, and evaporated (aspirator) to obtain the crude products. Reactions could be followed by the precipitation of alkyl halide which usually appears within a few minutes.

Methoxymethyl Methyl Cyanodithioimidocarbonate (Xa).—The reaction mixture was filtered and the acetone evaporated to leave 9.0 g (68%) of viscous, red oil.

Anal. Calcd for $C_5H_8N_2OS_2$: C, 34.07; H, 4.57; S, 36.38. Found: C, 34.04; H, 4.25; S, 34.24.

A 1.21-g portion of crude VII was purified by chromatography on 60 g of silicic acid to give 0.34 g of an oil.

Anal. Found: C, 33.83; H, 4.25; S, 35.98.

Dimethylcarbamoylmethyl Methyl Cyanodithioimidocarbonate (Xb).—The residue was recrystallized from chloroform (charcoal treatment of the hot chloroform solution) to give 9.7 g (44.7%) of white crystals, mp 102.5–103°.

Anal. Calcd for $C_7H_{11}N_3OS_2$: C, 38.69; H, 5.10; S, 29.51. Found: C, 39.34; H, 5.18; S, 28.72.

Ethylcarbamoylmethyl Methyl Cyanodithioimidocarbonate (Xc).—The crude product was recrystallized from acetone (hot acetone solution treated with charcoal) to give 7.5 g (46%) of a white solid, mp 125–126°.

Anal. Calcd for $C_7H_{11}N_3OS_2$: C, 38.69; H, 5.10; S, 29.51. Found: C, 38.49; H, 4.93; S, 29.26.

Carbamoylmethyl Methyl Cyanodithioimidocarbonate (Xd).—The solid residue obtained upon evaporation of the acetone was not taken up in chloroform, but stirred directly with water and recrystallized from ethanol to give 5.6 g (40%) of a solid, mp 152–154.5°.

Anal. Calcd for $C_5H_7N_3OS_2$: C, 31.73; H, 3.73; S, 33.88. Found: C, 31.40; H, 3.72; S, 33.65.

Carbethoxymethyl Methyl Cyanodithioimidocarbonate (Xe).—The oily residue crystallized upon standing. It was recrystal-

lized three times from ether and once from carbon disulfide to give 5.8 g (36%), mp 34–36°.

Anal. Calcd for $C_7H_{10}N_2O_2S_2$: C, 38.51; H, 4.62; S, 29.38. Found: C, 37.72; H, 4.99; S, 28.74.

The ether and carbon disulfide mother liquors were combined and evaporated. The residue was recrystallized twice from carbon disulfide to give 4.9 g, mp 30.8–35.8°.

Cyanomethyl Methyl Cyanodithioimidocarbonate (Xf).—Recrystallization of the crude product from ethanol–water gave 10.0 g (58%), mp 59–60°.

Anal. Calcd for $C_5H_5N_3S_2$: C, 35.07; H, 2.94; S, 37.45. Found: C, 35.24; H, 2.98; S, 37.84.

Allyl Methyl Cyanodithioimidocarbonate (Xg).—The crude product was an oil (9.8 g, 75%) and was not further purified.

Anal. Calcd for $C_6H_8N_2S_2$: C, 41.8; H, 4.68; S, 37.23. Found: C, 40.94; H, 4.53; S, 38.34.

2-Chloroallyl Methyl Cyanodithioimidocarbonate (Xh).—The crude product was a red oil which could not be distilled without decomposition, yield 8.6 g (56%).

Anal. Calcd for $C_6H_7ClN_2S_2$: C, 34.8; H, 3.66; S, 31.02. Found: C, 33.08; H, 3.08; S, 32.30.

Carboxymethyl Methyl Cyanodithioimidocarbonate (Xi).—A solution of 12.8 g (0.075 mole) of VI and 8.8 g (0.075 mole) of sodium chloroacetate in 65 ml of acetone and 17 ml of water (required to effect solution of the sodium chloroacetate) was refluxed for 3 hr under nitrogen. The two-phase liquid was filtered and evaporated with a rotary evaporator. The residue was stirred with 350 ml of water and the aqueous phase was decanted from the black, tarry residue. The solution was acidified in an ice bath and refrigerated overnight. The crude product was filtered off and recrystallized from ethanol–water (charcoal treatment of the hot solution) to give 1.3 g (9%), mp 104–109°.

Anal. Calcd for $C_5H_6N_2O_2S_2$: C, 34.8; H, 3.66; S, 31.02. Found: C, 33.08; H, 3.08; S, 32.30.

Bis(N-Cyanoimidomethylthiocarbonyl) Trithiocarbonate (VIII).—To a mixture of 14.5 g (0.085 mole) of potassium methyl cyanodithioimidocarbonate (VI) in 30 ml of diglyme (dried by distillation from LiAlH₄) cooled to 10° was added a solution of 10.3 g (0.09 mole) of thiophosgene in 30 ml of diglyme. The addition was exothermic and precipitation occurred immediately. The reaction mixture was stirred for 30 min at ambient temperature. The product was filtered off and washed with ether, two 50-ml and one 100-ml portions of boiling acetone, and two 100-ml portions of water to leave 3.9 g (10%): mp 199–202.0°; λmax 4.56 (C≡N), 6.73 (C=N), 9.74, 10.56 μ.

Anal. Calcd for $C_7H_6N_4S_5$: C, 27.43; H, 1.97; N, 18.28; S, 52.31. Found: C, 28.24; H, 2.38; N, 17.42; S, 50.59.

Ethoxycarbonyl Methyl Cyanodithioimidocarbonate (XI).—A solution of 17.0 g (0.1 mole) of potassium methyl cyanodithioimidocarbonate (VI) in 85 ml of acetone was cooled below 10° and 10.8 g (0.1 mole) of ethyl chloroformate was added dropwise under a nitrogen atmosphere. The reaction mixture was refluxed for 6 hr under a positive nitrogen pressure, during which time precipitate formed in the flask. The reaction mixture was allowed to cool to room temperature overnight. It was filtered and the filtrate was evaporated in a rotary evaporator and filtered once more to leave 15.9 g (78%) of a red oil: λmax 4.56 (C≡N), 5.75 (C=O), 7.05, 6.70, (C=N), 9.93, 10.45 μ.

Anal. Calcd for $C_6H_8N_2O_2S_2$: C, 35.28; H, 3.95; S, 31.39. Found: C, 35.62; H, 4.06; S, 31.68.

Reaction of I with Bromobenzene.—The reaction was based on the procedure of Reifschneider[6] for the reaction of substituted bromobenzenes with sodium methyl mercaptide in refluxing 2,4-lutidine, employing cuprous bromide catalyst. A suspension of 14.6 g (0.075 mole) of I, 21.5 g (0.15 mole) of CuBr, and 23.6 g (0.15 mole) of bromobenzene was refluxed for 24 hr in 100 ml of 2,4-lutidine (dried over KOH, then BaO, then distilled) under nitrogen. The mixing of reagents was exothermic (to 58°). The green liquid phase turned brownish black upon heating, and the solution became homogeneous at 115°. After reflux was completed, the reaction mixture was concentrated and taken up in 150 ml of hot chloroform. The chloroform was washed with two-100 ml portions of 3 N HCl and dried with MgSO₄. The chloroform was evaporated to leave an oil which was distilled to give three fractions: fraction 1 had bp 125–131° (2.3 mm); fraction 2 had bp 131–140° (2.2 mm); fraction 3 had bp 140–148° (2.1 mm). The pot residue was small, and its infrared spectrum did not show nitrile absorption. Upon refrigeration, fractions 2 and 3 deposited solid which was recrystallized from

ethanol. Its infrared spectrum was identical with that of authentic diphenyl disulfide. The liquid phases of fractions 2 and 3 were combined to give fraction 4. The infrared spectrum of fractions 1 and 4 and diphenyl sulfide were identical.

N-Cyano-2-imino-1,3-dithiolane (XI).—To a two-phase liquid mixture of 19.4 g (0.1 mole) of I in 70 ml of acetone and 85 ml of water was added dropwise (while stirring under nitrogen) 18.8 g (0.1 mole) of 1,2-dibromoethane in 5 ml of acetone, and the reaction mixture was stirred for 21 hr under nitrogen at room temperature as a precipitate slowly formed. The mixture was diluted with 290 ml of ice-cold water and filtered. The solid was recrystallized from ethanol–water to give 10.8 g (75%) of white needles: mp 79.2–81.2°; λ_{max} 4.58 (C≡N), 6.66 (C=N), 7.02, 9.94, 10.24 μ.

Anal. Calcd for $C_4H_4N_2S_2$: C, 33.31; H, 2.80; S, 44.47. Found: C, 33.90; H, 2.79; S, 44.96.

N-Cyano-2-imino-1,3-dithiane (XII).—To a solution of 19.4 g (0.1 mole) of I in 70 ml of acetone and 90 ml of water was added, dropwise at room temperature under nitrogen, 20.2 g (0.1 mole) of 1,3-dibromopropane. The dropping funnel was rinsed with 10 ml of acetone which was allowed to run into the reaction mixture. The 1,3-dibromopropane settled to the bottom of the flask. The temperature slowly climbed to 36° 30 min after the addition and began to drop after another 20 min, at which time the reaction mixture was homogeneous. After 21 hr, the reaction mixture was diluted with 290 ml of ice-cold water and filtered. The yellow solid was recrystallized twice from ethanol to give 6.5 g (41%) of pale yellow crystals: mp 99–102°; λ_{max} 4.62 (C≡N), 6.86 (C=N), 7.07, 9.95, 10.10 μ.

Anal. Calcd for $C_5H_6N_2S_2$: C, 37.95; H, 3.82; S, 40.53. Found: C, 37.78; H, 3.51; S, 40.60.

Cyclic Methylene Cyanodithioimidocarbonate.—To a suspension of 19.4 g (0.1 mole) of I in 100 ml of acetonitrile was added dropwise 26.8 g (0.1 mole) of methylene iodide. The suspension was stirred for 1 hr at room temperature and refluxed for 18 hr. The hot acetonitrile solution was decanted and the residue was treated with another 25 ml of hot acetonitrile which was combined with the decantate. The acetonitrile was evaporated and the residue was dissolved in acetone. The acetone solution was stirred with charcoal and filtered, and ether was added to precipitate a high-melting solid. The acetone–ether filtrate was evaporated and the residue was recrystallized from ethanol (charcoal) to give 3.8 g (29%): mp 93.5–94.5°, λ_{max} 4.61 (C≡N), 6.43 (C=N), 7.23, 9.92, 10.37 μ.

Anal. Calcd for $C_3H_2N_2S_2$: C, 27.67; H, 1.55; N, 21.52; S, 49.26. Found: C, 27.68; H, 1.58; N, 21.20; S, 49.04.

2-Carbamoylimino-1,3-dithiolane.—A mixture of 8.4 g (0.075 mole) of XI was stirred with 63 ml (0.75 mole) of concentrated HCl. After 20 min the reaction mixture became homogeneous and the temperature rose to 38°. After standing overnight, the solution was evaporated at 60° to leave 10.7 g of a white solid which was partially water soluble. A 9.9-g quantity (0.05 mole) was stirred with 40 ml of water and just neutralized with 22 ml (0.06 mole) of 10% NaOH. The neutralized mixture was refrigerated and filtered to give 5.2 g (46%, mp 154.2–159.8°) submitted as an analytical sample. Two recrystallizations of 0.5 g of the product gave 0.3 g: mp 156.7–161.2°; λ_{max} 3.01 (NH₂), 3.22 (NH₂), 6.13 (C=O), 6.26 (NH₂), 6.56 (C=N), 7.01, 10.25 μ.

Anal. Calcd for $C_4H_6N_2OS_2$: C, 29.6; H, 3.73; S, 39.53. Found: C, 30.03; H, 3.68; S, 39.58.

Conversion of N-Cyano-2-imino-1,3-dithiolane (XI) to a Mixture of the Imino Ethyl Ester Hydrochloride (XVI) and the Urea Hydrochloride (XVII).—A mixture of 14.4 g (0.1 mole) of XI, 4.80 g (0.104 mole) of absolute ethanol, and 70 ml of anhydrous ether was placed in a flask which had previously been dried and swept with nitrogen. The flask was cooled to 0°, and the temperature was held at 0° as HCl gas was passed in. After 3 hr the ice bath was removed and the HCl gas was passed through for another 4 hr. The reaction mixture was stirred overnight under nitrogen. The fine solid which had formed was rapidly filtered off, washed with dry ether, and placed in a desiccator over powdered P_2O_5 and NaOH pellets. After 2 hr of evacuation in the desiccator, a sample was withdrawn for an infrared spectrum. Contamination with starting nitrile was indicated by the weak band at 4.57 μ. The imino ether was indicated by bands at 3.40 (C_2H_5), and 6.00 μ (C=NH⁺).[8a] A band at 5.74 μ demonstrated the presence of the urea hydrochloride (XVII). After 48 hr a second sample was withdrawn from the desiccator. The band at 3.40 μ had disappeared and the band at 6.00 μ had greatly

decreased in intensity relative to the peak at 5.77 μ. A shoulder at 3.85 μ (NH_2·HCl[8b]) had appeared.

2-Carbamoylimino-1,3-dithiolane (XV) from Its Hydrochloride (XVII).—A suspension of 11.3 g (0.069 mole) of XVII (obtained from N-cyano-2-imino-1,3-dithiolane with HCl and ethanol in ether) in 15 ml (0.054 mole) of 3.6 M ammonia in absolute ethanol was stirred first in an ice bath and then for 3 days at room temperature. The reaction mixture was boiled with 100 ml of ethanol which was filtered hot. Upon cooling, the filtrate deposited 6.2 g of solid, mp 152.3–158.8°. The reaction mixture was treated similarly with another 100 ml of boiling ethanol, and 1.0 g of additional solid was obtained. The two solids were combined and recrystallized from ethanol to give 4.8 g (44%) of XV: mp 157.7–162.7°; λ_{max} 2.96, 3.17, 6.11, 6.23, 6.54, 6.99, 10.23 μ.

2-Carbamoylimino-1,3-dithiolane Hydrochloride (XVII).—A 0.2-g quantity (0.001 mole) of XV in 10 ml of anhydrous ether was stirred as anhydrous hydrogen chloride gas was bubbled in for 2 hr at room temperature. The product (0.21 g, 86%, mp 158–173° dec) showed infrared bands at 3.87 (NH_2·HCl),[8b] 3.12, 3.22 (NH), and 5.78 (C=O) μ.

2-Thiocarbamoylimino-1,3-dithiolane (XVIII).—A suspension of 6.5 g (0.045 mole) of N-cyano-2-imino-1,3-dithiolane (XI) and 3.4 g (0.045 mole) of thiolacetic acid (dried with $MgSO_4$) in 65 ml of anhydrous ether was cooled in an ice bath to 0° under nitrogen, and hydrogen chloride gas (dried by passing through concentrated H_2SO_4) was bubbled through the suspension for 3 hr at 0°. The color of the suspended solid changed from white to bright yellow. The reaction mixture was allowed to stand overnight. The solid was filtered off, washed with 500 ml of ethyl ether, and purified by dissolving in 5% NaOH and reprecipitating with 3 M HCl. The dried product weighed 3.0 g (37%): mp 135.7–138.1°; λ_{max} 6.25 (NH_2), 6.69 (C=N), 7.05, 9.94, 10.72 μ.

Anal. Calcd for $C_4H_6N_2S_3$: C, 26.94; H, 3.39; S, 53.95. Found: C, 26.50; H, 3.54; S, 54.22.

2-Imino-1,3-dithiolane Hydrochloride.—This compound was prepared by the method of Wheeler and Merriam.[11] A solution of 95.5 g (0.787 mole) of 2-chloroethyl thiocyanate[13] and 213.8 g (1.575 mole) of thiolbenzoic acid in 625 ml of sodium-dried benzene was refluxed for 45 min under sulfuric acid-dried nitrogen. The reaction mixture was cooled and filtered to give 129 g of crude product. This was dissolved in water and reprecipitated with acetone to give 76.9 g (62.8%): mp 215.4–220.4° (lit.[11] 212–216°); λ_{max} 3.67, 6.44, 6.77, 10.16, 10.38 μ.

Anal. Calcd for $C_3H_6ClNS_2$: C, 23.15; H, 3.88; S, 41.20. Found: C, 23.78; H, 4.00; S, 40.38.

Reaction of 2-Imino-1,3-dithiolane Hydrochloride with Isocyanates, Carbamoyl Chlorides, and Chloroformates.—A suspension of 7.8 g (0.05 mole) of 2-imino-1,3-dithiolane hydrochloride, 0.05 mole of the isocyanate, etc, and sodium bicarbonate (0.15 mole for isocyanates and isothiocyanates and 0.20 mole for chloroformates and carbamoyl chlorides) in 60 ml of acetone was refluxed 4 hr. As soon as the temperature reached *ca.* 40°, gas evolution was observed. The reaction mixture was cooled and filtered. The solid was washed with 150 ml of water and the water-insoluble portion was combined with the precipitate formed when the acetone filtrate was poured into 200 ml of water to give the combined crude product.

1-[2-(1,3-Dithiolaneidene)]-3-phenylurea (XIXa).—The recrystallized product weighed 7.8 g (66%): mp 171.0–173.0°; λ_{max} 3.01, 6.07, 6.58, 7.03, 9.88, 10.50 μ.

Anal. Calcd for $C_{10}H_{10}N_2OS_2$: C, 50.40; H, 4.23; S, 26.91. Found: C, 50.02; H, 4.06; S, 27.16.

1,1-Dimethyl-3-[2-(1,3-dithiolaneidene)]urea (XIXb).—The reaction mixture was refluxed for 18 rather than for 4 hr. The crude product, a waxy, yellow solid, was dissolved in chloroform, and ether was added. The water-soluble precipitate was discarded, and the filtrate was evaporated to leave 5.7 g, mp 58.8–63.8°. Sublimation at 60° (0.005 mm) gave 3.3 g (35%): mp 65.9–67.9° (softens 58.9°); λ_{max} 6.17, 6.75, 7.03, 9.98, 10.45 μ.

Anal. Calcd for $C_6H_{10}N_2OS_2$: C, 37.87; H, 5.29; S, 33.70. Found: C, 37.67; H, 5.28; S, 33.55.

1-(2-Chlorophenyl)-3-[2-(1,3-dithiolaneidene)]urea (XIXc).—The crude product was recrystallized from ethanol to give 11.0 g (80%) of colorless needles: mp 150.3–152.3°; λ_{max} 3.15, 6.02, 6.69, 7.07, 9.82, 10.41 μ.

Anal. Calcd for $C_{10}H_9ClN_2OS_2$: C, 44.03; H, 3.32; S, 23.50. Found: C, 43.61; H, 3.02; S, 24.09.

1-(3-Chlorophenyl)-3-[2-(1,3-dithiolaneidene)]urea (XIXd).— The crude product was recrystallized from ethanol to give 9.5 g (70%) of colorless needles: mp 134.6–136.1°; λ_{max} 2.98, 6.01, 6.75, 7.03, 9.89, 10.51 μ.

Anal. Calcd for $C_{10}H_9ClN_2OS_2$: C, 44.03; H, 3.32; S, 23.50. Found: C, 44.10; H, 3.11; S, 23.75.

1-(4-Chlorophenyl)-3-[2-(1,3-dithiolaneidene)]urea (XIXe).— The crude product was recrystallized from ethanol to give 9.9 g (72%) of colorless needles: mp 191.0–193.0°; λ_{max} 2.98, 6.03, 6.76, 7.03, 9.90, 10.39 μ.

Anal. Calcd for $C_{10}H_9ClN_2OS_2$: C, 44.03; H, 3.32; S, 23.50. Found: C, 44.99; H, 3.50; S, 24.25.

1-(3,4-Dichlorophenyl-3-[2-(1,3-dithiolanidene)]urea (XIXf).— The crude product was recrystallized from ethyl acetate to give 11.0 g (72%) of colorless crystals: mp 191.0–192.0°; λ_{max} 2.99, 6.01, 6.62, 7.06, 9.90, 10.37 μ.

Anal. Calcd for $C_{10}H_8Cl_2N_2OS_2$: C, 39.09; H, 2.62; S, 23.08. Found: C, 38.60; H, 2.69; S, 21.48.

1-[2-(1,3-Dithiolaneidene)]-3-(2-nitrophenyl)urea (XIXg).— The crude product was recrystallized twice from ethanol to give 3.0 g (21%) of light yellow needles: mp 168.0–170.5°; λ_{max} 3.04, 5.99, 6.35, 6.77, 7.06, 7.50, 9.94, 10.42 μ.

Anal. Calcd for $C_{10}H_9N_3O_3S_2$: C, 42.39; H, 3.20; S, 22.63. Found: C, 42.61; H, 3.49; S, 23.06.

1,1-Diphenyl-3-[2-(1,3-dithiolaneidene)]urea (XIXh).— The crude product was recrystallized from ethanol to give 7.7 g (49%) of colorless needles: mp 191.0–191.5°; λ_{max} 6.12, 6.75, 7.04, 9.94, 10.40 μ.

Anal. Calcd for $C_{16}H_{14}N_2OS_2$: C, 61.12; H, 4.49; S, 20.40. Found: C, 60.76; H, 4.11; S, 20.43.

1-[2-(1,3-Dithiolaneidene)]-3-phenyl-2-thiourea (XX).— The crude product was recrystallized from ethanol to give 11.0 g (86%) of bright yellow crystals: mp 116.9–118.5°; λ_{max} 3.22, 6.60, 7.01, 9.76, 10.61, 11.80 μ.

Anal. Calcd for $C_{10}H_{10}N_2S_3$: C, 47.21; H, 3.96; S, 37.81. Found: C, 46.64; H, 4.05; S, 39.08.

n-Hexyl N-[2-(1,3-dithiolaneidene)]carbamate (XXIa).— The work-up was varied from the general procedure. The reaction mixture was filtered and the filtrate was evaporated. The light brown, oily residue was dissolved in chloroform and the solution was dried with MgSO₄. The chloroform was evaporated to leave 9.6 g (78%) of a light brown liquid: λ_{max} 5.94, 6.60, 7.00, 9.81, 10.11 μ.

Anal. Calcd for $C_{10}H_{17}NO_2S_2$: C, 48.55; H, 6.93; S, 25.92. Found: C, 47.98; H, 6.99; S, 25.44.

Phenyl N-[2-(1,3-Dithiolaneidene)]carbamate (XXIb).— The crude product was recrystallized to 12.2 g (51%) of colorless plates: mp 110.5–111.0°; λ_{max} 5.91, 6.63, 7.03, 10.05, 10.61 μ.

Anal. Calcd for $C_{10}H_9NO_2S_2$: C, 50.19; H, 3.79; S, 26.80. Found: C, 49.56; H, 4.26; S, 27.13.

m-Chlorophenyl N-[2-(1,3-Dithiolaneidene)]carbamate (XXIc). — The crude product was recrystallized from ethanol to give 2.8 g (20%) of colorless needles; mp 128.1–129.1°; λ_{max} 5.93, 6.64, 7.07, 9.89, 10.60 μ.

Anal. Calcd for $C_{10}H_8ClNO_2S_2$: C, 43.87; H, 2.95; S, 23.43. Found: C, 43.46; H, 2.97; S, 23.87.

4-Chlorophenyl N-[2-(1,3-Dithiolaneidene)]carbamate (XXId). — The crude product was recrystallized from ethanol to give 4.8 g (35%) of colorless needles: mp 136.1–138.1°; λ_{max} 5.94, 6.74, 7.07, 9.98, 10.58 μ.

Anal. Calcd for $C_{10}H_8ClNO_2S_2$: C, 43.87; H, 2.95; S, 23.43. Found: C, 43.63; H, 3.09; S, 26.36.

3-Chloro-5-methylthio-1,2,4-thiadiazole (XXII).— Trichloromethanesulfenyl chloride (18.6 g, 0.10 mole) was added dropwise to a stirred solution of 17.0 g (0.10 mole) of monopotassium methyl N-cyanoimidodithiocarbonate (VI) in 200 ml of water previously cooled to 5°. The temperature was maintained near 5° during the addition which required approximately 1 hr. A yellow liquid separated at the bottom of the aqueous layer during this period. At the completion of the addition the reaction mixture was allowed to warm slowly to room temperature and stirred for an additional 0.5 hr. The reaction mixture was then transferred to a separatory funnel and extracted with ether, and the combined ether extracts were washed with water, dried over magnesium sulfate, filtered, and evaporated *in vacuo*. This treatment afforded a dark brown, heterogeneous solid. Extraction of the solid with hot ligroin (bp 60–90°) gave a brown solution which was charcoaled to remove most of the color. A colorless, crystalline solid (8.5 g, 50%) was obtained upon cooling the solution, mp 52.5–53.5°. Further recrystalliza-

tions from ligroin gave an analytical sample: mp 54–55°; the infrared spectrum of XXII showed (CHCl₃) 7.42, 9.50, 11.08, 9.35, 7.60 μ; (KBr) 7.00, 8.20, 9.35, 10.35 μ. The nmr spectrum of XXII in carbon tetrachloride showed a single peak at δ 2.82 relative to tetramethylsilane.

Anal. Calcd for $C_3H_3ClN_2S_2$: C, 21.62; H, 1.81; Cl, 21.27; S, 38.48; mol wt, 167. Found: C, 21.88; H, 1.70; Cl, 21.11; S, 38.16; mol wt, 150 (Rast).

Using acetone as a solvent, XXII was prepared in 16% yield by the above method. Compound XXII could also be prepared using sulfuryl chloride in place of the trichloromethanesulfenyl chloride in refluxing chloroform to give an 89% yield of crude product. The infrared spectrum of the crude product was identical with that of pure XXII, but purification lowered the final yield to 26%.

To a suspension of 12.8 g (0.075 mole) of potassium methyl cyanodithioimidocarbonate (VI) in 65 ml of dry chloroform was added dropwise 11.5 g (0.085 mole) of sulfuryl chloride while the temperature was held below 10°. The reaction mixture was stirred for 1 hr below 0° and for 1 hr at room temperature. The temperature was increased to reflux with gas evolution being apparent from 35°. The reaction mixture was refluxed for 3 hr and cooled. It was filtered, and the filtrate was evaporated to leave 11.2 g of a red oil which soon solidified. The product was recrystallized twice from ligroine (bp 60–90°) and twice from pentane (decolorizing charcoal) to give 3.2 g (26%) of XXII as tan plates, mp 52.1–52.6°, with XXII prepared above mmp 52.1–53.1°.

3-Chloro-5-(methylsulfonyl)-1,2,4-thiadiazole (XXIII).— 3-Chloro-5-methylthio-1,2,4-thiadiazole (8.3 g, 0.05 mole) in 25 ml of glacial acetic acid and 25 ml of acetic anhydride was cooled to 0° and 14.7 g (0.13 mole) of 30% hydrogen peroxide was added dropwise with stirring. At the completion of the addition the homogeneous solution was allowed to warm slowly to room temperature over a period of 3 hr. The solution was then stirred at ambient temperature for 2 days. Manganese dioxide was added to decompose excess peroxide, the mixture was filtered, the filtrate was concentrated *in vacuo*, and cold water was added to the resulting liquid residue to separate a colorless oil. Sodium bicarbonate was added to this mixture to neutralize residual acid, and the solution was extracted with ether. The combined ether extracts were washed with water, dried over magnesium sulfate, and filtered, and the filtrate was evaporated *in vacuo*, which gave 5.5 g (55%) of white solid, mp 73–78°. Several recrystallizations of this from ligroin (bp 60–90°) and a little ether gave 3 g of colorless, crystalline solid, mp 82–83°. The nmr spectrum of XXIII in carbon tetrachloride showed a single peak at δ 3.45 relative to tetramethylsilane.

Anal. Calcd for $C_5H_3ClN_2O_2S_2$: C, 18.14; H, 1.52; S, 32.28. Found: C, 18.44; H, 1.50; S, 32.32.

Reaction of 3-Chloro-5-(methylthio)1,2,4-thiadiazole (XXII) with Ammonium Hydroxide.— To 35 ml of concentrated, aqueous ammonium hydroxide (30%) was added 6.7 g (0.04 mole) of 3-chloro-5-(methylthio)-1,2,4-thiadiazole (XXII). The mixture was warmed to 60° and maintained at that temperature for 3 hr. Additional ammonium hydroxide was added from time to time. The reaction mixture was then cooled and the insoluble solid was filtered. Further work-up afforded 5.4 g (81% recovery) of starting material, mp 52–53°. No other product was isolated.

Reaction of 3-Chloro-5-(methylsulfonyl)-1,2,4-thiadiazole (XXIII) with Sodium Methylmercaptide.— Anhydrous methanol (20 ml) and 0.34 g (0.015 g-atom) of sodium metal were mixed and stirred until all of the sodium reacted. To the above was added, with stirring, 0.72 g (0.015 mole) of methyl mercaptan. The solution which resulted was cooled to 15° and 2.3 g (0.011 mole) of 3-chloro-5-(methylsulfonyl)-1,2,4-thiadiazole (XXIII) was added carefully with stirring. The reaction mixture was warmed to 35° and stirred for 16 hr at this temperature An insoluble, white solid (sodium chloride) was removed by filtration and the filtrate evaporated *in vacuo*. This treatment afforded a yellow, viscous oil. An infrared spectrum of the crude product exhibited a strong nitrile band at 4.55 μ. Attempts to isolate a characterizable product, however, were uniformly unsuccessful.

Reaction of 3-Chloro-5-methylthio-1,2,4-thiadiazole (XXII) with Sodium Methylmercaptide.— A solution of 1.46 g (0.027 mole) sodium methylate in 15 ml of anhydrous methanol was stirred in an ice bath as 0.87 g (0.018 mole) of methanethiol in 3 ml of methanol was added, followed by 3.0 g (0.018 mole) of XXII.

The solution was refluxed for 1 hr and another 0.44 g (0.009 mole) of methanethiol in 3 ml of methanol was added. Reflux was contained for another 7 hr. The mixture was filtered and the filtrate was evaporated. The residue was partitioned between 25 ml of chloroform and 25 ml of water. The chloroform layer was washed with 25 ml of water, dried with magnesium sulfate, and evaporated to leave a yellow solid. The solid was recrystallized from pentane–ether to give 0.5 g, mp 52.2–53.7°, with XXII mmp 52.1–53.3°. The infrared spectrum was identical with that of XXII.

Registry No.—IIIa, 10191-60-3; VI, 10191-61-4; VIII, 10191-62-5; IX, 10191-63-6; Xa, 10239-65-3; Xb, 10191-64-7; Xc, 10191-65-8; Xd, 10191-66-9; Xe, 10191-67-0; Xf, 10191-68-1; Xg, 10191-69-2; Xh, 10191-70-5; Xi, 10191-71-6; XI, 10191-72-7; XII, 10191-73-8; XV, 10191-74-9; XVII, 10191-75-0; XVIII, 10191-76-1; XIXa, 10191-77-2; XIXb, 10191-78-3; XIXc, 10191-79-4; XIXd, 10191-80-7; XIXe, 10191-81-8; XIXf, 10191-82-9; XIXg, 10191-83-0; XIXh, 10191-84-1; XX, 10191-85-2; XXIa, 10191-86-3; XXIb, 10191-87-4; XXIc, 10191-88-5; XXId, 10191-89-6; XXII, 10191-90-9; XXIII, 10191-91-0; cyanodithioimidocarbonic acid, 108-04-3; cyclic methylene cyanodithioimidocarbonate, 10191-92-1; 2-imino-1,3-dithiolane hydrochloride, 1072-49-7.

Arylenebis(tertiary phosphines) and -(phosphinic acids)

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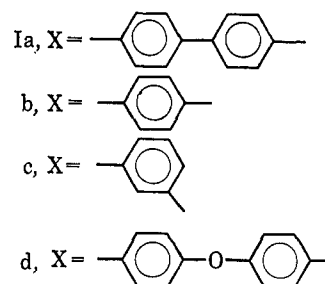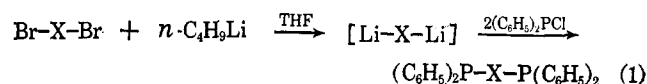
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n-Butyllithium has been effectively utilized to prepare arylenemono- or -dilithiums from which monosubstituted tertiary phosphines and phosphinic acids as well as bis(tertiary phosphines) and bis(phosphinic acids) have been obtained. Monobromo-substituted tertiary phosphines were similarly converted to bis(tertiary phosphines). The use of tetrahydrofuran as the reaction solvent at low temperatures (below −65°) generally provided the best reaction conditions.

In previous papers from this laboratory we have described the preparation of several arylenebisphosphorus compounds leading to *p*-phenylenebis(methylphosphinic acid)[1] and of several bis(tertiary phosphines).[2] While other recent papers have described several related *p*-phenylenebis(methyl- and phenylphosphinous esters and amides),[3] *p*-phenylenebis(phosphonous acid) and related compounds,[4] and several bis(tertiary phosphines),[5] this area of arylenebisphosphorus compounds has received relatively little attention. Since these bis compounds are of interest in several thermally stable polymer systems and as chelate ligands, we wish now to report the improved syntheses of arylenebis(tertiary phosphines) and the syntheses of arylenebis(phosphinic acids) and tris(tertiary phosphines).

Bis(tertiary phosphines).—Some of the problems encountered in the previous syntheses of arylenebis(tertiary phosphines) have been briefly described.[2,5] Thus, while reasonable yields of *p*-phenylenebis(diphenylphosphine) (Ib) have been obtained from the use of either the di Grignard reagent[2] or lithium diphenylphosphinide,[5c] extensions of these techniques to the syntheses of other bis(tertiary phosphines) have been of only limited success.[2] Thus, while 4,4′-biphenylenebis(diphenylphosphine) (Ia) has now been obtained from the di Grignard reagent using a tetrahydrofuran–benzene solvent mixture, the product was grossly contaminated, purification was tedious, and the yields were low. Our continued investigation of the syntheses of these compounds has shown that the

use of a hexane solution of *n*-butyllithium in tetrahydrofuran (THF) to form the necessary arylenedilithium intermediates, generally at low temperatures, frequently results in higher yields of more pure products in considerably shortened reaction times. However, as will be seen from the following discussion, the choice of reaction conditions can greatly effect the yield and even the product obtained (eq 1).

$$\text{Br-X-Br} + n\text{-C}_4\text{H}_9\text{Li} \xrightarrow{\text{THF}} [\text{Li-X-Li}] \xrightarrow{2(\text{C}_6\text{H}_5)_2\text{PCl}}$$

$$(\text{C}_6\text{H}_5)_2\text{P-X-P(C}_6\text{H}_5)_2 \quad (1)$$

Ia, X = [biphenylene structure]

b, X = [phenylene structure]

c, X = [phenylene structure]

d, X = [diphenyl ether structure]

Thus, high yields (94–98%) of 4,4′-biphenylenebis(diphenylphosphine) (Ia) were obtained when a hexane solution of *n*-butyllithium was added to 4,4′-dibromobiphenyl in tetrahydrofuran at −66°, or vice versa, and the mixture was warmed over 0.5 hr to 0° and then recooled to −66° before the addition of 2 equiv of diphenylchlorophosphine was begun. However, elimination of the warm-up step decreased the yield to 64% of less pure Ia. The use of 20 and 30% excesses of *n*-butyllithium resulted in roughly 80 and 70% yields of Ia, respectively.

However, when *p*-dibromobenzene was treated similarly with first *n*-butyllithium and then diphenylchlorophosphine, only a 57% yield of (4-bromophenyl)diphenylphosphine (IIIa) was obtained. Subsequently, the best yield of *p*-phenylenebis(diphenylphosphine) (58%) was obtained by refluxing 4 equiv of *n*-butyllith-

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