tillation exhibited bp 68° (0.04 mm). *Anal.* Calcd for $C_{10}H_{16}O_2S_2$: C, 51.69; H, 6.94. Found: C, 51.63; H, 6.90.

4-Methyl-1,3-dithiol-2-one (5a). Dithiocarbonate **4a** (2.9 g, 81% pure) suspended in cold aqueous H_2SO_4 (80%, 5 ml) was stirred for 4 min and then heated at 67° for 20 min and at 54° for an additional 15 min. The mixture was cooled, poured into ice-water, and worked up as described for **3a** to yield 1.83 g (88%) of crude **5a**, purity *ca.* 77% (pmr assay). Evaporative distillation [40° (0.05 mm)] afforded pure **5a** in 63% yield (based on **4a**): pmr ($CDCl_3$) δ 2.25 (d, 3, J = 1.4 Hz) and 6.32 (q, 1, J = 1.4 Hz); ir ($CHCl_3$) 1725, 1685, and 1640 cm^{-1}; mass spectrum (molecular ion) theoretical 132, found 132. *Anal.* Calcd for $C_4H_4OS_2$: C, 36.34; H, 3.05; S, 48.51. Found: C, 36.50; H, 3.20; S, 48.43.

4,5-Diphenyl-1,3-dithiol-2-one (5b). Dithiocarbonate **4b** (150 mg) suspended in cold aqueous H_2SO_4 (80%, 0.55 ml) was stirred for 5 min and heated for 20 min at 60° (oil bath). The mixture was cooled and diluted with ice and water. Filtration yielded 105 mg (85%) of **5b:** mp 104–106°; pmr ($CDCl_3$) δ 7.2 (m, 10); ir ($CHCl_3$) 1690 and 1635 cm^{-1}. Recrystallization from diethyl ether afforded an analytical sample, mp 109.5–110.5°. *Anal.* Calcd for $C_{15}H_{10}OS_2$: C, 66.64; H, 3.72; S, 23.71. Found: C, 66.90; H, 3.83; S, 23.55.

4-Ethyl-5-methyl-1,3-dithiol-2-one (5c). Potassium *O*-isopropyl xanthate (5.5 g) was treated for 10 min with a solution of 2-bromo-3-pentanone (4.2 g, *ca.* 84% purity) in acetone (50 ml). Work-up as described for **2a** yielded 5.5 g of crude **4c:** purity *ca.* 77% (pmr assay); pmr ($CDCl_3$) δ 1.09 (t, 3, J = 7.0 Hz), 1.38 (d, 6, J = 6.5 Hz), 1.45 (d, 3, J = 7.0 Hz), 2.66 (m, 2), 4.40 (q, 1, J = 7.0 Hz), and 5.71 (h, 1, J = 6.5 Hz); ir (CCl_4) 1720, 1240, 1090, and 1035 cm^{-1}. Perchloric acid (70%, 1.5 ml) was slowly added to a solution of crude **4c** (2.0 g) in 1:1 ether–$CHCl_3$ (16 ml). After the solution was refluxed for 1.5 hr it was worked up as described for **3a**, yielding 1.4 g (96%) of crude **5c**, purity *ca.* 68% (pmr assay). Chromatography on alumina using petroleum ether (bp 66–67°) as eluent afforded pure **5c:** pmr ($CDCl_3$) δ 1.16 (t, 3, J = 7.5 Hz), 2.13 (s, 3), and 2.56 (q, 2, J = 7.5 Hz); ir ($CHCl_3$) 1642 and 1595 cm^{-1}; mass spectrum (molecular ion) theoretical 160, found 160.

4,5-Cyclohexano-1,3-dithiol-2-one (5d). Perchloric acid (70%, 4.0 ml) was slowly added to a solution of dithiocarbonate **4d** (3.0 g, 93% pure) in 1:1 ether–CH_2Cl_2 (30 ml). After the solution was stirred for 10 hr, it was worked up as described for **3a**, yielding 2.1 g (93%) of **5d**, purity 94% (pmr assay). Chromatography on alumina using petroleum ether as eluent afforded pure **5d:** mp 33°; pmr ($CDCl_3$) δ 1.70–1.97 (m, 4) and 2.25–2.53 (m, 4); ir ($CHCl_3$) 1738, 1670, 1635, and 1600 cm^{-1}; mass spectrum (molecular ion) theoretical 172, found 172. *Anal.* Calcd for $C_7H_8OS_2$: C, 48.81; H, 4.68; S, 37.23. Found: C, 49.06; H, 4.76; S, 37.45.

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Registry No. 2a, 42574-08-3; **2b,** 42574-09-4; **2c,** 42588-16-9; **2d,** 42574-10-7; **2e,** 42574-11-8; **2f,** 42574-12-9; **3a,** 939-11-7; **3b,** 42574-13-0; **3c,** 42574-14-1; **3d,** 42573-96-6; **3e,** 42573-97-7; **4a,** 42573-98-8; **4b,** 42573-99-9; **4d,** 42574-00-5; **5a,** 42574-01-6; **5b,** 42574-02-7; **5c,** 42574-03-8; **5d,** 698-41-9; α-bromoacetophenone, 70-11-1; α-bromo(*p*-phenyl)acetophenone, 135-73-9; *p*-bromophenacyl bromide, 99-73-0; *O*-ethyl-*S*-(*p*-bromophenacyl)dithiocarbonate, 1861-48-9; *p*-trifluoromethylphenacyl bromide, 383-53-9: α-bromo-2′,5′-dimethoxyacetophenone, 1204-21-3; *p*-nitrophenacyl bromide, 99-81-0; α-chloroacetone, 78-95-5; desyl chloride, 447-31-4; 2-chlorocyclohexanone, 882-87-7; 2-bromo-3-pentanone, 815-52-1.

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(3) For a recent review of the chemistry of 1,3-dithioles, see E. Campaigne and R. D. Hamilton, *Quart. Rep. Sulfur Chem.*, **5**, 275 (1970).

(4) Ketothiol **1** has been prepared by other methods; see R. G. Hiskey, J. A. Kepler, and B. D. Thomas, *J. Org. Chem.*, **29**, 3684 (1964), and references cited therein.

(5) It is noteworthy that Campaigne, *et al.* (ref 2d), found that in the reaction of several *O-ethyl* β-ketodithiocarbonates corresponding to **2** with perchloric acid much decomposition occurred and in most cases (including that of the *O*-ethyl analog of **2c**) no product was isolable, with the exception that **3f** was obtained from the *O*-ethyl analog of **2f**. In our work (see Experimental Section) we have found that the *O*-ethyl analog of **2c** was *also* readily converted at elevated temperature into **3c**, suggesting that under suitable acidic conditions analogs of **3** can indeed be obtained from analogs of **2** having *O*-alkyl groups other than *O*-isopropyl.

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(7) Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer. Nmr spectra were recorded using a Varian Associates A-60A instrument. Mass spectra were obtained using a Varian Model M-66 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Reactions at elevated temperatures were carried out in a nitrogen atmosphere.

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Reaction of a Phosphorus Ylide with Aliphatic Acyl Cyanides

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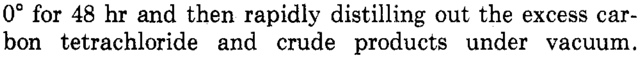
The phosphorus ylide, dichloromethylenetriphenylphosphorane (II), is most conveniently prepared by the addition of triphenylphosphine to an excess of carbon tetrachloride.[1] The concurrent production of triphenylphosphine dichloride appears to present no problems in the Wittig reactions of II with aldehydes,[1,2] ketones,[1] keto esters,[2] or aroyl cyanides[3] to give substituted 1,1-dichloroethylene derivatives.

In our previous studies of the reactions of II with aroyl cyanides, aliquots of the reaction mixtures were analyzed by an ir spectrophotometer to determine when the reaction was complete. It was found that the aroyl cyanide carbonyl stretching band was absent after 2–4 hr at reflux or 48–72 hr at room temperature. Under these same conditions aliphatic acyl cyanides Ia and Ib appeared to undergo an aldol type side reaction[4] giving only red-colored resinous residues and a strong odor of hydrogen cyanide.



$$\mathrm{R\overset{O}{\overset{\|}{C}}CN} + (\mathrm{Ph})_3\mathrm{P{=}CX_2} \longrightarrow \mathrm{X_2C{=}\overset{R}{\overset{|}{C}}CN} + (\mathrm{Ph})_3\mathrm{PO}$$

Ia, R = CH_3 II, X = Cl IIIa–d, X = Cl
b, R = C_2H_5 IV, X = Br Va, b, X = Br
c, R = $CH(CH_3)_2$
d, R = $C(CH_3)_3$

It has now been found that deleterious side reactions can be minimized by maintaining the reaction mixture at 0° for 48 hr and then rapidly distilling out the excess carbon tetrachloride and crude products under vacuum. Yields were greatly reduced when the reaction time was changed to 24 or 72 hr at 0°. Higher temperatures invariably produced red, tarry residues and little or no product. In a typical reaction, excess dry carbon tetrachloride and 1.0 equiv of triphenylphosphine were mixed for 30 min at 0° under a nitrogen atmosphere, then 0.5 equiv of the acyl cyanide, Ia–d, was added and the reaction mixture was stirred at 0° for approximately 48 hr. The disappearance of the carbonyl stretching band and the appearance of a strong band in the 920–940-cm^{-1} region (=CCl_2 stretch[5]) was an effective means of determining the reaction end point. After the reaction mixture was quickly warmed, the excess carbon tetrachloride and liquid products were rapidly removed by vacuum distillation. With the exception of IIId, the 2-alkyl-3,3-dichloroacrylonitriles were contaminated with by-products which could not be easily separated from the desired products by simple distillation. In two cases, IIIb and IIIc, analytically pure samples were obtained by preparative vpc.

When carbon tetrabromide (0.5 equiv) was added to a cold solution of benzene and 1.0 equiv of triphenylphosphine, an immediate reaction occurred resulting in a precipitate and a bright orange colored solution. Addition of acyl cyanide Ia or Ib to this solution required efficient ice cooling, as a rapid exothermic reaction resulted. An infrared carbonyl absorption was not detectable in this mixture after 5 min. Work-up of these reaction mixtures was carried out in a manner similar to that described above when carbon tetrachloride was used. Purification of the products Va and Vb was simplified owing to the absence of unwanted by-products.

The sensitivity of the acrylonitrile carbon–carbon double bond infrared absorption to substituent effects has been noted previously.[5] A smooth correlation of $+I$ effects and shift of the double bond absorption to lower frequencies were observed for IIIa–d. The dichlorovinylidene stretching frequency ($=CCl_2$) was also shifted to lower positions as the α substituent in III was changed from methyl to *tert*-butyl. Loss of molecular coplanarity owing to steric interaction by bulkier α groups and the cis β chlorine atom were most likely responsible for a portion of the observed shift.

The dibromovinylidene stretching frequency in Va,b appeared as a very strong absorption in the 840–850-cm^{-1} region.

Experimental Section

All temperatures are uncorrected. Elemental analyses were performed by Huffman Laboratories, Wheatridge, Colo. A Beckman IR-8 was used to obtain the infrared spectra, which were calibrated at 2849.9 and 1601.0 cm^{-1} by polystyrene film. All ylide reactions were carried out under dry nitrogen, and maintained at 0° by use of an ice–water bath.

Aliphatic Acyl Cyanides. The following acyl cyanides were prepared by heating a mixture of 1.0 mol of acyl bromide and 1.4 mol of cuprous cyanide in *o*-dichlorobenzene to approximately 120° for 4 hr and then carefully distilling the reaction mixture:[6] acetyl cyanide (Ia), bp 92–93°, n^{22}D 1.3905 (lit.[7] bp 92–93°, n^{20}D 1.3743); propionyl cyanide (Ib), bp 110–111°, n^{20}D 1.3225 (lit.[7] bp 110°, n^{20}D 1.3225); isobutyryl cyanide (Ic), bp 117–118°, n^{22}D 1.3847 (lit.[7] bp 118°, n^{20}D 1.3790); pivaloyl cyanide (Id), bp 120°, n^{20}D 1.3961 (lit.[8] bp 120°, n^{20}D 1.3961). Three variations of this basic technique[9] were used in the attempted synthesis of trichloroacetyl cyanide. The reaction was run with and without the use of *o*-dichlorobenzene as solvent, and by substituting potassium cyanide for cuprous cyanide; all attempts to synthesize trichloroacetyl cyanide were unsuccessful.

3,3-Dichloro-2-methylacrylonitrile (IIIa). Into a 250-ml, three-necked flask fitted with nitrogen inlet and drying tube was added 80 ml of dry carbon tetrachloride and 40.0 g (0.152 mol) of triphenylphosphine. The reaction mixture was stirred (magnetic stirrer) for 30 min at 0°, then 5.25 g (0.076 mol) of Ia was added quickly and stirring was continued at 0° for 40 hr. At this time the mixture was heated under vacuum to first remove excess carbon tetrachloride and then the crude product. This crude distillate was then carefully refractionated to yield 6.33 g (61%) of IIIa, bp 68° (28 mm). The ir spectrum of IIIa was identical with that of the known compound.[5]

3,3-Dichloro-2-ethylacrylonitrile (IIIb). In a manner similar to that described above, 80 ml of dry carbon tetrachloride and 40.0 g (0.152 mol) of triphenylphosphine were stirred for 30 min at 0°, then 6.34 g (0.076 mol) of Ib was added and the mixture was stirred at 0° for 44 hr. The reaction mixture was heated to remove the excess carbon tetrachloride and then placed under vacuum to distil out 15.34 g (45%[9]) of crude product. Purification of the crude product by distillation was complicated by closely boiling by-products. An analytically pure sample was obtained by preparative vpc: bp 75–78° (28 mm); n^{20}D 1.4829; ir (neat) 2990, 2890, 2220, 1590, 1460, and 930 cm^{-1} ($=CCl_2$).

Anal. Calcd for $C_5H_5Cl_2N$: C, 40.04; H, 3.33; N, 9.34; Cl, 47.28. Found: C, 40.38; H, 3.49; N, 9.27; Cl, 46.98.

3,3-Dichloro-2-(isopropyl)acrylonitrile (IIIc). Dry carbon tetrachloride (80 ml) was mixed with 40.0 g (0.152 mol) of triphenylphosphine and the mixture was stirred for 30 min at 0°, then 7.40 g (0.076 mol) of Ic was added quickly. The mixture, stirred at 0° for 40 hr, then was heated under vacuum to distil out the excess carbon tetrachloride and 6.5 g (40%[9]) of crude product. Purification was complicated by the presence of closely boiling by-products. An analytically pure sample was obtained by preparative vpc: bp 85–87° (28 mm); n^{22}D 1.4824; ir (neat) 2980, 2940, 2885, 2230, 1580, 1460, and 935 cm^{-1} ($=CCl_2$).

Anal. Calcd for $C_6H_7Cl_2N$: C, 43.85; H, 4.26; N, 8.54; Cl, 43.21. Found: C, 43.85; H, 4.39; N, 8.44; Cl, 42.95.

3,3-Dichloro-2-(*tert*-butyl)acrylonitrile (IIId). Dry carbon tetrachloride (80 ml) was mixed with 40.0 g (0.152 mol) of triphenylphosphine, and the mixture was stirred for 15 min at 0°. To this was added 8.47 g (0.076 mol) of Id and the mixture was stirred at 0° for 45 hr. The mixture was then heated under vacuum to first distil the excess carbon tetrachloride and then crude product. The crude product was carefully refractionated to yield 6.55 g (48%) of IIId: bp 102–105° (28 mm); n^{23}D 1.4829; ir (neat), 2980, 2940, 2920, 2880, 2220, 1550, and 920 cm^{-1} ($=CCl_2$).

Anal. Calcd for $C_7H_9Cl_2N$: C, 47.23; H, 5.05; N, 7.86; Cl, 39.83. Found: C, 47.41; H, 5.04; N, 7.59; Cl, 39.44.

3,3-Dibromo-2-methylacrylonitrile (Va). Into a 250-ml, three-necked flask provided with nitrogen inlet and drying tube was added 80 ml of dry benzene and 40.0 g (0.152 mol) of triphenylphosphine. After all the triphenylphosphine had dissolved, the solution was cooled to 0° and 25.31 g (0.076 mol) of carbon tetrabromide was slowly added. This addition resulted in a highly exothermic reaction which gave a bright orange colored solution and a copious amount of precipitate. The reaction mixture was held at 0° while 5.25 g (0.076 mol) of Ia was added dropwise. This addition produced a second highly exothermic reaction coupled with the complete decolorization of the solution. The mixture was mechanically stirred at 0° for 5 min and then rapidly distilled under vacuum to remove the crude product and solvent. The higher boiling fractions which solidified were washed with cold ligroin to remove unreacted carbon tetrabromide and then refractionated to yield 11.5 g (68%) of Va: bp 94–95° (28 mm); mp 62–63°; ir (KBr pellet), 2230, 1575, 1030, and 850 cm^{-1} ($=CBr_2$).

Anal. Calcd for $C_4H_3Br_2N$: C, 21.52; H, 1.33; N, 6.23; Br, 71.09. Found: C, 21.82; H, 1.62; N, 6.23; Br, 71.07.

3,3-Dibromo-2-ethylacrylonitrile (Vb). In a manner similar to that described for Va, 40.0 g (0.152 mol) of triphenylphosphine was dissolved in 80 ml of dry benzene and the mixture was cooled to 0°. Carbon tetrabromide (25.31 g, 0.076 mol) was slowly added, yielding an orange-colored solution and a precipitate. The mixture was held at 0° while 6.34 g (0.076 mol) of Ib was added. The mixture was stirred for 5 min and then rapidly heated under vacuum to distil out solvent and crude product. The crude product was refractionated to yield 10.51 g (58%) of Vb: bp 99–102° (28 mm); n^{24}D 1.5430; ir (neat) 2980, 2840, 2885, 2225, 1565, 1455, and 840 cm^{-1} ($=CBr_2$).

Anal. Calcd for $C_5H_5Br_2N$: C, 25.31; H, 2.11; N, 5.91; Br, 66.66. Found: C, 25.30; H, 2.27; N, 5.87; Br, 66.20.

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Registry No. Ia, 631-57-2; Ib, 4390-78-7; Ic, 42867-39-0; Id, 42867-40-3; II, 6779-08-4; IIIa, 31413-58-8; IIIb, 42791-06-0; IIIc, 42867-43-6; IIId, 42867-44-7; IV, 42867-45-8; Va, 42867-46-9; Vb, 42867-47-0.

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