comparison with authentic 4-acetoxyacetanilide indicated that no detectable amount of this compound was formed in the reaction.

Deoxygenation of *p*-Nitrosotoluene in the Presence of Acetic Anhydride. The reaction was carried out as described for nitrosobenzene. 2-Acetoxy-4-methylacetanilide (**20**, 46%) crystallized from the crude product, mp 154–155° (lit.[20] mp 153–154°), and was identified by spectral data and hydrolysis to 2-hydroxy-4-methylacetanilide which was identical with an authentic sample.[17] A small amount (2%) of 4-methylacetanilide was isolated from the mother liquors.

Deoxygenation of *o*-Nitrosotoluene in the Presence of Acetic Anhydride. The reaction was carried out as for nitrosobenzene. Trituration of the crude product with hot hexane gave 2-acetoxy-6-methylacetanilide (**21**, 16%), mp 142–143° (lit.[21] mp 141–143°),[22] after recrystallization from ether–hexane. The identification was accomplished by partial hydrolysis to 2-hydroxy-6-methylacetanilide, mp 161–162° (lit.[17] mp 160–161°), and complete hydrolysis by 2-hr reflux with 15% aqueous sodium hydroxide to 2-hydroxy-6-methylaniline, mp 149–150.5° (lit.[24] mp 150°).

***O,N*-Diacetyl-4-methylphenylhydroxylamine (22).** 4-Methylphenylhydroxylamine[25] (2.0 g, 16 mmol) was dissolved in ether (20 ml) containing pyridine (2 ml) and treated with a solution of acetyl chloride (2.6 g, 32 mmol) in ether (10 ml) at 0°. The solution was washed with water, dried over sodium sulfate, and evaporated to give the product as an oil purified by distillation at diffusion pump vacuum: ir (neat) 1800, 1690 cm^{-1}; nmr ($CDCl_3$) δ 7.2–7.6 (m, 4), 2.40 (s, 3), 2.20 (s, 3), 2.05 (s, 3).

Stability of *O,N*-Diacetyl-4-methylphenylhydroxylamine under Deoxygenation Conditions. A solution of **22** (0.30 g, 1.45 mmol), TEP (15 ml), acetic anhydride (15 ml), and benzene (6 ml) was stirred at 0° under nitrogen for 2 hr. The benzene was removed at reduced pressure and TEP and acetic anhydride were removed at 0.1 mm. Chromatography of the residue gave 97% recovery of **22**.

Registry No. **1a**, 98-95-3; **1b**, 99-99-0; **1c**, 88-72-2; **1d**, 89-87-2; **2a**, 586-96-9; **2b**, 623-11-0; **2c**, 611-23-4; **4**, 31238-50-3; **5**, 42822-57-1; **8**, 42822-58-2; **11**, 42822-59-3; **12**, 42822-60-6; **14**, 42822-61-7; **15**, 42822-62-8; **16**, 42822-63-9; **19**, 42822-64-0; **22**, 27451-20-3; 4-methylphenylhydroxylamine, 623-10-9.

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A General Synthesis of 1,3-Dithiol-2-ones

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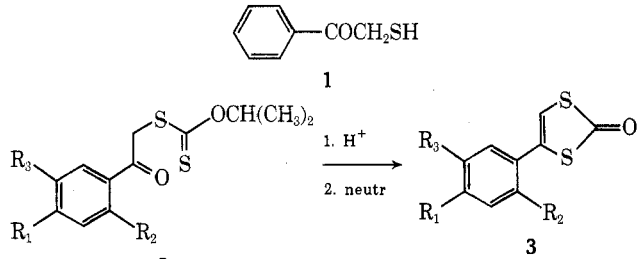
Although specific preparations of 1,3-dithiol-2-one[1] (vinylene dithiocarbonate) and of several substituted analogs[2] have been described, a general synthesis of compounds in this series has never been reported.[3]

In the course of another investigation an attempt was made to prepare ketothiol **1**[4] by heating a solution (CCl_4) of *O*-isopropyl *S*-phenacyl dithiocarbonate (**2a**) in contact with 70% perchloric acid. Upon neutralization and work-up of the reaction mixture, a fair yield of 4-phenyl-1,3-dithiol-2-one (**3a**) was obtained. Further investigation of this reaction led to a general preparation of 1,3-dithiol-2-ones **3a–f** and **5a–d** from the readily accessible β-keto *O*-isopropyl dithiocarbonates **2a–f** and **4a–d**.[5]

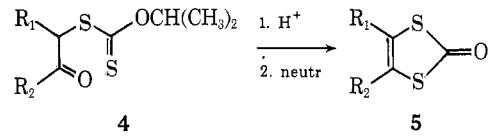


1

2

3

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = Ph$; $R_2 = R_3 = H$
c, $R_1 = Br$; $R_2 = R_3 = H$
d, $R_1 = CF_3$; $R_2 = R_3 = H$
e, $R_1 = H$; $R_2 = R_3 = OCH_3$
f, $R_1 = NO_2$; $R_2 = R_3 = H$



4 **5**

a, $R_1 = H$; $R_2 = CH_3$
b, $R_1 = R_2 = Ph$
c, $R_1 = CH_3$; $R_2 = C_2H_5$
d, $R_1, R_2 = -(CH_2)_4-$

The 1,3-dithiol-2-ones described herein should also serve as useful precursors of the corresponding 2-hydroxy-1,3-dithiolium cations, which are of some theoretical interest.[3,6]

Experimental Section[7]

***O*-Isopropyl *S*-Phenacyl Dithiocarbonate (2a).** Potassium *O*-isopropyl xanthate[8] (11.3 g) was treated in small quantities during 10 min with a solution of α-bromoacetophenone (12.0 g) in acetone (140 ml). The solvent was removed *in vacuo*. Water was added to the solid residue and the resulting suspension was acidified with dilute HCl and extracted with diethyl ether. The combined extracts were washed with water followed by brine and dried ($MgSO_4$). The solvent was removed *in vacuo*, yielding 14.9 g of crude **2a**: mp 65–67°; purity (pmr assay) *ca.* 90%; pmr ($CDCl_3$) 1.33 (d, 6, J = 6.5 Hz), 4.60 (s, 2), 5.70 (h, 1, J = 6.5 Hz), 7.27–7.63 (m, 3), and 7.88–8.08 (m, 2); ir (CCl_4) 1690, 1240, 1090, 1053, and 686 cm^{-1}. Recrystallization from diethyl ether afforded 12.7 g (83%) of pure **2a**, mp 68–69°. An analytical sample exhibited mp 68–69°. *Anal.* Calcd for $C_{12}H_{14}O_2S_2$: C, 56.66; H, 5.55. Found: C, 56.72; H, 5.46.

***O*-Isopropyl *S*-(*p*-Phenylphenacyl) Dithiocarbonate (2b).** Potassium *O*-isopropyl xanthate (3.0 g) was treated (10 min) in small quantities with a solution of α-bromo(*p*-phenyl)acetophenone (4.0 g) in acetone (40 ml). Work-up as described for **2a** yielded 5.0 g of crude product. Recrystallization from diethyl

ether afforded **2b:** mp 72–74°; pmr ($CDCl_3$) δ 1.35 (d, 6, J = 6.5 Hz), 4.63 (s, 2), 5.73 (h, 1, J = 6.5 Hz), 7.3–7.7 (m, 5), and an A_2B_2 multiplet centered at δ 7.68 and 8.08; ir (CCl_4) 1683, 1606, 1240, 1090, 1050, and 697 cm^{-1}. An analytical sample had mp 74–75°. *Anal.* Calcd for $C_{18}H_{18}O_2S_2$: C, 65.42; H, 5.49. Found: C, 65.53; H, 5.55.

***O*-Isopropyl *S*-(*p*-Bromophenacyl) Dithiocarbonate (2c).**[8] Potassium *tert*-butoxide (2.24 g) was dissolved in a solution of 2-propanol (7 ml) in benzene (35 ml). Cooling (ice bath) was followed by slow addition of carbon disulfide (2.25 g) in benzene (5.0 ml) to the sitrred solution. After the solution was stirred for 20 min longer, *p*-bromophenacyl bromide (4.73 g) and benzene (20 ml) were added and the solution was refluxed for 2 hr under N_2. The reaction mixture was cooled and filtered. Removal of the solvent *in vacuo* left 5.1 g (*ca.* 100%) of crude product, mp 89–90°. Recrystallization from diethyl ether afforded **2c:** mp 90–91° (lit.[8] mp 90–91°); pmr ($CDCl_3$) δ 1.38 (d, 6, J = 6.5 Hz), 4.60 (s, 2), 5.76 (h, 1, J = 6.5 Hz), and an A_2B_2 pattern centered at δ 7.81; ir (CCl_4) 1690, 1585, 1240, 1090, and 1045 cm^{-1}; mass spectrum (molecular ion) theoretical 332, found 332.

***O*-Ethyl *S*-(*p*-Bromophenacyl) Dithiocarbonate.**[2d,5] Potassium *O*-ethyl xanthate (2.8 g) was added to a solution of *p*-bromophenacyl bromide (4.17 g) in acetone (50 ml) and the suspension was heated in a water bath at *ca.* 50° for 5 min. The reaction mixture was worked up as described for **2a,** yielding 4.4 g (92%) of crude product, purity *ca.* 84% (pmr assay). Recrystallized product had mp 82–83° (lit.[2d] mp 81–82°); pmr ($CDCl_3$) δ 1.35 (t, 3, J = 7.0 Hz), 4.58 (s, 2), 4.60 (q, 2, J = 7.0 Hz), and an A_2B_2 pattern centered at δ 7.73.

***O*-Isopropyl *S*-(*p*-Trifluoromethylphenacyl) Dithiocarbonate (2d).** Potassium *O*-isopropyl xanthate (1.5 g) was treated in small amounts during 20 min with a solution of *p*-trifluoromethylphenacyl bromide (1.94 g) in acetone (30 ml). The solution was warmed in a water bath (*ca.* 50°) for 15 min and worked up as described for **2a,** yielding 2.17 g (92%) of crude **2d.** Recrystallization from ether afforded pure **2d** (pmr assay): mp 97–99°; pmr ($CDCl_3$) δ 1.35 (d, 6, J = 6.5 Hz), 3.75 (s, 3), 3.88 (s, 3), 4.56 (s, 2), Hz), and an A_2B_2 pattern centered at δ 7.93; ir (CCl_4) 1710, 1692, 1330, 1245, 1090, and 1045 cm^{-1}; mass spectrum (molecular ion) theoretical 322, found 322. An analytical sample had mp 98.5–99.5°. *Anal.* Calcd for $C_{13}H_{13}F_3O_2S_2$: C, 48.44; H, 4.06. Found: C, 48.20; H, 4.05.

***O*-Isopropyl *S*-(2′,5′-Dimethoxyphenacyl) Dithiocarbonate (2e).** Potassium *O*-isopropyl xanthate (7.3 g) was treated in small amounts with a solution of α-bromo-2′,5′-dimethoxyacetophenone (8.0 g) in acetone (125 ml). The solution was allowed to stand at room temperature (40 min). Work-up as described for **2a** yielded 8.7 g (89%) of crude **2e** which was 90% pure by pmr assay: pmr ($CDCl_3$) δ 1.35 (d, 6, J = 6.5 Hz), 3.75 (s, 3), 3.88 (s, 3), 4.56 (s, 2), 5.68 (h, 1, J = 6.5 Hz), and 6.81–7.35 (m, 3); ir (CCl_4) 1670, 1235, 1090, and 1050 cm^{-1}; mass spectrum (molecular ion) theoretical 314, found 314. An analytical sample exhibited mp 49.5–50.5°. *Anal.* Calcd for $C_{14}H_{18}O_4S_2$: C, 53.48; H, 5.77. Found: C, 53.62; H, 5.81.

***O*-Isopropyl *S*-(*p*-Nitrophenacyl) Dithiocarbonate (2f).** Potassium *O*-isopropyl xanthate (6.2 g) was added in small portions to a solution of *p*-nitrophenacyl bromide (9.32 g) in acetone (75 ml) and the mixture was heated on a water bath (*ca.* 50°) for 3 min. The reaction mixture was filtered and washed with acetone (75 ml), and the solvent was removed *in vacuo.* Work-up as described for **2a** afforded 11.2 g (90%) of crude **2f:** mp 68–70°; purity *ca.* 90% (pmr assay); pmr ($CDCl_3$) δ 1.36 (d, 6, J = 6.3 Hz), 4.63 (s, 2), 5.68 (h, 1, J = 6.3 Hz), and an A_2B_2 pattern centered at δ 8.22. An analytical sample exhibited mp 72.5–73.5°. *Anal.* Calcd for $C_{12}H_{13}NO_4S_2$: C, 48.14; H, 4.38. Found: C, 48.37; H, 4.50.

4-Phenyl-1,3-dithiol-2-one (3a). Perchloric acid (70%, 2.0 ml) was slowly added to a solution of dithiocarbonate **2a** (2.5 g, *ca.* 90% pure) in 1:2 ether–$CHCl_3$ (18 ml). The solution was refluxed for 1 hr and poured into ice-water. Extraction with ether followed by a normal work-up yielded 1.8 g (92%) of crude **3a,** purity *ca.* 76% (pmr assay). Recrystallization from ether afforded pure **3a:** mp 96–97.5° (lit.[2b] mp 93–95°); pmr ($CDCl_3$) δ 6.82 (s, 1) and 7.40 (s, 5); ir ($CHCl_3$) 1733, 1690, and 1650 cm^{-1}; mass spectrum (molecular ion) theoretical 194, found 194.

4-(*p*-Phenylphenyl)-1,3-dithiol-2-one (3b). Perchloric acid (70%, 1.5 ml) was slowly added to a solution of the dithiocarbonate **2b** (2.0 g) in 1:2 ether–$CHCl_3$ (15 ml). The solution was refluxed for 15 min, cooled, and poured into ice-water. Extraction with $CHCl_3$ and work-up as described for **3a** afforded 1.6 g of crude **3b,** purity *ca.* 70% (pmr assay). Recrystallization from CH_2Cl_2 afforded pure **3b:** mp 184–186°; pmr ($CDCl_3$–CF_3CO_2D, 2:1) δ 6.95 (s, 1) and 7.36–7.78 (m, 9); ir (CH_2Cl_2) 1642 cm^{-1}; mass spectrum (molecular ion) theoretical 270, found 270. An analytical sample exhibited mp 186–187°. *Anal.* Calcd for $C_{15}H_{10}OS_2$: C, 66.64; H, 3.72; S, 23.71. Found: C, 66.53; H, 3.74; S, 23.53.

4-(*p*-Bromophenyl)-1,3-dithiol-2-one (3c). Method A. Perchloric acid (70%, 1.6 ml) was slowly added to a solution of dithiocarbonate **2c** (0.8 g) in 1:1 ether–CH_2Cl_2 (6.4 ml). After the solution was stirred for 7 hr at room temperature, it was poured into ice-water. Extraction with ether followed by a normal work-up afforded 0.63 g of crude **3c,** purity *ca.* 85% (pmr assay). Recrystallized material had mp 97–98°; pmr ($CDCl_3$) δ 6.90 (s, 1) and an A_2B_2 pattern centered at *ca.* δ 7.43; ir (CCl_4) 1732, 1700, and 1650 cm^{-1}; mass spectrum (molecular ion) theoretical 272, found 272. *Anal.* Calcd for $C_9H_5BrOS_2$: C, 39.57; H, 1.85; S, 23.26. Found: C, 39.72; H, 1.84; S, 23.00.

Method B. *O*-Ethyl *S*-(*p*-bromophenacyl) dithiocarbonate[2d,5] (600 mg) was stirred with cold aqueous H_2SO_4 (80%, 2.0 ml) for 5 min. The solution was then heated for 0.5 hr in an oil bath (77–79°), cooled, diluted with ice-water, and extracted with ether. The combined extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo,* yielding 450 mg (87%) of crude **3c,** purity 65% (pmr assay). Recrystallization from ether afforded pure **3c,** mp 97–98°.

4-(*p*-Trifluoromethylphenyl)-1,3-dithiol-2-one (3d). Dithiocarbonate **2d** (480 mg, *ca.* 95% pure) was suspended in cold aqueous H_2SO_4 (0.4 ml) and heated for 15 min at 75°. The mixture was cooled and poured into ice-water. The solid obtained on filtration was washed with water and dried, yielding 460 mg (*ca.* 100%) of crude **3d,** purity *ca.* 60% (pmr assay). Recrystallized product had mp 97–99°; pmr ($CDCl_3$) δ 7.03 (s, 1) and an A_2B_2 pattern centered at δ 7.6; ir (CH_2Cl_2) 1645 and 1330 cm^{-1}; mass spectrum (molecular ion) theoretical 262, found 262. An analytical sample exhibited mp 98–99°. *Anal.* Calcd for $C_{10}H_5F_3OS_2$: C, 45.80; H, 1.92; S, 24.45. Found: C, 45.76; H, 2.06; S, 24.45.

4-(2′,5′-Dimethoxyphenyl)-1,3-dithiol-2-one (3e). Perchloric acid (70%, 2.0 ml) was slowly added to a solution of dithiocarbonate **2e** (1.5 g, *ca.* 90% pure) in 8 ml of ether–CH_2Cl_2 (9:7). The solution was refluxed for 10 hr, cooled, poured into ice-water, and worked up as described for **3a,** yielding 0.9 g (74%) of crude **3e,** purity 82% (pmr assay). Recrystallization from ether afforded pure **3e:** mp 86–87°; pmr ($CDCl_3$) δ 3.76 (s, 3), 3.81 (s, 3), 6.86 (s, 2) and an AB pattern centered at δ 6.91 (J = 7.5 Hz); ir ($CHCl_3$) 1640, 1220, and 1045 cm^{-1}; mass spectrum (molecular ion) theoretical 254, found 254. *Anal.* Calcd for $C_{11}H_{10}O_3S_2$: C, 51.95; H, 3.96; S, 25.21. Found: C, 51.88; H, 3.90; S, 25.04.

4-(*p*-Nitrophenyl)-1,3-dithiol-2-one (3f).[2d,5] A suspension of dithiocarbonate **2f** (340 mg, 90% pure) and cold aqueous sulfuric acid (0.6 ml) was heated for 5 min at 72°, cooled, and poured into ice-water. Extraction with CH_2Cl_2 afforded 260 mg of crude **3f,** purity *ca.* 94% (pmr assay), pmr data identical with those already reported.[2d] The recrystallized product had mp 208–209.5° (lit.[2d] mp 205–208°).

***O*-Isopropyl *S*-Acetonyl Dithiocarbonate (4a).** Potassium *O*-isopropyl xanthate (9.0 g) was treated during 15 min with small portions of 5.0 g of α-chloroacetone in 60 ml of acetone. Work-up as described for **2a** yielded 8.8 g of crude **4a:** purity *ca.* 81% (pmr assay); pmr ($CDCl_3$) δ 1.37 (d, 6, J = 6 Hz), 2.29 (s, 3), 3.97 (s, 2), and 5.70 (h, 1, J = 6 Hz); ir ($CHCl_3$) 1710, 1245, 1085, and 1042 cm^{-1}; mass spectrum (molecular ion) theoretical 192, found 192. An analytical sample was procured by distillation and exhibited bp 42° (0.05 mm). *Anal.* Calcd for $C_7H_{12}O_2S_2$: C, 43.72; H, 6.29. Found: C, 43.63; H, 6.23.

***O*-Isopropyl *S*-(α-Phenylphenacyl) Dithiocarbonate (4b).** Sodium *O*-isopropyl xanthate (5 g) was treated at room temperature during 2 hr with desyl chloride (4.6 g) in acetone (70 ml). Work-up as described for **2a** yielded 6.7 g (100%) of crude **4b,** purity *ca.* 80% (pmr assay). Recrystallization from ether afforded pure **4b:** mp 95–96°; pmr ($CDCl_3$) δ 1.23 (d, 6, J = 6.3 Hz), 5.66 (h, 1, J = 6.3 Hz), 6.65 (s, 1), 7.2–7.6 (m, 8), and 8.0–8.2 (m, 2); ir (CCl_4) 1690, 1235, 1090, 1045, and 695 cm^{-1}; mass spectrum (molecular ion) theoretical 330, found 330. *Anal.* Calcd for $C_{18}H_{18}O_2S_2$: C, 65.42; H, 5.49. Found: C, 65.20; H, 5.46.

***O*-Isopropyl *S*-(2-Cyclohexanonyl) Dithiocarbonate (4d).** Potassium *O*-isopropyl xanthate (7.0 g) was added in small amounts to a solution of 5.0 g of 2-chlorocyclohexanone in acetone (100 ml). The suspension was refluxed for 45 min and worked up as described for **2a** to yield 8.5 g (91%) of crude **4d** as a liquid: purity *ca.* 93% (pmr assay); pmr ($CDCl_3$) δ 1.36 (d, 6, J = 6.2 Hz), 1.7–2.8 (m, 8), 4.5 (m, 1), and 5.7 (h, 1, J = 6.2 Hz); ir (CCl_4) 1720, 1235, 1087, and 1045 cm^{-1}. An analytical sample obtained by dis-

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.

References and Notes

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(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.

$$\underset{\text{Ia, R = CH}_3;\ \text{b, R = C}_2\text{H}_5;\ \text{c, R = CH(CH}_3)_2;\ \text{d, R = C(CH}_3)_3}{\text{RCCN}} + \underset{\text{II, X = Cl;\ IV, X = Br}}{(\text{Ph})_3\text{P=CX}_2} \longrightarrow \underset{\text{IIIa–d, X = Cl;\ Va, b, X = Br}}{\text{X}_2\text{C=CCN}} + (\text{Ph})_3\text{PO}$$

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 rap-