Our modified procedure described below includes removal of excess phthalimide on the basis of its low solubility in chloroform, does not require, as in other procedures,[1,4] the formation of potassium phthalimide, avoids the use of protic solvents in the purification, and affords pure 1 in high yields.

Experimental Section[9]

Modified Procedure for *N*-(Ethoxycarbonyl)phthalimide. Ethyl chloroformate (115 mL, 1.29 mol) was added dropwise over a period of 90 min to a stirred solution of phthalimide (149.9 g, 1.02 mol) and triethylamine (160 mL, 1.15 mol) in dimethylformamide (500 mL) at 0–5 °C under argon. The reaction mixture was allowed to warm to room temperature and stand for 4 h. It then was slowly added to an agitated mixture of ice and water (3 L). The solid product was collected and extracted with two portions of chloroform (450 mL and then 50 mL). The extract was dried (Na_2SO_4), cooled overnight in the refrigerator, and filtered to remove phthalimide (mp 238 °C). The chloroform solution was concentrated to about 350 mL, diluted with petroleum ether (bp 60–80 °C; 350 mL) and allowed to stand at room temperature to give *N*-(ethoxycarbonyl)phthalimide (179 g, followed by two additional crops for a total of 212 g, 95% yield): mp 83 °C; IR (KBr) 1720, 1765, 1805 cm^{-1}; NMR ($CDCl_3$) δ 1.46 (t, 3 H, J = 7.2 Hz, OCH_2CH_3), 4.51 (q, 2 H, J = 7.2 Hz, OCH_2CH_3), 7.96 (d, 4 H, J = 2 Hz, aromatic H); UV λ_{max} (CH_3CN) 216 nm (ϵ 48 000), 263 (1400), 292 (1400); gas chromatographic analysis on a high-performance column (3% Carbowax on Chromosorb W (20 M); $^1/_8$ in. × 6 ft; 200 °C) exhibited one sharp peak. Anal. Calcd for $C_{11}H_9NO_4$: C, 60.28; H, 4.14; N, 6.39. Found: C, 60.36; H, 4.15; N, 6.32.

Alcoholysis of *N*-(ethoxycarbonyl)phthalimide (1). A. A solution of 1 (1.02 g, 4.66 mmol) in reagent-grade methanol (25 mL) was stirred and heated under reflux for 1 h and then concentrated under reduced pressure to afford a viscous oil (1.2 g). Crystallization from 2-propanol (20 mL) at −5 °C gave ethyl *N*-[2-(methoxycarbonyl)benzoyl]carbamate (**2**, R = CH_3): 765 mg, followed by additional crops for a total of 1.18 g, 100% yield; mp 86–87 °C; IR (KBr) 1680, 1718, 1760 cm^{-1}; NMR ($CDCl_3$) δ 1.17 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 3.89 (s, 3 H, OCH_3), 4.11 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 7.45 (m, 3 H, aromatic H), 8.00 (m, 1 H, aromatic H), 8.65 (br s, 1 H, exchangeable with D_2O, –CONHCO–). Anal. Calcd for $C_{12}H_{13}NO_5$: C, 57.37; H, 5.22; N, 5.58. Found: C, 57.57; H, 5.24; N, 5.36.

B. In a similar manner, a solution of 1 in reagent-grade ethanol was heated under reflux for 2 h. Concentration gave an impure white solid (mp 60–70 °C) which by recovery of 1 by crystallization from 2-propanol appeared to be a mixture of 1 (65%) and ethyl *N*-[2-(ethoxycarbonyl)benzoyl]carbamate (**2**, R = CH_2CH_3; 35%) isolated as a clear viscous oil which could not be crystallized. The same proportions of 1 and **2** (R = CH_2CH_3) were indicated by treatment of the mixture with aqueous sodium bicarbonate solution for 8 h at 22 °C to convert 1 to sodium *N*-[2-(ethoxycarbonyl)benzoyl]carbamate and then extraction of the mixture with dichloromethane followed by concentration of the extract to afford **2** (R = CH_2CH_3) as a clear oil: IR (CCl_4) 3420 (NH), 1765 (C=O), 1720 (C=O), 1705 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.17 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 1.33 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 4.11 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 4.33 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 7.40 (m, 3 H, aromatic H), 7.95 (m, 1 H, aromatic H), 8.73 (br s, 1 H, exchangeable with D_2O, –CONHCO–); mass spectrum, m/e 265 (M^+).

Similarly, when a solution of 1 in ethanol was heated for 12 h, 1 was recovered (20%) and **2** (R = CH_2CH_3) was produced (80%). After 36 h, the proportions were ~2% 1 and ~98% **2** (R = CH_2CH_3).

C. In a similar manner, a solution of 1 in 2-propanol was heated for 2 h to produce a mixture of 1 (93%) and **2** (R = $CH(CH_3)_2$) (7%). After the mixture was heated in 2-propanol for 60 h, the proportions were 50% 1 and 50% **2** (R = $CH(CH_3)_2$). Ethyl *N*-[2-(2-propoxycarbonyl)benzoyl]carbamate (**2**, R = $CH(CH_3)_2$) was isolated as a clear viscous oil: IR (CCl_4) 3420 (NH), 1770 (C=O), 1720 (C=O), 1710 cm^{-1} (sh, C=O); NMR ($CDCl_3$) δ 1.20 (t, 3 H, J = 7.0 Hz, CH_2CH_3), 1.33 (d, 6 H, J = 6.0 Hz, $CH(CH_3)_2$), 4.11 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 5.20 (m, 7 peaks, 1 H, J = 6.0 Hz, $OCH(CH_3)_2$), 7.2–7.6 (7, 3 H, aromatic), 7.8–8.1 (m, 1 H, aromatic H), 8.48 (br s, 1 H, exchangeable with D_2O, –CONHCO–).

Acknowledgment. We thank the National Research Council of Canada and the Faculty of Science, York University, for financial support.

Registry No. 1, 22509-74-6; **2**, R = CH_3, 71964-88-0; **2**, R = CH_2CH_3, 71964-89-1; **2**, R = $CH(CH_3)_2$, 71964-90-4; phthalimide, 85-41-6; ethyl chloroformate, 541-41-3; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0.

(9) Melting points are uncorrected. Microanalyses were performed by A. B. Gygli, Toronto, Ontario, Canada. The NMR spectra were determined on an EM 360 Varian spectrometer, the IR spectra on an SP1000 Infrared Pye Unicam spectrometer, the UV spectra on a Hitachi Perkin-Elmer 340 spectrometer, and the gas chromatographic analyses on a Perkin-Elmer 990 gas chromatograph.

Efficient and General Synthesis of 1,3-Dithiole-2-thiones

Neil F. Haley* and Michael W. Fichtner

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

Received July 30, 1979

Recently we reported a novel synthesis of 1,3-dithiole-2-thiones with a variety of functional groups from sodium *tert*-butyl trithiocarbonate and propargyl halides.[1] Although this synthesis allowed the introduction of many substituents, some of which are unavailable by other methods, the limited availability of acetylenic halides precluded broad application of this technique.[2] We now report an expansion of the synthetic utility of sodium *tert*-butyl trithiocarbonate in the synthesis of 1,3-dithiole-2-thiones (**3**) by the acid-catalyzed ring closure of β-keto *tert*-butyl trithiocarbonates (**1**) which are readily available from α-halo ketones (Scheme I) and sodium *tert*-butyl trithiocarbonate. We also report the ring closure of acetylenic trithiocarbonate **4** with bromine to give the highly reactive 4-(bromomethyl)-1,3-dithiole-2-thione (**7**) (Scheme II).

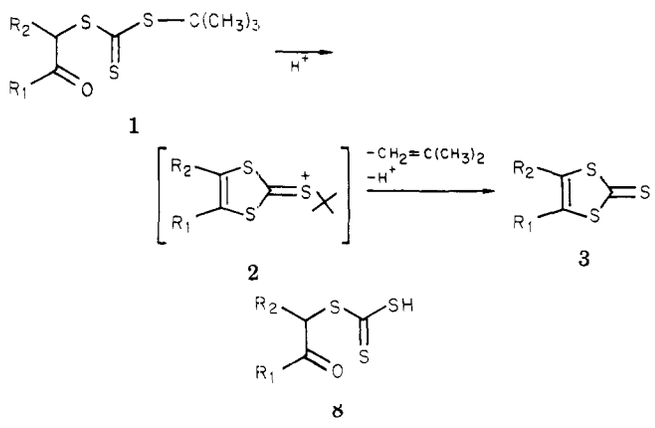
Although specific preparations of 1,3-dithiolylium salts via the acid-catalyzed ring closures of substituted methyl trithiocarbonates have been disclosed, which would give compounds similar to **2**, the reported cyclizations are specific only for phenacyl-substituted methyl trithiocarbonates; acetonyl methyl trithiocarbonates were reported not to yield any 1,3-dithiolylium salts.[3] Since we have by our method isolated high yields of 4-methyl-1,3-dithiole-2-thione (**3c**) from acetonyl *tert*-butyl trithiocarbonates as well as other compounds such as **3b,e,f**, the mechanistic question arises: When is isobutylene lost, before or after cyclization? The actual intermediate leading to **3** may be **8** rather than **2**. Our experimental technique did not allow us to answer this mechanistic question.

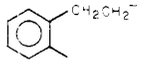
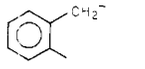
However, an example of cyclization before loss of isobutylene was found when acetylenic trithiocarbonate **4** cyclized stereospecifically to salt **5**. This parallels the

(1) Haley, N. F. *Tetrahedron Lett.* **1978**, 5161.
(2) Recent syntheses of dithioles from acetylenes, carbon disulfide, and bis(amine) disulfides suffer from the same limitation. See: Grumwell, J. R. *J. Org. Chem.* **1978**, *43*, 2917.
(3) Hamilton, R. D.; Campaigne, E. *Chem. Heterocycl. Compd.* **1977**, *30*, 171.

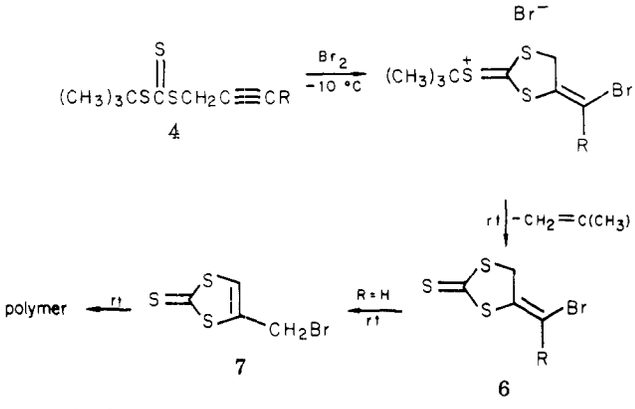
0022-3263/80/1945-0175$01.00/0

Scheme I



	R_1	R_2	% 3
a	C_6H_5	H	67
b	CH_2OCOCH_3	H	98
c	CH_3	H	98
d		H	78
e	CH_3	CH_3	90
f	$CH_2CH_2CH_2$		71
			97
h			60
i			86

Scheme II



$R = H, C_6H_5$

previously reported cyclization of **4** with acid catalysts.[1] When allowed to stand overnight, crystalline **5** slowly evolves isobutylene, yielding **6**. Traces of acid convert **6**, with its exo double bond, into **7**, which polymerizes rapidly. We tentatively assigned the polymer structure as a salt resulting from an alkylation between the thione sulfur and the bromomethyl group.

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. NMR spectra were recorded on a Varian EM-390 spectrometer with Me_4Si as an internal standard. Mass spectra were taken on an AEI MS-90 mass spectrometer.

Sodium *tert*-Butyl Trithiocarbonate Dihydrate. Sodium hydride dispersion (60% NaH in mineral oil, 40 g) suspended in 800 mL of THF at 0 °C was treated in small quantities with *tert*-butyl mercaptan (90 g). A thick paste formed, and stirring was continued for 16 h at 20 °C. Carbon disulfide (80 g) was added in small quantities at 0 °C. The paste dissolved, and after a small quantity of insoluble material was removed, 1200 mL of diethyl ether was added to the filtrate. Water (36 mL) was added, and the yellow crystalline solid was filtered and dried in air: 212 g (95%); mp >300 °C; IR (KBr) 3300, 2857, 1351, 1020, 995, 840 cm^{-1}.

Anal. Calcd for $C_5H_9NaS_3 \cdot 2H_2O$: C, 26.77; H, 5.84; Na, 10.3. Found: C, 26.5; H, 5.9; Na, 10.7.

General Procedure for the Synthesis of 1 or 4. The appropriate α-halo ketone or propargyl halide (0.01 mol) was dissolved in 25 mL of acetone, and sodium *tert*-butyl trithiocarbonate dihydrate (0.01 mol) was added in small quantities at 10 °C. The suspension was stirred for 2 h at 20 °C, and then 100 mL of water was added. The resulting solid was collected and recrystallized, or the oil was extracted with diethyl ether (2 × 50 mL), dried ($MgSO_4$), and either distilled or used directly. These compounds were susceptible to decomposition at temperatures above 110 °C. They were usually pure enough to be used in the next syntheses.

Phenacyl *tert*-Butyl Trithiocarbonate (1a). From phenacyl bromide, 28 g (96%) of trithiocarbonate was obtained after recrystallization from ethanol: mp 61–62 °C; IR (KBr) 2859, 1667, 1190, 1053, 980, 806, 747, 690 cm^{-1}; NMR ($CDCl_3$) δ 8.0 (m, 2 H), 7.5 (m, 3 H), 4.8 (s, 2 H), 1.6 (s, 9 H).

Anal. Calcd for $C_{13}H_{16}OS_3$: C, 54.89; H, 5.69; S, 33.81. Found: C, 54.7; H, 5.5; S, 33.6.

3-Acetoxyacetonyl *tert*-Butyl Trithiocarbonate (1b). From 1-acetoxy-3-chloroacetone, 2.6 g (93%) of trithiocarbonate was obtained after distillation at 0.01 torr: bp 98–100 °C; IR (neat) 2899, 1739, 1730, 1351, 1222, 1064, 1031, 806 cm^{-1}; NMR ($CDCl_3$) δ 4.8 (s, 2 H), 4.1 (s, 2 H), 2.0 (s, 3 H), 1.7 (s, 9 H).

Anal. Calcd for $C_{10}H_{16}O_3S_3$: C, 42.85; H, 5.71; S, 34.32. Found: C, 42.6; H, 5.5; S, 34.0.

Acetonyl *tert*-Butyl Trithiocarbonate (1c). From chloroacetone, 2.1 g (95%) of trithiocarbonate was obtained after distillation at 0.01 torr: bp 106–108 °C; IR (neat) 2857, 1709, 1351, 1143, 1064, 806 cm^{-1}; NMR ($CDCl_3$) δ 4.1 (s, 2 H), 2.2 (s, 3 H), 1.6 (s, 9 H).

Anal. Calcd for $C_8H_{14}OS_3$: C, 43.23; H, 6.30; S, 43.27. Found: C, 43.0; H, 6.0; S, 43.1.

Bis(*p*-phenacyl *tert*-butyl trithiocarbonate) (1d). From 1,4-bis(bromoacetyl)benzene and sodium *tert*-butyl trithiocarbonate (0.02 mol), 2.7 g (78%) of bis(trithiocarbonate) was obtained after recrystallization from acetic acid: mp 129–130 °C dec; IR (KBr) 2899, 1672, 1212, 1047, 810 cm^{-1}; NMR ($CDCl_3$) δ 8.0 (s, 4 H), 4.8 (s, 4 H), 1.7 (s, 9 H).

Anal. Calcd for $C_{20}H_{26}O_2S_3$: C, 42.08; H, 1.75; S, 56.17. Found: C, 41.8; H, 1.7; S, 55.8.

2-(3-Oxobutyl) *tert*-Butyl Trithiocarbonate (1e). From 3-bromo-2-butanone, 2.1 g (89%) of trithiocarbonate was obtained and was used directly for next synthesis: IR (neat) 2899, 1701, 1439, 1351, 1149, 1064, 794 cm^{-1}; NMR ($CDCl_3$) δ 4.8 (q, J = 7 Hz, 1 H), 2.3 (s, 3 H), 1.6 (s, 9 H), 1.5 (d, J = 7 Hz, 3 H).

Anal. Calcd for $C_9H_{16}OS_3$: C, 45.75; H, 6.77; S, 40.71. Found: C, 45.8; H, 6.7; S, 41.0.

2-(1-Oxocyclopentyl) *tert*-Butyl Trithiocarbonate (1f). From 2-chlorocyclopentanone, 2.3 g (93%) of trithiocarbonate was obtained and used directly in next synthesis: IR (neat) 2899, 1739, 1538, 1439, 1331, 1143, 1064, 800 cm^{-1}; NMR ($CDCl_3$) δ 4.5 (t, 1 H), 2.7–1.8 (m, 6 H), 1.6 (s, 9 H).

Anal. Calcd for $C_{10}H_{16}OS_3$: C, 48.37; H, 6.44; S, 38.74. Found: C, 48.4; H, 6.2; S, 38.5.

2-(*tert*-Butyl Trithiocarbonato)-α-tetralone (1g). From 2-bromo-α-tetralone, 3.0 g (92%) of trithiocarbonate was obtained after recrystallization from ethanol: mp 100–101 °C; IR (KBr) 1667, 1587, 1439, 1294, 1212, 1064, 800, 791, 741 cm^{-1}; NMR ($CDCl_3$) δ 7.9 (m, 1 H), 7.2 (m, 3 H), 5.1 (dd, 1 H), 3.1 (m, 2 H), 2.5 (m, 2 H), 1.7 (s, 9 H).

Anal. Calcd for $C_{15}H_{18}OS_3$: C, 58.05; H, 5.80; S, 30.99. Found: C, 57.9; H, 5.6; S, 29.9.

2-(*tert*-Butyl Trithiocarbonato)-1-indanone (1h). From 2-bromo-1-indanone, 2.0 g (67%) of trithiocarbonate was obtained and used directly for conversion to **3g**: IR (KBr) 2857, 1709, 1600, 1449, 1266, 1064, 1042, 813, 741 cm^{-1}; NMR ($CDCl_3$) δ 7.9–7.3 (m, 4 H), 5.0 (dd, 1 H), 3.9 (dd, 1 H), 3.1 (dd, 1 H), 1.7 (s, 9 H).

Anal. Calcd for $C_{14}H_{16}OS_3$: C, 56.74; H, 5.40; S, 32.46. Found: C, 56.5; H, 5.4; S, 32.0.

2-(*tert*-Butyl Trithiocarbonato)acenaphthylenone (1i). From 2-chloroacenaphthylenone, 3.0 g (90%) of trithiocarbonate was obtained after recrystallization from ethanol: mp 106–107 °C; IR (KBr) 2941, 2740, 1718, 1351, 1064, 995, 791, 772, 755 cm^{-1}; NMR ($CDCl_3$) δ 8.1–7.6 (m, 6 H), 6.3 (s, 1 H), 1.7 (s, 9 H).

Anal. Calcd for $C_{17}H_{16}OS_3$: C, 61.43; H, 4.81; S, 28.94. Found: C, 61.0; H, 4.5; S, 28.5.

General Method for Preparation of 1,3-Dithiole-2-thiones (3). The appropriate trithiocarbonate (1; 0.01 mol) was dissolved in a mixture of trifluoroacetic acid (10 mL), acetic acid (10 mL), and *p*-toluenesulfonic acid (0.1 g). The solution was warmed on a steam bath for 30 min and then refluxed for 30 min more. If the trithione **3** did not crystallize from the cooled solution, water (75 mL) was added, and the resulting oil was extracted with diethyl ether (75 mL), dried ($MgSO_4$), and evaporated under vacuum. The resulting oil was distilled under vacuum.

4-Phenyl-1,3-dithiole-2-thione (3a). From **1a**, 1.4 g (67%) of trithione was obtained: mp 116–117 °C (lit.[4] mp 117–118 °C); IR (KBr) 3100, 1486, 1446, 1055, 1045, 890, 740, 675 cm^{-1}.

4-(Acetoxymethyl)-1,3-dithiole-2-thione (3b). From **1b**, 2.0 g (98%) of trithione was obtained: bp 140–143 °C (0.05 torr); IR (neat) 2985, 1748, 1370, 1227, 1064, 1031 cm^{-1}; NMR ($CDCl_3$) δ 7.0 (t, J = 2.1 Hz, 1 H), 4.9 (d, J = 2.1 Hz, 2 H), 2.1 (s, 3 H).

Anal. Calcd for $C_6H_6O_2S_3$: C, 34.94; H, 2.91; S, 46.63. Found: C, 34.7; H, 2.8; S, 46.3.

4-Methyl-1,3-dithiole-2-thione (3c). From **1c**, 1.45 g (98%) of trithione was obtained and recrystallized from diethyl ether at −30 °C (60% yield); mp 30–31 °C (lit.[4,5] mp 32 °C); bp 90–93 °C (0.05 torr); NMR ($CDCl_3$) δ 6.7 (q, J = 1.2 Hz, 1 H), 2.3 (d, J = 1.2 Hz, 3 H).

1,4-Phenylenebis(1,3-dithiole-2-thione) (3d). From **1d**, 2.7 g (78%) of trithione was obtained, mp 345–347 °C (lit.[6] mp 347 °C).

4,5-Dimethyl-1,3-dithiole-2-thione (3e). From **1e**, 1.5 g (90%) of trithione was obtained after recrystallization from methanol, mp 95–96 °C (lit.[5] mp 96 °C).

4,5-Trimethylene-1,3-dithiole-2-thione (3f). From **1f**, 1.2 g (70%) of trithione was obtained after recrystallization from ethyl acetate, mp 107–108 °C (lit.[5] mp 109 °C).

4,5-Dihydronaphtho[3,4-*d*]-1,3-dithiole-2-thione (3g). From **1g**, 2.3 g (87%) of trithione was obtained after recrystallization from ethyl acetate: mp 114–116 °C (lit.[5] mp 116 °C); NMR ($CDCl_3$) δ 7.2 (m, 3 H), 7.0 (m, 1 H), 3.0 (m, 2 H), 2.8 (m, 2 H); mass spectrum, m/e 236 (M^+), 203, 192, 160, 128, 115.

Indeno[2,3-*d*]-1,3-dithiole-2-thione (3h). From **1h**, 1.3 g (60%) of trithione was obtained: mp 127–129 °C (lit.[5] mp 131 °C); NMR ($CDCl_3$) δ 5–7.2 (m, 4 H), 4.7 (s, 2 H).

4,5-(1,8-Naphtho)-1,3-dithiole-2-thione (3i). From **1i**, 2.2 g (86%) of trithione was obtained after recrystallization from dioxane: mp 234–235 °C; IR (KBr) 1429, 1099, 1053, 800, 758 cm^{-1}; mass spectrum, m/e 258 (M^+), 214, 170, 138, 126, 107, 93, 69.

Anal. Calcd for $C_{13}H_6S_3$: C, 60.44; H, 2.30; S, 37.23. Found: C, 60.8; H, 2.2; S, 37.2.

3-Propynyl *tert*-Butyl Trithiocarbonate (4, R = H). From 3-bromo-1-propyne, 2.0 g (100%) of trithiocarbonate was obtained and distilled at 0.1 torr: mp 78–80 °C (94% yield); IR (neat) 3330, 2857, 2128 (w), 1351, 1064, 800 cm^{-1}; NMR ($CDCl_3$) δ 4.0 (d, J = 2.1 Hz, 2 H), 2.2 (t, J = 2.1 Hz, 1 H), 1.6 (s, 9 H).

Anal. Calcd for $C_8H_{12}S_3$: C, 47.02; H, 5.92; S, 47.06. Found: C, 46.8; H, 5.7; S, 46.8.

1-Phenyl-3-propynyl *tert*-Butyl Trithiocarbonate (4, R = C_6H_5). From 3-bromo-1-phenyl-1-propyne,[7] 2.7 g of trithiocarbonate was obtained and used directly in the next syntheses: IR (neat) 2899, 2247 (w), 1508, 1355, 1163, 1064, 800, 758, 687 cm^{-1}; NMR ($CDCl_3$) δ 7.3 (m, 5 H), 4.3 (s, 2 H), 1.6 (s, 9 H).

Anal. Calcd for $C_{14}H_{16}S_3$: C, 59.98; H, 5.71; S, 34.31. Found: C, 59.6; H, 5.8; S, 33.9.

4-(Bromomethylene)-2-(*tert*-butylthio)-1,3-dithiolylium Bromide (5, R = H). A solution of 2 g of 4 (R = H) in 25 mL of dichloromethane at −10 °C was treated dropwise with a solution of 1.6 g of bromine in 25 mL of dichloromethane. A precipitate formed immediately and was collected and air-dried. The yellow solid (3.5 g, 97%) was stable for a short time but began to lose isobutylene at room temperature: NMR (HOAc-d_4) δ 6.8 (t, J = 2.5 Hz, 1 H), 4.9 (d, J = 2.5 Hz, 2 H), 1.9 (s, 9 H); IR (KBr) 2899, 1412, 1227, 1072 (vs), 903, 779, 719 cm^{-1}.

4-(Bromomethylene)-1,3-dithiolane-2-thione (6). From **5**, when the mixture was allowed to stand overnight at room temperature, 2.2 g (100%) of trithione was obtained: NMR ($CDCl_3$) δ 6.2 (t, J = 2.0 Hz, 1), 4.6 (d, J = 2.0 Hz, 2 H); IR (KBr) 3030 (w), 1587 (w), 1379, 1258, 1055 (vs), 1042, 893, 781, 717 cm^{-1}.

Anal. Calcd for $C_4H_3BrS_3$: C, 21.15; H, 1.32; S, 42.35; Br, 35.18. Found: C, 20.8; H, 1.3; S, 42.0; Br, 34.8.

When the mixture was allowed to stand, a mixture of **7** and an insoluble polymer was formed. We detected **7** by its NMR spectrum when the mixture was extracted with deuteriochloroform: NMR ($CDCl_3$) δ 6.9 (t, J = 0.9 Hz, 1 H), 4.4 (d, J = 0.9 Hz, 2 H).[8] Yellow polymer slowly precipitated from the chloroform.

4-(α-Bromobenzylidene)-1,3-dithiolane-2-thione (6, R = C_6H_5). Compound **6** was prepared from **4** (R = C_6H_5) and bromine in a manner similar to that of the reaction of **4** (R = H) except aqueous $NaHCO_3$ (25 mL, saturated solution) was added, followed by solid $Na_2S_2O_5$ until the solution was colorless. The dichloromethane solution was separated, dried ($MgSO_4$), and evaporated. The yellow solid (2.8 g, 93%) was a mixture of cis and trans exo isomers in a ratio of 1.8:1: NMR ($CDCl_3$) δ 7.4 (m, 5 H), 4.8 (s, 1.3 H), 4.3 (s, 0.7 H). This mixture did not change on recrystallization from ethanol, nor did it isomerize to a compound like **7**.[9]

Anal. Calcd for $C_{10}H_7BrS_3$: C, 39.61; H, 2.31; S, 31.72, Br, 26.35. Found: C, 39.4; H, 2.2; S, 31.6; Br, 26.0.

Registry No. **1a**, 71988-71-1; **1b**, 72030-06-9; **1c**, 71988-72-2; **1d**, 71988-73-3; **1e**, 71988-74-4; **1f**, 71988-75-5; **1g**, 71988-76-6; **1h**, 71988-77-7; **1i**, 71988-78-8; **3a**, 2314-61-6; **3b**, 71988-79-9; **3c**, 3608-38-6; **3d**, 68144-36-5; **3e**, 17534-27-9; **3f**, 17534-29-1; **3g**, 17784-42-8; **3h**, 17534-42-8; **3i**, 71988-80-2; **4** (R = H), 71127-44-1; **4** (R = C_6H_5), 71127-45-2; **5** (R = H), 71988-81-3; **6** (R = H), 71988-82-4; *cis*-**6** (R = C_6H_5), 71988-83-5; *trans*-**6** (R = C_6H_5), 71988-84-6; **7**, 71988-85-7; sodium *tert*-butyltrithiocarbonate, 71127-42-9; *tert*-butylmercaptan, 75-66-1; carbon disulfide, 75-15-0; phenacyl bromide, 70-11-1; 1-acetoxy-3-chloroacetone, 40235-68-5; chloroacetone, 78-95-5; 1,4-bis(bromoacetyl)benzene, 946-03-2; 3-bromo-2-butanone, 814-75-5; 2-chlorocyclopentanone, 694-28-0; 2-bromo-α-tetralone, 13672-07-6; 2-bromo-1-indanone, 1775-27-5; 2-chloroacenaphthylenone, 16269-26-4; 3-bromo-1-propyne, 106-96-7; 3-bromo-1-phenyl-1-propyne, 1794-48-5.

(4) Lever, D.; Robertson, W. A. H.; McKinnon, D. M. *J. Chem. Soc.* **1962**, 5104.
(5) Fanghänel, E. *J. Prakt. Chem.* **1975**, *317*, 123.
(6) Schukat, G.; VanHinh, L.; Fanghänel, E.; Libera, L. *J. Prakt. Chem.* **1978**, *320*, 404.
(7) Smith, L.; Swenson, J. *J. Am. Chem. Soc.* **1957**, *79*, 2962.
(8) The NMR spectrum of **7** is similar to that of 4-(bromomethyl)-1,3-dithiol-2-one prepared by an alternative unambiguous synthesis.
(9) The conjugative effect of the phenyl ring probably prevents the isomerization to an endo double bond.

Photodimerization of Propellanones Involving a Cyclobutanone Moiety via an Oxacarbene Intermediate

Yoshihiro Fukuda,* Toshihiko Negoro, Koji Kimura, and Yoshinobu Odaira

Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Received August 3, 1979

There has been remarkable interest recently in the chemistry of propellane systems, particularly in view of structure–reactivity relationships,[1] and the above relationships on various [*n*.3.2]propellanes have attracted our

(1) For a review: Ginsburg, D. "Propellanes, Structure and Reactions"; Verlag Chemie: Weinheim/Bergstr., Germany, 1975. See also: Paquette, L. A.; Photis, J. M.; Micheli, R. P. *J. Am. Chem. Soc.* **1977**, *99*, 7899 and references cited therein.

0022-3263/80/1945-0177$01.00/0