Ethylene Thionocarbonate and 1,3-Oxathiolane-2-thione

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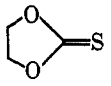
Syntheses and reactions of the title compounds are reported. These compounds are isomerized to thiol- and dithiolcarbonates by halide ions. Alkylation with alkyl halides gives unstable intermediates which rearrange to β-haloethyl thiol- and dithiolcarbonates. Acids induce polymerization to polythiol and polydithiolcarbonates. Both 1 and 2 give ethylene when treated with triphenylphosphine. Nmr and ir spectral comparisons of the six possible ethylene carbonates with sulfur substituted for oxygen are tabulated.

Corey and Winter discovered that cyclic 1,2-thionocarbonates and 1,2-trithiocarbonates are converted into olefins by *cis* elimination in high yields when treated with tertiary phosphines or phosphites.[1,2] This new olefin synthesis is broadly useful for stereospecific syntheses of olefins and provides the first synthesis of the strained *trans*-cycloheptene.[2] Cyclic 1,3-trithiocarbonates, however, are converted into phosphorus ylides by sulfur–phosphite exchange,[3] and intermediate ylides have been implicated in the reaction of 1,2-trithiocarbonates with phosphites.[3]

Previous work on cyclic 1,2-thionocarbonates has centered on substituted cases and has been concerned primarily with their conversion into olefins. The parent ethylene thionocarbonate (1) has not been described. Synthesis of the related compound 1,3-oxathiolane-2-thione (2) has been reported,[4] but we have been unable to repeat this synthesis. Earlier reports of 2 are clearly erroneous. In this paper, we describe satisfactory syntheses of 1 and 2 and studies of their chemistry.



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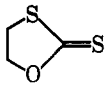

2

Results

Compound 1 was synthesized directly from thiophosgene and ethylene glycol in 33% yield. The most successful technique was slow addition of the glycol in tetrahydrofuran (THF) to a boiling mixture of thiophosgene, methylene chloride, and potassium carbonate (eq 1).

$$HOCH_2CH_2OH + Cl_2C{=}S \xrightarrow[CH_2Cl_2\text{–}THF]{K_2CO_3;\ 45°} 1 \qquad (1)$$

Compound 2 was synthesized indirectly from a lead salt of 2-mercaptoethanol and thiophosgene in 46% yield (eq 2). Other heavy metal salts of 2-mercaptoethanol gave lower yields.

$$HOCH_2CH_2SH \xrightarrow{Pb(OAc)_2} (HOCH_2CH_2S)Pb(OAc) \xrightarrow[CH_2Cl_2]{Cl_2CS} 2 \qquad (2)$$

Compound 1 is a colorless solid, mp 55–55.5°; compound 2 is a pale yellow oil, mp *ca.* −20°. Both 1 and 2 are thermally unstable, decomposing appreciably at 100°, and both are reactive toward acids, bases, and moisture. Synthesis of 1 and 2 makes available for characterization the six possible ethylene carbonates in which S is systematically substituted for O. Physical and spectral data for these six compounds are assembled in Table I. These data establish the structures of 1 and 2.

The CH_2O hydrogens in ethylene carbonate and 3 exhibit decreased nmr shielding in the presence of the thiocarbonyl function in 1 and 2, respectively. In both cases the CH_2O hydrogens are more shielded than the CH_2O hydrogens in 1,3-dioxolanes, whose peaks fall at *ca.* τ 6.[5] The presence of two sulfur atoms in 2 results in a paramagnetic shift for the CH_2O relative to 1. Similarly, the CH_2S protons in ethylene trithiocarbonate and 2 show corresponding downfield shifts compared with carbonyl compounds 4 and 3, respectively. Finally, two sulfurs in the ring in the trithiocarbonate and 4 result in a downfield shift for the CH_2S protons relative to 2 and 3, respectively.

The C═S stretching frequencies in 1, 2, and ethylene trithiocarbonate (1303, 1368, 1181, 1234, and 1069) are consistent for these structures[6] when account is taken of the anticipated shift to higher frequencies due to the five-membered ring. Spectra of related heterocycles, including ethylene dithiol- and trithiocarbonates, have been analyzed.[7]

Reactions of 1 and 2 are outlined in Scheme I. Compounds 1 and 2 are readily isomerized to 3 and 4, respectively, by halide ions. We postulate that the reaction involves nucleophilic displacement to give intermediates 3′ and 4′ (not detected) followed by ring closure. Bond energy data[8] indicate that isomerization of thionocarbonates to the corresponding thiolcarbonates should be exothermic by about 24 kcal/mol. Other examples which illustrate the instability of thionocarbonates relative to thiolcarbonates are the Schönberg rearrangement of diarylthionocarbonates[9] and the well-known tendency of monothio acids to exist almost exclusively in the thiol form.

The ease with which 1 and 2 isomerize indicates that earlier workers,[4,10] who claimed to have prepared 2, had

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(1) E. J. Corey and R. E. A. Winter, *J. Amer. Chem. Soc.*, **85** 2677 (1963).

(2) E. J. Corey, F. A. Carey, and R. E. A. Winter, *ibid.*, **87**, 934 (1965).

(3) E. J. Corey and G. Markl, *Tetrahedron Lett.*, No. 33, 3201 (1967); R. Hull and R. Farrand, *Chem. Commun.*, 164 (1967)

(4) V. S. Etlis, *J. Org. Chem. USSR*, **34**, 3032 (1964).

(5) E. Caspi, T. A. Wittstruck, and D. M. Piatek, *J. Org. Chem.*, **27**, 3183 (1962); E. Caspi, H. Zajac, and T. A. Wittstruck, *ibid.*, **29**, 640 (1964).

(6) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958, p 356; Jones, Kynaston, and Hales, *J. Chem. Soc.*, 614 (1957).

(7) R. Mecke, R. Mecke, and A. Luttringhaus, *Chem. Ber.*, **90**, 975 (1957).

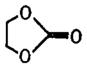
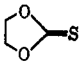
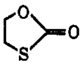
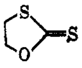
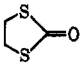
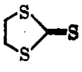
(8) E. S. Kooyman in "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience Publishers, New York, N. Y., 1967, Chapter 1.

(9) A. Schönberg and L. Vargha, *Chem. Ber.*, **63**, 178 (1930); A. Schönberg, L. Vargha, and W. Paul, *Ann.*, **483**, 107 (1930); H. R. Al-Kazimi, D. S. Tarbell, and D. Plant, *J. Amer. Chem. Soc.*, **77**, 2479 (1955); D. H. Powers and D. S. Tarbell, *ibid.*, **78**, 70 (1956).

(10) A. Husemann, *Ann.*, **126**, 268 (1863).

Table I

Properties of Ethylene Carbonate and Thiocarbonates

Compd	Registry no.	Color	Mp, °C	Chemical shift (τ), ppm[a]	Ir absorption,[b] cm⁻¹				
	96-49-1	None	38.5–39[c]	5.45	1076	1153	1779	1808	
 (1)	20628-59-5	None	55–55.5	5.22	955	1013	1151	1303	1368
 (3)	3326-89-4	None		A_2B_2[d] 6.41, 5.47	1037	1074	1739		
 (2)	20628-60-8	Pale yellow	Ca. −20	A_2B_2[d] 6.27, 5.02	924	1003	1057	1181	1231
 (4)	2080-58-2	None	35[e]	6.28	827	885	1637	1672	
	822-38-8	Yellow	40–41[f]	5.99	832	880	1074		

[a] Measured at 60 MHz in $CDCl_3$. [b] Strongest peaks only; $CHCl_3$ solutions. [c] J. Nemirowsky, *J. Prakt. Chem.*, [2] **28**, 493 (1883). [d] Pair of triplets with fine splitting; J = 7 Hz. [e] See ref 22. [f] A. Miolati, *Ann. Chem.*, **262**, 61 (1891).

Table II

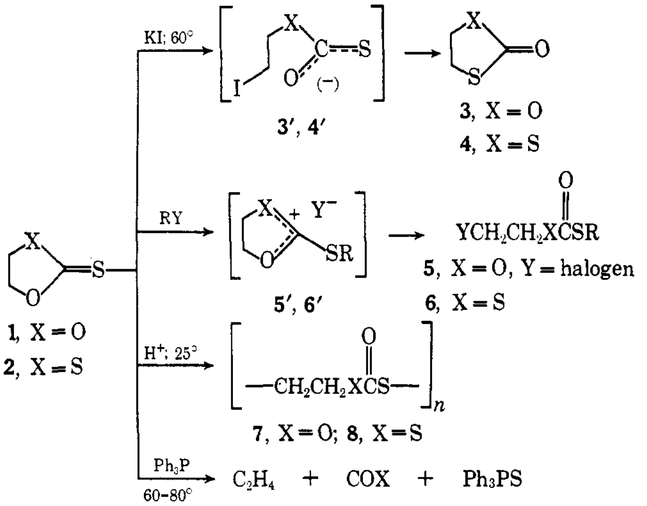
Data for Compounds 

$\mathrm{YCH_2CH_2X}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{SR}$

Compd	R	X	Y	Time, hr	Temp, °C	Yield, %	Bp (mm) or mp, °C	Formula	% C Calcd	% C Found	% H Calcd	% H Found	% other Element	% other Calcd	% other Found	C=O peak, cm⁻¹ ±3
5a	CH_3	O	I	72[a]	25	72	93 (5)	$C_4H_7IO_2S$	19.52	19.60	2.87	2.84	S	13.03	13.22	1715
5b	$C_6H_5CH_2$	O	Br	0.5[b]	200	98	Oil	$C_{10}H_{11}BrO_2S$	43.65	43.94	4.03	3.98	Br	29.04	28.61	1709
5c	$C_6H_5CH_2$	O	I	18[a]	25	40	Oil[c]	$C_{10}H_{11}IO_2S$	37.29	37.14	3.44	3.50	S	9.95	10.23	1712
5d	4-$O_2NC_6H_4CH_2$	O	Br	72[a]	82	62	81–83.5[d]	$C_{10}H_{10}BrNO_4S$	37.51	37.24	3.15	3.05	Br	24.92	25.11	1709
5e	2,4-$Cl_2C_6H_3CH_2$	O	Cl	8[a]	150	11	29–31[f]	$C_{10}H_9Cl_3O_2S$	40.09	39.91	3.03	3.05	Cl	35.50	35.09	1712
5f	$(C_6H_5)_2CH$	O	Cl	16[b]	120	..	Oil	$C_{16}H_{15}ClO_2S$	62.64	62.55	4.93	4.84	S	10.45	10.74	1715
5g	$(C_6H_5)_3C$	O	Cl	140[a]	25	44	119–121.5[g]	$C_{22}H_{19}ClO_2S$	69.01	69.31	5.00	5.09	S	8.37	8.35	1724
5h	$CH_2{=}CHCH_2$	O	Br	5[h]	70	26	96 (5)	$C_6H_9BrO_2S$	32.01	32.18	4.03	3.97	Br	35.50	35.50	1712
5i	$HOOCCH_2$	O	I	18[a]	25	34	109–110.5[f]	$C_5H_7IO_4S$	20.70	20.92	2.43	2.45	I	43.75	42.91	1706
5j	$HC{\equiv}CCH_2$	O	Cl	18[i]	125	67	~120 (0.0001)	$C_6H_6ClNO_2S$	33.43	33.36	3.37	3.33	Cl	19.74	19.61	1727
6a	CH_3	S	I	14[a]	82	90	90–95 (1)	$C_4H_7IOS_2$	18.33	18.75	2.69	2.73	S	24.46	24.69	1650
6b	4-$O_2NC_6H_4CH_2$	S	Br	18[a]	82	43	66–67[f]	$C_{10}H_{10}BrNO_3S_2$	35.72	35.64	3.00	3.22	S	19.07	19.12	1645

[a] Reaction solvent was acetonitrile. [b] No solvent; equimolar amounts of reagents were used. [c] Product was flash distilled at 0.0001 mm. [d] Recrystallized from pentane–methylene chloride. [e] A steel pressure vessel was used. [f] Recrystallized from hexane–methylene chloride. [g] Recrystallized from hexane. [h] Compound **1** was added to refluxing, excess allyl bromide during 3 hr. [i] The solvent was excess chloroacetonitrile at reflux.

Scheme I



actually obtained **4**. Attempted synthesis of **2** from 2-mercaptoethanol and thiophosgene in the presence of aqueous NaOH as described by Etlis[4] gave **4** but not **2**. Compound **2** is rapidly hydrolyzed by dilute aqueous NaOH.

The ring-opening alkylation of **1** and **2** was used to synthesize twelve unsymmetrical β-haloethyl thiolcarbonates (**5a–j**) and dithiolcarbonates (**6a–b**), generally in good yield. The alkyl halides used, conditions, and yields are specified in Table II. The only apparent limitation in scope is that the alkyl halide must be of reactivity comparable with or greater than that of the product. Unreactive alkyl halides such as *t*-butyl bromide give polymers **7** or **8**, even when used in excess. The ring-opening alkylation is analogous to the previously observed ring-opening alkylation of 1,3-oxazolidine-2-thione with methyl iodide.[11]

The ring-opening reaction presumably involves intermediate salts, such as **5′** and **6′**, analogous to the 1,3-dioxolenium salts[12] or to the formation of intermediate alkylthiuronium salts from thiourea and alkyl halides.[13]

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(11) T. Mukaiyama, I. Kuwajima, and K. Mixui, *J. Org. Chem.*, **31**, 32 (1966).

(12) H. E. Zaugg and R. J. Michals, *Tetrahedron*, **18**, 893 (1962).

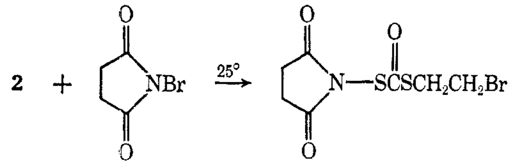
(13) F. G. Bordwell, "Organic Chemistry," The Macmillan Co., Inc., New York, N. Y., 1963, p 210.

Ring-opening polymerizations of **1** and **2** to polymers **7** and **8**, respectively, were effected by treatment with anhydrous acids at 25°. Trifluoroacetic acid appears to form a 1:1 complex with **1** which polymerizes when the acid is volatilized. Polymers **7** and **8** were unstable above 200°. Analogous ring-opening polymerizations of 1,3-oxazolidine-2-thiones are known.[11]

Treatment of **1** with triphenylphosphine at 60° caused rapid evolution of CO_2 and ethylene, as expected from previous work.[1,2] The yield of ethylene was only 10%. Similar treatment of **2** gave COS and ethylene in 42% yield; this is the first example of a Corey–Winter reaction of a dithiocarbonate.

Heating compound **1** at 140° caused decomposition to mixtures of isomer **3**, polymer **7**, and other substances. Heating **2** at 120° gave a similar mixture.

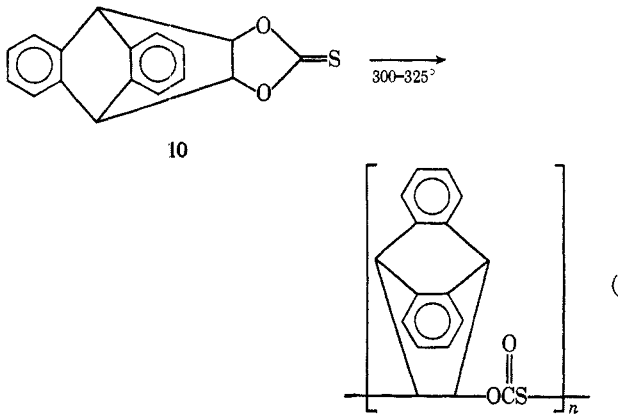
Treatment of **2** with N-bromosuccinimide (NBS) gave a 1:1 adduct tentatively assigned structure **9** (eq 3) on the basis of spectroscopic data. Formation of N–S bonds in reactions of NBS have been noted.[14]



(3)

9

Anthracene-substituted derivative **10** was synthesized by heating 9,10-dihydro-9,10-ethanoanthracene-11,12-diol[15] with N,N′-thiocarbonyldiimidazole.[16,17] When heated at 325°, compound **10** gave polymer **11** (eq 4).



10

(4)

11

Experimental Section[18]

Ethylene Thionocarbonate (**1**).—In a 1-l. 4-neck flask was placed a mixture of 550 ml of methylene chloride, 120 g of anhydrous potassium carbonate, and 50 ml (74 g, 0.65 mol) of thiophosgene. The orange mixture was stirred mechanically and heated at reflux as a solution of 40 g (0.65 mol) of dry, redistilled ethylene glycol in 125 ml of tetrahydrofuran was added dropwise during 2 hr. Refluxing was continued for 16 hr. The mixture was filtered; the liquid was concentrated to give 58 g of partly crystalline residue. (*Caution:* The temperature must be kept at 25° or below during the late stages of solvent removal. The concentrated residue contains by-products which can undergo violent exothermic decomposition.)

The residue was recrystallized by dissolving in 300 ml of methanol, filtering, and cooling to −78° to give 28 g of solid, mp 48–52°, containing orange impurities and polymer. This solid was sublimed at a pressure of 0.05 μ using a controlled oil bath temperature of 58–62° to give 23.5 g of sublimate. Recrystallization from 300 ml of methanol gave 22.7 g (33%) of **1** as colorless needles, mp 54.5–55.5°. Compound **1** should be stored under dry, dark, cold conditions.

Anal. Calcd for $C_3H_4O_2S$: C, 34.60; H, 3.87; S, 30.71. Found: C, 34.63; H, 3.85; S, 30.73.

The ultraviolet spectrum of **1** in ethanol had λ_{max} 304 (ϵ 28) and 235 mμ (ϵ 14,100). Winter reports that *trans*-4,5-dimethylethylenethionocarbonate has λ_{max} 302 (ϵ 33) and 236 mμ (ϵ 16,100).[19] The strongest peaks in the mass spectrum were at *m/e* (rel intensity) 60 (1.00), 104 (molecular ion, 0.87), 29 (0.82), 45 (0.81), 32 (0.65), 59 (0.59), and 43 (0.48).

1,3-Oxathiolane-2-thione (**2**).—Lead(II) mono(β-hydroxyethylmercaptide)monoacetate was prepared by stirring a mixture of 500 g (1.3 mol) of lead(II) acetate trihydrate, 150 g (1.9 mol) of 2-mercaptoethanol, and 300 ml of ethanol overnight in the dark. Powerful stirring is required, particularly during addition of the lead acetate. The cream-colored product was collected and washed three times with ethanol, three times with tetrahydrofuran, and twice with methylene chloride. The product was dried by prolonged pumping at 0.5 mm. The yield was 400 g (87%) of finely divided solid, mp 180–190° dec (lit.[20] mp 173–176° dec).

A 1-l. 3-neck flask containing 172 g (0.50 mol) of the above lead compound and 600 ml of methylene chloride was surrounded by a large bath of water at about 15°. The slurry was stirred as 35 ml (52 g, 0.45 mol) of thiophosgene was added by means of pipets. The mixture was stirred for 20 hr with minimum exposure to light. During the first 5 hr, the temperature was maintained at 18–25° by occasional addition of ice to the water bath to keep it at 10–15°. Later, the bath and the reaction flask were allowed to warm to ambient temperature. The mixture was filtered. The liquid was concentrated on a rotary evaporator, keeping the temperature below 25°, to give 55 g of pale yellow oil. The oil was chromatographed on a 9.5-cm column of 1 kg of neutral silica gel (Woelm activity I) using methylene chloride to elute the product. Most by-products, including substantial amounts of $(HOCH_2CH_2S)CS$, were not eluted. The yellow-orange eluent was collected in fractions. Concentration of the earlier fractions gave 25 g (46%) of product **2**, containing a few per cent isomer **4**. Distillation using a high-vacuum Vigreux apparatus gave 18 g of pale yellow liquid, bp 56–62° (0.08–0.1 μ). All fractions contained about 5% isomer **4**. The product should be stored under cold, dry, dark conditions. Further purification by zone refining did not remove isomer **4**.

Anal. Calcd for $C_3H_4OS_2$: C, 29.98; H, 3.35; S, 53.35. Found: C, 30.00; H, 3.50; S, 53.44.

Isomerization Reactions.—A mixture of 0.52 g (5 mmol) of compound **1**, 3 g of KI, and 20 ml of acetonitrile was stirred and heated at 60° for 68 hr. Removal of solvent and salts gave 0.4 g of essentially pure ethylene thiolcarbonate (**3**), identical with a sample prepared as described.[21] (See Table I for nmr and ir spectra.)

Similar treatment of compound **2** caused essentially complete isomerization to ethylene dithiocarbonate (**4**) identical with a sample, mp 30–30.5° (lit.[22] mp 35°), prepared as described.[22]

Reactions with Alkyl Halides.—These reactions were performed in acetonitrile solution or using the neat alkyl halide as solvent. The products were isolated by distillation, recrystallization, or volatilization of starting materials, as appropriate. The data for individual reactions and the properties of the products are collected in Table II. The ir spectra of thiocarbonates **5a–j** showed C=O peaks in the range 1706–1727 cm^{-1}; the corresponding peaks in the spectra of dithiolcarbonates were at 1645–1650 cm^{-1}. Similar frequencies were noted in the spectra of cyclic carbonates **3** and **4** (see Table I). The nmr spectra of these products were consistent with the assigned structures. Typically, the β-haloethyl groups in **5a–j** give rise to 6-line A_2B_2 patterns,

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[14] D. S. Tuleen and D. N. Buchanan, *J. Org. Chem.*, **32**, 465 (1967).

[15] T. L. Patton, U. S. Patent 2,857,434 (1958).

[16] H. A. Staab and G. Walther, *Ann.*, **657**, 98 (1962).

[17] T. J. Pullokat and G. Urry, *Tetrahedron Lett.*, 1953 (1967).

[18] Melting and boiling points are uncorrected. Infrared spectra were recorded linearly in wavelength on a Perkin-Elmer 21 spectrophotometer. Nmr spectra were produced at 60 MHz using Varian A-60 and A-56-60 devices; the solvent was deuteriochloroform doped with Me_4Si except where noted.

[19] R. E. A. Winter, Ph.D. Dissertation, Harvard University, Cambridge, Mass., 1964, p 64.

[20] A. Schoberl and G. Wiehler, *Ann.*, **595**, 101 (1955).

[21] D. D. Reynolds, *J. Amer. Chem. Soc.*, **79**, 4951 (1957).

[22] C. G. Overberger and P. V. Bonsignore *ibid.*, **80**, 5427 (1958).

J = 6–8 Hz. For example, the nmr spectrum of **5a** had peaks at τ 7.65 (s, 3, SCH_3), 6.68 (t, 2, J = 7 Hz, OCH_2), and 5.53 (t, 2, J = 7 Hz, ICH_2). The nmr spectrum of compound **6a** had peaks at τ 7.55 (s, 3, SCH_3) and 6.60 (m, 4, ICH_2CH_2S).

Reaction of 1 with *t*-Butyl Bromide.—A solution of 1.04 g (10 mmol) of compound **1** in 25 ml of *t*-butyl bromide was heated at 78° overnight. Polymeric material began to separate within a few minutes. The solid was filtered and dried. The yield was 0.80 g of white polymer, substantially identical with polymer **7** (see below). *The soluble fraction appeared to contain telomers.*

Ring-Opening Polymerizations.—A solution of 2.08 g (0.020 mol) of **1**, 4.5 g (6.040 mol) of trifluoroacetic acid, and 30 ml of methylene chloride was kept for 3 days at 25°. The solvent was removed under high vacuum to give 2.1 g of white polymer **7**: mp 128°, η_{inh} 0.08 (0.1% in dimethylformamide); ir 1715 cm^{-1} (C=O). The polymer was a crystalline substance which could be drawn into fibers. Thermogravimetric analysis (TGA) showed decomposition at 200–250°.

Anal. Calcd for $(C_3H_4O_2S)_x$: C, 34.60; H, 3.87; S, 30.71. Found: C, 34.54; H, 3.88; S, 30.27.

This polymer was insoluble in chloroform, but readily dissolved when 1 equiv of trifluoroacetic acid was added: nmr ($CDCl_3$) τ −0.93 (br), 5.50 (t, J = 6 Hz), and 6.78 (t, J = 6 Hz). A solution having an identical nmr spectrum was formed from monomeric **1** and trifluoroacetic acid. Formation from **1** of the species which gives the pair of triplets was 93% complete in about 10 min.

A solution of 1.2 g of **2** in 2.4 g of trifluoroacetic acid was kept overnight to give a precipitate of white polymer **8**: mp 191–194° dec; ir (KBr) 1655 (C=O).

Anal. Calcd for $(C_3H_4OS_2)_x$: C, 29.98; H, 3.35; S, 53.35. Found: C, 30.12; H, 3.45; S, 52.29.

Reaction with Triphenylphosphine.—A mixture of 1.04 g (10 mmol) of **1** and 10 g of triphenylphosphine was heated to 80° in an evacuated flask with a manometer. As soon as the solids melted (about 60°), 11.7 mmol of gas evolved. Mass spectroscopic and infrared analysis showed this to consist mainly of CO_2 and C_2H_4 in a 92:8 ratio.

Similar treatment of **2** gave 0.012 mol of gas. Mass spectroscopic and infrared analysis showed carbonyl sulfide and ethylene in a 65:35 ratio, a 42% conversion to ethylene.

S-(β-Bromoethyl)-S-(N-succinimido)dithiocarbonate (9).—A solution of 6.0 g (0.045 mol) of **2** (90% pure) and 8.0 g (0.045 mol) of N-bromosuccinimide in 70 ml of methylene chloride was stirred at 0° for 3 hr and then at ambient temperature overnight. The solution was filtered and concentrated to give 13.2 g of solid. Two recrystallizations from a mixture of carbon tetrachloride, methylene chloride, and pentane gave 4.4 g (34%) of colorless solid, mp 111–113°. Further recrystallization gave a sample which melted at 117.5–118.5°; nmr τ 6.52 (s, 4) and 7.03 (s, 4); ir (KBr) 1650 and 1730 cm^{-1}.

Anal. Calcd for $C_7H_8BrNO_3S_2$: C, 28.19; H, 2.70; Br, 26.80; N, 4.70; S, 21.50. Found: C, 28.16; H, 3.31; Br, 27.36; N, 5.07; S, 21.77.

Treatment of a solution of **2** *in carbon tetrachloride with NBS* gave the same product.

"Anthracene–Vinylene Thionocarbonate Adduct" (10).—The adduct of anthracene with vinylene carbonate was prepared as described.[23] Hydrolysis to 9,10-dihydro-9,10-ethanoanthracene-11,12-diol, mp 204–206°, was done by Patton's procedure.[15]

A mixture of 32.0 g (0.134 mol) of the above diol, 23.9 g (0.134 mol) of N,N′-thiocarbonyldiimidazole,[16,17] and 400 ml of toluene was heated at reflux under nitrogen for 18 hr. The solution was washed with water while warm. Cooling to 0° gave crystals which were collected, dried, and recrystallized from toluene (Darco) to give 34 g (91%) of product **10**: mp 228–230°; nmr (acetone-d_6–TMS) τ 4.65 (t, 2, J = 2 Hz), 5.06 (t, 2, J = 2 Hz), and aromatic (m, 8).

Anal. Calcd for $C_{17}H_{12}O_2S$: C, 72.83; H, 4.32; S, 11.43. Found: C, 72.83; H, 4.37; S, 11.51.

Polymerization of 10.—Solid **10** (1.0 g) was placed in a sublimer containing N_2 at 400 mm. The sublimer was partly immersed for 5 min in a fluidized-bed sand bath heated at 315–325°. Partial sublimation of starting material (0.3 g) occurred. The remainder (0.69 g) was molten polymer which solidified when cooled: ir 1690 (C=O) and 1275 cm^{-1}; TGA decomposition at 350–375°.

Anal. Calcd for $(C_{17}H_{12}O_2S)_x$: C, 72.83; H, 4.32. Found: C, 72.91; H, 4.43; η_{inh} = 0.31 (0.1% in toluene at 25°).

Registry No.—**5a**, 20628-63-1; **5b**, 20628-64-2; **5c**, 20628-65-3; **5d**, 20628-66-4; **5e**, 20628-67-5; **5f**, 20628-68-6; **5g**, 20628-69-7; **5h**, 20628-70-0; **5i**, 20628-71-1; **5j**, 20628-72-2; **6a**, 20628-73-3; **6b**, 20628-74-4; **9**, 20628-75-5; **10**, 20628-76-6; 9,10-dihydro-9,10-ethanoanthracene-11,12-diol, 20678-93-7.

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[23] N. D. Field, *J. Am. Chem. Soc.*, **83**, 3504 (1961).