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The Reductive Acylation of Organic Disulfides with Aldehydes under Photochemical and Radical Conditions[1)]

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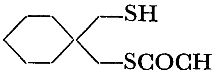
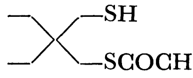
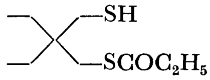
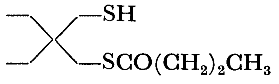
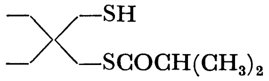
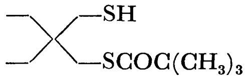
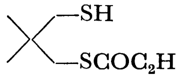
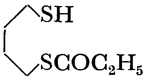
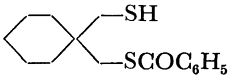
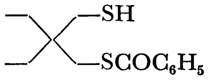
The irradiation of organic disulfides in aldehyde solvents resulted in the reductive fission of the S–S linkage, giving an equimolar mixture of the corresponding thiol and the thiol acylate in a good yield. The cyclic disulfides gave mono *S*-acylated dithiols. The reaction proceeded by means of the photo-initiated radical chain mechanism, and AIBN (azobisisobutyronitrile) effected the same reaction under thermal conditions.

In previous communications, a photochemical reductive acylation of organic disulfides with aldehydes has been described, with particular emphasis on the synthesis and the reaction of the 8-*S*-acylated derivative of coenzyme lipoic acid.[2–4)] The present report includes some of the experimental details. In addition, the reactions under radical conditions are described; these data, combined with those of other photochemical studies, suggest that the photo-reaction of organic disulfides with aldehydes proceeds by means of a photo-initiated radical chain mechanism.

Results

Photo-reactions. Reactions were carried out for 0.5—1×10^{-2} M (1 M=1 mol dm^{-3}) solutions of the disulfide in aldehyde at ≤5 °C under nitrogen or argon, using liquid-filtered ($\lambda<330$ nm removed) radiation from a 100-W immersion-type high-pressure mercury lamp. A radiation through a Pyrex filter ($\lambda<300$ nm removed) may be used with a slight decrease in the yields of the products. The concentration of the disulfides may be increased to 0.2—0.7 M (see the reaction under radical conditions), but the reaction is cleaner when the concentration is lower. The reaction could be followed by TLC or GLC. For 1,2-dithiolane compounds, the color (yellow) disappearance indicated the completion of the reaction. After 1—2 h of irradiation, followed by concentration under reduced pressure, the residue was purified by distillation or column chromatography on silica gel. The experimental procedure has been described in detail elsewhere.[3)] The colorless liquid obtained was identified by elemental and spectral analyses.

TABLE 1. PHOTO-REACTION OF SYMMETRICAL CYCLIC DISULFIDES WITH ALIPHATIC ALDEHYDES

Disulfide	Aldehyde	Irradiation time/min	Product	Yield[a)] %
1	CH_3CHO	90		**5** (71)
2	CH_3CHO	50		**6** (73)
2	C_2H_5CHO	90		**7** (68)
2	$CH_3(CH_2)_2CHO$	25		**8** (89)
2	$(CH_3)_2CHCHO$	90		**9** (85)
2	$(CH_3)_3CCHO$	60		**10** (71)
3	C_2H_5CHO	80		**11** (42[b)])
4	C_2H_5CHO	90		**12** (90)
1	C_6H_5CHO	75		**13** (59)
2	C_6H_5CHO	110		**14** (69)

a) Isolated yields. b) The lower yield is due to the polymerization of the starting disulfide before irradiation.

Table 2. Photo-reaction of symmetrical linear disulfides with propionaldehyde

Disulfide	Irradiation time/min	Product, yield/%	
		R′COSR	RSH
$(n\text{-}C_4H_9S)_2$	150	$C_2H_5COSC_4H_9$ (97)	C_4H_9SH (87)
$(C_6H_5S)_2$	150	$C_2H_5COSC_6H_5$ (54)	C_6H_5SH (58)
$(i\text{-}C_3H_7S)_2$	240	$C_2H_5COSC_3H_7$ (≤ 40)	C_3H_7SH (≤ 40)
$(t\text{-}C_4H_9S)_2$	360	a)	a)

a) No reaction; $(t\text{-}C_4H_9S)_2$ recovered.

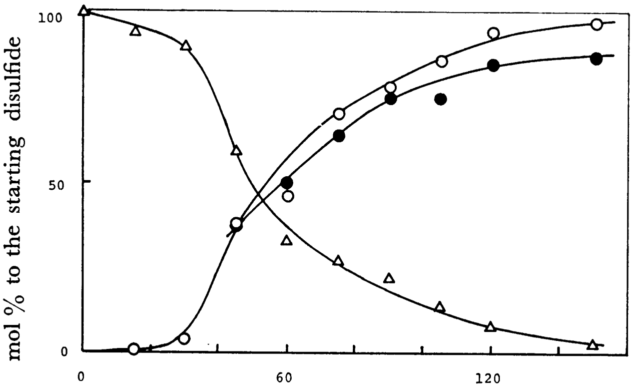


Fig. 1. Photo-reaction of dibutyl disulfide with propionaldehyde.
△, $(n\text{-}C_4H_9S)_2$; ●, $n\text{-}C_4H_9SH$; ○, $n\text{-}C_4H_9SCOC_2H_5$. GLC: column Apiezon L (2%); internal standard, $n\text{-}C_{12}H_{26}$; column temperature, 50→150 °C.

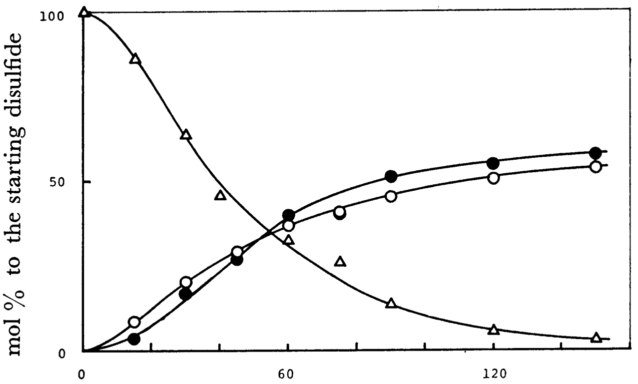
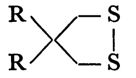


Fig. 2. Photo-reaction of diphenyl disulfide with propionaldehyde.
△, $(C_6H_5S)_2$; ●, C_6H_5SH; ○, $C_6H_5SCOC_2H_5$. GLC: column Apiezon L (2%); internal standard, $n\text{-}C_8H_{18}$; column temperature, 60→150 °C.

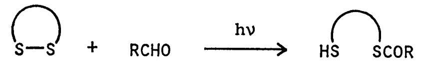
Reaction of Symmetrical Disulfides: The results with cyclic disulfides and aliphatic aldehydes are summarized in Table 1.



1, (R, R) = $(CH_2)_5$
2, R = C_2H_5
3, R = CH_3

4

All the aliphatic aldehydes reacted with similar ease, and the effect on the reactivity of branching on the α-carbon of the aldehyde is unimportant. The effect of the disulfide-ring size, whether five- or six-membered, is also trivial. The reactivities of cyclic disulfides and linear disulfides are similar insofar as the carbons bound to sulfur are not branched (see below). No by-products were detected by either TLC or GLC. Thus, the reaction may be formulated simply by Eq. 1:



(1)

The reactions with aromatic aldehydes were not straightforward. The isolation of the reaction products was not easy, since the benzoins were formed in a considerable amount, along with other unidentifiable, high-boiling by-products. In the reaction of *p*-anisaldehyde with **2**, the formation of the thioester was suggested by the results of spectral analysis, but the isolation was not successful due to the overwhelming side reactions. In view of the complexity of the reaction and the unavailability of the liquid aromatic aldehydes, the photo-reaction with disulfides would not have practical value. Pyruvic acid and formate esters did not react under the conditions of Table 1.

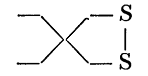
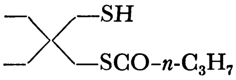
The reaction of symmetrical linear disulfides is shown in Table 2 and Eq. 2.

$$\text{RSSR} + \text{R'CHO} \xrightarrow{h\nu} \text{RSH} + \text{RSCOR'} \qquad (2)$$

The reaction of dibutyl disulfide with propionaldehyde was monitored by a direct GLC analysis of the reaction mixture, the results are shown in Fig. 1. The reaction of diphenyl disulfide with propionaldehyde is similarly illustrated in Fig. 2. The reaction in Fig. 1 was intentionally chosen from among several similar experiments, since it happened to show an "induction period." The induction period does not appear when the reactants are carefully purified. Aldehydes have to be distilled just before use. For dibutyl disulfide, the reaction approached a theoretical completion (Fig. 1), but for diphenyl disulfide the yields of the products leveled off at 50—60% of the theoretical yield, while the starting disulfide was almost 100% consumed. The fate of the unbalanced sulfur compound is not clear. The decrease in reactivity of aliphatic disulfides as the carbon bound to sulfur becomes branched is obvious in Table 2, suggesting the steric influence on the ease of the reaction.

Reaction of Unsymmetrical Disulfides: Unsymmetrical disulfides were allowed to react with aliphatic aldehyde to clarify the selectivity of *S*-acylation among different thiyl groups. The disulfides used were butyl isopropyl disulfide, *t*-butyl ethyl disulfide, and

Table 3. Radical reaction of symmetrical disulfide with butyraldehyde[a)]

Disulfide	mmol	Aldehyde ml	AIBN mmol	Reaction time/h	Product	yield/%[b)]
$(n\text{-}C_4H_9S)_2$	10	50	1.2	2	$n\text{-}C_4H_9SCO\text{-}n\text{-}C_3H_7$	79
$(n\text{-}C_4H_9S)_2$	2.0	10	0	32	c)	
$(n\text{-}C_4H_9S)_2$	25	10[d)]	0.3	13	c)	
$(i\text{-}C_3H_7S)_2$	6.7	10	1.5	4	$i\text{-}C_3H_7SCO\text{-}n\text{-}C_3H_7$	71
$(t\text{-}C_4H_9S)_2$	5.6	10	1.2	12	c)	
	3.1	10	0.6	2		80

a) Reaction temperature, 76 °C (refluxing). b) Isolated yield. c) No reaction, starting disulfide being recovered. d) Propionaldehyde was used. Reaction temperature, 48 °C.

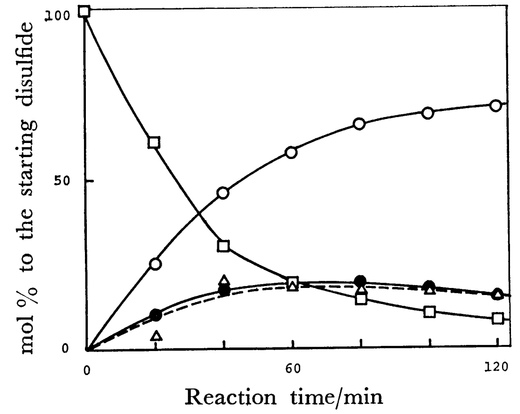


Fig. 3. Photo-reaction of butyl isopropyl disulfide with propionaldehyde.
□, $n\text{-}C_4H_9SS\text{-}i\text{-}C_3H_7$; ○, $C_2H_5COS\text{-}n\text{-}C_4H_9$; ●, $C_2H_5COS\text{-}i\text{-}C_3H_7$; △, $n\text{-}C_4H_9SH$; $i\text{-}C_3H_7SH$, not determined. GLC: column, Apiezon L (2%); internal standard, $n\text{-}C_{11}H_{24}$; column temperature, 40—150 °C.

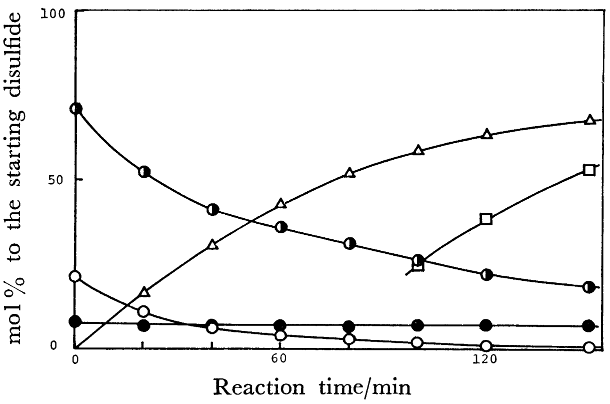


Fig. 4. Photo-reaction of *t*-butyl ethyl disulfide with acetaldehyde. The starting disulfide contained diethyl disulfide (21%) and di-*t*-butyl disulfide (8%).
◑, $t\text{-}C_4H_9SSC_2H_5$; ○, $(C_2H_5S)_2$; ●, $(t\text{-}C_4H_9S)_2$; △, $C_2H_5SCOCH_3$; □, $t\text{-}C_4H_9SH$; no formation of $t\text{-}C_4H_9SCOCH_3$. GLC: column, Apiezon L (2%); internal standard, $n\text{-}C_8H_{18}$; column temperature, 20→160 °C.

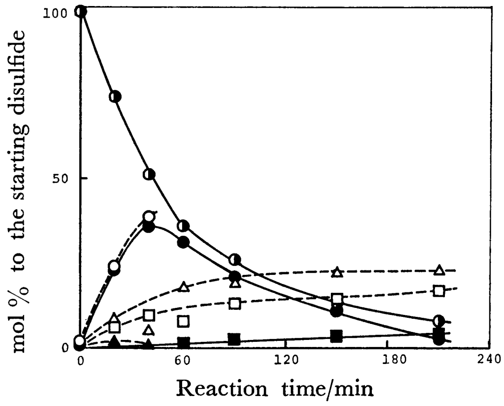


Fig. 5. Photo-reaction of butyl phenyl disulfide with propionaldehyde.
◑, $n\text{-}C_4H_9SSC_6H_5$; ●, $(C_6H_5S)_2$; ○, $(n\text{-}C_4H_9S)_2$; △, $n\text{-}C_4H_9SCOC_2H_5$; ▲, $C_6H_5SCOC_2H_5$; □, $n\text{-}C_4H_9SH$; ■, C_6H_5SH. GLC: column, Silicone SE 30 (10%); internal standard, $n\text{-}C_{14}H_{30}$; column temperature, 20→180 °C.

butyl phenyl disulfide. The progress of the reaction was monitored by means of GLC analysis of the reaction mixture (Figs. 3, 4, and 5). The reaction is formulated by Eq. 3;

$$RSSR' + R''CHO \xrightarrow{h\nu} RSH + R'SH + RSCOR'' + R'SCOR'' \qquad (3)$$

Butyl isopropyl disulfide gave *S*-*n*-butyl propionate and *S*-isopropyl propionate in a ratio of more than 7:2 in favor of the former at the completion of the reaction (Fig. 3), indicating that the sulfur bound to primary (butyl) carbon is more than three times as reactive as that bound to secondary (isopropyl) carbon. Even more pronounced is the reaction of *t*-butyl ethyl disulfide (Fig. 4). Only *S*-ethyl acetate was formed, no *S*-*t*-butyl acetate at all being detected. These results are in harmony with those in Table 2, where diisopropyl disulfide is less reactive than dibutyl disulfide, and where di-*t*-butyl disulfide is entirely unreactive. The reactivity difference between aliphatic and aromatic sulfur could not be assessed clearly, because the disproportionation of the unsymmetrical disulfide to symmetrical disulfides took place rapidly (Fig. 5). However, Fig. 5 indicates that the aliphatic sulfur (butylthio group) is more reactive toward the acyl group than the aromatic. The disproportionation did not occur without light, suggesting the introduction of radical species under photo-conditions.

As an unsymmetrical cyclic disulfide, 3-methyl-1,2-dithiane (**15**) was allowed to react with acetaldehyde;

it was found to give the dithiol monoacetate, **16**, in a 96% yield, where the primary thiol was selectively acetylated and the isomeric product could not be detected. The same reactivity has been observed with lipoic acid.[2,3] Thus, the selectivity of acylation among primary and secondary thiyl groups is much more strict in cyclic disulfides than in linear disulfides.

Reactions under Radical Conditions. The disulfides were dissolved in a 0.2—0.7 M concentration in an aldehyde solvent, followed by the addition of AIBN in a 10 mol % concentration of the disulfides. The atmosphere was then replaced with nitrogen, and the mixture was heated to initiate the radical reaction. The products were isolated and identified in a manner similar to that above. The results are summarized in Table 3. Some of the reactions were followed by GLC analysis; the results showed that the progress of the reaction was strikingly similar to those for the photo-reactions, including the appearance of the induction period and the disproportionation of unsymmetrical disulfides.

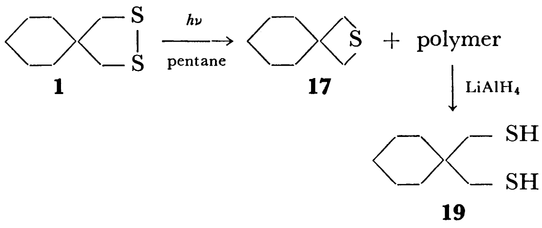
That the reaction proceeds by means of radical chain mechanism is obvious from the facts that it required only a catalytic amount of AIBN and that it did not take place in the absence of AIBN. Peroxides failed to initiate the reaction, and so the RSH–Fe(III) combination failed. Peroxides probably reacted with thiol or thiol acylate and were deactivated. At present, AIBN is the sole radical initiator effective in this reaction.

Discussion

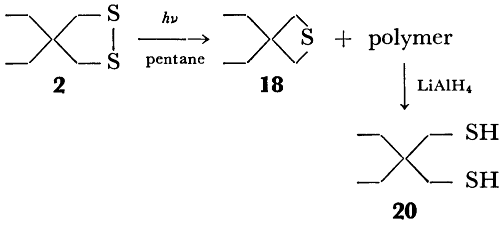
The resemblance between the photo- and the radical reactions suggests that the former is, in fact, a photo-induced radical reaction. The fact that the photo-reaction occurs with non-light-absorbing aliphatic linear disulfides as well indicates that the disulfide is not responsible for the primary photo-act; *i.e.*, it is not the disulfide molecule which is photo-activated and produces radicals. Aliphatic aldehydes have weak absorption maxima in the 290—300 nm region, and since the compounds are used as reaction solvents, the effective absorption extends up over 365 nm, where the major radiation from the high-pressure mercury lamp falls. A radical formation from aldehydes according to Eq. 4 is well documented in the literature.[5)]

$$\mathrm{RCHO} \longrightarrow \mathrm{R}\cdot + \cdot\mathrm{CHO} \qquad (4)$$

1,2-Dithiolanes have absorption maxima around 334 nm (ε, 150—200),[6,7)] and the possibility could not be excluded that these disulfides accepted the radiation to form radicals, thus initiating the reaction with aldehydes. The formation of the thiyl radical from the cyclic disulfides under photo-irradiation has been shown by Calvin *et al.*[8,9)] in their early works on 1,2-dithiolane as well as by other investigators.[10,11)] In this context, the photochemical behavior of **1** and **2** was studied. A 1×10^{-3} M solution of **1** or **2** in pentane was irradiated by means of a high-pressure mercury lamp in the usual manner for 100 min. The reaction was followed by GLC and UV spectroscopy (λ_{max}, 334 nm). The subsequent work-up of the mixture gave **17** (19% yield from **1**) and **18** (8% from **2**) along with the recovery of the starting disulfide (50%) and a polymeric material (Eqs. 5 and 6). The polymeric material gave two dithiol compounds, **19** and **20**, upon reduction with lithium aluminium hydride. However, an appreciable amount of the polymer yet remained unconverted to the dithiols, suggesting that the polymer chain was not composed of mere S–S linkages. Thus, the photo-activated 1,2-dithiolanes seem to perform a complicated series of radical reactions, including a desulfurization to thietanes. The formation of radicals under photo-irradiation was readily indicated by the polymerization of such added vinyl monomers as styrene, butyl vinyl ether, and acrylonitrile. To the authors' knowledge, a photo-desulfurization with ring contraction has not been documented in the literature, and it is quite possible that the unknown photo-products from lipoic acid reported by Brown *et al.*[11)] involved a similar structure.



(5)



(6)

It is also possible that the above-mentioned photo-desulfurization was a result of the particular reaction conditions, where good hydrogen donors to the thiyl radicals were not available. When 2-propanol instead of pentane was used as a solvent, two 1,3-dithiols, **19** and **20** (as determined by iodometry), were formed, and the yield of the thietanes, **17** and **18** was greatly reduced (<1%). It should be stressed, however, that the desulfurized products were formed even in a good hydrogen-donating solvent such as 2-propanol when the disulfide was photo-activated.

As has been noted earlier,[3)] the photo-reaction of 1,2-dithiolanes in aldehydes is less clean when the concentration of the disulfide is high. At a concentration below 1×10^{-2} M, the fraction of radiation absorbed by the sulfur compound is unimportant because of the overwhelming absorption by the aldehyde solvent. As the concentration increases, more of the light is absorbed by the sulfur compound, leading to the introduction of side reactions. Thus, the activation of 1,2-dithiolane is not a necessity for the reductive acylation to take place.

The reaction most probably involves the following sequence of events:

(initiation)

$$\text{initiator} \xrightarrow{\Delta} \text{In}\cdot$$

$$(\text{or RCHO} \xrightarrow{h\nu} \text{R}\cdot + \cdot\text{CHO})$$

$$\text{In}\cdot(\text{or R}\cdot) + \text{RCHO} \longrightarrow$$

$$\text{InH (or RH)} + \text{R}\dot{\text{C}}\text{=O} \qquad (7)$$

$$\text{In}\cdot(\text{or R}\cdot) + \text{R'SSR'} \longrightarrow$$

$$\text{In}-\text{SR' (or RSR')} + \text{R'S}\cdot \qquad (7')$$

(propagation)

$$\text{R}\dot{\text{C}}\text{=O} + \text{R'SSR'} \longrightarrow \text{R'S}\cdot + \text{R'SCOR} \qquad (8)$$

$$\text{R'S}\cdot + \text{RCHO} \longrightarrow \text{R'SH} + \text{R}\dot{\text{C}}\text{=O} \qquad (9)$$

A selectivity in acylation appears when the acyl radical attacks the disulfide on a sterically less hindered sulfur. An electronic factor is not responsible for the selectivity, since the electron density on sulfur would not be much different among primary, secondary, and tertiary disulfides in view of the small variation in the acid-dissociation constants of the corresponding thiols.[12] Moreover, an electronegative acyl radical should show a preferred reactivity for the electropositive tertiary thiyl sulfur if the electronic factor were indeed controlling.

Mechanistically related to the present reaction is the photochemical decarbonylation of aliphatic aldehydes at elevated temperatures. The reaction is strongly accelerated by the presence of a catalytic amount of either disulfides or thiols (Eq. 10).[13] An induction period has been reported for the catalysis of disulfides, but not for that of thiols. It is very probable that the reductive acylation of the disulfide first took place to afford the thiol and the thiol acylate, though the formation of the latter had not been studied. After most of the disulfides were consumed, the unimolecular decomposition of the acyl radical became predominant under high-temperature conditions (>140 °C), thus giving carbon monoxide and alkyl radical (decarbonylation, Eq. 11). The alkyl radical then abstracts hydrogen either from thiol or aldehyde to form an alkane molecule (RH) and a chain-propagating radical (either R'S· or R$\dot{\text{C}}$=O). The decarbonylation from the acyl radical is obviously not important at lower temperatures (76 °C, Table 3).

$$\text{RCHO} \xrightarrow[\text{R'SH or (R'S)}_2]{h\nu,\ >140\,^\circ\text{C}} \text{RH} + \text{CO} \qquad (10)$$

$$\text{R}\dot{\text{C}}\text{=O} \xrightarrow{>140\,^\circ\text{C}} \text{R}\cdot + \text{CO} \qquad (11)$$

Experimental

Materials. The cyclic disulfides, **1**,[14] **2**,[14] **3**,[14] **4**,[8] and **15**,[8] were prepared according to the reported procedures. Butyl isopropyl disulfide, butyl phenyl disulfide, and *t*-butyl ethyl disulfide were prepared by oxidizing the corresponding thiol mixtures.[15] Compound **2**, prepared according to the previously reported procedure,[14] showed a small absorption peak at 330 nm in addition to the normal absorption at 334 nm. The former absorption was eliminated by reduction with lithium aluminum hydride, followed by reoxidation with iodine. No differences in reactivity or other spectral characteristics (NMR and IR) were observed between the two methods of preparation. A very minute impurity seems to be responsible for the 330 nm absorption.

Photo-reactions. High-pressure mercury lamps, UVL-100HA (100 W output) and UVL-400HA (400 W) (Riko Kagaku Co.), fitted with Pyrex glass-made double jackets, were used as light sources. The sample solutions, 100—200 ml in volume, were internally irradiated by a liquid-filtered light ($\lambda \leq 330$ nm removed) under nitrogen or argon at ≤5 °C. The reaction mixture was analyzed by GLC, using appropriate straight-chain alkanes as internal standards (Figs. 1—5). The reaction product was isolated either by distillation or by column chromatography. The detailed experimental procedure has been described elsewhere.[3]

Radical Reactions. In 10—50 ml of freshly distilled aldehyde we dissolved an appropriate amount of the organic disulfide to give a 0.2—0.7 M solution. AIBN was then added in a 10 mol% concentration of the disulfide, and the mixture was heated under nitrogen or argon to reflex. The reaction was monitored by GLC. The work-up of the reaction mixture was similar to that used in the photo-reactions.

Reaction Products. The simple thiocarboxylates and thiols were identified by comparisons on GLC with authentic samples. The dithiol monocarboxylates were isolated and identified by the spectral method (IR, NMR, and MS) as well as by elemental analysis.

5: Isolated by distillation; 91—92 °C/1 mmHg (1 mmHg=133 Pa); IR (neat) 2580 (SH) and 1695 cm^{-1} (CO); NMR (CCl$_4$) δ=1.02 (1H, t, J=8.8 Hz, SH), 1.40 (10H, m, cyclic CH$_2$), 2.28 (3H, s, COCH$_3$), 2.42 (2H, d, $\mathrm{C\underline{H}_2SH}$), 3.01 (2H, s, CH$_2$SCO). Found: C, 54.88; H, 8.28%. Calcd for $\mathrm{C_{10}H_{18}OS_2}$: C, 55.00; H, 8.30%.

6: Isolated by distillation; 95 °C/2.5 mmHg; IR (neat) 2580 (SH) and 1695 cm^{-1} (CO); NMR (CCl$_4$) δ=0.78 (6H, t, J=7.1 Hz, $\mathrm{C\underline{H}_3CH_2}$), 1.07 (1H, t, J=8.8 Hz, SH), 1.36 (4H, q, $\mathrm{CH_3C\underline{H}_2}$), 2.29 (3H, s, COCH$_3$), 2.37 (2H, d, $\mathrm{C\underline{H}_2SH}$), 2.92 (2H, s, CH$_2$SCO). Found: C, 52.36; H, 8.80%. Calcd for $\mathrm{C_9H_{18}OS_2}$: C, 52.38; H, 8.79%.

7: Isolated by chromatography (silicagel, benzene); colorless liquid; IR (neat) 2580 (SH) and 1695 cm^{-1} (CO); NMR (CCl$_4$) δ=0.79 (6H, t, J=7.0 Hz, $\mathrm{\underline{CH_3}CH_2C\lessdot}$), 1.10 (1H, t, J=8.5 Hz, SH), 1.17 (3H, t, J=7.5 Hz, $\mathrm{\underline{CH_3}CH_2CO}$), 1.36 (4H, q, $\mathrm{CH_3\underline{CH_2}C\lessdot}$), 2.38 (2H, d, $\mathrm{\underline{CH_2}SH}$), 2.55 (2H, q, $\mathrm{CH_3\underline{CH_2}CO}$), 2.93 (2H, s, CH$_2$SCO); MS (*m/e*), 220 (M$^+$), 163 (M$^+$−C$_2H_5$CO), 57 (C$_2H_5$CO). Found: C, 54.78; H, 9.20%. Calcd for $\mathrm{C_{10}H_{20}OS_2}$: C, 54.50; H, 9.15%.

8: Isolated by chromatography (silica gel, hexane containing 1% ether); colorless liquid; IR (neat) 2580 (SH) and 1695 cm^{-1} (CO); NMR (CCl$_4$) δ=0.79 (6H, t, J=7.0 Hz, $\mathrm{C\underline{H}_3CH_2C\lessdot}$), 0.95 (3H, t, J=7.0 Hz, $\mathrm{C\underline{H}_3CH_2}$-$\mathrm{CH_2CO}$), 1.07 (1H, t, J=8.6 Hz, SH), 1.36 (4H, q, $\mathrm{CH_3\underline{CH_2}C\lessdot}$), 1.58 (2H, sex, J=7.0, 7.6, $\mathrm{CH_3\underline{CH_2}CH_2CO}$), 2.38 (2H, d, $\mathrm{\underline{CH_2}SH}$), 2.49 (2H, t, $\mathrm{CH_3CH_2\underline{CH_2}CO}$), 2.92 (2H, s, $\mathrm{\underline{CH_2}SCO}$). Found: C, 57.03; H, 9.45%. Calcd for $\mathrm{C_{11}H_{22}OS_2}$: C, 56.36; H, 9.46%.

9: Isolated by chromatography (silica gel, hexane); colorless liquid; IR (neat) 2580 (SH) and 1695 cm^{-1} CO); NMR (CCl$_4$) δ=0.78 (6H, t, $\mathrm{\underline{CH_3}CH_2C\lessdot}$), 1.03 (1H, t, J=7.0 Hz, SH), 1.17 (6H, d, J=6.8 Hz, $\mathrm{CH(\underline{CH_3})_2}$), 1.35 (4H, q, $\mathrm{CH_3\underline{CH_2}C\lessdot}$), 2.37 (2H, d, $\mathrm{\underline{CH_2}SH}$), 2.72 (1H, sep, $\mathrm{\underline{CH}(CH_3)_2}$), 2.89 (2H, s, CH$_2$SCO). Found: C, 56.27; H, 9.42%. Calcd for $\mathrm{C_{11}H_{22}OS_2}$: C, 56.36; H, 9.46%.

10: Isolated by chromatography (silica gel, hexane containing 5% ether); colorless liquid; IR (neat) 2580 (SH) and 1695 cm^{-1} (CO); NMR (CCl$_4$) δ=0.79 (6H, t, J=7.0 Hz, $\mathrm{\underline{CH_3}CH_2C\lessdot}$), 1.03 (1H, t, J=8.5 Hz, SH), 1.21

(9H, s, $C(CH_3)_3$), 1.36 (4H, q, $CH_3\underline{CH_2}C\langle$), 2.37 (2H, d, $\underline{CH_2}SH$), 2.87 (2H, s, CH_2SCO). Found: C, 58.22; H, 9.75%. Calcd for $C_{12}H_{24}OS_2$: C, 58.01; H, 9.73%.

13: Isolated by chromatography (silica gel, hexane containing 5% ether); colorless liquid; IR (neat) 3060 (aromatic CH), 2580 (SH), and 1665 cm^{-1} (CO); NMR (CCl_4) $\delta=$ 1.09 (1H, t, $J=8.5$ Hz, SH), 1.46 (10H, m, cyclic CH_2), 2.50 (2H, d, $\underline{CH_2}SH$), 3.22 (2H, s, CH_2SCO), 7.2—7.5 (3H, m, aromatic *m*- and *p*-H), 7.8—8.0 (2H, m, aromatic *o*-H). Found: C, 64.82; H, 7.21%. Calcd for $C_{15}H_{20}OS_2$: C, 64.24; H, 7.18%. a contamination from by-products.

14: Isolated by chromatography (silica gel, hexane containing 2% ether); colorless liquid; IR (neat) 3060 (aromatic CH), 2580 (SH), and 1665 cm^{-1} (CO); NMR (CCl_4) $\delta=$ 0.81 (6H, t, $J=7.0$ Hz, $\underline{CH_3}CH_2$), 1.10 (1H, t, $J=8.5$ Hz, SH), 1.39 (4H, q, $CH_3\underline{CH_2}$), 2.41 (2H, d, $\underline{CH_2}SH$), 3.10 (2H, s, CH_2SCO), 7.2—7.5 (3H, m, aromatic *m*- and *p*-H), 7.8—8.0 (2H, m, aromatic *o*-H); MS (*m*/*e*), 268 (M^+), 163 ($M^+-C_6H_5CO$), 105 (C_6H_5CO). Found: C, 63.87; H, 7.34%. Calcd for $C_{14}H_{20}OS_2$: C, 62.64; H, 7.51%. a contamination from by-products.

16: Isolated by distillation, 95 °C/3 mmHg; IR (neat) 2580 (SH) and 1695 cm^{-1} (CO); NMR (CCl_4) $\delta=1.32$ (3H, d, $J=6.5$ Hz, $\underline{CH_3}CH(SH)CH_2$), 1.37 (1H, d, $J=6.3$ Hz, SH), 1.5—1.9 (4H, m, $CH_3CH(SH)\underline{CH_2}\underline{CH_2}CH_2S$), 2.28 (3H, s, CH_3CO), 2.6—3.0 (3H, m, $CH_3\underline{CH}(SH)CH_2$-$CH_2\underline{CH_2}S$). Found: C, 47.24; H, 7.98%. Calcd for $C_7H_{14}OS_2$: C, 47.15; H, 7.91%.

17: Isolated by distillation, 80 °C/1.3 mmHg; IR (neat) 2925, 2850 (CH), and 1452 cm^{-1} (CH); UV (pentane) λ_{max} 266 nm, ε 70; NMR (CCl_4) $\delta=1.50$ (10H, m, 6-membered cyclic CH_2), 2.81 (4H, s, CH_2S). Found: C, 67.73; H, 9.93%. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92%.

18: Isolated by distillation, 53 °C/10 mmHg; IR (neat) 2925, 2850 (CH), and 1450 cm^{-1} (CH); NMR (CCl_4) $\delta=$ 0.83 (6H, t, $J=7.5$ Hz, CH_3), 1.63 (4H, q, $CH_3\underline{CH_2}$), 2.79 (4H, s, CH_2S). Found: C, 65.45; H, 11.07%. Calcd for $C_7H_{14}S$: C, 64.55; H, 10.83%.

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