ml tall beaker. The solution was electrolyzed at 30° using 3-cm² platinum foils without separation of an anodic compartment from a cathodic. One equivalent of constant current (200 mA) was applied while the terminal voltage was 6–10 V. An electrolysis in which an anodic compartment was separated from a cathodic was done using a cell described previously[1].

**Product Analysis and Assignment.**—The reaction mixture was combined with 0.100 g ($5 \times 10^{-4}$ mol) of benzyl phenyl sulfide as an internal standard for vpc and evaporated by suction. The resulting oily materials were extracted with chloroform. The extract was washed with water, dried ($Na_2SO_4$), and concentrated. The residual oil was dissolved in 50 ml of ether and stirred for 30 min. Ether was removed by decantation. The ether-insoluble product was washed twice again with each 50 ml of ether and dried under vacuum, giving 0.41 g of a slightly brown colored amorphous solid. The solid, diphenyl *p*-(phenylthio)phenyl sulfonium perchlorate (**3**), showed a positive Beilstein test: ir (Nujol) 1573 (m, SPh), 1080–1100 (s, broad, sulfonium), 815 (w), 745 (s), 683 cm$^{-1}$ (m); nmr ($CDCl_3$) $\tau$ 2.30 (s, 10), 2.53 (s, 5), 2.41 (d, 2, $J$ = 9 Hz), and 2.74 (d, 2, $J$ = 9 Hz).

The ether layer was dried ($Na_2SO_4$) and concentrated, giving an oily material. The oil was then subjected to vpc analysis (SE-30, 1-m column, 170°) showing the existence of products, **1**, **4**, and **5**. Yields of sulfoxide **4** and sulfides **1** and **5** were obtained by calculating each peak area as compared with that of the internal standard.

To the sulfonium salt **3** (0.30 g) dissolved in 10 ml of acetic acid, 0.2 g of 30% aqueous hydrogen peroxide was added dropwise. The mixture was stirred at room temperature for 1 hr and at 50° for 1 hr and evacuated by suction to remove acetic acid. The resulting oil was dissolved in 50 ml of chloroform. The extract was washed with 5% aqueous sodium hydroxide and twice with water, dried ($Na_2SO_4$), and concentrated. After the resulting product was washed twice with each 50 ml of ether, the ether-insoluble product was dried and solidified under vacuum, giving diphenyl *p*-(phenylsulfonyl)phenyl sulfonium perchlorate (**6**) as an almost colorless amorphous solid (0.28 g): ir (Nujol) 1590 (w), 1330 and 1160 (s, $-SO_2-$), 1090–1100 (vs, sulfonium), 830 (w), 750 cm$^{-1}$ (vs); nmr ($CDCl_3$) $\tau$ 2.28 (s, 10, $Ph_2S^+-$), 1.75–2.55 (m, 9).

*Anal.* Calcd for $C_{24}H_{19}O_6S_2Cl$: C, 57.30; H, 3.81. Found: C, 56.94; H, 3.95.

**Reaction of 6 with Sodium Ethoxide.**—Sulfonium salt **6** (0.3 g, $6 \times 10^{-4}$ mol) was dissolved in 5 ml of tetrahydrofuran and 2 ml of ethanol containing 50 mg of sodium metal. The reaction mixture was stirred at room temperature for 1 day and at 70° for 20 min and then combined with 50 mg ($2.5 \times 10^{-4}$ mol) of benzyl phenyl sulfide as an internal standard for vpc analysis and suctioned out to remove solvent. The resulting products were washed with water and extracted with chloroform. The extract was concentrated to give oily products, which were analyzed by vpc (SE-30, 80-cm column, at 120–190°, scan rate 4°/min) giving **1** (50%), **7** (62%), **8** (2%), and **9** (2%). The product mixture was kept at room temperature overnight to crystallize in part. The crude crystals were collected and recrystallized from *n*-hexane–benzene to give colorless crystals whose ir spectrum and melting point are consistent with those of the authentic sample **7**.

**Reaction of 6 with Thiophenol.**—Sulfonium salt **6** (0.32 g) was stirred with 1 g of thiophenol and 1.5 g of pyridine at room temperature for 2 days. Products were analyzed by vpc as similarly as described above giving **1** (62%) and **8** (68%). Crystals obtained from the product mixture were recrystallized from *n*-hexane–benzene and were identified by comparing with authentic sample **8**.

**Registry No.** —**1**, 139-66-2; **3**, 32958-90-0; **6**, 32958-91-1; **7**, 14193-13-6; **8**, 32846-68-7.

# The Alkaline Decomposition of Organic Disulfides. VI. Further Examples of Elimination Reactions (1,2-Dithiolanecarboxylic Acids) and of Nucleophilic Substitution

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*Received July 20, 1971*

In aqueous, alkaline solution 1,2-dithiolane-4-carboxylic acid (**1**) appears to undergo a $\beta$ elimination, the primary product of which decomposes to yield $\alpha$-(mercaptomethyl)acrylic acid, which has been isolated as its *S*-ethyl derivative, and hydrogen sulfide. The corresponding polymeric disulfide, $(-SCH_2CH(COOH)CH_2S-)_n$, depolymerizes to **1** instantly in alkaline solution and at measurable rates at pH values as low as 4.2. The profile of pH *vs.* rate suggests that the carboxylate ion participates in this depolymerization, a conclusion which is confirmed by the stability of the methyl ester of the polymer. In aqueous, alkaline solution both *rac*- and *meso*-1,2-dithiolane-3,5-dicarboxylic acids decompose at the same rate to yield 2-mercapto-2-pentenedioic acid by a process which is probably an $\alpha$ elimination initially. Dithiobis(methylcyclopropane-1-carboxylic acid) decomposes very slowly by direct nucleophilic attack of hydroxide ion on disulfide sulfur.

It has been amply demonstrated experimentally that the alkaline decomposition of organic disulfides takes place by one of three alternative pathways, as determined by secondary features of their molecular structures:[2] $\alpha$ elimination,[3,4] $\beta$ elimination,[5] or direct nucleophilic displacement of sulfur from sulfur by hydroxide ion.[5-7] Several more disulfides have now been found to decompose *via* the pathways predictable from their structures. However, those of this group which undergo an initial elimination gave unstable intermediates which decompose further to unsaturated compounds which were not anticipated.

Jansen[8] isolated from asparagus a crude disulfide which he could not crystallize but which he successfully reduced to 2-mercaptomethyl-3-mercaptopropionic acid. Schotte and Ström[9] found that the 1,2-dithiolane-4-carboxylic acid (**1**) which they obtained by the aerial oxidation of the dithiol was appreciably contaminated by the isomeric polymeric disulfide **2**. Pure **1** was obtained by recrystallization from benzene, in which **2** is insoluble. Schotte and Ström conjectured that **1** exists in the asparagus plant and that some of it had undergone polymerization during Jansen's recovery procedure. Analogously, we recently suggested that "...

(1) Postdoctoral Research Associate, 1969–1971.
(2) J. P. Danehy, *Int. J. Sulfur Chem. B*, **6**, 103 (1971).
(3) J. P. Danehy and J. A. Kreuz, *J. Amer. Chem. Soc.*, **83**, 1109 (1961).
(4) J. P. Danehy and V. J. Elia, *J. Org. Chem.*, **36**, 1394 (1971).
(5) J. P. Danehy and W. E. Hunter, *ibid.*, **32**, 2047 (1967).
(6) J. P. Danehy and K. N. Parameswaran, *ibid.*, **33**, 568 (1968).
(7) J. P. Danehy, C. J. Lavelle, and V. J. Elia, *ibid.*, **36**, 1003 (1971).
(8) E. F. Jansen, *J. Biol. Chem.*, **176**, 657 (1948).
(9) L. Schotte and H. Ström, *Acta Chem. Scand.*, **10**, 687 (1956).

all of the dihtiol passes through the dithiolane form upon oxidation by iodine."[10] As will be shown a little later, a quite different view of the relation between **1** and **2** has emerged from the present study.

The quantitative data obtained for the decomposition of **1** in aqueous, alkaline solutions are presented in Table I. Several generalizations can be drawn from them. The initial rates of decomposition are, approximately, directly proportional to the concentration of sodium hydroxide. As with so many other disulfides, there appear to be asymptotically approached levels of decomposition corresponding to each concentration of base: ~15, 37, and 45% at 0.2, 0.5, and 1.0 *N* NaOH, respectively. The ratio of $H_2S$ to RSH increases both with increasing percentage decomposition and with increasing time to an observed high value of ~0.5. When the initial concentration of disulfide is increased ~10-fold, the ratio of $H_2S$ to RSH does not increase further; if anything, it is somewhat lower than might have been expected. The percentage of sulfur accounted for as RSH and $H_2S$ formed, and RSSR remaining, slowly and steadily decreases with time.

TABLE I

DECOMPOSITION OF 1,2-DITHIOLANE-4-CARBOXYLIC ACID (1) IN AQUEOUS ALKALINE SOLUTIONS AT 35.2° [a]

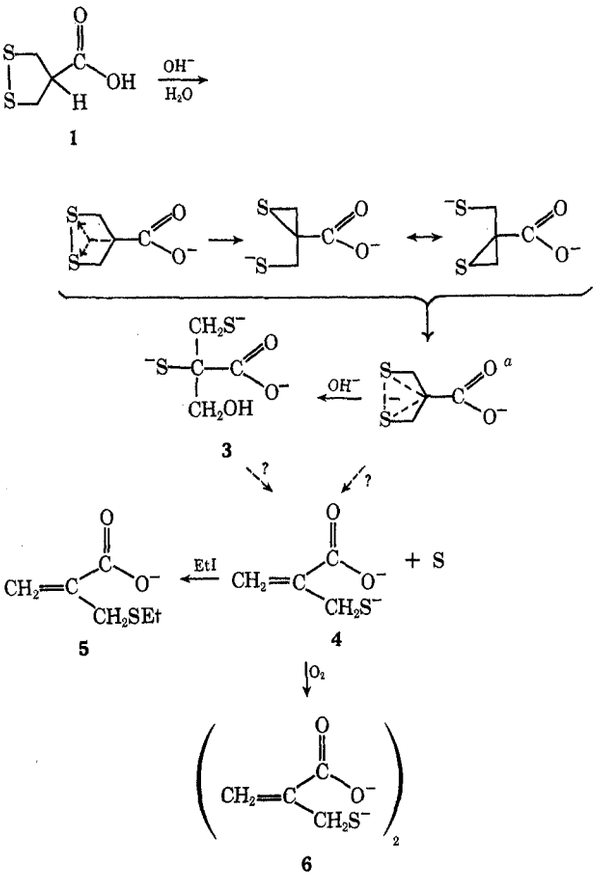
| Time, hr | RSSR | RSH | $H_2S$ | % dec | % S accounted for |
|---|---|---|---|---|---|
| 0 | 9.36[b] | | | | |
| 0.33 | 9.14 | 0.44[b] | 0.00[b] | 2.4 | 100.0 |
| 0.67 | 9.01 | 0.77 | 0.00 | 3.7 | 100.2 |
| 1.0 | 8.56 | 0.98 | 0.00 | 8.5 | 96.8 |
| 2.0 | 8.42 | 1.15 | 0.00 | 10.1 | 96.3 |
| 7.0 | 8.24 | 1.26 | 0.14 | 12.1 | 95.5 |
| 23.0 | 8.03 | 1.45 | 0.14 | 14.2 | 94.4 |
| 0 | 9.49[c] | | | | |
| 0.33 | 8.99 | 0.99[c] | 0.00[c] | 5.3 | 100.0 |
| 0.67 | 8.78 | 1.41 | 0.00 | 7.4 | 100.0 |
| 1.0 | 8.54 | 1.79 | 0.31 | 9.0 | 100.9 |
| 2.0 | 8.36 | 2.03 | 0.36 | 11.8 | 100.6 |
| 23.0 | 7.59 | 2.56 | 0.52 | 20.0 | 96.3 |
| 168.0 | 5.97 | 3.36 | 1.82 | 37.0 | 90.4 |
| 0 | 10.50[d] | | | | |
| 0.33 | 9.09 | 2.82[d] | 0.00[d] | 13.5 | 100.0 |
| 0.67 | 8.52 | 3.97 | 0.00 | 18.8 | 100.0 |
| 1.0 | 8.38 | 4.25 | 0.32 | 20.3 | 101.3 |
| 2.0 | 7.59 | 4.85 | 0.69 | 27.8 | 98.7 |
| 6.0 | 7.36 | 4.53 | 0.70 | 29.8 | 95.0 |
| 8.5 | 6.55 | 4.65 | 0.72 | 37.6 | 88.0 |
| 24.0 | 6.03 | 5.45 | 1.63 | 42.6 | 91.2 |
| 52.0 | 5.90 | 5.72 | 2.32 | 43.8 | 89.8 |
| 0 | 97.5[e] | | | | |
| 0.33 | 78.2 | 26.2[e] | 0.00[e] | 19.8 | 93.7 |
| 0.67 | 69.1 | 39.3 | 3.70 | 29.2 | 93.5 |
| 1.0 | 68.7 | 40.1 | 4.5 | 29.6 | 93.4 |
| 2.0 | 64.3 | 46.5 | 7.2 | 34.0 | 93.6 |
| 5.0 | 60.8 | 37.7 | 12.0 | 37.7 | 88.0 |
| 10.0 | 59.6 | 40.1 | 14.8 | 38.9 | 89.3 |

[a] The methods by which the data have been obtained were fully described.[3] [b] $M \times 10^4$ in 0.2018 *N* NaOH. [c] $M \times 10^4$ in 0.508 *N* NaOH. [d] $M \times 10^4$ in 1.010 *N* NaOH. [e] $M \times 10^4$ in 1.102 *N* NaOH.

(10) J. P. Danehy, C. P. Egan, and J. Switalski, *J. Org. Chem.*, **36**, 2530 (1971).

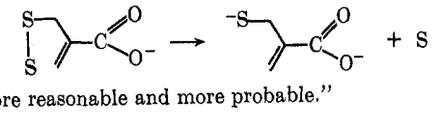
Preparative experiments, designed to isolate the thiol formed as its *S*-ethyl derivative, yielded substantial amounts of a product, mp 49–51°, whose elemental analysis and nmr spectrum are in agreement with the structure of 2-(ethylthiomethyl)acrylic acid (**5**). Somewhat smaller amounts were obtained of a product, mp 167–173°, whose nmr spectrum and the fact that it gives a positive test with Folin's reagent[3] after reduction with zinc amalgam in aqueous hydrochloric acid are consistent with the structure for the disulfide **6** corrresponding to 2-(mercaptomethyl)acrylic acid (**4**). The mechanism presented in Scheme I accounts for, or is at least consistent with, all of these facts. The delayed appearance of the hydrogen sulfide, particularly at higher concentrations of alkali at which the initial reaction is more rapid, suggests that hydrogen sulfide arises from a secondary decomposition. The gradually decreasing sulfur balance corresponds to the stoichiometric requirement that one-third of the inorganic sulfur formed should be sulfite, which we have not determined.

SCHEME I



$$3S + 4OH^- \longrightarrow SO_3^{2-} + 2SH^- + H_2O$$

[a] A referee has suggested that



is "... more reasonable and more probable."

What we have suggested in Scheme I is a $\beta$ elimination, formally similar to that invoked in the case of the decomposition of 3,3′-dithiodipropionic acid[5] but with several specific differences. First, the "episulfide" here

is actually a resonance-stabilized anion and can have only a partial episulfide character. Second, the hydrogen sulfide does not arise as the indirect result of a thiol–disulfide exchange reaction, as it appears to have done in the earlier case, for the relative amount of the hydrogen sulfide does not increase upon increasing the initial concentration of disulfide. Third, the eliminated moiety here remains part of the same molecule, as it did in the case of the dithiane derivatives recently reported.[4] Finally, the most striking difference is that here the first product of elimination, either the resonance-stabilized anion or **3**, undergoes a second elimination to form **4** and inorganic sulfur.

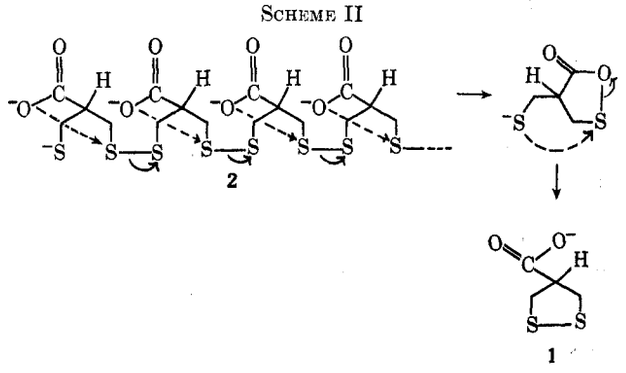
The polymeric disulfide **2** was readily prepared by heating the fused monomer **1** (mp 77°) at 130–140° for a few minutes. Traces of monomer were removed by extraction with benzene.

The results of several quantitative experiments on the alkaline decomposition of **2** matched the corresponding results for the alkaline decomposition of **1** within the range of experimental variance. This apparent identity was completely elucidated on the basis of uv absorption measurements.

Schotte[11] reported the uv absorption spectra of **1** and of its sodium salt in water, both of which have a $\lambda_{max}$ at 330 nm and a $\lambda_{min}$ at 280 nm. We have now found that **2** begins to absorb weakly at ~425 nm, has less than half the absorbance of **1** at the latter's maximum, but absorbs very strongly below 300 nm. Therefore, the maximum at 330 nm is a sensitive quantitative measure of the formation of **1** at the expense of **2**.

When **2** was dissolved at room temperature in 0.20 *N* NaOH, and in aqueous buffer solutions at pH 12.0, 10.7, 9.2, and 7.3, the results were the same in each case: immediate and quantitative transformation of **2** into **1**. At pH 6.40 and 5.75 the depolymerization was ~80% completed in 2 and 15 min, respectively. In 1:1 ethanol–water (v/v), self pH of 4.22, **2** was ~25, 50, and 80% depolymerized in 2, 7, and 14 days, respectively. The range of the strong dependence of the rate of decomposition on pH suggests neighboring group participation by the carboxylate anion.[12] Reference to molecular models shows that the mechanism of Scheme II is sterically very favored. The plausi-

SCHEME II



bility of this view is increased by the fact that the methyl ester of **2** in aqueous *p*-dioxane buffer at pH 9.20 shows no sign of depolymerization, even after 24 hr.

These phenomena are not without precedent. Thomas and Reed[15] have studied the linear polymeric disulfide that is related to α-lipoic acid (1,2-dithiolane-3-valeric acid) in the same way that **2** is related to **1**. They have observed both thermal polymerization of the monomer and depolymerization of the polymer in aqueous solution, but the latter ". . . did not proceed to a measurable extent in the absence of alkali . . ." so that the much more remote carboxylate anion is not likely to be involved.

Although it is of lesser interest, it may be noted that alkaline solutions of **1** undergo changes in their uv spectra at rates which depend on the concentration of base. The absorption at 280 nm increases until it no longer represents a minimum and the original $\lambda_{max}$ at 330 nm is completely engulfed in the intense continuous absorption below 350 nm. These changes, of course, reflect the reactions reported quantitatively in Table I.

Racemic 1,2-dithiolane-3,5-dicarboxylic acid (**7**) was synthesized by Schotte,[16] who subsequently determined its uv and ir spectra[17,18] and resolved its enantiomorphs.[18] The crystalline structure of **7** was determined by Foss and Reistad.[19]

*A priori* one might expect **7** to undergo an α elimination in alkaline solution, initiated by the abstraction of a proton from one of the two equivalent carbons bonded to both sulfur and carboxylate anion. The subsequent course might correspond to that undergone by the acyclic analog, 2,2′-dithiodipropionic acid,[3] or it might resemble that of the 1,2-dithiane-3,6-dicarboxylic acids.[4] *I.e.*, the initially formed carbanion might isomerize to the thioketone **8**, which would hydrolyze to a ketone and hydrosulfide, or the hemidithioketal **9** could stabilize the molecule against loss of inorganic sulfur (Scheme III).

The quantitative data obtained for the decomposition of **7** in aqueous alkaline solutions are presented in Table II. The eventual attainment of a ~1:1 value for the ratio of hydrogen sulfide to thiol and the high values for accounting of sulfur support the α elimination of Scheme III. They also indicate that **9**, if formed at all, has only a transitory existence, as might have been predicted from its highly strained four-membered ring. The possibility of calculating reasonably satisfactory pseudo-first-order rate constants for these solutions in which alkali is in large excess suggests that proton abstraction is the rate-controlling factor and that collapse of the carbanion to form thiol (either **8** or **9** or both) is relatively rapid. The sensitivity of **7** to alkali more nearly approximates than of the *rac*-1,2-dithiane-3,6-dicarboxylic acid[4] than it does that of the much more sensitive acyclic analog.[3] One might have expected the highly strained ring (27° dihedral angle for the sulfur–sulfur bond in **7**[19] *vs.* ~90° in acyclic disulfides) to potentiate alkaline cleavage, but this is not true.

Yet **12** is not the only final product if, indeed, it is one at all. A preparative experiment, including alkyla-

(11) L. Schotte, *Ark. Kemi*, **9**, 441 (1956).
(12) An exactly analogous five-membered cyclic intermediate, a sulfenic carboxylic anhydride, has recently been invoked twice.[13,14]
(13) J. P. Danehy and M. Y. Oester, *J. Org. Chem.*, **32**, 1491 (1967).
(14) L. Field, P. M. Giles, and D. L. Tuleen, *ibid.*, **36**, 623 (1971).
(15) R. C. Thomas and L. J. Reed, *J. Amer. Chem. Soc.*, **78**, 6148 (1956).
(16) L. Schotte, *Acta Chem. Scand.*, **8**, 130 (1954).
(17) L. Schotte, *Ark. Kemi*, **8**, 579 (1956).
(18) L. Schotte, *ibid.*, **9**, 429 (1956).
(19) O. Foss and T. Reistad, *Acta Chem. Scand.*, **11**, 1427 (1957).

SCHEME III

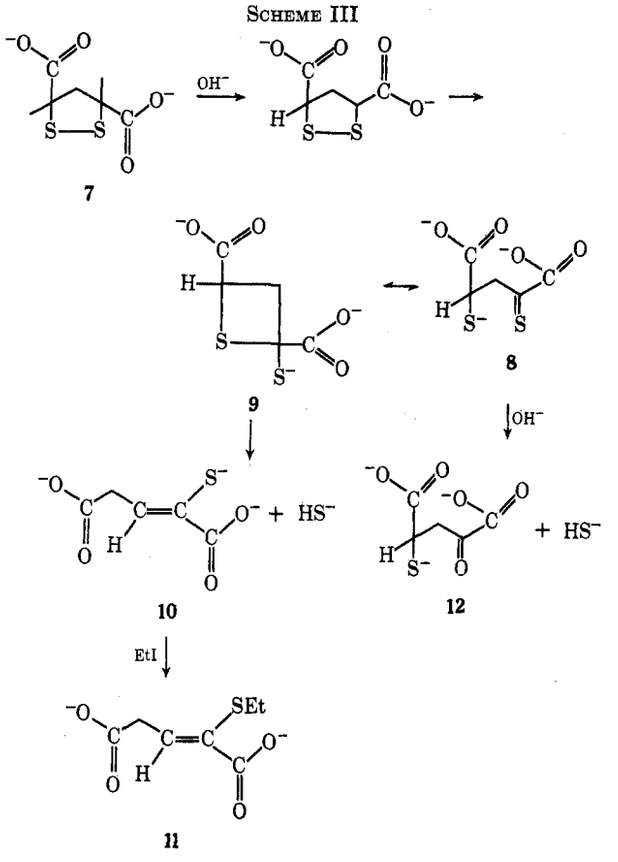


TABLE II

DECOMPOSITION OF *rac*-1,2-DITHIOLANE-3,5-DICARBOXYLIC ACID (7) IN AQUEOUS ALKALINE SOLUTIONS AT 35.2° [a]

| Time, hr | RSSR | RSH | $H_2S$ | % dec | % S accounted for | $k \times 10^6$, $sec^{-1}$ |
|---|---|---|---|---|---|---|
| 0 | 8.51[b] | | | | | |
| 3.0 | 8.02 | 0.64[b] | 0.32[b] | 5.7 | 99.9 | 5.48 |
| 6.0 | 7.30 | 1.02 | 0.72 | 14.2 | 96.3 | 7.09 |
| 10.0 | 6.62 | 1.32 | 1.24 | 22.2 | 93.0 | 6.97 |
| 24.0 | 5.24 | 2.70 | 3.09 | 38.3 | 95.8 | 5.62 |
| 0 | 7.66[b] | | | | | |
| 3 | 7.16 | 0.53[b] | 0.25[b] | 6.6 | 98.5 | 6.25 |
| 6 | 6.54 | 0.94 | 0.52 | 14.7 | 95.1 | 7.32 |
| 10.0 | 5.85 | 1.22 | 1.10 | 23.6 | 91.4 | 7.48 |
| 24.0 | 4.90 | 2.38 | 2.93 | 36.2 | 98.7 | 5.17 |
| 0 | 8.29[b] | | | | | |
| 3.0 | 7.84 | 0.80[b] | 0.24[b] | 5.4 | 100.8 | 5.19 |
| 6.0 | 7.25 | 1.00 | 0.50 | 12.5 | 96.7 | 6.23 |
| 24.0 | 5.08 | 2.76 | 2.87 | 38.6 | 95.4 | 5.68 |
| 0 | 10.32[c] | | | | | |
| 1.0 | 9.78 | 0.80[c] | 0.16[c] | 5.3 | 99.5 | 14.9 |
| 5.0 | 7.22 | 2.47 | 1.44 | 30.2 | 88.9 | 19.9 |
| 7.0 | 6.34 | 2.94 | 2.45 | 38.6 | 87.7 | 19.4 |
| 10.0 | 5.12 | 3.29 | 3.07 | 50.5 | 80.5 | 19.5 |
| 24.0 | 2.89 | 5.92 | 4.89 | 72.0 | 80.5 | 14.8 |

[a] See footnote *a* of Table I. [b] $M \times 10^4$ in 0.5190 *N* NaOH; average $k = 6.2 \times 10^{-6}$ $sec^{-1}$. [c] $M \times 10^4$ in 0.7785 *N* NaOH; average $k = 18. \times 10^{-6}$ $sec^{-1}$.

tion with ethyl iodide, gave a 30% yield of **11**, the structure for which is in agreement with elemental analysis, mass spectrum, nmr, and the fact that it slowly reacts with Folin's reagent,[3] characteristic of vinyl alkyl sulfides.

The quantitative data obtained for the decomposition of *meso*-1,2-dithiolane-3,5-dicarboxylic acid (**13**)[20] in aqueous alkaline solutions are presented in Table III.

TABLE III

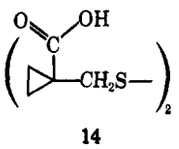
DECOMPOSITION OF *meso*-1,2-DITHIOLANE-3,5-DICARBOXYLIC ACID (13) IN AQUEOUS ALKALINE SOLUTIONS AT 35.2° [a]

| Time, hr | RSSR | RSH | $H_2S$ | % dec | % S accounted for | $k \times 10^6$ $sec^{-1}$ |
|---|---|---|---|---|---|---|
| 0 | 7.97[b] | | | | | |
| 1.5 | 7.73 | 0.16[b] | 0.04[b] | 3.2 | 98.3 | 5.68 |
| 3.0 | 7.42 | 0.27 | 0.10 | 6.8 | 95.4 | 6.62 |
| 6.0 | 7.13 | 0.68 | 0.42 | 10.5 | 96.4 | 5.13 |
| 10.0 | 6.14 | 1.08 | 1.08 | 23.0 | 90.7 | 6.58 |
| 24.0 | 5.10 | 2.20 | 3.07 | 36.2 | 97.2 | 5.18 |
| 0 | 8.62[c] | | | | | |
| 2.0 | 7.79 | 1.08[c] | 0.26[c] | 9.6 | 98.3 | 14.08 |
| 3.0 | 7.05 | 1.73 | 0.66 | 18.2 | 95.7 | 18.60 |
| 5.0 | 5.85 | 2.42 | 1.73 | 32.1 | 92.0 | 21.48 |
| 7.0 | 5.45 | 2.74 | 2.30 | 36.8 | 92.7 | 18.20 |
| 10.0 | 4.83 | 3.18 | 2.95 | 43.9 | 91.8 | 16.08 |
| 24.0 | 2.46 | 5.09 | 5.25 | 71.5 | 88.5 | 14.50 |

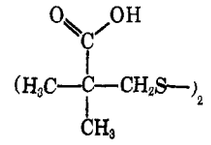
[a] See footnote *a* in Table I. [b] $M \times 10^4$ in 0.5200 *N* NaOH; average $k = 5.8 \times 10^{-6}$ $sec^{-1}$. [c] $M \times 10^4$ in 0.7785 *N* NaOH; average $k = 17. \times 10^{-6}$ $sec^{-1}$.

Comparison of the data in Tables II and III shows that the stereomers are equally sensitive to alkaline cleavage. This conclusion is in striking contrast to that drawn from the study of the corresponding dithianedicarboxylic acids[4] in which it was found that the racemic compound decomposed about 100 times more rapidly than the meso one. In that case the result was rationalized by considering that equatorial hydrogens should be more easily abstracted from a dithiane ring than the axial ones, but examination of models shows no reason why, in the rather flat dithiolane cycles, axial ones should be more difficult to abstract.

The quantitative data obtained for the decomposition of dithiobis(methylcyclopropane-1-carboxylic acid) (**14**)[21] in aqueous alkaline solutions are presented in Table IV. This compound, with protons on the carbon



**14**



**15**

$\alpha$ to the sulfur, but without protons on the carbon $\beta$ to the sulfur, is structurally quite analogous to dithiodipivalic acid[5] (**15**), which was found to decompose, but very slowly, probably by direct nucleophilic attack of hydroxide ion on disulfide sulfur. The data in Table IV confirm the prediction: **14** is quite resistant to aqueous alkali, no hydrogen sulfide is formed at all, and at 26% decomposition the percentage of sulfur accounted for (89.8%) corresponds fairly well to the calculated value (93.5%) based on the assumption of the Schiller–Otto stoichiometry[5,6] that 75% of the sulfur from decomposed

(20) A sample of this compound (as well as a sample of **7**) was generously supplied to us by Professor Arne Fredga of the University of Uppsala. **13** had been prepared by Dr. Mats-Olov Hedblom [*Tetrahedron Lett.*, 5159 (1970)] by the oxidation of *meso*-2,4-dimercaptoglutaric acid with aqueous potassium triiodide.

(21) Again we are indebted to Professor Arne Fredga for a sample of **14** which has not yet been described in the literature.

TABLE IV

DECOMPOSITION[a] OF DITHIOBIS(METHYLCYCLOPROPANE-1-CARBOXYLIC ACID) (14) IN AQUEOUS ALKALINE SOLUTIONS AT 35.2° [b]

| Time | RSSR | RSH | % dec | % S accounted for |
|---|---|---|---|---|
| 0 day | 10.22[c] | | | |
| 1 day | 9.9 | 0.62[c] | 3.1 | 100.0 |
| 2 days | 9.86 | 0.73 | 3.6 | 100.0 |
| 5 days | 9.73 | 0.87 | 4.8 | 99.4 |
| 10 days | 9.73 | 0.87 | 4.8 | 99.4 |
| 0 hr | 10.47[d] | | | |
| 6.0 hr | 9.86 | 0.87[d] | 5.5 | 98.3 |
| 11.5 hr | 9.44 | 1.54 | 10.0 | 97.5 |
| 23.0 hr | 8.89 | 2.55 | 15.2 | 97.0 |
| 48.0 hr | 8.45 | 2.93 | 19.3 | 94.7 |
| 96.0 hr | 7.75 | 3.29 | 26.0 | 89.8 |

[a] No $H_2S$ detected at any time. [b] See footnote *a* in Table I. [c] $M \times 10^4$ in 1.002 *N* NaOH. [d] $M \times 10^4$ in 2.50 *N* NaOH.

disulfide shows up as thiol and that 25% of it shows up as sulfinic acid, which we do not measure. In both compounds $\beta$ elimination is precluded by the absence of appropriately located protons, the carboxylate anion is too remote to labilize protons for an $\alpha$ elimination, and the thiolate anion displaced by nucleophilic attack is a poor leaving group ($pK_a$ of the conjugate thiol > 10.3 in each case).

## Experimental Section

**Materials.**—2-Mercaptomethyl-3-mercaptopropionic acid[22] was a gift from Dr. Daniel L. Klayman of the Walter Reed Army Medical Center, Washington, D. C. 1,2-Dithiolane-4-carboxylic acid (1) (mp 76–78°) was prepared in ~90% yield by the aerial oxidation of the dithiol according to Schotte and Ström[9] with the slight modification that the pH value of the solution was kept between 8 and 9 with sodium bicarbonate so that any polymeric disulfide 2 which might be formed would immediately be isomerized to monomer 1. The methyl ester of 1 was prepared by adding 1.20 g of 1 in 25 ml of ethyl ether to a freshly prepared solution of diazomethane in ethyl ether, allowing the solution to stand overnight, and evaporating the ethereal solution. The neutral yellow oil has a uv spectrum qualitatively identical with that of 1: $\lambda_{max}$ at 330 nm and $\lambda_{min}$ at 280 nm; nmr (benzene) $\delta$ 2.66–3.58 ($J$ = 160–215 Hz, multiplet, 5 H), 3.30 ($J$ = 198 Hz, s, 3 H, ester methyl). From a solution of the methyl ester of 1 in ethanol the methyl ester of 2 slowly separates as a white, amorphous solid. The uv spectrum of the latter in aqueous *p*-dioxane is qualitatively identical with that of 2. The statement, already made, that the methyl ester of 2 does not undergo depolymerization in aqueous *p*-dioxane, is to be read in the light of the fact that 2 itself does undergo depolymerization as readily in aqueous *p*-dioxane as it does in aqueous solutions at the same pH values. Polymeric disulfide 2 was prepared by heating fused 1 in the absence of air at 130–140° for several minutes until it set to a rubbery solid. The crude product was triturated with benzene to remove residual 1 and dried *in vacuo*. Both racemic 1,2-dithiolane-3,5-dicarboxylic acid (7), meso compound 13, and dithiobis(methylcyclopropane-1-carboxylic acid) (14) were gifts from Professor Fredga.

(22) Prepared by the method of J. R. Piper and T. P. Johnston, *J. Org. Chem.*, **32**, 1261 (1967).

**Transformation of 1,2-Dithiolane-4-carboxylic Acid (1) into 2-(Mercaptomethyl)acrylic Acid (4) and of the Latter into 2-(Ethylthiomethyl)acrylic Acid (5).**—1 (1.015 g) was dissolved in 200 ml of aqueous sodium hydroxide (40 g of NaOH) under nitrogen at 35.2°. After 2 hr the solution was cooled in an ice bath and neutralized to pH 10 with hydrochloric acid. Ethyl iodide (3.0 g) in 150 ml of ethanol was added and the solution held for several hours until a negative test with Folin's reagent demonstrated the absence of thiol. The solution was evaporated to less than half its original volume on a rotary evaporator, the residue was acidified to pH 1 with hydrochloric acid and extracted four times with 200-ml portions of ethyl ether, and the combined ethereal extracts were dried and evaporated to dryness to leave 0.90 g of yellow oil. The portion of the oil which was soluble in chloroform was placed on a silica gel column from which was eluted, by Skellysolve B with increasing increments of ethyl ether, 0.110 g of white, crystalline material melting at 49–51°: nmr ($CDCl_3$) $\delta$ 1.23 ($J$ = 74 Hz, t, 3 H, methyl), 2.50 ($J$ = 150 Hz, q, 2 H, methylene), 3.40 ($J$ = 204 Hz, s, 2 H, methylene), 5.77 (346 Hz, d, 1 H, $J$ = 1.5 Hz, vinyl), 6.37 ($J$ = 381 Hz, d, 1 H, $J$ = 1.5 Hz, vinyl), 11.4 ($J$ = 683 Hz, s, 1 H, carboxyl).

*Anal.* Calcd for $C_6H_{10}O_2S$ (5): C, 49.29; H, 6.91; S, 21.96. Found: C, 49.64; H, 7.17; S, 21.18.

The residue of the oil after extraction with chloroform was a white solid, melting at 167–173°. After passing through zinc amalgam with dilute hydrochloric acid it gave a strong positive test with Folin's reagent: nmr $\delta$ 3.69 ($J$ = 221 Hz, s, methylene), 5.84 ($J$ = 350 Hz, d, vinyl), 6.47 ($J$ = 388 Hz, d, vinyl), in agreement with 6.

**Transformation of *rac*-1,2-Dithiolane-3,5-dicarboxylic Acid (7) into 2-Mercapto-2-pentenedioic Acid (10) and of the Latter into 2-Ethylthio-2-pentenedioic Acid (11).**—7 (0.535 g) was dissolved in 200 ml of 0.950 *N* NaOH under nitrogen at 35.2°. Analysis[8] showed that decomposition was ~90% complete in 15 hr. The solution was cooled, acidified to pH 1–2 with concentrated hydrochloric acid, and aspirated with nitrogen to remove hydrogen sulfide. The solution was readjusted with aqueous sodium hydroxide to pH 10–11, 1.5 g of ethyl iodide in 150 ml of ethanol was added, and the solution was allowed to stand at room temperature under nitrogen until thiol had disappeared (Folin's reagent). After concentration to half volume on a rotary evaporator the solution was reacidified to pH 1–2 with hydrochloric acid and extracted four times with 200-ml portions of ethyl ether, and the combined ethereal extracts were dried and evaporated to give an oil which, upon elution from a silica gel column with Skellysolve B–ethyl ether, yielded a white product which, after recrystallization from chloroform–Skellysolve B, amounted to 0.150 g, mp 134–136°. With Folin's reagent faint color appears after 15–30 min and rises to a maximal value in ~24 hr. The mass spectrum gave $m/e$ 190 along with informative fragmentation; ir (KBr) 5.9 $\mu$ (=C=O), 6.2 (C=C); nmr (DMSO-$d_6$) $\delta$ 1.08 ($J$ = 65 Hz, t, 3 H, methyl), 2.70 ($J$ = 162 Hz, q, 2 H, methylene), 3.40 ($J$ = 204 Hz, d, methylene), 7.15 ($J$ = 429 Hz, t, 1 H, vinyl). This pattern agrees unequivocally with 11 rather than the isomeric possibility, $HO_2CCH{=}CHCH(SEt)CO_2H$.

*Anal.* Calcd for $C_7H_{10}O_4S$: C, 44.19; H, 5.25; S, 16.86. Found: C, 43.91; H, 5.31; S, 16.97.

**Registry No.**—**1**, 2224-02-4; **5**, 32687-42-6; **7**, 19307-93-8; **11**, 32687-44-8; **13**, 31413-40-8; **14**, 32687-46-0.

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