refluxing, an additional 2.5 ml of the chloroplatinic acid solution was introduced, and the mixture was continuously heated under reflux for a total of 87 hr. The excess X and volatile materials were stripped off *in vacuo* at room temperature, and the resulting crude product (148 g) was purified using a molecular still to yield 58 g (34.5% yield) of slightly impure $ClSi(CH_3)(CF_3CH_2CH_2)CH_2CH_2CF_2CF_2(CF_3C_3N_3)CF_2CF_2CH_2CH_2(CF_3CH_2CH_2)(CH_3)SiCl$ (XI), $n^{25}D$ 1.4050. The data for the fractionation are shown in Table III. A large amount of diadduct XI is believed to have been lost during the six passes.

TABLE III

PURIFICATION OF XI BY A MOLECULAR STILL[a]

Run	Temp, °C	Pressure, μ	Time, hr	Distillate, g	Residue, g
1	25–35	25–90	1.5	2	137
2	50–60	30–50	1.5	23	106
3	65–70	20–30	1.0	15	82
4	75–80	70–75	1.0	3	75
5	75–80	20–25	1.3	5	63
6	120–130	~20	4.4	58 (XI)	2

[a] ASCO Model 50-2 Rota-Film molecular still was employed.

Anal. Calcd for $C_{20}H_{22}Cl_2F_{17}N_3Si_2$: C, 31.84; H, 2.93; Cl, 9.40. Found: C, 32.2; H, 2.96; Cl, 8.12.

The ^{19}F resonance spectrum was consistent with the assigned structure, XI. The spectrum ($CDCl_3$) showed a triplet centered at δ +69.2 (6 F), a singlet at +72.2 (3 F), a triplet centered at +114.9 (4 F), and a broad unresolved signal centered at +117.7 ppm (4 F). The infrared spectrum (CCl_4) showed a strong band at *ca.* 1565 cm^{-1} (characteristic of triazine) and a weak band in the ≡SiOH region, indicating the presence of the hydrolysate of XI. The proton resonance spectrum (CCl_4) was in agreement with the assigned structure, XI, with the exception that the spectrum indicated the presence of $(CH_3)(OH)Si<$.

Hydrolysis of Diadduct XI.—To a saturated aqueous sodium bicarbonate solution (120 ml) was added 14 g of XI in 70 ml of ether while stirring at room temperature. After stirring for 1.5 hr, the ether solution was separated, washed with a 5% aqueous sodium chloride solution, and dried over Drierite. After evaporation of the ether *in vacuo* at room temperature, the resulting viscous liquid product was placed under vacuum (*ca.* 0.1 mm) at room temperature for 24 hr to yield 13 g of fairly pure $HOSi(CH_3)(CF_3CH_2CH_2)CH_2CH_2CF_2CF_2(CF_3C_3N_3)CF_2CF_2CH_2CH_2(CF_3CH_2CH_2)(CH_3)SiOH$ (XII).

Anal. Calcd for $C_{20}H_{24}F_{17}N_3Si_2O_2$: OH, 4.74. Found: OH, 4.59.

The ^{19}F resonance spectrum ($CDCl_3$) was comprised of a triplet centered at δ +69.4 (6 F), a singlet at +72.1 (3 F), a triplet centered at +115.1 (4 F), and a broad unresolved signal centered at +117.5 ppm (4 F). The proton resonance spectrum (CCl_4) was in agreement with the assigned structure, XII, but showed that more than a trace amount of ether was present. The molecular weight by vapor phase osmometry was found to be 795 (calcd 717). The infrared spectrum (CCl_4) showed a strong band at *ca.* 1565 cm^{-1} (characteristic of triazine) and bands in the ≡SiOH region (*ca.* 3400 and 3700 cm^{-1}). The above analytical and spectral data suggest that diol XII was fairly pure, although the molecular weight determination suggested that some condensation might have occurred. Diol XII prepared in this manner was used for polymerization without further purification.

Polymerization of Diol XII.—A mixture of 19 g of XII and 5 drops of tetramethylguanidine–trifluoroacetic acid (1:3) solution was heated, while mixing by rotation, at 70–75° *in vacuo* (*ca.* 15 mm) for 27 hr, at 80° under *ca.* 0.3-mm pressure for 16 hr, and at 100° under *ca.* 0.2-mm pressure for 45 min. The resulting polymer, 17.5 g, was a rubbery gum (XIII) which was soluble in isopropyl acetate.

Anal. Calcd for $(-C_{20}H_{22}F_{17}N_3Si_2O-)_n$: C, 34.34; H, 3.17. Found: C, 34.8; H, 3.47.

The infrared spectrum (film) was qualitatively in agreement with the assigned polymer structure, $[-Si(CH_3)(CF_3CH_2CH_2)CH_2CH_2CF_2CF_2(CF_3C_3N_3)CF_2CF_2CH_2CH_2(CF_3CH_2CH_2)(CH_3)SiO-]_x$ (XIII).

Registry No.—IIa, 18321-45-4; IIb, 18321-46-5; IIIa, 18321-47-6; IVa, 18339-04-3; IVb, 18320-81-5; VI, 18320-82-6; VII, 18320-83-7; VIII, 18320-84-8; IX, 18320-85-9; XI, 18320-86-0; XII, 18320-87-1; ethyl 2,2,3,3-tetrafluoropentanoate, 18320-88-2; 3-(vinyl)perfluoropropionamide, 18320-89-3; 5-(vinyl)-perfluoropentanamide, 18320-90-6.

Acknowledgment.—This investigation was supported in part by Contract F33615-67-C-1350, Elastomers and Coatings Branch, Air Force Materials Laboratory. The authors are indebted to Mr. J. C. Lavis for his technical assistance, to Dr. L. H. Toporcer for the isolation and characterization of ethyl 2,2,3,3-tetrafluoropentanoate, and to Dr. D. R. Chapman for a generous supply of (3,3,3-trifluoropropyl)methylchlorosilane.

Mass Spectra of Bis-1,3-dithiolanes and Bis-1,3-dithianes. Mechanism of the Ring-Cleavage Reactions of Malonaldehyde Bisthioacetals and Structures of Glyoxal Bisthioacetals

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Received July 18, 1968

α cleavage and two ring-cleavage reactions constitute the major fragmentation pathways of malonaldehyde bisthioacetals. The mechanisms of the ring-cleavage reactions have been elucidated and one of them has been shown to proceed with McLafferty rearrangement of the angular hydrogen of the distal ring to the departing chain of the fragmenting ring. α cleavage is the only major fragmentation reaction of glyoxal bisthioacetals and biacetyl bisthioketals, establishing the pendant rather than the fused bicyclic systems as the correct structures of these compounds.

We have recently carried out an investigation of the electron-impact-induced fragmentation reactions of bis-1,3-dithiolanylmethanes and bis-1,3-dithianylmethanes.[1] The major fragmentation reactions observed in this system were α cleavage and two ring-cleavage reactions, designated as type I and type II, in which the expelled neutral fragment contained one and two sulfur atoms, respectively.

Both ring-cleavage reactions proceed with the simultaneous loss of an angular hydrogen atom and both reactions were completely blocked when the two angular

(1) R. H. Shapiro, T. E. McEntee, and D. L. Coffen, *Tetrahedron*, **24**, 2809 (1968).

hydrogen atoms were replaced by methyl groups. This observation and the appearance in the spectra of appropriate metastable peaks indicated that hydrogen migration and ring fragmentation are concerted processes. The data available at that time did not permit an unequivocal distinction between the possibility of hydrogen migration from the angular position of the fragmenting (proximal) ring or that of the distal ring, although extrapolation of the results obtained with 2-phenyl-1,3-dithiane suggested the proximal position for the type I cleavage and distal position for the type II cleavage.

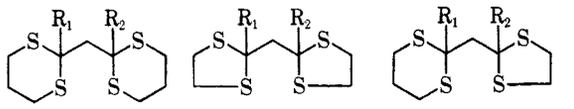
We have now extended this investigation to members of the series in which both the two angular substituents (H *vs.* D or H *vs.* CH_3) and the two rings (five membered *vs.* six membered) are differentiated from each other. The mass spectra of these substances clearly establish that hydrogen migration occurs from the distal angular position in both ring-cleavage reactions.

As a further extension of this investigation, we have examined the mass spectra of the ethylene and trimethylene bisthioacetals and bisthioketals of glyoxal and biacetyl. In each case, the single major fragmentation reaction was α cleavage of a 2,2′-bi(1,3-dithiolanyl) or of a 2,2′-bi(1,3-dithianyl). This observation resolves the long-standing ambiguity regarding the structures of these and related compounds,[2] a distinction between the pendant and fused-ring systems being not previously possible.

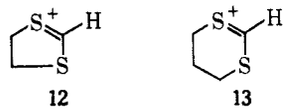
Results and Discussion

The information necessary for the elucidation of the mechanisms of the ring-cleavage fragmentation reactions required the synthesis of 2-(1,3-dithiolanyl)-2-(1,3-dithianyl)methanes in which the angular substituents differed from one another. The replacement of one of the two angular hydrogens of compound **3** by deuterium with defined selectivity appeared *a priori* to be possible from earlier observations made on compounds **1** and **2** and other members of this series. While compound **1**[1,3] and other 1,3-dithianes[4] are readily converted into their monolithio derivatives with *n*-butyllithium, we have never been able to generate any detectable trace of the lithio derivative of compound **2**, notwithstanding the fact that greater kinetic acidity in 1,3-dithiolanes than in 1,3-dithianes has been demonstrated.[5] Thus, as anticipated, sequential treatment with *n*-butyllithium and deuterium oxide effected exchange of the angular proton of the 1,3-dithianyl ring of compound **3** selectively.

Both the nmr and mass spectra of product **6** established which of the two protons had been exchanged. For all aldehydes examined, we have observed that the proton at the 2 position of the derived 1,3-dithiolane invariably shows a larger chemical shift than that same proton in the derived 1,3-dithiane (see Table I). The angular protons of compound **3** give rise to triplets at 4.12 and 4.76 ppm. The deuterium-exchange procedure reduced the intensity of the signal at 4.12 ppm to *ca.* 20% of its original intensity while the signal at 4.76 ppm remained unchanged. The α-cleavage reaction produces peaks at *m/e* 105 and 119, corresponding to ions **12** and **13**, in the mass spectrum of compound **3**. These peaks appear at *m/e* 105 and 120 in the spectrum of compound **6** (see Table II).



1, $R_1 = R_2 = H$ **2**, $R_1 = R_2 = H$ **3**, $R_1 = R_2 = H$
4, $R_1 = R_2 = CH_3$ **5**, $R_1 = R_2 = CH_3$ **6**, $R_1 = D; R_2 = H$
7, $R_1 = H; R_2 = CH_3$ **8**, $R_1 = H; R_2 = CH_3$ **9**, $R_1 = H; R_2 = CH_3$
10, $R_1 = CH_3; R_2 = H$
11, $R_1 = D; R_2 = CH_3$



12 **13**

TABLE I

CHEMICAL SHIFTS[a] OF PROTONS AT C_2 IN 1,3-DITHIOLANES AND 1,3-DITHIANES

Aldehyde	1,3-Dithiolane	1,3-Dithiane
Malonaldehyde	4.68	4.32
Acetylacetaldehyde	4.57	4.09
Propionaldehyde	4.36	3.94
Glyoxal	4.76	4.45
Benzaldehyde	5.52	5.01
Compound **3**	4.76	4.12
Compound **22**	5.01	4.10

[a] In parts per million from internal tetramethylsilane.

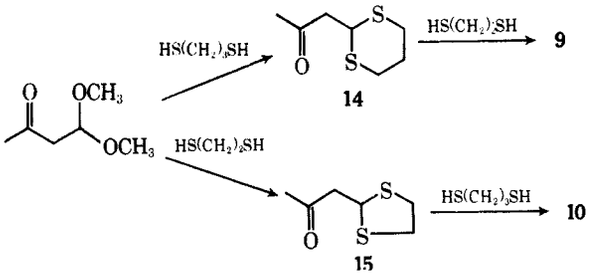
TABLE II

PRINCIPAL PEAKS IN THE 70-eV MASS SPECTRA OF 2-(1,3-DITHIOLANYL)-2-(1,3-DITHIANYL)METHANES[a]

Compd	α cleavage (%)	Type I cleavage	Type II cleavage
3	105 (100), 119 (51)	163 (11), 177 (12)	131 (97), 145 (36)
6	105 (100), 120 (48)	164 (13), 177 (9)	132 (100), 145 (35)
9	119 (100)	191 (41)	159 (94)
10	105 (98), 133 (43)	177 (24)	145 (100)
11	119 (100), 120 (40)	191 (33)	159 (87)

[a] Data for the symmetrical analogs are given in Table I of ref 1.

Three additional 2-(1,3-dithiolanyl)-2-(1,3-dithianyl)-methanes in which the angular substituents are differentiated were synthesized to corroborate the conclusions drawn from the mass spectrum of compound **6**. Two of these substances (**9** and **10**) were obtained by sequential condensation of acetylacetaldehyde dimethyl acetal with 1,2-ethanedithiol and 1,3-propanedithiol; the third (**11**) was obtained by applying the deuterium-exchange procedure to compound **9**.



The reaction of acetylacetaldehyde dimethyl acetal with 1 equiv of the appropriate dithiol proceeds cleanly to the thioacetals **14** and **15**. The sequential reaction of malonaldehyde bisdimethyl acetal with 1,2-ethane-

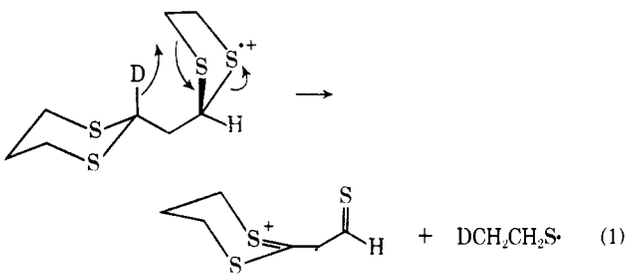
(2) M. Prostenik and K. Balenovic, *J. Org. Chem.*, **17**, 379 (1952).
(3) D. Seebach, N. R. Jones, and E. J. Corey, *ibid.*, **33**, 300 (1968).
(4) D. Seebach and E. J. Corey, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1075, 1077 (1965).
(5) S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 427 (1964).

dithiol and 1,3-propanedithiol, however, produced a mixture of compounds **1**, **2**, and **3**. Fortunately these compounds were cleanly separated on tlc and adequate samples of **3** could be obtained by preparative layer chromatography.

The peaks in the mass spectra of the 2-(1,3-dithiolanyl)-2-(1,3-dithianyl)methanes arising from the three major fragmentation pathways are listed in Table II.

The spectrum obtained from compound **6** clearly shows that both type I and type II cleavages of the six-membered ring proceed with retention of the deuterium atom (expulsion of C_3H_7S and $C_3H_7S_2$) giving rise to the ions $C_5H_6DS_3^+$ (*m/e* 164) and $C_5H_6DS_2^+$ (*m/e* 132), respectively. Conversely both type I and type II cleavages of the five-membered ring proceed with the loss of the deuterium atom (expulsion of C_2H_4DS and $C_2H_4DS_2$) giving rise to the ions $C_6H_9S_3^+$ (*m/e* 177) and $C_6H_9S_2^+$ (*m/e* 145), respectively. Thus both of these fragmentation pathways proceed with migration of the angular hydrogen (deuterium) of the *distal* ring.

Equation 1 represents one of the more reasonable pathways by which migration of the hydrogen atom of the distal ring to the departing chain of the fragmenting ring can take place. The resulting cation,

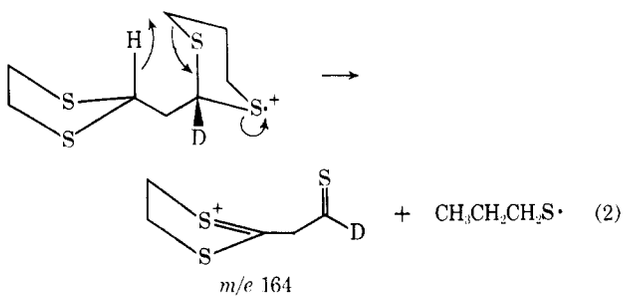


+ $DCH_2CH_2S\cdot$ (1)

m/e 177

thioaldehyde, and sulfur radical are all relatively stable entities, well known in solution chemistry. A similar process (eq 2) accounts for fragmentation of the six-membered ring to produce the ion with *m/e* 164.

A second pathway in which the sulfur radical cation site is the terminus of the hydrogen migration accommodates the data equally as well; however, a primary carbon radical rather than a sulfur radical is now generated from the fragmenting ring. The process



+ $CH_3CH_2CH_2S\cdot$ (2)

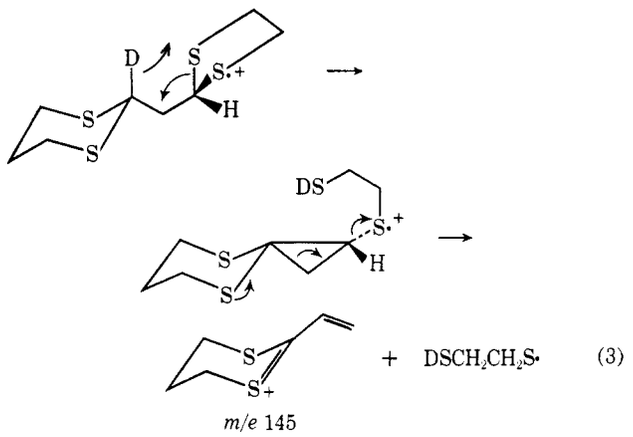
m/e 164

indicated in eq 1 and 2 formally resembles a McLafferty rearrangement, although such a rearrangement to an sp^3 carbon atom has not previously been identified.[6]

From the data made available by our initial study,[1] it was construed that type II cleavage proceeds with migration of a hydrogen atom from the distal ring.

(6) For a discussion of various types of McLafferty rearrangements, see J. K. MacLeod and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 5182 (1967).

Thus the mechanism previously advanced for this cleavage is in accord with the new results. A similar



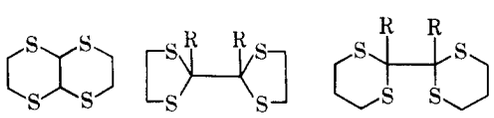
+ $DSCH_2CH_2S\cdot$ (3)

m/e 145

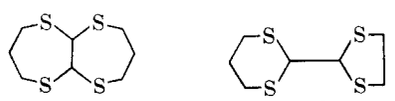
process accounts for type II cleavage of the six-membered ring with retention of the deuterium atom. From eq 1, 2, and 3 it can be construed that whether the molecular ion elects to undergo type I or type II cleavage may be predicated on whether the surviving ring is axial (type I) or equatorial (type II) to the fragmenting ring. In support of this observation it may be noted that peaks arising from type II cleavage are consistently more intense than those from type I cleavage (see Table I and ref 1).

The mass spectra of compounds **9**, **10**, and **11** are fully in accord with the above conclusions. Since only α cleavage occurs in compounds **4** and **5**, both type I and type II cleavages are effectively blocked by angular methyl groups, although all three reactions occur in compounds **7** and **8**. The mechanistic pathways described above require that blocking of the ring-cleavage reactions will occur only if the angular position of the distal ring is occupied by a methyl group. Thus, as anticipated, type I and type II cleavage reactions occur only in the five-membered ring of compounds **9** and **11**, with the expected loss of deuterium in the latter, giving ions with *m/e* 191 and 159, respectively, and only in the six-membered ring of compound **10** giving ions with *m/e* 177 and 145, respectively.

Glyoxal and Biacetyl Derivatives.—The unusual mass spectral behavior of the bisthioacetals of malonaldehyde and related 1,3-dicarbonyl compounds prompted a similar investigation of the bisthioacetals of glyoxal and bisthioketals of biacetyl. The preparation of the bisethylenethioacetal of glyoxal from either glyoxal itself or from 2,3-dichloro-1,4-dioxane produced the same product, precluding a distinction between the two possible structures, **16** and **17**, by synthesis.[2] Similarly the reaction of 1,3-propanedithiol with 1,3-di-



16 **17**, R = H; **20**, R = CH_3 **19**, R = H; **21**, R = CH_3



18 **22**

chloro-1,4-dioxane[2] and with 2-formyl-1,3-dithiane[7] produced identical products, **18** or **19**.

The mass spectra of compounds **17** (or **16**) and **19** (or **18**) exhibited, in addition to the molecular ion peak, only one intense peak with m/e $^1/_2M^+$ (see Table III). This mode of fragmentation, α cleavage, clearly excludes the fused bicyclic structures **16** and **18**. The dimethyl analogs **20** and **21**, obtained in low yields from biacetyl and the appropriate dithiol, and compound **22**, obtained from 2-formyl-1,3-dithiane and 1,2-ethanedithiol, also undergo α cleavage as the only significant fragmentation reaction.

TABLE III

PRINCIPAL PEAKS IN THE 70-eV MASS SPECTRA OF 2,2′-BI(1,3-DITHIOLANYLS) AND 2,2′-BI(1,3-DITHIANYLS)

Compd	M^+ (%)	α cleavage (%)
17	210 (6)	105 (100)
19	238 (5)	119 (100)
20	238 (6)	119 (100)
21	266 (3)	133 (100)
22	224 (8)	105 (31), 119 (100)

Mass spectrometry has previously been applied to the problem of distinguishing pendant from alternative ring systems in the structure elucidation of a group of steroidal lactones.[8]

Experimental Section

Mass spectra were obtained by Mr. J. R. Sadecky on a CEC 21-103-C mass spectrometer using a direct inlet system. Melting points are uncorrected. Ir and nmr spectra were measured on Perkin-Elmer Model 137 and Varian A-60A instruments using, in the latter case, TMS as internal standard. Published procedures were utilized for the preparation of compounds **17**,[2] **19**,[2,7] and **21**.[7]

2-(1,3-Dithiolanyl)-2-(1,3-dithianyl)methane (3).—1,3-Propanedithiol (2.16 g, 0.02 mol) in benzene (25 ml) was added slowly to a refluxing solution of malonaldehyde bisdimethyl acetal (3.28 g, 0.02 mol) and *p*-toluenesulfonic acid (40 mg) in benzene (50 ml). After 3 hr, a solution of 1,2-ethanedithiol (1.88 g, 0.02 mol) in benzene (10 ml) was added and heating under reflux continued for 6 hr. The cooled reaction mixture was diluted with methylene chloride, washed with aqueous $NaHCO_3$, dried over Na_2SO_4 and the solvents were evaporated under reduced pressure. The residue was a mixture of three compounds (**1**, **2**, and **3**). Column chromatography on alumina with benzene followed by preparative layer chromatography of the purest fraction on silica gel (benzene) gave a pure sample of compound **3** as a colorless oil: nmr ($CDCl_3$) 2.10 (2 H, multiplet), 2.19 (2 H, triplet, J = 7 cps), 2.80 (4 H, unsymmetric triplet), 3.21 (4 H, singlet), 4.12 (1 H, triplet, J = 7 cps), and 4.76 ppm (1 H, triplet, J = 7 cps); mol wt 238.

2-(1,3-Dithiolanyl)-2-(2-deuterio-1,3-dithianyl)methane (6).—The dithiolanyldithianylmethane (90 mg) in dry ether (30 ml) was cooled in a Dry Ice–CCl_4 bath while stirring under nitrogen. *n*-Butyllithium in hexane (2 ml of 2 *M* solution) was added and stirring continued for 3 hr. After quenching with D_2O (2 ml), the mixture was diluted with methylene chloride, dried over $MgSO_4$ and the solvents were evaporated. The product was purified by preparative layer chromatography (silica gel–benzene) giving 32 mg of colorless oil. The nmr signal at 4.76 ppm was reduced in relative intensity to *ca.* 20% of that in compound **3**. The mass spectrum gave mol wt 239 (a peak with one-fourth the intensity appeared at 238). The product was further purified by evaporative distillation [108° (0.005 mm)] before measuring the mass spectrum.

2-(1,3-Dithianyl)acetone (14).—Acetylacetaldehyde dimethyl acetal (13.2 g, 0.1 mol), 1,3-propanedithiol (10.8 g, 0.1 mol) and *p*-toluenesulfonic acid (100 mg) in benzene (100 ml) were heated under reflux for 16 hr. The residue left after evaporation of the solvent was triturated with ether, filtered and washed with ether giving 12.0 g (69%) of brownish white crystals. Recrystallization from ethanol gave a pure, colorless sample with mp 61–62°; ν_{max}^{Nujol} 1715 cm^{-1}; nmr ($CDCl_3$) 2.10 (2 H multiplet), 2.22 (3 H, singlet), 2.90 (6 H, multiplet), and 4.51 ppm (1 H, triplet, J = 7 cps); mol wt 176.

2-(2-Methyl-1,3-dithiolanyl)-2-(1,3-dithianyl)methane (9).—2-(1,3-Dithianyl)acetone (3.52 g, 0.02 mol) and 1,2-ethanedithiol (1.88 g, 0.02 mol) in absolute ethanol (25 ml) was saturated with anhydrous HCl. The resulting solution was heated under reflux for 30 min, cooled, and poured into excess saturated aqueous K_2CO_3 solution. The resulting mixture was extracted with methylene chloride; the extract was dried and evaporated. The product was purified by kugelrohr distillation [160° (0.04 mm)] giving 4.70 g (93%) of very pale yellow oil: nmr (CCl_4) 1.82 (3 H, singlet), 2.0 (2 H, multiplet), 2.28 (2 H, doublet, J = 6 cps), 2.8 (4 H, multiplet), 3.32 (4 H, singlet) and 4.09 ppm (1 H, triplet, J = 6 cps); mol wt 252.

2-(1,3-Dithiolanyl)acetone (15).—Acetylacetaldehyde dimethyl acetal (2.64 g, 0.02 mol), 1,2-ethanedithiol (1.88 g, 0.02 mol) and *p*-toluenesulfonic acid (50 mg) in benzene (30 ml) were heated under reflux for 16 hr. The cooled solution was diluted with methylene chloride, washed with aqueous $NaHCO_3$, dried and the solvent evaporated. The product was purified by vacuum distillation giving 2.22 g (44%) of colorless oil: bp 85–87° (0.1 mm); ν_{max}^{film} 1710 cm^{-1}; nmr (CCl_4) 2.13 (3 H, singlet), 3.01 (2 H, doublet, J = 7 cps), 3.21 (4 H, singlet), and 4.72 ppm (1 H, triplet, J = 7 cps); mol wt 162.

2-(1,3-Dithiolanyl)-2-(2-methyl-1,3-dithianyl)methane (10).—2-(1,3-Dithiolanyl)acetone (1.32 g, 8.15 mmol) and 1,3-propanedithiol (0.875 g, 8.10 mmol) in absolute ethanol (25 ml was saturated with anhydrous HCl. The resulting solution was heated under reflux for 1.5 hr, then cooled, diluted with methylene chloride, washed with aqueous $NaHCO_3$, dried, and the solvent evaporated. The crude product, 2.10 g (100%), was purified by kugelrohr distillation at 160° (0.05 mm) giving a colorless oil: nmr (CCl_4) 1.55 (3 H, singlet), 1.90 (2 H, multiplet), 2.54 (2 H, doublet, J = 6 cps), 2.7 (4 H, multiplet), 3.19 (4 H, broad singlet), and 4.57 ppm (1 H, triplet, J = 6 cps); mol wt 252.

Deuteration of 9 to 11.—Compound **9** was deuterated using the procedure described above for compound **3** except that stirring with butyllithium at −40° was continued for 5 hr. Deuteration was approximately 50% (mass spectrum and nmr) complete.

2,2′-Bi(2-methyl-1,3-dithiolanyl) (20).—A solution of biacetyl (4.30 g, 0.05 mol), 1,2-ethanedithiol (9.4 g, 0.1 mol) and *p*-toluenesulfonic acid (200 mg) in benzene (100 ml) was heated under reflux for 24 hr while collecting the water formed in a trap. The solution was cooled, washed with aqueous $NaHCO_3$, dried, and evaporated leaving a green oil. After it stood for several days, crystals of the crude product began to separate. These were filtered and washed with hexane giving 1.65 g (14%) of greenish white crystals. Vacuum sublimation followed by two recrystallizations from ethanol gave pure, colorless crystals: mp 82–83°; nmr (CCl_4) 2.00 (6 H, singlet) and 3.36 ppm (8 H, AB quartet); mol wt 238.

2-[2-(1,3-Dithiolanyl)]-1,3-dithiane (22).—A crude sample of 2-formyl-1,3-dithiane[7] (200 mg, 1.4 mmol), 1,2-ethanedithiol (127 mg, 1.4 mmol), and *p*-toluenesulfonic acid (25 mg) in benzene (25 ml) was heated under reflux for 40 hr. The cooled solution was washed with aqueous $NaHCO_3$, dried, and the solvent evaporated. The residue was taken up in hot ethanol, filtered through Celite and stored in the cold giving 141 mg (45%) of yellowish white crystals. Vacuum sublimation followed by recrystallization from ethanol gave pure, colorless needles: mp 81°; nmr ($CDCl_3$) 2.0 (2 H, multiplet), 2.9 (4 H, multiplet), 3.32 (4 H, singlet), 4.10 (1 H, doublet, J = 9 cps), and 5.01 ppm (1 H, doublet, J = 9 cps); mol wt 224.

Registry No.—**3**, 18554-35-3; **6**, 18554-36-4; **9**, 18554-37-5; **10**, 18554-38-6; **14**, 18554-39-7; **15**, 14860-12-9; **20**, 18554-41-1; **22**, 18554-42-2.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this project.

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