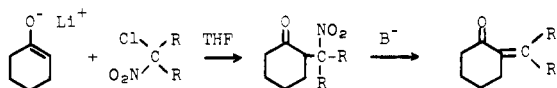


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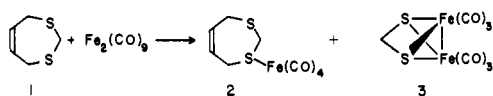
Received October 2, 1978

## Reductive Decyclization of Organosulfur Compounds. Preparation and Crystal Structure of $\mu, \mu'$ -Dithiolato-methanehexacarbonyldiiron(I)

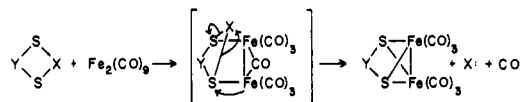
Sir:

Desulfurization with organometallic complexes is a topic of current interest and development.<sup>1</sup> During a study on the coordination chemistry of cyclic organosulfur compounds, we have discovered a decarbasulfurization reaction. The parent molecules undergo novel cleavage reactions whereby organosulfur fragments are incorporated in complexes of general formula  $(\text{RS})_2(\text{CO})_6\text{Fe}_2$ . We are prompted to communicate these unexpected results because of the importance of the two classes of molecules involved. In addition, organometallic complexes of novel structures have been prepared.

1,3-Dithia-5-cycloheptene<sup>2</sup> (**1**) has two potential ligating sites; the olefin and the sulfur atoms. Upon reaction with  $\text{Fe}_2(\text{CO})_9$  in tetrahydrofuran, at room temperature, a complex mixture resulted. Chromatography on alumina permitted **2**<sup>3</sup> and **3**<sup>4</sup> to be isolated as oils which were crystallized from hexane. The structure of **2**, an expected product, was assigned



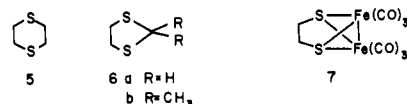
## Scheme I



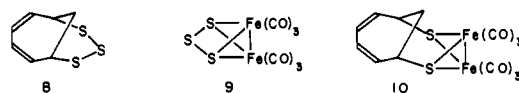
by comparison of its spectroscopic properties to those of the analogous complexes  $\text{LFe}(\text{CO})_4$ .<sup>5</sup> The structure of the unexpected product, **3**, was assigned by comparison of its spectroscopic properties with those of  $[(\text{RS})(\text{CO})_3\text{Fe}]_2$ .<sup>6,7</sup> Unbridged complexes such as  $[(\text{C}_2\text{H}_5\text{S})(\text{CO})_3\text{Fe}]_2$  (**4**) have stereochemically nonrigid  $\text{Fe}(\text{CO})_3$  groups.<sup>8</sup> Compound **3** is also fluxional at room temperature, showing only one line<sup>9</sup> in the carbonyl region of the <sup>13</sup>C NMR spectrum. At  $-85^\circ\text{C}$ , two lines, approximately in the intensity ratio 2:1, are observed, consistent with the symmetrical structure expected for **3**.

The preparation of **3** was quite unexpected, involving the cleavage of two carbon-sulfur bonds. Little, if any, **3** is formed when  $\text{Fe}(\text{CO})_5$  is used in the reaction, while a large excess of  $\text{Fe}_2(\text{CO})_9$  raises the yield. An atmosphere of CO prevents formation of **3** with **2** being the major product. This implies that an unsaturated dimeric carbonyl species is required. Possible precursors, such as dithiacyclopropane<sup>10</sup> or methanedithiol,<sup>11</sup> are unlikely to be produced from **1** under the reaction conditions. We propose that **3** may be produced via reductive decyclization of an intermediate such as  $(\text{XYS})_2(\text{CO})_7\text{Fe}_2$  (Scheme I). Complexes of the type  $(\text{L-L})\text{Fe}_2(\text{CO})_7$  are known in iron carbonyl chemistry.<sup>12</sup> Such a complex containing 1,3-dithiacyclohexane has been reported but not characterized.<sup>13</sup>

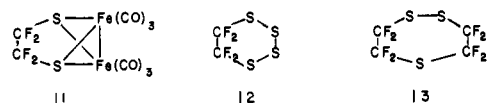
Compounds **5** and **6** undergo decarbasulfurization to give **7** in addition to products analogous to **2**.<sup>14a</sup> In **8** there is the



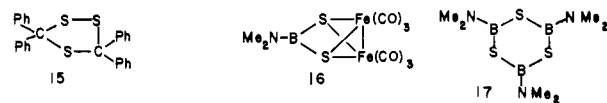
possibility of cleaving either two carbon-sulfur bonds or two sulfur-sulfur bonds to give **9** or **10**, respectively. Only **10** is



isolated,<sup>14b</sup> which suggests that sulfur-sulfur bond cleavage is preferred. Scheme I is consistent with previously unrelated reactions such as the preparation<sup>15</sup> of **11** from **12** and **13**. In



addition, complex **14**, which has aryl groups replacing the methylene hydrogens of **3**, has been isolated from reactions of diaryl thioketones and  $\text{Fe}_2(\text{CO})_9$ .<sup>16</sup> It was proposed that these thioketones may rearrange in solution to give **15** which falls into the general category. Finally, the recently reported<sup>17</sup> synthesis of **16** from **17** indicates that this reaction may be applicable to other classes of cyclic sulfur compounds.



The structure of **3**, with its bridging methylene group, is particularly relevant to unbridged complexes of the general formula  $[(\text{RS})(\text{CO})_3\text{Fe}]_2$ .<sup>18</sup> Three different isomers can exist depending on the arrangement of the R groups. The presence of two of the three isomers can be detected in solution.<sup>6</sup> For  $\text{R} = \text{C}_2\text{H}_5$  (**4**)<sup>19</sup> and  $\text{C}_6\text{H}_5$ <sup>20</sup> and for the structural analogue

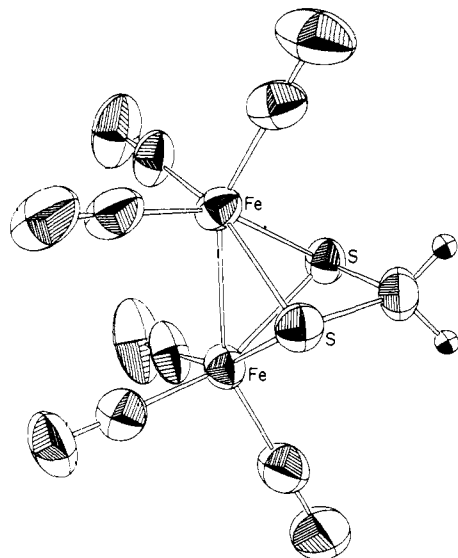


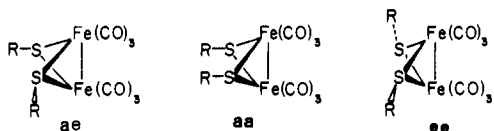
Figure 1. ORTEP drawing of  $(\text{CH}_2\text{S}_2)(\text{CO})_6\text{Fe}_2$ .

Table I. Comparison of Selected Distances (Å) and Angles (Degrees) for Complexes 3, 4, and 18<sup>a</sup>

complex	Fe-Fe	Fe-S	S-S	Fe-S-Fe	S-Fe-S
3	2.485 (1)	2.262 (1)	2.673 (2)	66.64 (4)	72.45 (4)
4	2.537 (10)	2.259 (7)	2.932 (14)	68.3 (3)	81.0 (3)
18	2.552 (2)	2.228 (2)	2.007 (5)	69.9 (1)	53.5 (1)

<sup>a</sup> Data for complexes 4 and 18 taken from ref 19 and 29, respectively.

$[(\text{C}_6\text{H}_5\text{S})(\eta^5\text{-C}_5\text{H}_5)\text{Rh}]_2$ ,<sup>21</sup> the axial-equatorial (ae) conformation is observed in the crystal. Unfavorable van der Waals contacts were calculated<sup>19</sup> for the axial-axial (aa) isomer; thus the equatorial-equatorial (ee) structure was proposed for the other species in solution although some doubt still remains.<sup>8</sup> Complex 3 is formally analogous to an axial-axial isomer.



The structure of  $\text{CH}_2\text{S}_2\text{Fe}_2(\text{CO})_6$  (Figure 1) displays an interesting quadricyclic  $\text{CH}_2\text{S}_2\text{Fe}_2$  ring system similar to the normal "butterfly" structure<sup>19-21</sup> except for the addition of a bridging methylene group that serves to pin back the sulfur atoms. While the gross structural features are similar to other members of this class,<sup>26</sup> the presence of the bridging methylene group has some interesting consequences. The S-CH<sub>2</sub>-S bridging angle, for example, is only 94.55 (3)°. While not extraordinary,<sup>27</sup> it is indicative of the strain in the  $\text{CH}_2\text{S}_2\text{Fe}_2$  ring system.<sup>28</sup> This strain is also reflected in the bond lengths and angles of 3 when compared with 4 and  $[\text{S}(\text{CO})_3\text{Fe}]_2$  (18), the latter containing a direct S-S bond (Table I). The sulfur atoms are much closer together in 3 than they are in 4. The Fe-Fe bond length of 2.485 (1) Å is the shortest reported for these compounds.<sup>30</sup> The short Fe-Fe distance is accompanied by relatively long Fe-S distances, as expected.<sup>31</sup> The Fe-S-Fe angles are somewhat compressed while the S-Fe-S are intermediate between those for 4 and 18.

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facilities, to Dr. G. Hamer for the <sup>13</sup>C NMR spectra, and to Professor J. Takats for the mass spectra.

**Supplementary Material Available:** A table of atomic positional and thermal parameters (1 page). Ordering information is given on any current masthead page.

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- 3: IR (hexane)  $\nu(\text{CO})$  2079 (m), 2039 (s), 2008 (s), 1999 (s), 1988 (w)  $\text{cm}^{-1}$ ; Raman  $\nu(\text{Fe-Fe})$  204  $\text{cm}^{-1}$ ; NMR ( $(\text{CD}_3)_2\text{CO}$ ) 4.9 ppm (s); mass spectrum  $m/e$  358 ( $\text{M}^+$ ), 330 ( $\text{M}^+ - \text{CO}$ ), 302 ( $\text{M}^+ - 2\text{CO}$ ), 274 ( $\text{M}^+ - 3\text{CO}$ ), 246 ( $\text{M}^+ - 4\text{CO}$ ), 218 ( $\text{M}^+ - 5\text{CO}$ ), 190 ( $\text{M}^+ - 6\text{CO}$ ), 188 ( $[\text{Fe}_2\text{S}_2\text{C}]^+$ ), 176 ( $[\text{Fe}_2\text{S}_2]^+$ ), 144 ( $[\text{Fe}_2\text{S}]^+$ ), 112 ( $[\text{Fe}_2]^+$ ), 88 ( $[\text{FeS}]^+$ ); yield, 25%. Anal. Calcd for  $\text{C}_7\text{H}_2\text{S}_2\text{Fe}_2\text{O}_6$ : C, 23.6; H, 0.56. Found: C, 23.4; H, 0.53.
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- All calculations were performed on an IBM 370/158 computer employing the programs of "XRAY-76" edited by J. M. Stewart, Technical Report 446, Computer Science Center, University of Maryland, College Park, Md.
- Unweighted full-matrix least-squares refinement, employing anisotropic thermal parameters for all nonhydrogen atoms and arbitrary  $U = 0.10$  Å<sup>2</sup> isotropic thermal parameters for the two methylene hydrogen atoms.
- $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_2 = [\sum (|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$ . The function minimized during least-squares refinement was  $R_2$ .
- 3 possesses effective  $C_{2v}$ - $mm2$  symmetry. The dihedral angle between the basal planes of the two distorted square pyramids is 63.7° (69.5° in 4<sup>19</sup>). The two iron atoms are displaced 0.35 Å, (0.38 Å in 4<sup>19</sup>) from their respective basal planes in the direction of the axial carbonyl groups.
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complex formation or extensive coupling with other low frequency modes. See W. M. Scovell and T. G. Spiro, *Inorg. Chem.*, **13**, 304 (1974), for a comparison of  $[\text{S}(\text{CO})_3\text{Fe}]_2$  and  $[(\text{CH}_3\text{S})(\text{CO})_3\text{Fe}]_2$ .

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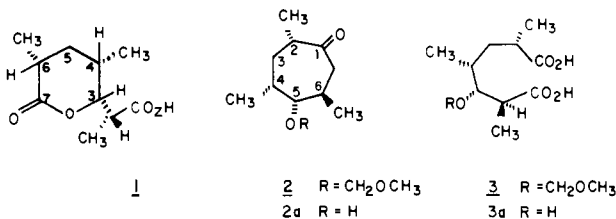
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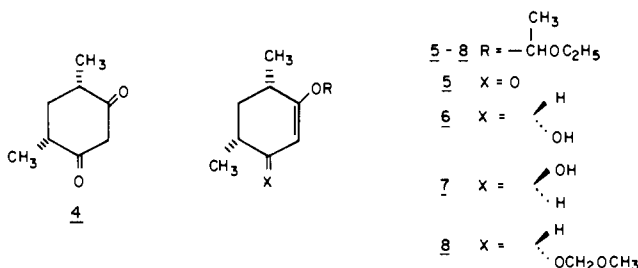
## A Stereocontrolled Synthesis of the ( $\pm$ ) Djerassi-Prelog Lactonic Acid

Sir:

The lactonic acid<sup>1,2</sup> **1** is a key degradation product of the macrolide antibiotic methymycin. Its structure was established by Djerassi,<sup>3</sup> while the stereochemical assignments were completed by Rickards.<sup>4</sup> Significantly, **1** retains the structural fragment C-1 through C-7 and four of the six chiral centers of the aglycone methynolide, and this fact has been exploited in the total synthesis of the latter by Masamune.<sup>5</sup>



We now report a stereocontrolled and efficient synthesis of *rac*-**1**. A strategy involving the construction of the cycloheptanone **2** and its oxidative fragmentation to the diacid precursor **3** was considered an ideal route to the lactone **1**. *cis*-4,6-Dimethyl cyclohexane-1,3-dione (**4**) was used to provide the *cis* geometry of the 2,4-methyl groups in **2**. A single stereoisomer

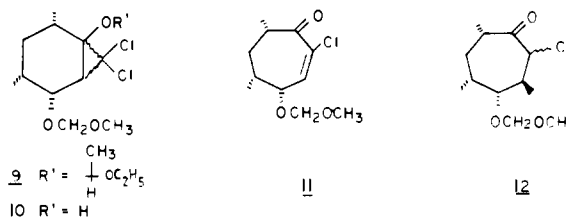


of **4** was obtained by the reaction of butanone with methyl methacrylate<sup>6</sup> (NaOMe, benzene, 0 °C, 6 h), mp 110–113 °C, in 30% yield; mass spectrum  $m/e$  140 ( $M^+$ ); IR ( $\text{CHCl}_3$ ) 5.8, 5.9, 6.55  $\mu$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.2 (6 H, d,  $J = 6$  Hz,  $-\text{CHCH}_3$ ), 3.45 (2 H, s,  $\text{COCH}_2\text{CO}$ ). The stereochemistry of **4** was established by its periodate oxidation<sup>7</sup> to afford the known *meso*-2,4-dimethylglutaric acid.<sup>8</sup> Reaction of **4** with ethyl vinyl ether (hydrochloric acid catalysis, room temperature, 12 h), gave the acetal **5**, bp 98–100 °C ( $\sim 0.2$  mm), in 83% yield; IR (neat) 6.0, 6.27  $\mu$  (Fermi resonance); NMR ( $\text{CCl}_4$ )  $\delta$  5.2 (1 H, m,  $-\text{C}=\text{CH}$ ).

The desired *cis* axial alcohol **6** was obtained from **5** by reduction with lithium Selectride<sup>9</sup> (THF, 0 °C, 1.5 h), followed by oxidative workup, as a single isomer in 94% yield; IR (neat) 3.0, 6.08  $\mu$  (enol ether); NMR ( $\text{CCl}_4$ )  $\delta$  4.85 (1 H, d,  $J = 8$  Hz,  $-\text{C}=\text{CH}$ ). The expected stereochemical assignment for **6** was supported by the reduction of **5** with lithium aluminum hydride (THF, 0 °C, 1.5 h) when an isomeric alcohol **7** was obtained; NMR ( $\text{CCl}_4$ )  $\delta$  4.6 (1 H, s,  $-\text{C}=\text{CH}$ ). The alcohol **6**, when treated with chloromethyl methyl ether in the presence of ethyl

diisopropylamine (0 °C, 12 h) afforded the acetal **8**, bp 90–91 °C (0.5 mm), in 85% yield; mass spectrum  $m/e$  285 ( $M^+$ ); IR (neat) 6.08  $\mu$  ( $=\text{C}-\text{O}$ ); NMR ( $\text{CDCl}_3$ )  $\delta$  3.38 (3 H, s,  $\text{OCH}_3$ ), 4.7 (2 H, AB,  $J_{\text{AB}} = 4$  Hz,  $-\text{OCH}_2\text{O}$ ), 4.95 (1 H, d,  $J = 7$  Hz,  $-\text{C}=\text{CH}$ ).

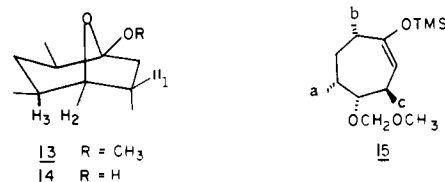
The stage was now set for the addition of a methylene equivalent to **8**, and the subsequent ring expansion to a cycloheptenone. This was done by the addition of dichlorocarbene ( $\text{CHCl}_3$ , 50% aqueous NaOH, benzyl triethylammonium chloride<sup>10</sup>). The reaction afforded the *gem*-dichlorocyclopropyl compound<sup>11</sup> **9** in 97% yield. Treatment of **9** with



aqueous acetic acid (90%), containing sodium acetate, transformed it smoothly, via **10**, to the chloroenone **11** (82% yield, bp 107 °C (0.06 mm)) as a thick oil with a characteristic odor; mass spectrum:  $m/e$  232 ( $M^+$ ); IR (neat) 5.92, 6.35  $\mu$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  0.95 (3 H, d,  $J = 6$  Hz,  $\text{CH}_3$  at C-5), 1.2 (3 H, d,  $J = 6$  Hz,  $\text{CH}_3$  at C-7) 3.2 (3 H, s,  $\text{OCH}_3$ ), 4.7 (2 H, s,  $\text{OCH}_2\text{O}$ ), 6.8 (1 H, d,  $J = 4$  Hz,  $-\text{C}=\text{CH}$ ).

The last methyl group was introduced by the addition of lithium dimethylcuprate to **11** (ether, 0 °C, 1.5 h). The chloroketone **12** was obtained as a mixture epimeric at C-2, bp 103–105 °C (0.05 mm), in 97% yield; NMR ( $\text{CDCl}_3$ )  $\delta$  5.28 (1 H, 2 d,  $J = 3$  Hz, H at C-2). Reductive dehalogenation of **12** with chromous perchlorate<sup>12</sup> (DMF, 0 °C, 6 h) afforded the cycloheptanone<sup>13</sup> **2** as a colorless oil, bp 78–80 °C (0.05 mm), in 62% yield; mass spectrum  $m/e$  214 ( $M^+$ ); IR (neat), 5.85  $\mu$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.9 (3 H, d,  $J = 8$  Hz,  $\text{CH}_3$  at C-4), 1.1 (6 H, d,  $J = 8$  Hz,  $\text{CH}_3$  at C-2 and C-6), 3.4 (3 H, s,  $\text{OCH}_3$ ), 4.7 (2 H, AB,  $J_{\text{AB}} = 4$  Hz,  $\text{OCH}_2\text{O}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  16.77 ( $\text{CH}_3$  at C-4), 19.33 ( $\text{CH}_3$  at C-6), 21.41 ( $\text{CH}_3$  at C-2), 33.33 (C-3), 33.57 (C-6), 33.62 (C-4), 41.41 (C-7), 55.68 ( $\text{OCH}_3$ ) 83.84 (C-5), 96.32 ( $-\text{OCH}_2\text{O}$ ), 215.8 (C=O).

Support for the assignment at C-5 and C-6 was derived from NMR studies on the ketal **13**, obtained from **2** with dilute hydrochloric acid, followed by methanol and acid, via the alcohol **2a** which is in equilibrium with the hemiketal **14**. Examination of the molecular models of **13** reveals dihedral angles of 0° between H-1 and H-2 and 90° between H-2 and H-3. As expected, the NMR spectrum of **13** exhibits H-2 as a doublet at  $\delta$  4.35 ( $J = 7$  Hz) coupled to H-1 (irradiation of H-1 collapses H-2 into a singlet, whereas irradiation of H-3 has no effect on the H-2 signal). The configurations of the methyl at



C-6 and methoxyl at C-5 in **13**, and therefore of the methyl and alkoxy groups in **2**, clearly follow from the above NMR results.<sup>14</sup> Conclusive evidence for these stereochemical assignments was provided by transformation of **2** to the ( $\pm$ ) Djerassi-Prelog lactone. The ketone **2** was converted by trapping the kinetic enolate (LDA, THF, 0 °C) with trimethylchlorosilane<sup>15</sup> to the silyl enol ether **15**, bp 84 °C (0.05 mm), in 84% yield; mass spectrum  $m/e$  286 ( $M^+$ ); IR (neat) 6.02  $\mu$  ( $\text{C}=\text{CHOTMS}$ ); NMR ( $\text{CDCl}_3$ )  $\delta$  0.2 (9 H, s,  $\text{SiCH}_3$ ), 0.9 (3 H,