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Novel W(CO)$_6$-Promoted C-S Bond Cleavage Reactions of Dithianes. X-ray Structure of 9,9′:9,9″-Terfluorene[1]

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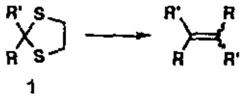
The reactions of dithianes with W(CO)$_6$ in refluxing chlorobenzene give dimeric alkenes and their reduced products; fluorenone derivative yielding trimer **8**. A radical mechanism is suggested. The structure of **8** has been determined by a single-crystal X-ray diffraction study. Crystal data: $P2_1/n$; $a = 11.948(5)$, $b = 16.8795(14)$, $c = 13.491(6)$ Å, $\beta = 105.03(3)°$, $Z = 4$, $V = 2628(2)$ Å^3; $R_F = 0.061$, $R_{WF} = 0.051$ for 2142 reflections and 353 variables.

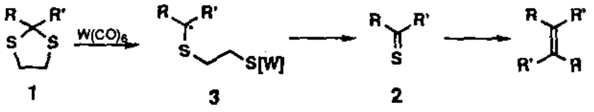
INTRODUCTION

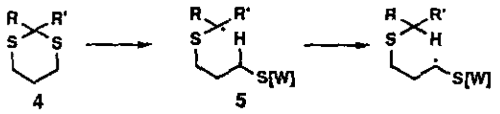
The conversion of the carbon-sulfur bonds in dithioacetals into the carbon-carbon bonds has been exceedingly useful in organic synthesis.[2-4] To illustrate, desulfurdimerization of five-membered-ring dithiolanes **1** with W(CO)$_6$ gives in good yields the corresponding dimeric alkenes (Eq. 1).[3] These coupling reactions can be intermolecular[3a] or intramolecular[3b] and can be applied to polymer synthesis.[3c] The mechanism of this newly discovered reaction has been investigated and thioketone **2** is the key intermediate (Scheme I).[3a] It is known that the W(CO)$_6$-mediated C-S bond cleavage reaction occurs via a free radical mechanism.[5] Accordingly, the formation of **2** may arise from a similar process. The homolytic cleavage of one of the carbon-sulfur bonds in **1** may afford the radical **3** which may undergo fragmentation process yielding **2** and ethylene. Desulfurdimerization of a thioketone to give a dimeric alkene is well documented.[2a,6] Although the formation of **3** can be rationalized from the product distribution and supported by a simulation study,[3a] a direct evidence for the involvement of intermediate **3** is still lacking. It is well established that a radical can readily undergo an intramolecular 1,5-atom transfer reaction.[7] As such, when a six-membered dithiane **4** is employed in the W(CO)$_6$-mediated reaction, it is conceivable that intermediate **5** would undergo such an intramolecular hydrogen atom migration (Eq. 2) leading to various reduced product(s). In this paper, we report for the first time the details of W(CO)$_6$-promoted reactions of dithianes.



(1)

Scheme I





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RESULTS AND DISCUSSION

Our initial effort was to treat fluorenone derivative **6a** with 2.5 equivalents of W(CO)$_6$ in refluxing chlorobenzene for 24 h. After usual work-up and chromatographic separation, the dimeric bifluorenylidene **7** and trimeric 9,9':9,9"-terfluorene **8** were obtained in 28% and 54% yields, respectively. The structure of **8**[8] was unambiguously confirmed by spectroscopic means and by the X-ray crystallography (Fig. 1). Bond lengths and angles are tabulated in Table 1. Our X-ray structure of **8** confirms that the molecule has an apparent C_2 symmetric axis, the rotation about the C_9-$C_{9'}$ (or C_9-$C_{9''}$) being hindered.

It is noted both five-membered and open-chained dithioacetals (**6b** and **6c**) give **7** in excellent yields (>90%) and no further reduced product(s) was detected at all.[3a] The isolation of **8** indicates that the reaction behavior be-

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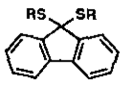
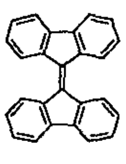
Dedicated to Professor Yau-Tang Lin (林耀堂) on the occasion of his eightieth birthday.

tween **6a** and **6b** is different. Structurally, these two substrates differ only by one CH_2 moiety. Consequently, the homolytic cleavage of one of the carbon-sulfur bonds in **6a** would lead to **9**. Intramolecular hydrogen atom transfer in **9** via a similar path shown in Eq. 2 may lead to **10**. This step may be responsible for the formation of the C-H bond. Further homolytic cleavage of the remaining carbon-sulfur bond in **10** may then occur yielding 9-fluorenyl radical **11**. The coupling of **11** with **9** will lead to **12** which may further react giving **8**. The reason why **8** was formed in such a significant yield remained unclear. Presumably, a highly stable planar 9-fluorenyl radical would give such a unique and interesting result.



6a R-R = $(CH_2)_3$
6b R-R = $(CH_2)_2$
6c R = Ph



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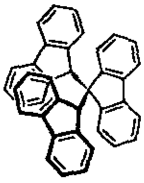

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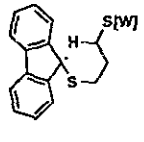

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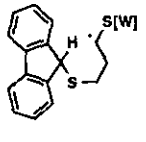

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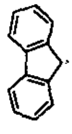

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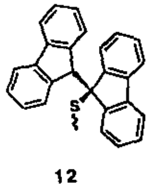

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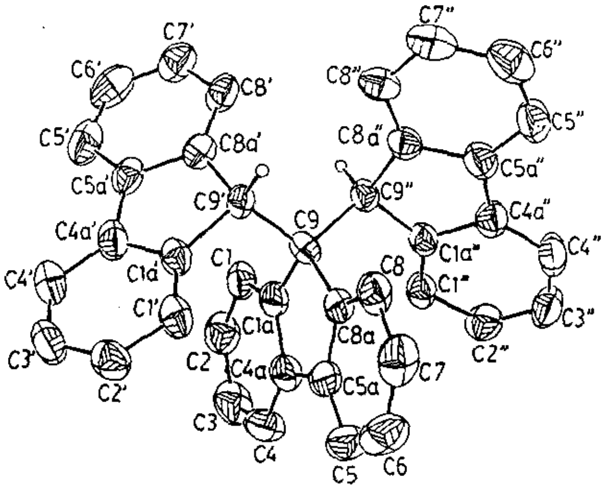
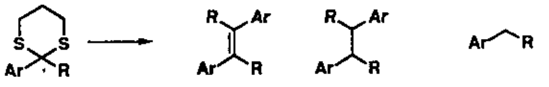


Fig. 1. ORTEP drawing of the molecule **8** with 50% probability.

Table 1. Bond Distances and Bond Angles of **8**

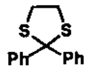
Bond Distances			
C(1)-C(1A)	1.393(7)	C(4A')-C(5A')	1.473(8)
C(1)-C(2)	1.399(8)	C(5')-C(5A')	1.397(8)
C(1A)-C(4A)	1.398(7)	C(5')-C(6')	1.388(9)
C(1A)-C(9)	1.522(7)	C(5A')-C(8A')	1.420(7)
C(2)-C(3)	1.382(9)	C(6')-C(7')	1.383(9)
C(3)-C(4)	1.392(9)	C(7')-C(8')	1.378(8)
C(4)-C(4A)	1.401(8)	C(8')-C(8A')	1.368(7)
C(4A)-C(5A)	1.474(8)	C(8A')-C(9')	1.523(7)
C(5)-C(5A)	1.384(8)	C(1")-C(1A")	1.399(7)
C(5)-C(6)	1.362(9)	C(1")-C(2")	1.406(7)
C(5A)-C(8A)	1.390(7)	C(1A")-C(4A")	1.417(7)
C(6)-C(7)	1.378(9)	C(1A")-C(9")	1.514(7)
C(7)-C(8)	1.393(8)	C(2")-C(3")	1.376(8)
C(8)-C(8A)	1.370(7)	C(3")-C(4")	1.398(8)
C(8)-C(9)	1.517(7)	C(4")-C(4A")	1.404(7)
C(9)-C(9')	1.569(7)	C(4A")-C(5A")	1.427(7)
C(9)-C(9")	1.580(7)	C(5")-C(5A")	1.394(8)
C(1')-C(1A')	1.363(7)	C(5")-C(6")	1.373(8)
C(1')-C(2')	1.382(7)	C(5A")-C(8A")	1.415(7)
C(1A')-C(4A')	1.402(7)	C(6")-C(7")	1.404(8)
C(1A')-C(9')	1.547(7)	C(7")-C(8")	1.415(8)
C(2')-C(3')	1.397(9)	C(8")-C(8A")	1.394(7)
C(3')-C(4')	1.353(9)	C(8A")-C(9")	1.526(7)
C(4')-C(4A')	1.380(7)		
Bond Angles			
C(1A)-C(1)-C(2)	119.9(5)	C(5A')-C(5')-C(6')	117.5(5)
C(1)-C(1A)-C(4A)	120.3(5)	C(4A')-C(5A')-C(5')	129.8(5)
C(1)-C(1A)-C(9)	129.8(5)	C(4A')-C(5A')-C(8A')	109.2(4)
C(4A)-C(1A)-C(9)	109.8(4)	C(5')-C(5A')-C(8A')	121.0(5)
C(1)-C(2)-C(3)	119.4(5)	C(5')-C(6')-C(7')	121.8(5)
C(2)-C(3)-C(4)	121.4(5)	C(6')-C(7')-C(8')	119.8(5)
C(3)-C(4)-C(4A)	119.2(5)	C(7')-C(8')-C(8A')	120.9(5)
C(1A)-C(4A)-C(4)	119.7(5)	C(5A')-C(8A')-C(8')	118.9(5)
C(1A)-C(4A)-C(5A)	108.9(5)	C(5A')-C(8A')-C(9')	109.5(4)
C(4)-C(4A)-C(5A)	131.3(5)	C(8')-C(8A')-C(9')	131.6(5)
C(5A)-C(5)-C(6)	118.9(5)	C(9)-C(9')-C(1A')	110.6(4)
C(4A)-C(5A)-C(5)	130.4(5)	C(9)-C(9')-C(8A')	114.5(4)
C(4A)-C(5A)-C(8A)	108.4(4)	C(1A')-C(9')-C(8A')	102.3(4)
C(5)-C(5A)-C(8A)	121.1(5)	C(1A")-C(1")-C(2")	118.9(5)
C(5)-C(6)-C(7)	120.1(5)	C(1")-C(1A")-C(4A")	119.9(4)
C(6)-C(7)-C(8)	121.7(5)	C(1")-C(1A")-C(9")	130.2(4)
C(7)-C(8)-C(8A)	118.0(5)	C(4A")-C(1A")-C(9")	109.9(4)
C(5A)-C(8A)-C(8)	120.1(5)	C(1")-C(2")-C(3")	122.0(5)
C(5A)-C(8A)-C(9)	110.7(4)	C(2")-C(3")-C(4")	119.3(5)
C(8)-C(8A)-C(9)	129.0(5)	C(3")-C(4")-C(4A")	120.5(5)
C(1A)-C(9)-C(8A)	102.2(4)	C(1A")-C(4A")-C(4")	119.5(5)
C(1A)-C(9)-C(9')	110.3(4)	C(1A")-C(4A")-C(5A")	109.0(4)
C(1A)-C(9)-C(9")	109.1(4)	C(4")-C(4A")-C(5A")	131.5(5)
C(8A)-C(9)-C(9')	110.7(4)	C(5A")-C(5")-C(6")	119.5(5)
C(8A)-C(9)-C(9")	111.1(4)	C(4A")-C(5A")-C(5")	129.7(5)
C(9')-C(9)-C(9")	112.9(4)	C(4A")-C(5A")-C(8A")	109.5(4)
C(1A')-C(1')-C(2')	118.6(5)	C(5")-C(5")-C(8A")	120.7(5)
C(1')-C(1A')-C(4A')	120.2(4)	C(5")-C(6")-C(7")	120.6(5)
C(1')-C(1A')-C(9')	129.9(5)	C(6")-C(7")-C(8")	120.8(5)
C(4A')-C(1A')-C(9')	109.9(4)	C(7")-C(8")-C(8A")	118.2(5)
C(1')-C(2')-C(3')	120.4(5)	C(5A")-C(8A")-C(8")	120.1(5)
C(2')-C(3')-C(4')	121.5(5)	C(5A")-C(8A")-C(9")	109.3(4)
C(3')-C(4')-C(4A')	117.9(5)	C(8")-C(8A")-C(9")	130.5(5)
C(1A')-C(4A')-C(4')	121.3(5)	C(9)-C(9")-C(1A")	112.2(4)
C(1A')-C(4A')-C(5A')	108.8(4)	C(9)-C(9")-C(8A")	114.3(4)
C(4')-C(4A')-C(5A')	129.9(5)	C(1A")-C(9")-C(8A")	102.0(4)

We have also investigated other benzylic systems for comparison. Thus, the reaction of **13a** with 2.5 equiv of $W(CO)_6$ under the same conditions yielded a mixture of the dimeric olefin **14a**, the reduced dimer **15a** and trace amount of the reduced monomer **16a** (Eq. 3). Again, it is noted that the yield of **14a** was much lower than those obtained from the reaction of dithiolane **17**.[3a] However, no trimeric product similar to **8** was detected at all. The formation of **15a** or **16a** may arise from the intramolecular hydrogen transfer in a similar manner as depicted above.



(3)

	13	14	15	16
a	Ar = R = Ph	24%	50%	trace
b	Ar = p-$CH_3C_6H_4$, R = H	29%	4%	--



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The reaction of simple benzylic dithiane **13b** with $W(CO)_6$ under the same conditions afforded a mixture of stilbene **14b** and bibenzyl **15b** in 34% and 4% yields, respectively (Eq. 3). Again, this result, is consistent with the radical mechanism depicted earlier. The yields of the "reduced" products seem to reflect the relative stability of the radical intermediates.

In summary, we have demonstrated the interesting behaviour of the six-membered ring dithianes in the $W(CO)_6$-mediated desulfurization reactions. Our results confirmed the radical mechanism of the $W(CO)_6$-mediated carbon-sulfur bond cleavage reactions.

EXPERIMENTAL SECTION

Melting points are uncorrected. ^1H NMR spectra were obtained on a Bruker AC200 (200 MHz) NMR spectrometer. Chemical shifts are reported in δ scale using tetramethylsilane as the internal standard, and deuteriochloroform was used as the solvent. ^{13}C NMR spectra were recorded on a Bruker AC200 spectrometer operating at 50 MHz using deuteriochloroform (δ 77.0) as the internal standard. Mass spectral data (MS) were obtained on a Finigan TSQ-16C mass spectrometer. All solvents were purified by standard methods.

Reaction of 6a with $W(CO)_6$

A mixture of **6a** (1.00 g, 3.7 mmol) and $W(CO)_6$ (3.26 g, 9.26 mmol) in chlorobenzene (10 mL) was heated under reflux for 24 h. After being cooled to room temperature, the mixture was filtered and the solid residue was triturated with ethyl acetate. The combined organic solutions were evaporated in vacuo. The residue was subjected to flash chromatography using hexane as the eluent to give bifluorenyli-dene **7** (0.14 g, 24%); mp 190-191°C (lit.[3a] 191-192°C) and terfluorene **8** (0.33 g, 54%); mp 291-293°C (lit.[8] 293°C); ^1H NMR δ 5.35 (*br. d*, J = 7.8 Hz, 2H, $H_{1'}$, $H_{1''}$), 5.41 (*s*, 2H, $H_{9'}$, $H_{9''}$), 6.30 (*br. d*, J = 7.8 Hz, 2H, H_1, H_8), 6.52 (*br. t*, J = 7.6 Hz, 2H, $H_{2'}$, $H_{2''}$), 6.86 (*br. t*, J = 7.6 Hz, 2H, H_2, H_7), 6.97 (*br. t*, J = 7.4 Hz, 2H, $H_{3'}$, $H_{3''}$), 7.12 (*br. t*, J = 7.4 Hz, 2H, H_3, H_6), 7.31 (*br. d*, J = 7.8 Hz, 2H, H_4, H_5), 7.44 (*br. d*, J = 7.6 Hz, 2H, $H_{4'}$, $H_{4''}$), 7.50-7.64 (*m*, 4H, $H_{6'}$, $H_{6''}$, $H_{7'}$, $H_{7''}$), 7.83 (*br. d*, J = 8.0 Hz, 2H, $H_{5'}$, $H_{5''}$), 8.51 (*br. d*, J = 7.1 Hz, 2H, $H_{8'}$, $H_{8''}$); ^{13}C NMR δ 52.8, 59.0, 118.9, 119.1, 120.3, 123.4, 124.5, 125.8, 126.1, 126.7, 126.8, 127.3, 127.5, 128.0, 140.9, 141.6, 143.8, 144.2, 146.1.

Reaction of 13a with $W(CO)_6$

By using a similar procedure described above, a solution of **13a** (1.02 g, 3.75 mmol) and $W(CO)_6$ (3.25 g, 9.26 mmol) in chlorobenzene was allowed to reflux for 24 h to give, after work-up and chromatographic separation, **14a** (0.31 g, 50%); mp 205-206°C (lit.[9] 206°C), **15a** (0.15 g, 24%); mp 222-223°C (lit.[3a] 222-223°C), and **16a** (trace) which exhibited identical spectroscopic properties as those of an authentic sample.

Reaction of 13b with $W(CO)_6$

According to a similar procedure described above, **13b** (1.02 g, 4.86 mmol) was allowed to react with $W(CO)_6$ (6.1 g, 17.5 mmol) in refluxing chlorobenzene (10 mL) to give **14b** (144 mg, 29%); mp 176-177°C (1it.[10] 178-180°C) and **15b** (18 mg, 4%) which exhibited the same spectroscopic properties as those of an authentic sample.

Crystal structure of 8

$C_{39}H_{26}$, monoclinic, space group $P2_1/n$, a = 11.948(5), b = 16.8795(14), c = 13.491(6) Å, β = 105.03(3)°, Z = 4,

$V = 2628(2)$ Å^3, $D_c = 1.25$ g cm^{-1}, $F(000) = 1039.87$, λ(Mo-$K\alpha$) = 0.7093 Å, $\mu = 0.07$ mm^{-1}, Crystal dimensions, 0.3 x 0.4 x 0.5 mm, $R_F = 0.061$, $R_{WF} = 0.051$ for 2142 unique reflections with $I > 2\sigma(I)$ and 353 variables. Data were collected on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by the direct method. All carbon atoms were refined with anisotropic thermal parameters, all hydrogen atoms were added at idealized positions and included in the structure factor calculation. Atomic coordinates, thermal parameters and structure factor lists can be obtained from the authors.

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Key Words

C-S Cleavage; $W(CO)_6$; Radical mechanism; Dithioacetal; 9,9':9,9''-Terfluorene.

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