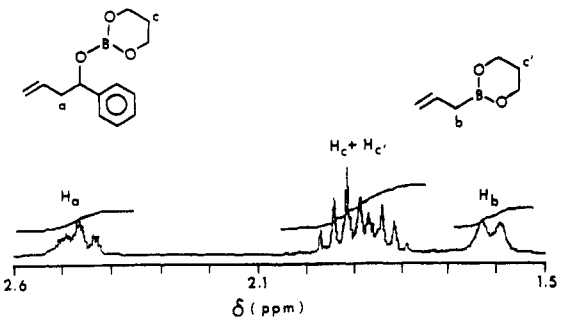


Figure 3. The progress of allylboration of benzaldehyde with *B*-allyl-1,3,2-dioxaborinane (**11**) in dichloromethane-d_2 at 0 °C by 200-MHz ^{1}H NMR spectroscopy.

0.5 mmol) and the solution of benzaldehyde (0.5 mL, 1.0 M, 0.5 mmol) were mixed together (by using standard syringing techniques[17]) in an NMR tube, and the progress of the reaction was continuously monitored by ^{11}B NMR[18] (on either Varian FT-80A or Varian XL-200 NMR instruments) by quantifying the relative amounts of starting material and product peaks (see for example, Figure 1). Thus the reaction mixtures were 0.5 M in each of the two components. No attempt was made to correct for the minor variations in concentrations resulting from the contraction of solutions at low temperatures.

General Procedures for the Determination of Rates of Allylborations by ^{1}H NMR Method. Two procedures were found to be reliable by ^{1}H NMR for quantifying the progress of allylborations:

Procedure A.[20] Benzaldehyde (0.1062 g, 1 mmol) and hexamethylethane (0.0155 g, 0.1357 mmol) were weighed into a 1-mL volumetric flask and dichloromethane-d_2 (or tetrahydrofuran-d_8) was added up to the mark to obtain a 1.0 M solution of the aldehyde. Next, the solution of the allylboron reagent (0.5 mL, 1.0 M, 0.5 mmol) and the solution of benzaldehyde (0.5 mL, 1.0 M, 0.5 mmol) were mixed in an NMR tube at the desired temperature (note: prior to mixing, the reagent and aldehyde solutions were maintained at the desired temperature for 2 h in all cases), and the progress of the reaction was monitored by ^{1}H NMR (on the Varian XL-200 NMR instrument) continuously by quantifying the relative amount of the aldehyde against the internal standard peak.

Procedure B.[20,21] In this method, no internal standard was taken. The solutions of the reagent (0.5 mL, 1.0 M, 0.5 mmol) and the aldehyde (0.5 mL, 1.0 M, 0.5 mmol) were mixed together at the desired temperature in an NMR tube, and the progress of the reaction was continuously monitored by ^{1}H NMR spectroscopy (on Varian XL-200 NMR instrument) by quantifying the relative amounts of the peaks corresponding to the allylic protons of the starting material and product (viz., the boron adduct resulting from the addition of allylboron reagent to benzaldehyde). Since the allylic protons of the starting material and the product are well resolved in the 200-MHz ^{1}H NMR spectrum in most cases (without interference from other protons; see, for example, Figure 3) this method was more commonly employed for the rate studies.

Acknowledgment. We gratefully acknowledge the financial support of the National Institutes of Health (Grant GM 10937), which made this research possible. We also wish to thank Professor William R. Roush for kindly sharing with us some unpublished allylboration data from his laboratories and for his helpful discussions. We thank Professor M. T. Reetz for providing us with some detailed experimental procedures for the preparation of his reagent.

Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra for the title compounds **11**, **16–24**, and **26** (22 pages). Ordering information is given on any current masthead page.

(18) The boronates (δ 30–37 ppm) and the borinates (δ 18–24 ppm) are well resolved in ^{11}B NMR and permit quantification, generally up to −50 °C. However, we have found that, due to quadrupolar broadening effects, ^{11}B NMR does not permit reliable quantitative rate determinations below −50 °C.

(19) This reagent was prepared in dichloromethane and used without isolation as it was unstable in distillation.

(20) Procedures A and B gave identical results for **11** at 0 °C.

(21) The ^{11}B NMR method and the ^{1}H NMR method (procedure B) also gave essentially identical results for **11** at 0 °C.

(22) After we completed the present work, Corey and co-workers reported yet another reagent for the asymmetric allylation of aldehydes. See ref 4p. Although this reagent falls into the category of 1,3,2-diazaborolidines, it can be, for practical purposes, treated as a homologue of the reagent **20**, in the category of 1,3,2-oxazaborolidines.

$W(CO)_6$-Mediated Desulfurdimerization of Dithioketals. Evidence for a Thione Intermediate†,1

Lam Lung Yeung,[2a,3] Yu Chi Yip,[2a] and Tien-Yau Luh*,[2a-c]

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, and Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

Received July 18, 1989

Upon treatment with $W(CO)_6$, dithioketals undergo desulfurdimerization to give the corresponding dimeric olefins in good to excellent yields. The mechanism of this newly discovered reaction has been investigated. Thioketones have been isolated from the reactions of highly crowded dithioketals. The mechanism for the formation of thioketones has been shown to occur via a new type of radical fragmentation process of dithiolane. Thermolysis of 2,2-dimethylindan-1-yl 2-thiophenoxyethyl sulfide in the presence of *tert*-butyl adamantane-1-peroxycarboxylate (a typical radical initiator) has been studied for comparison. Thioketones react with $W(CO)_6$, giving dimeric olefins and/or undergoing carbene-like insertion reactions.

Transition-metal-mediated C–S bond cleavage reactions are useful in organic synthesis.[4] Various metal carbonyls have been shown to be thiophilic, hence, organosulfur compounds can be reduced under different conditions.[4] Upon treatment with metal carbonyls, certain thioethers[5a] and thioketones[5b,c] readily undergo desulfurdimerization

† Dedicated to Professor Wei Chuan Lin on the occasion of his 70th birthday.

(1) Part 28 of the series "Transition Metal Promoted Reactions".

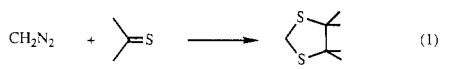
(2) (a) The Chinese University of Hong Kong. (b) National Taiwan University. (c) To whom correspondence should be addressed at NTU.

(3) Recipient of the Croucher Foundation studentship, 1987–89.

(4) For a review, see: Luh, T.-Y.; Ni, Z.-J. *Synthesis*, in press.

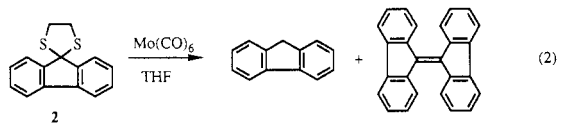
0022-3263/90/1955-1874$02.50/0

to give dimeric products. It is noteworthy that the reductive coupling of a carbonyl equivalent provides a versatile method for carbon–carbon double bond formation.[6] Dithioketals have two carbon–sulfur bonds. The coupling of a carbene precursor and 2 equiv of thioketone can afford dithioketals (eq 1).[7] The reverse reaction, considering



(1)

dithioketal functionality as a carbene synthon, has not been explored.[8] We recently found that group 6 metal carbonyl mediated desulfurization proceeds via homolytic cleavage of the carbon–sulfur bond.[5a] Fluorenone dithioketal gives a mixture of fluorene and bifluorenylidene upon treatment with $Mo(CO)_6$ in THF (eq 2).[9] It has been



(2)

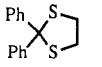
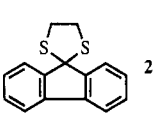
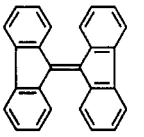
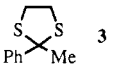
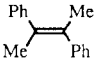
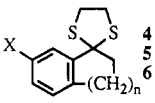
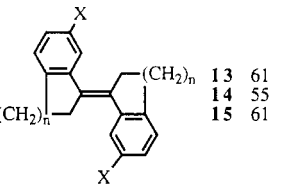
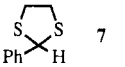
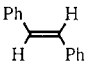
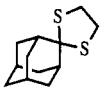
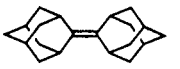
envisaged that the reduction may arise by a stepwise hydrogen abstraction from the solvent by some radical species generated during the reaction. Bifluorenylidene may be formed from the dimerization of two carbene-like moieties.[9] Chlorobenzene has been shown to be a useful solvent for the coupling of two radical intermediates in the metal carbonyl mediated C–X bond cleavage reactions.[5a,10] In this case, no hydrogen is available for radical abstraction. Accordingly, the reaction of dithioketals under these conditions may lead to cleavage of both carbon–sulfur bonds, yielding a carbene equivalent which dimerizes to give the olefin. As part of our continuing interest in the synthetic applications of dithioacetal functionality,[11] we hereby report a detailed investigation of this reaction. Synthetic as well as mechanistic features of the reactions are discussed.

Results and Discussion

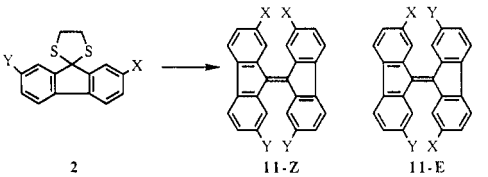
Treatment of dithioketals with $W(CO)_6$ in refluxing chlorobenzene afforded the corresponding dimeric products in good to excellent yields. The results are compiled in Table I.

Benzophenone and fluorenone dithioketals **1** and **2a** gave in excellent yields the respective dimers **10** and **11a**. Indanone and tetralone derivatives (**4–6**), on the other hand, gave the dimers **13–15** in slightly lower yields. *trans*-Stilbene **16** was obtained from the reaction of the benzaldehyde derivative **7**. Again, only the *E* isomer was obtained. It is noted that *E*/*Z* isomerization was observed when *cis*-stilbene was treated with 2 equiv of $W(CO)_6$ in refluxing chlorobenzene. Adamantanone dithioketal (**8**) also afforded the desired olefin **17** in good yield. Even ketene dithioacetal **9** can be converted into cumulene **18**.

Table I. Intermolecular Desulfurdimerization of Dithioketals

substrate	product	% yield
 **1**	$Ph_2C{=}CPh_2$ **10**	97
 **2**	 **11a**	93
 **3**	 **12** E/Z = 1:1	62
 **4** n=1 X=H **5** n=1 X=OMe **6** n=2 X=H		**13** 61 **14** 55 **15** 61
 **7**	 **16**	45
 **8**	 **17**	71
$Ph_2C{=}C(SPh)_2$ **9**	$Ph_2C{=}C{=}C{=}CPh_2$ **18**	71

As can be seen from Table I, the reaction shows stereoselectivity in cases with a significant difference in steric environment between the olefinic isomers. When this discrepancy is lifted, the selectivity no longer holds. As a result, acetophenone dithioketal **3** yielded a mixture of (*E*)- and (*Z*)-dimethylstilbenes **12**. In a similar manner, reactions of 2-substituted fluorenone dithioketal **2** gave *E*/*Z* isomeric mixture of bifluorenylidenes **14** (eq 3). Stereospecific syntheses of *Z*-disubstituted bifluorenylidenes, however, can be achieved by employing the bridging strategy and intramolecular desulfurdimerization.[12]



(3)

2 **11-Z** **11-E**

	X	Y	%Yield	Z/E
a	H	H	93	
b	Br	Br	96	
c	OMe	H	84	1/1
d	Br	H	93	1/1
e	CO_2Me	H	95	2/1

(5) (a) Ng, C. T.; Wang, X.-j.; Luh, T.-Y. *J. Org. Chem.* **1988**, *53*, 2536. (b) Alper, H. *J. Organomet. Chem.* **1974**, *73*, 357. (c) Alper, H.; Park, H.-N. *J. Org. Chem.* **1977**, *42*, 3522.

(6) (a) Lai, Y.-H. *Org. Prep. Pr. Int.* **1980**, *12*, 361. (b) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405.

(7) (a) Schönberg, A.; König, B.; Singer, E. *Chem. Ber.* **1967**, *100*, 767. (b) Ohno, A.; Ohnishi, Y.; Fukuyama, M.; Tsuchihashi, G. *J. Am. Chem. Soc.* **1968**, *90*, 7038.

(8) Although the reactions of dithioacetals with metal carbonyls have been studied and C–S bond cleavages have been recorded, no carbene complexes have been reported. Cf.: Raubenheimer, H. G.; Linford, L.; Lombard, A. v. A. *Organometallics* **1989**, *8*, 2062 and references therein.

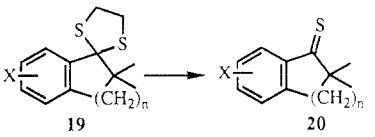
(9) Luh, T.-Y.; Wong, C. S. *J. Org. Chem.* **1985**, *50*, 5413.

(10) Luh, T.-Y.; Lee, K. S.; Tam, S. W. *J. Organomet. Chem.* **1983**, *248*, 221.

(11) (a) Wong, C. S.; Leung, W. S.; Yeung, L. L.; Luh, T.-Y. *J. Organomet. Chem.* **1986**, *307*, C49. (b) Yeung, L. L.; Yip, Y. C.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1987**, 981. (c) Ni, Z.-J.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1515. (d) Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1988**, *53*, 2129. (e) Ni, Z.-J.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1011. (f) Ng, D. K. P.; Luh, T.-Y. *Tetrahedron Lett.* **1988**, *29*, 5131. (g) Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1988**, *53*, 5582. (h) Wang, X.-j.; Luh, T.-Y. *J. Org. Chem.* **1989**, *54*, 263. (i) Yang, P.-F.; Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1989**, *54*, 2261. (j) Ng, D. K. P.; Luh, T.-Y. *J. Am. Chem. Soc.* **1989**, *111*, 9119.

(12) Yip, Y. C.; Wang, X.-j.; Ng, D. K. P.; Mak, T. C. W.; Chiang, P.; Luh, T.-Y. *J. Org. Chem.*, following paper in this issue.

Table II. The Yield of 20 from the Reaction of 19 with $W(CO)_6$ in Chlorobenzene



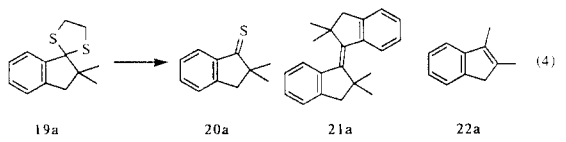
19 20

X	n	reaction time, h	% yield
a, H	1	18	30
b, 5-OMe	1	24	26
c, 6-OMe	1	8	36
d, 5-Me	1	8	38
e, 6-Me	1	18	42
f, 5-CN	1	72	0[a]
g, H	2	24	9

[a] Starting material was recovered.

It has been established that the tungsten-mediated carbon–sulfur bond cleavage reactions of mercaptans and thioethers occur via a free-radical mechanism.[5a] The two carbon–sulfur bonds in dithioketals may cleave at different stages, and it would be highly interesting if any intermediate(s) could be detected. The intrinsic idea of designing such an experiment is to treat a highly crowded dithioketal under reaction conditions such that the intermolecular coupling step might be very slow and the intermediate species might be isolated. As can be seen from Table I, indanone dithioketals gave the corresponding dimers in good yields. When methyl groups are introduced in the C_2-position, the dimerization step may be hindered because of increasing steric crowding around the reaction center.

These considerations lead us to study the reaction of dithioketal **19a** with $W(CO)_6$. A mixture of thione **20a**, dimeric olefin **21a** and rearranged monomeric alkene **22a** was obtained (eq 4). The yield of **20a** was somewhat



19a 20a 21a 22a (4)

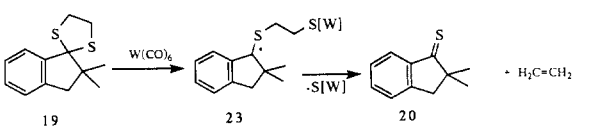
time-dependent, and the dimeric olefin **21a** was labile under the reaction conditions. Consequently, prolonged heating of **19a** resulted in lower yields of **20a** and **21a**. The reactions with other dithioketals **19b–g** behaved similarly, and the yields of **20a–g** are summarized in Table II. Electron-donating substituents on the aromatic ring in **19** facilitated the reactions, giving slightly higher yields of **20** and requiring shorter reaction times. Substrates containing an electron-withdrawing group (e.g. **19f**) did not react under the reaction conditions.

The formation of thioketones revealed an unprecedented type of the fragmentation of the dithiolane moiety. The gaseous product of the reaction was also carefully examined. Thus, the reaction was carried out in a closed system and any gas formed during the course of the reaction was introduced directly into a carbon tetrachloride solution of bromine. Dibromoethane was obtained in 92% yield. This result indicated that ethylene was liberated from the reaction.

On the basis of these experimental results and in comparison with related work,[5a] a plausible mechanism is proposed (Scheme I). The first carbon–sulfur bond of the dithiolane **19** is cleaved homolytically to give radical **23**, which may then undergo fragmentation step to yield thioketone **20** and ethylene.

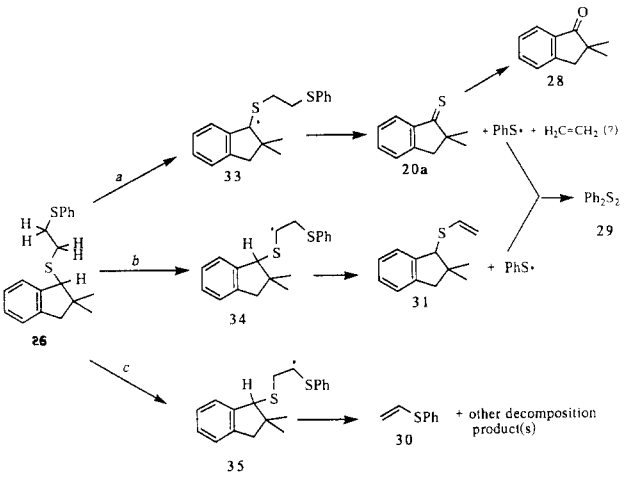
Group 6 metal carbonyls are thiophilic. C–S bond cleavage should be more favorable than the breakage of

Scheme I

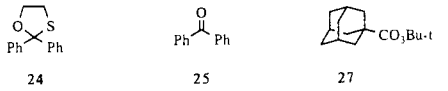


19 23 20

Scheme II

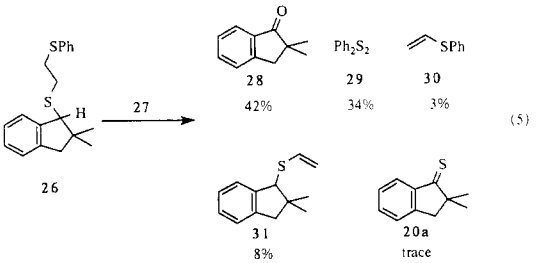


the C–O bond under the reaction conditions. If the mechanism shown in Scheme I is correct, thermolysis of oxthiolane in the presence of $W(CO)_6$ would yield the corresponding ketone via a similar fragmentation process. It is interesting to note that the fragmentation of α-alkoxy-substituted radicals to yield carbonyl compounds is well-documented.[13] In this study, treatment of **24** with $W(CO)_6$ in refluxing chlorobenzene afforded **25** in 99% yield. Dibromoethane was also detected. This observation supports the mechanism shown in Scheme I.



24 25 27

In order to establish the radical intermediate in the overall reaction, we have synthesized thioether **26** to simulate the tungsten-mediated reaction. Thermolysis of **26** in the presence of 1 equiv of *tert*-butyl adamantane-1-peroxycarboxylate (**27**) in chlorobenzene gave the following mixture of products:[14] 2,2-dimethylindan-1-one (**28**, 42%), diphenyl disulfide (**29**, 34%), phenyl vinyl sulfide (**30**, 3%), 2,2-dimethylindan-1-yl vinyl sulfide (**31**, 8%), and a trace amount of **20a** (eq 5). The structure of vinyl sulfide **31** was proved by an independent synthesis from **32**.



26 28 42% 29 34% 30 3% 31 8% 20a trace (5)

The thermal decomposition of **27** occurs via a free-radical mechanism.[15] Adamantyl and *tert*-butoxy radicals thus generated may abstract hydrogens in **26** to generate

(13) (a) Gritter, R. J.; Wallace, T. J. *J. Org. Chem.* **1961**, *26*, 282, 5256. (b) Huyser, E. S.; Garcia, Z. *J. Org. Chem.* **1962**, *27*, 2716.
(14) Starting material **26** was recovered in 35% yield.
(15) Luh, T.-Y.; Stock, L. M. *J. Org. Chem.* **1978**, *43*, 3271 and references cited therein.

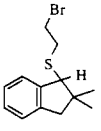
radicals **33–35**, which may undergo further fragmentation processes to yield the various decomposition products (Scheme II). Path a would generate thioketone **20a** and thiophenoxy radical. The latter may dimerize to yield **29**. Attempts to trap ethylene with bromine in carbon tetrachloride by a similar procedure described above were unsuccessful. Presumably, the radical species generated in situ may rapidly react with ethylene before it can escape from the reaction mixture. Path b would yield **30**[16] and path c **29** and **31**. The product distribution in this reaction apparently reflects the relative stability of the radical intermediates **33–35**.

The isolation of **28** is interesting. It is noted that thioketones are unstable under these conditions. Treatment of **20a** with **27** in refluxing chlorobenzene gave **28** in 97% yield based on unrecovered **20a**. Consequently, in situ conversion of **20a** to **28** may occur during the course of the thermolysis of **26** in the presence of **27**.

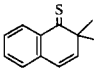
The observation of the radical-initiated reaction of **26** is compatible with that of the $W(CO)_6$-mediated fragmentation of **19** As a result, it seems plausible that the latter reaction proceeds via a similar radical mechanism shown in Scheme I.

It is known that thioketones undergo desulfurdimerization to olefins upon treatment with manganese or cobalt carbonyls.[5b,c] We also found that the reaction of **20a** with $W(CO)_6$ in refluxing chlorobenzene for 24 h gave **21a** in 24% yield in addition to recovered starting material **20a** (65%). Prolonged heating of the reaction mixture of **20a** and $W(CO)_6$ for 72 h, however, gave **21a** and the insertion product **22a** in 19 and 34% yields, respectively. The isolation of dimeric products further supports the view that desulfurdimerization of dithioacetal occurs via a thioketone intermediate.

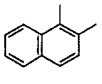
The mechanism for the conversion of the thioketones into dimeric olefins is not clear. A metallocarbene intermediate is envisaged. Indeed, when thionocarbonate is treated with iron carbonyl, an iron carbene complex was isolated.[17] Dimerization[18] and insertion[19] are two common types of reaction of metallocarbenes. As just mentioned, an insertion product was indeed obtained from the reaction of **20a**. Furthermore, the reaction of **36** under similar conditions gave **37** in 45% yield. All these results are reconcilable with the involvement of the carbenoid intermediate.



32



36



37

In conclusion, we have demonstrated a new desulfurdimerization reaction of dithioacetals leading to the formation of carbon–carbon double bonds. The procedure is simple, and starting materials are easily accessible. The reaction provides a useful method for the dimerization of carbonyl equivalents under neutral conditions. Our mechanistic investigations shows that the reaction proceeds via a thioketone intermediate which then dimerizes to give the coupling product. A new type of fragmentation of dithiolane has been discovered. The overall process suggests that dithioacetals can serve as carbene synthons. The synthetic applications of these reactions are under investigation.[12]

Experimental Section

Melting points are uncorrected. All ^1H NMR spectra were recorded at 60 or 250 MHz. All ^{13}C NMR spectra were taken at 62.5 MHz. Reagent-grade tungsten hexacarbonyl (Aldrich or Fluka) was used without further purification. Chromatographic separation was performed on silica gel (Merck, 70–230 mesh). All solvents were purified by standard procedure[20] prior to use. Chlorobenzene was distilled from calcium hydride and stored over molecular sieve (4A). The purity of all title compounds without elemental analyses was judged to be >95%. Copies of the 250-MHz ^1H NMR spectra of thioketones **20a–e** and **20g** are included in the supplementary material.

General Procedure for the Synthesis of Unhindered Dithioketal. A chloroform solution (100 mL) of carbonyl compound (0.2 mol) was mixed with 1,2-ethanedithiol (16 mL, 0.2 mol) and boron trifluoride etherate (1 mL). The mixture was allowed to reflux for 3 h. After being cooled to room temperature, the solution was washed with aqueous NaOH (10%) and the organic layer was dried over anhydrous magnesium sulfate. After filtration, the filtrate was evaporated in vacuo and the residue was purified by recrystallization to give the desired dithioketal.

General Procedure for Desulfurdimerization of Dithioketals. A chlorobenzene solution (4 mL) of dithioketal (0.50 mmol) and $W(CO)_6$ (1–2 mmol) was heated to 160 °C under nitrogen atmosphere for 24–48 h. After the solution was cooled to room temperature, the solvent was removed in vacuo and the black residue was triturated with ether and filtered. The filtrate was evaporated in vacuo, and the residue was chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to give the desired product.

Tetraphenylethene (10). According to the general procedure, benzophenone dithioketal **1** (123 mg, 0.47 mmol) was allowed to react with $W(CO)_6$ (352 mg, 1.00 mmol) to give **10** (81 mg, 97%): mp 225 °C (lit.[21] mp 222 °C); *m/z* 332, 167, 165; ^1H NMR δ ($CDCl_3$) 7.20 (m).

Bifluorenylidene (11a). Compound **2a** (270 mg, 0.36 mmol) was desulfurdimerized according to the general procedure with $W(CO)_6$ (530 mg, 1.5 mmol) in chlorobenzene (15 mL) for 24 h to afford, after column chromatography (eluent: hexane–ethyl acetate, 6:1), **11a** (0.16 g, 93%): mp 190–191 °C (lit.[9] mp 190–191.5 °C). The product showed the same physical properties as those of the authentic sample.

(*E*)-1,1′-Biindanylidene (13). Via the general procedure, a mixture of **4** (102 mg, 0.50 mmol) and $W(CO)_6$ (352 mg, 1.00 mmol) was allowed to react for 24 h to give **13** (35.9 mg, 62%): mp 140–142 °C (lit.[22] 142–143 °C); *m/z* 232, 116, 115; ^1H NMR δ 3.16 (8 H, s), 7.20 (4 H, m), 7.32 (2 H, m), 7.64 (2 H, d, J = 8 Hz).

(*E*)-6,6′-Dimethoxy-1,1′-biindanylidene (14). A chlorobenzene solution (5 mL) of 6-methoxy-1,1-(ethylenedithio)indan **5** (238 mg, 1.00 mmol) and tungsten hexacarbonyl (528 mg, 1.50 mmol) was allowed to react for 24 h according to the general procedure. After workup, the residue was chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to afford **14** (80.3 mg, 55%): mp 187–188 °C; IR (KBr) ν 2925, 2833, 1597, 1483, 1323, 1286, 1214, 1199, 1158, 1096, 1030, 961, 926, 850, 822, 751 cm^{-1}; ^1H NMR δ 3.12 (s, 8 H), 3.83 (s, 6 H), 6.70–7.22 (m, 6 H); ^{13}C NMR δ 30.2, 32.5, 55.6, 110.4, 113.0, 125.2, 135.8, 139.5, 144.5, 158.8; accurate mass calcd for $C_{20}H_{20}O_2$ 292.1463, found 292.1463. Anal. Calcd: C, 82.16; H, 6.89. Found: C, 81.43; H, 6.36.

(*E*)-1,1′-Bitetralinylidene (15). According to the general procedure, a mixture of **6** (111 mg, 0.50 mmol) and $W(CO)_6$ (352 mg, 1.00 mmol) was refluxed for 24 h to give **15** (39.6 mg, 61%): mp 117–120 °C; *m/z* 260, 129, 130; ^1H NMR δ 1.80 (4 H, m), 2.77

(16) The other residue which may be formed via path b may further react under the reaction conditions to afford **28**.

(17) Daub, J.; Endress, G.; Erhardt, U.; Jogun, K. H.; Kappler, J.; Laumer, A.; Pfiz, R.; Stezowski, J. J. *Chem. Ber.* **1982**, *115*, 1787.

(18) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983; p 196.

(19) Casey, C. P.; Neumann, S. M. *J. Chem. Soc., Chem. Commun.* **1975**, 895.

(20) Perrin, D. R.; Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford; 1988.

(21) Schlenk, W.; Bergmann, E. *Ann.* **1928**, *463*, 1.

(22) Lenoir, D.; Lemmen, P. *Chem. Ber.* **1980**, *113*, 3112.

(8 H, m), 7.13 (4 H, m), 7.47 (2 H, m), 7.87 (2 H, m).[23]

(*E*)- and (*Z*)-2,3-Dimethylstilbene (12). Via the general procedure, **3** (98 mg, 0.50 mmol) and $W(CO)_6$ (352 g, 1.00 mmol) were transformed into a mixture of (*E*)- and (*Z*)-**15** (30.7 g, 62%). The methyl groups of both isomers showed ^1H NMR absorptions at δ 1.90 and 2.20[24] in the ratio of approximately 1:1.

(*E*)-Stilbene (16). By use of the general procedure, the reaction between **7** (91 mg 0.50 mmol) and $W(CO)_6$ (352 mg, 1.00 mmol) afforded **16** (20 mg, 45%), which exhibited identical physical properties with those of the authentic compound.

(*E*)-2,2′-Biadamantylidene (17). According to the general procedure, **8** (113 mg, 0.50 mmol) was allowed to react with $W(CO)_6$ (352 mg, 1.00 mmol) to give **17** (475 mg, 71%): mp 183–184 °C (lit.[25] mp 183–185 °C).

1,1,4,4-Tetraphenylbutatriene (18). Similar to the general procedure, **9** (198 mg, 0.5 mmol) and $W(CO)_6$ (352 mg, 1.00 mmol) were converted to **18** (66.7 mg, 75%), which exhibited the same physical properties as those of the literature compound.[26]

2,2′,7,7′-Tetrabromobifluorenylidene (11b). A mixture of **2b** (0.33 g, 0.8 mmol) and $W(CO)_6$ (0.66 g, 1.9 mmol) in chlorobenzene (15 mL) was allowed to react according to the general procedure to give **11b** (0.25 g, 96%): mp >300 °C (toluene; lit.[27] mp 425 °C); ^1H NMR ($CDBr_3$) δ 7.51 (d, J = 8 Hz, 4 H), 7.60 (d, J = 8 Hz, 4 H), 8.35 (br s, 4 H); m/z 640, 642, 644, 646, 648.

(*E*)- and (*Z*)-2,2′-Dimethoxybifluorenylidene (11c). According to the general procedure, **2c** (0.89 g, 3.1 mmol) was desulfurdimerized with $W(CO)_6$ (2.03 g, 5.7 mmol) in chlorobenzene (20 mL) for 30 h to afford, after columh chromatography (eluent: hexane–ethyl acetate, 4:1), a 1:1 mixture of (*Z*)- and (*E*)-**11c** (0.51 g, 84%): IR (KBr) ν 3020, 2930, 780 cm^{-1}; ^1H NMR δ 3.76 (s, 6 H), 3.78 (s, 6 H), 6.89 (dd, J = 2, 8 Hz, 4 H), 7.10 (m, 4 H), 7.25 (m, 4 H), 7.55 (m, 8 H), 7.95 (d, J = 2 Hz, 2 H, of *E* isomer, 16% NOE upon irradiation at δ 8.39), 8.05 (d, J = 2 Hz, 2 H, of *Z* isomer, no NOE upon irradiation at δ 8.30), 8.30 (d, J = 8 Hz, 2 H, of *Z* isomer), 8.39 (d, J = 8 Hz, 2 H, of *E* isomer); ^{13}C NMR δ 55.7, 111.6, 111.9, 116.0, 119.1, 119.2, 120.5, 125.8, 125.9, 126.4, 126.7, 129.3, 129.4, (C-1, C-1′, C-3 to C-8, C-3′ to C-8′), 134.8, 138.1, 138.3, 139.3, 141.4, 141.6 (C-9 to C-13, C-9′ to C-13′), 159.3 (C-2, C-2′); accurate mass calcd for $C_{28}H_{20}O_2$ 388.1463, found 388.1451.

(*E*)- and (*Z*)-2,2′-Dibromobifluorenylidene (11d). Via the general procedure, compound **2d** (0.78 g, 2.3 mmol) was desulfurdimerized with $W(CO)_6$ (1.73 g, 4.9 mmol) in chlorobenzene (30 mL) for 12 h to give, after recrystallization from benzene, a 1:1 mixture of (*Z*)- and (*E*)-2,2′-dibromo-9,9′-biflurenylidene (**11d**) (0.52 g, 93%): IR (KBr) ν 1610, 725, 415 cm^{-1}; ^1H NMR δ 7.20–7.70 (m, 20 H), 8.28 (d, J = 8 Hz, 2 H, of *E* isomer, 18% NOE upon irradiation at 8.48), 8.32 (d, J = 8 Hz, 2 H, or *Z* isomer, no NOE upon irradiation at 8.42), 8.42 (br s, 2 H, of *Z* isomer), 8.48 (br s, 2 H, of *E* isomer); ^{13}C NMR δ 120.1, 121.2, 126.7, 126.8, 127.4, 127.5, 129.3, 129.5, 129.8, 132.2 (C-1, C-1′, C-3 to C-8, C-3′ to C-8′ of *Z*/*E* isomers), 120.7 (C-2, C-2′), 137.7, 137.8, 139.6, 139.8, 140.2, 140.7, 140.9 (C-9 to C-13, C-9′ to C-13′ of *Z*/*E* isomers); accurate mass calcd for $C_{26}H_{14}{}^{79}Br_2$ 483.9461, $C_{26}H_{14}{}^{79}Br^{81}Br$ 485.9442, $C_{26}H_{14}{}^{81}Br_2$ 487.9421; found 483.9468, 485.9427, 487.9424.

9,9-(Ethylenedithio)fluorene-2-carboxylic Acid. A mixture of 9-fluorenone-2-carboxylic acid (5 g, 22.3 mmol), 1,2-ethanedithiol (2.5 mL, 29 mmol), and boron trifluoride etherate (1.0 mL) in acetic acid (150 mL) was refluxed overnight. After being cooled to room temperature, the solid was filtered and recrystallized from acetone to give the desired product as colorless solid (6.0 g, 90%): mp 257–259 °C; IR (KBr) ν 1695, 1620, 1430, 1310, 1270, 755, 740 cm^{-1}; m/z 300, 292, 240, 227; accurate mass calcd for $C_{16}H_{12}O_2S_2$ 300.0278, found 300.0236.

2-(Methoxycarbonyl)-9,9-(ethylenedithio)fluorene (2e). To a methanolic solution (10 mL) of 9,9-(ethylenedithio)-fluorene-2-carboxylic acid (0.5 g, 1.67 mmol) was added a few drops of concentrated sulfuric acid. The mixture was refluxed overnight. After being cooled to room temperature, the crystal was collected and recrystallized from chloroform to yield **2e** (0.46 g, 91%): mp 215–217 °C; IR (KBr) ν 3040, 2930, 1715, 1620, 1445, 1425, 1290, 1270, 1220, 750 cm^{-1}; ^1H NMR δ 8.32 (s, 1 H,), 8.09 (dd, J = 2, 8 Hz, 1 H), 7.27–7.77 (m, 5 H); 3.78 (m, 4 H), 3.90 (s, 3 H); m/z 314, 286. Anal. Calcd for $C_{17}H_{14}O_2S_2$: C, 64.94; H, 4.49. Found: C, 64.87; H, 4.36.

2,2′-Bis(methoxycarbonyl)bifluorenylidene (11e). A chlorobenzene solution (30 mL) of **2e** (314 mg, 1.0 mmol) and $W(CO)_6$ (0.70 g, 2 mmol) was refluxed for 36 h. After being cooled to room temperature, the mixture was filtered and the filter cake was washed with chloroform, and then was allowed to stand at room temperature overnight to crystallize the *Z* form of product (101 mg). Evaporation of mother liquid gave the residue, which contained a mixture of *Z* and *E* isomers (108 mg, 1:1); total yield (209 mg, 95% and the overall *Z*/*E* ratio is 2:1). Physical properties for *Z* isomer: mp >300 °C; IR (KBr) ν 3070, 1730, 1685, 1440, 1425, 1270, 760, 730 cm^{-1}; ^1H NMR δ 9.05 (s, 2 H), 8.35 (d, J = 8 Hz, 2 H), 8.06 (dd, J = 2, 8 Hz, 2 H), 7.76–7.80 (m, 4 H), 7.30–7.44 (m, 4 H), 3.90 (s, 6 H); accurate mass calcd for $C_{30}H_{20}O_4$ 444.1361, found 444.1360. The unambiguous stereochemical assignment for the *Z* isomer has been determined.[12] The ^1H NMR data for *E* isomer: δ 8.98 (s, 2 H), 8.43 (d, J = Hz, 2 H), 8.05 (dd, J = 2, 8 Hz, 2 H), 7.76–7.80 (m, 4 H), 7.30–7.44 (m, 4 H), 3.88 (s, 6 H).

General Procedure for the Synthesis of 2,2-Dimethylindan-1-one. A solution of 1-indanone (10 mmol) in dimethoxyethane (10 mL) was added dropwise to a slurry containing sodium hydride (80%, 0.90 g, 30 mmol) in dimethoxyethane (20 mL) under a nitrogen atmosphere. The mixture was stirred for 5 min, and methyl iodide (2 mL, 30 mmol) in dimethoxyethane (5 mL) was added over a period of 5–15 min. After being stirred for 15 min to 18 h, water (40 mL) was added and the mixture was extracted with ether. The combined organic solutions were washed with water, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was evaporated in vacuo. The residue was purified by chromatography on silica gel or by distillation to give the desired product.

General Procedure for the Synthesis of Hindered Dithioketal 19. A mixture of ketone (10 mmol), 1,2-ethanedithiol (2.8 mL, 15 mmol), and boron trifluoride etherate (0.5 mL, 3.5 mmol) was heated to 140 °C for 2 h. The reaction mixture was cooled to room temperature, diluted with chloroform, and poured into aqueous sodium hydroxide (40 mL, 10%). The organic layer was separated, and the aqueous solution was extracted with chloroform. The combined organic solutions were dried over anhydrous magnesium sulfate and filtered, and the filtrate was evaporated in vacuo to afford the residue, which was then chromatographed on silica gel to give the desired product.

2,2-Dimethyl-1,1-(ethylenedithio)indan (19a). According to the general procedure, a mixture of 2,2-dimethylindan-1-one (1.60 g, 10 mmol) and 1,2-ethanedithiol (2.8 mL, 15 mmol) with boron trifluoride etherate (0.5 mL) was heated to 140 °C for 2 h to give **19a** (1.60 g, 71%): bp 125 °C (0.2 mm, Kugelrohr); IR (neat) ν 3019, 2963, 2924, 2864, 1601, 1465, 1419, 1379, 1276, 744, 435 cm^{-1}; ^1H NMR δ 1.21 (s, 6 H), 2.78 (s, 2 H), 3.24–3.36 (m, 2 H), 3.36–3.48 (m, 2 H), 7.08–7.28 (m, 3 H), 7.48 (d, J = 8 Hz, 1 H); ^{13}C NMR δ 24.6, 40.2, 46.1, 50.1, 82.6, 124.3, 124.7, 126.9, 127.6, 140.5, 148.3; m/z 236, 208. Anal. Calcd for $C_{13}H_{16}S_2$: C, 66.05; H, 6.82. Found: C, 65.99; H, 6.92.

2,2-Dimethyl-5-methoxy-1,1-(ethylenedithio)indan (19b). A mixture of 2,2-dimethyl-5-methoxyindan-1-one (1.90 g, 10 mmol) and 1,2-ethanedithiol (2.8 mL, 15 mmol) with boron trifluoride etherate (0.5 mL) was allowed to react for 2 h according to the general procedure described above. After workup, the mixture was chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to give **19b** (2.20 g, 83%): mp 49–50 °C; IR (KBr) ν 3005, 2930, 1588, 1482, 1441, 1376, 1358, 1313, 1270, 1142, 1109, 1085, 1026, 842, 789, 709 cm^{-1}; ^1H NMR δ 1.20 (s, 6 H), 2.73 (s, 2 H), 3.22–3.34 (m, 2 H), 3.34–3.48 (m, 2 H), 3.80 (s, 3 H), 6.68 (s, 1 H), 6.76 (d, J = 8 Hz, 1 H), 7.40 (d, J = 8 Hz, 1 H); ^{13}C NMR δ 24.7, 40.2, 46.3, 50.5, 55.5, 82.3, 110.1, 112.9, 125.2, 140.3, 142.1, 159.8; m/z 266, 238. Anal. Calcd for $C_{14}H_{18}OS_2$: C, 63.12; H, 6.81. Found: C, 63.12; H, 6.96.

2,2-Dimethyl-6-methoxy-1,1-(ethylenedithio)indan (19c). In accordance with the general procedure, a mixture of 6-methoxy-2,2-dimethylindan-1-one (1.90 g, 10 mmol), 1,2-ethanedithiol

(23) Lemmen, P.; Lenoir, D. *Chem. Ber.* **1984**, *117*, 2300.
(24) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krespki, L. R. *J. Org. Chem.* **1978**, *43*, 3255.
(25) Geluk, H. W. *Synthesis* **1970**, 652.
(26) Brand, K. *Ber.* **1921**, *54*, 1987.
(27) Suzuki, K.; Minabe, M.; Fujimoto, M.; Nohara, N. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1609.

(2.8 mL, 15 mmol), and boron trifluoride etherate (0.5 mL) was heated to 140 °C for 2 h to yield **19c** (2.60 g, 98%): bp 144 °C (0.2 mm, Kugelrohr); IR (neat) ν 3080, 2960, 1606, 1450, 1398, 1370, 1320, 1270, 1240, 1182, 1150, 1090, 1034, 850, 800, 750 cm^{-1}; ^1H NMR δ 1.23 (s, 6 H), 2.77 (s, 2 H), 3.24–3.36 (m, 2 H), 3.26–3.48 (m, 2 H), 3.87 (s, 3 H), 6.72 (dd, J = 2, 8 Hz, 1 H), 7.02 (d, J = 8 Hz, 1 H), 7.04 (s, 1 H); ^{13}C NMR δ 24.6, 40.2, 45.3, 50.6, 55.5, 82.8, 108.8, 114.0, 125.3, 132.6, 149.7, 159.3; m/z 266, 238. Anal. Calcd for $C_{14}H_{18}OS_2$: C, 63.12; H, 6.81. Found: C, 63.02; H, 6.96.

2,2,5-Trimethyl-1,1-(ethylenedithio)indan (19d). According to the general procedure, a mixture of 2,2,5-trimethylindan-1-one (1.74 g, 10 mmol) and 1,2-ethanedithiol (2.8 mL, 15 mmol) with boron trifluoride etherate (0.5 mL) was heated to 140 °C for 2 h. After workup, the crude product was distilled to give **19d** (2.15 g, 86%): bp 132 °C (0.2 mm, Kugelrohr); IR (neat) ν 3005, 2963, 2922, 2863, 2837, 1464, 1359, 1275, 814, 789 cm^{-1}; ^1H NMR δ 1.24 (s, 6 H), 2.32 (s, 3 H), 2.76 (s, 2 H), 3.24–3.36 (m, 2 H), 3.36–3.48 (m, 2 H), 6.96 (s, 1 H), 7.02 (d, J = 8 Hz, 1 H), 7.36 (d, J = 8 Hz, 1 H); ^{13}C NMR δ 21.3, 24.7, 40.2, 46.0, 50.2, 82.0, 124.1, 125.3, 127.7, 137.4, 140.6, 145.5. Anal. Calcd for $C_{14}H_{18}S_2$: C, 67.15; H, 7.19. Found: C, 66.78; H, 7.31.

2,2,6-Trimethyl-1,1-(ethylenedithio)indan (19e). By using the general procedure, a mixture of 2,2,6-trimethylindan-1-one (1.74 g, 10 mmol) and 1,2-ethanedithiol (2.80 mL, 15 mmol) with boron trifluoride etherate (0.5 mL) was treated at 140 °C for 2 h to yield **19e** (1.65 g, 66%); bp 135 °C (0.2 mm, Kugelrohr); IR (neat) ν 3017, 2962, 2922, 2863, 2837, 1488, 1455, 1378, 1359, 1276, 794 cm^{-1}; ^1H NMR δ 1.24 (s, 6H), 2.35 (s, 3H), 2.76 (s, 2H), 3.24–3.36 (m, 2H), 3.36–3.48 (m, 2H), 6.98 (d, J = 8 Hz, 1H), 7.02 (d, J = 8 Hz, 1H), 7.30 (br s, 1H); ^{13}C NMR δ 21.4, 24.6, 40.3, 45.7, 50.3, 82.6, 124.4, 124.8, 128.6, 136.5, 137.6, 148.2. Anal. Calcd for $C_{14}H_{18}S_2$: C, 67.15, H, 7.19. Found: C, 66.95, H, 7.25.

5-Cyano-2,2-dimethyl-1,1-(ethylenedithio)indan (19f). According to the general procedure, a mixture of 5-cyano-2,2-dimethylindan-1-one (1.85 g, 10 mmol) and 1,2-ethanedithiol (2.8 mL, 15 mmol) with boron trifluoride etherate (0.5 mL) was treated at 140 °C for 2 h to give the crude product, which was recrystallized from ethanol to afford **19f** (2.30 g, 92%): mp 93–95 °C; IR (KBr) ν 3000, 2961, 2226, 1605, 1463, 1381, 1364, 1294, 1278, 1245, 1183, 1105, 974, 927, 878, 866, 791, 739, 712 cm^{-1}; ^1H NMR δ 1.21 (s, 6 H), 2.80 (s, 2 H), 3.28–3.47 (m, 4 H), 7.42 (s, 1 H), 7.51 (d, J = 8 Hz, 1 H), 7.57 (d, J = 8 Hz, 1 H); ^{13}C NMR δ 24.2, 20.4, 45.4, 50.0, 81.7, 111.1, 119.1, 125.0, 128.3, 131.2, 141.5, 154.0. Anal. Calcd for $C_{14}H_{15}NS_2$: C, 64.33, H, 5.78, N, 5.36; found: C, 64.22, H, 5.39, N, 5.18.

2,2-Dimethyl-1,1-(ethylenedithio)tetralin (19g). By using the method described in the general procedure, a mixture of 2,2-dimethyltetralone (1.74 g, 10 mmol) and 1,2-ethanedithiol (2.8 mL, 15 mmol) with boron trifluoride etherate (0.5 mL) was heated to 140 °C for 2 h to give **19g** (1.90 g, 77%): mp 76–77 °C; IR (KBr) ν 3020, 2855, 1933, 1600, 1427, 1378, 1354, 1278, 1240, 1154, 1101, 1016, 946, 899, 845, 762, 728 cm^{-1}; ^1H NMR δ 1.20 (s, 6 H), 1.93 (t, J = 6 Hz, 2 H), 2.83 (t, J = 6 Hz, 2 H), 3.32–3.44 (m, 2 H), 3.44–3.56 (m, 2 H), 6.98 (d, J = 8 Hz, 1 H), 7.06–7.22 (m, 2 H), 7.92 (d, J = 8 Hz, 1 H); ^{13}C NMR δ 25.4, 26.0, 35.9, 40.0, 42.5, 80.0, 126.0, 126.5, 128.4, 130.3, 134.5, 142.7; m/z 250, 166. Calcd for $C_{14}H_{18}S_2$: C, 67.15; H, 7.19. Found: C, 67.12; H, 7.19.

4-Bromo-2,2-dimethyltetralone. A mixture of 2,2-dimethyltetralone (1.80 g, 0.01 mol), *N*-bromosuccimide (1.80 g, 0.01 mol), and AIBN (0.1 g) in carbon tetrachloride (30 mL) was refluxed for 3 h and then cooled to room temperature. After filtration, the filtrate was washed with sodium thiosulfate (20%, 50 mL) and water (50 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was evaporated in vacuo to give the oil, which was then chromatographed on silica gel and eluted with hexane–ethyl acetate (15:1) to yield 4-bromo-2,2-dimethyltetralone (2.00 g, 79%): IR (neat) ν 3070, 3033, 2934, 1699, 1603, 1472, 1455, 1385, 1330, 1300, 1202, 1184, 1160, 1125, 1097, 1012, 992, 969, 947, 808, 795, 741 cm^{-1}; ^1H NMR δ 1.23 (s, 3 H), 1.33 (s, 3 H), 2.70 (d, J = 8 Hz, 2 H), 5.80 (t, J = 8 Hz, 1 H), 7.07–7.77 (m, 3 H), 8.03 (dd, J = 2, 8 Hz, 1 H). This product was used for the next operation without further purification.

2,2-Dimethyl-1,2-dihydronaphthalen-1-one. A mixture of 4-bromo-2,2-dimethyltetralone (1.50 g, 6 mmol) and potassium *tert*-butoxide (2.00 g, 18 mmol) in *tert*-butyl alcohol (25 mL) was refluxed for 1 h. The mixture was poured into water (30 mL) and was extracted with ether. The combined organic solutions were washed with water, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was evaporated in vacuo to afford the residue which was purified by chromatography on silica gel and eluted with hexane–ethyl acetate (15:1) to yield 2,2-dimethyl-1,2-dihydronaphthalen-1-one (1.00 g, 99%): bp 86 °C (0.2 mm); IR (neat) ν 3064, 3032, 2968, 2929, 1671, 1646, 1599, 1469, 1453, 1370, 1306, 1235, 1217, 1191, 989, 969, 880, 791, 718 cm^{-1}; ^1H NMR δ 1.20 (s, 6 H), 6.32 (d, J = 10 Hz, 1 H), 6.58 (d, J = 10 Hz, 1 H), 7.70–7.77 (m, 3 H), 8.05 (dd, J = 2, 8 Hz, 1 H); accurate mass calcd for $C_{12}H_{12}O$ 172.0888, found 172.0878.

2,2-Dimethyl-1,2-dihydronaphthalene-1-thione (36). A mixture of 2,2-dimethyl-1,2-dihydronaphthalen-1-one (0.50 g, 2.91 mmol) and phosphorous pentasulfide (0.20 g, 0.90 mmol) in pyridine (25 mL) was heated to 90 °C overnight. The reaction mixture was poured into hydrochloric acid (10%, 40 mL) and was extracted with hexane. The combined organic solutions were washed with water, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was evaporated in vacuo to give the blue oil, which was then chromatographed on silica gel and eluted with hexane to afford **36** (0.50 g, 91%): bp 96 °C (0.2 mm, Kugelrohr); IR (neat) ν 3067, 3038, 2973, 2871, 1677, 1647, 1602, 1578, 1478, 1466, 1315, 1289, 1256, 1159, 1097, 910, 792, 734 cm^{-1}; ^1H NMR δ 1.20 (s, 6 H), 6.32 (d, J = 10 Hz, 1 H), 6.58 (d, J = 10 Hz, 1 H), 7.00–7.73 (m, 3 H), 8.40 (dd, J = 1, 8 Hz, 1 H); ^{13}C NMR δ 32.0, 54.1, 123.3, 126.5, 127.3, 127.9, 129.8, 132.0, 134.0, 144.6, 247.6; accurate mass calcd for $C_{12}H_{12}S$ 188.0660, found 188.0639.

General Procedure for the Reaction of 19 with $W(CO)_6$. Dithioketal (1.00 mmol) and $W(CO)_6$ (530 mg, 1.50 mmol) were dissolved in chlorobenzene (5 mL). The solution was heated to 160 °C under nitrogen atmosphere for 8–24 h. After being cooled to room temperature, chlorobenzene was removed by vacuum distillation. The blackish residue was then taken up in chloroform. After filtration, the filtrate was evaporated in vacuo and the residue was chromatographed on silica gel and the product(s) was (were) subjected to spectroscopic and/or elementary analysis.

Reaction of 2,2-Dimethyl-1,1-(ethylenedithio)indan (19a) with $W(CO)_6$. According to the general procedure, a mixture of **19a** (236 mg, 1.00 mmol) and $W(CO)_6$ (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was treated for 18 h. After workup, the mixture was chromatographed on silica gel and eluted with hexane to yield **22a**[28] (14.1 mg, 10%): ^1H NMR δ 2.03 (s, 6 H), 3.27 (s, 2 H), 6.90–7.55 (m, 4 H). **21a** (44.4 mg, 31%): mp 127–129 °C (lit.[22] mp 129–130 °C); m/z 288, 271; ^1H NMR δ 1.33 (s, 12 H), 2.80 (s, 4 H), 7.12–7.24 (m, 6 H), 7.48–7.56 (m, 2 H); ^{13}C NMR δ 27.7, 50.7, 52.3, 124.2, 124.9, 127.2, 128.0, 143.0, 145.3, 146.1. Anal. Calcd for $C_{22}H_{24}$: C, 91.96; H, 8.39. Found: C, 91.51; H, 8.42. **20a** (52.8 mg, 30%): bp 80 °C (0.2 mm, Kugelrohr); IR (neat) ν 3070, 2963, 2864, 1601, 1578, 1464, 1433, 1378, 1322, 1291, 1265, 1150, 1119, 1101, 1078, 1016, 971, 770, 715 cm^{-1}; ^1H NMR δ 1.33 (s, 6 H), 3.13 (s, 2 H), 7.36 (t, J = 8 Hz, 1 H), 7.48 (d, J = 8 Hz, 1 H), 7.64 (t, J = 8 Hz, 1 H), 7.94 (d, J = 8 Hz, 1 H); ^{13}C NMR δ 29.7, 46.8, 56.8, 125.2, 126.2, 127.7, 134.7, 145.4, 152.2, 254.7. Anal. Calcd for $C_{11}H_{12}S$: C, 74.95; H, 6.86. Found: C, 74.18; H, 6.70.

Reaction of 2,2-Dimethyl-5-methoxy-1,1-(ethylenedithio)indan (19b) with $W(CO)_6$. By employing the general procedure, a mixture of **19b** (266 mg, 1.00 mmol) and $W(CO)_6$ (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was refluxed for 24 h. After usual workup, the mixture was chromatographed on silica gel and eluted with hexane to give **20b** (53.9 mg, 26%): bp 116 °C (0.2 mm, Kugelrohr); IR (neat) ν 3057, 3006, 2963, 2927, 1610, 1577, 1486, 1464, 1429, 1379, 1357, 1336, 1313, 1282, 1170, 1026, 985, 862, 819, 761 cm^{-1}; ^1H NMR δ 1.38 (s, 6 H), 3.04 (s, 2 H), 3.83 (s, 3 H), 7.23 (dd, J = 3, 8 Hz, 1 H), 7.33 (d, J = 8 Hz, 1 H), 7.36 (d, J = 3 Hz, 1 H); ^{13}C NMR δ 29.8, 46.3, 55.7, 57.5, 106.5, 124.5, 127.0, 145.4, 146.5, 160.0, 254.3; accurate mass calcd for $C_{12}H_{14}OS$ 206.0765, found 206.0762.

Reaction of 2,2-Dimethyl-6-methoxy-1,1-(ethylenedithio)indan (19c) with $W(CO)_6$. By using the general procedure, **19c** (266 mg, 1.00 mmol) and $W(CO)_6$ (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) were refluxed for 8 h. After workup, the mixture was chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to afford **20c** (74.8 mg, 36%) as purple

(28) Buddrus, J. *Chem. Ber.* **1968**, *101*, 4152.

oil: bp 110 °C (0.2 mm, Kugelrohr); IR (neat) ν 3050, 2926, 2840, 1605, 1485, 1443, 1322, 1264, 1249, 1197, 1176, 1139, 1078, 1024, 881, 867, 825, 761, 736 cm^{-1}; ^1H NMR δ 1.32 (s, 6 H), 3.05 (s, 2 H), 3.87 (s, 3 H), 6.83–6.87 (m, 2 H), 7.87 (d, J = 9 Hz, 1 H); ^{13}C NMR δ 29.6, 48.8, 55.7, 56.3, 108.8, 116.0, 127.1, 139.8, 155.3, 166.0, 250.6; accurate mass calcd for $C_{12}H_{14}OS$ 206.0765, found 206.0768.

Reaction of 2,2,5-Trimethyl-1,1-(ethylenedithio)indan (19d) with $W(CO)_6$. A solution of **19d** (250 mg, 1.00 mmol) and $W(CO)_6$ (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was treated according to the general procedure for 8 h. After workup, the mixture was chromatographed on silica gel and eluted with hexane to yield **20d** (72.2 mg, 38%) as red oil: bp 100 °C (0.2 mm, Kugelrohr); IR (neat) ν 3040, 2962, 2864, 1607, 1576, 1465, 1434, 1379, 1358, 1312, 1292, 1264, 1248, 1177, 1129, 1085, 1034, 973, 932, 822, 743 cm^{-1}; ^1H NMR δ 1.33 (s, 6 H), 2.37 (s, 3 H), 3.04 (s, 2 H), 7.14 (d, J = 8 Hz, 1 H), 7.23 (s, 1 H), 7.84 (d, J = 8 Hz, 1 H); ^{13}C NMR δ 22.1, 29.7, 46.6, 56.6, 125.1, 126.4, 128.7, 129.1, 146.2, 152.6, 254.9; accurate mass calcd for $C_{12}H_{14}S$ 190.0816, found 190.0812.

Reaction of 2,2,6-Trimethyl-1,1-(ethylenedithio)indan (19e) with $W(CO)_6$. According to the general procedure, a mixture of **19e** (250 mg, 1.00 mmol) and $W(CO)_6$ (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was allowed to react for 18 h. After workup, the mixture was chromatographed on silica gel and eluted with hexane to afford **20e** (79.8 mg, 42%) as purple oil: bp 96 °C (0.2 mm, Kugelrohr); IR (neat) ν 3029, 2964, 2924, 2865, 1614, 1574, 1487, 1464, 1437, 1419, 1380, 1357, 1413, 1279, 1265, 1224, 1190, 1167, 1097, 1074, 1033, 973, 893, 812, 756 cm^{-1}; ^1H NMR δ 1.33 (s, 6 H), 2.40 (s, 3 H), 3.07 (s, 2 H), 7.32 (d, J = 8 Hz, 1 H), 7.43 (d, J = 8 Hz, 1 H), 7.75 (s, 1 H); ^{13}C NMR δ 20.9, 29.7, 46.4, 56.9, 125.0, 125.8, 136.1, 137.6, 145.4, 149.5, 254.5; accurate mass calcd for $C_{12}H_{14}S$ 190.0816, found 190.0825.

Reaction of 2,2-Dimethyl-1,1-(ethylenedithio)tetralin (19g) with $W(CO)_6$. Via the general procedure, a mixture of **19g** (250 mg, 1.00 mmol) and $W(CO)_6$ (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was refluxed for 24 h. After workup, the mixture was chromatographed on silica gel and eluted with hexane–ethyl acetate (20:1) which gave **21g** (23.7 mg, 15%): mp 194–196 °C (lit.[23] mp 195 °C); ^1H NMR δ 0.64 (s, 6 H), 1.06 (s, 6 H), 1.53–2.80 (m, 8 H), 7.00–7.20 (m, 8 H). **20g** (15.8 mg, 9%): ^1H NMR δ 1.37 (s, 6 H), 1.97 (t, J = 6 Hz, 2 H), 3.00 (t, J = 6 Hz, 2 H), 6.18 (t, J = 8 Hz, 1 H), 7.26 (d, J = 8 Hz, 1 H), 7.47 (t, J = 8 Hz, 1 H), 8.35 (d, J = 8 Hz, 1 H); ^{13}C NMR δ 26.5, 29.6, 36.7, 49.5, 126.6, 128.9, 130.7, 132.8, 137.0, 139.3, 250.0; accurate mass calcd for $C_{12}H_{14}S$ 190.0816, found 190.0822.

Reaction of 2,2-Dimethylindan-1-thione (20a) with $W(CO)_6$. Via the same procedure as described above, a mixture of **20a** (300 mg, 1.70 mmol) and $W(CO)_6$ (897 mg, 2.55 mmol) in chlorobenzene (5.0 mL) was treated for 24 h. After workup, the residue was chromatographed on silica gel and eluted with hexane to give **21a** (60.0 mg, 24%) and **20a** (195 mg, 65%), which exhibited same physical properties as those of the authentic samples.

In a separate run, a mixture of **20a** (264 mg, 1.50 mmol) and $W(CO)_6$ (792 mg, 2.25 mmol) in chlorobenzene (5.0 mL) was treated in the same manner as described above for 72 h to give **22a** (74.3 mg, 34%) and **21a** (41.0 mg, 19%).

Reaction of 2,2-Dimethyl-1,2-dihydronaphthalene-1-thione (36) with $W(CO)_6$. A chlorobenzene solution (5 mL) of **36** (190 mg, 1.00 mmol) and $W(CO)_6$ (528 mg, 1.50 mmol) was allowed to react for 24 h according to the general procedure. After workup, the residue was chromatographed on silica gel and eluted with hexane to afford 1,2-dimethylnaphthalene (70.2 mg, 45%): ^1H NMR δ 2.47 (s, 3 H), 2.57 (s, 3 H), 7.07–8.07 (m, 6 H).[29]

Reaction of 2,2-Diphenyl-1,3-oxathiolane (24) with $W(CO)_6$. According to the general procedure, a mixture of **24** (242 mg, 1.00 mmol) and $W(CO)_6$ (528 mg, 1.50 mmol) in chlorobenzene (5.0 mL) was refluxed 24 h. After workup, the crude product was chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to afford benzophenone (**25**) (180 mg, 99%), which showed the same physical properties as the authentic sample.

Ethene Determination from the Reaction of 19a with $W(CO)_6$. A mixture of **19a** (760.1 mg, 3.22 mmol) and $W(CO)_6$ (1700 mg, 4.83 mmol) in chlorobenzene (15 mL) was flushed with nitrogen and then heated to 160 °C for 24 h. The outlet of the reaction flask was connected to a tube dipped into a carbon tetrachloride solution (100 mL) containing bromine (1 mL). The reaction mixture was allowed to cool to room temperature, and the carbon tetrachloride solution was washed with sodium thiosulfate (20%, 100 mL), dried over anhydrous magnesium sulfate, and filtered, and the filtrate was diluted to 100 mL in a volumetric flask. Three standard dibromoethane solutions in carbon tetrachloride with different concentrations (0.0144, 0.0298, and 0.0577M) were prepared for calibration purpose. The samples were subjected to the NMR analyses, and the yield of dibromoethane was estimated to be 92%.

Ethene Determination from the Reaction of 2,2-Diphenyl-1,3-oxathiolane (24) with $W(CO)_6$. According to the procedure describe above, a mixture of **24** (972.4 mg, 4.00 mmol) and $W(CO)_6$ (1400 mg, 4.00 mmol) in chlorobenzene (20 mL) was refluxed for 24 h. The outlet of the reaction flask was connected to a tube dipped into a carbon tetrachloride solution (100 mL) containing bromine (1 mL). After workup, the carbon tetrachloride solution was diluted to 100 mL in a volumetric flask and subjected to the NMR analysis in the same manner as described above. The yield of dibromoethane was estimated to be 62%.

2,2-Dimethylindan-1-thiol. Under nitrogen atmosphere, a solution of **20a** (3.50 g, 0.02 mol) in THF (5 mL) was added dropwise to a slurry containing lithium aluminum hydride (0.8 g, 0.021 mol) in THF (20 mL). The mixture was stirred for 0.5 h, water (30 mL) was added, and the mixture was extracted with ether. The combined organic solutions were washed with water, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was evaporated in vacuo. The crude product was distilled to yield 2,2-dimethylindan-1-thiol (3.40 g, 96%): bp 74 °C (0.2 mm, Kugelrohr); IR (neat) ν 3073, 3028, 2901, 2843, 1956, 1609, 1589, 1467, 1384, 1366, 1297, 1266, 1234, 1208, 1764, 1107, 1022, 940, 929, 760, 735 cm^{-1}; ^1H NMR δ 1.03 (s, 3 H), 1.20 (s, 3 H), 1.47 (d, J = 8 Hz, 1 H), 2.73 (br, 2 H), 4.00 (d, J = 8 Hz, 1 H), 7.07–7.43 (m, 4 H); ^{13}C NMR δ 23.6, 26.9, 44.9, 45.9, 54.4, 124.5, 124.7, 126.6, 127.2, 141.6, 145.4. This compound was used for the next operation without further purification.

2,2-Dimethylindan-1-yl 2-Bromoethyl Sulfide (32). A solution of 2,2-dimethylindan-1-thiol (1.00 g, 5.70 mmol) in dimethoxyethane (10 mL) was added dropwise to a slurry containing sodium hydride (80%, 0.30 g, 10 mmol) in dimethoxyethane (20 mL) under nitrogen atmosphere. The mixture was stirred for 10 min and was syringed to dibromoethane (5 mL, 5.8 mmol) in dimethoxyethane (10 mL) over a period of 15 min. After the mixture was stirred for 30 min, water (40 mL) was added, and the mixture was extracted with ether. The combined organic solutions were washed with water, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was evaporated in vacuo. Dibromoethane was removed by vacuum distillation to give the residue, which was chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to yield 2,2-dimethylindan-1-yl 2-bromoethyl sulfide (1.00 g, 69%): IR (neat) ν 3073, 3027, 2961, 2869, 1608, 1437, 1383, 1365, 1299, 1256, 1231, 1189, 1106, 1022, 938, 899, 792, 732, 609 cm^{-1}; ^1H NMR δ 1.10 (s, 3 H), 1.20 (s, 3 H), 2.77 (m, 2 H), 2.80–3.17 (m, 2 H), 3.27–3.63 (m, 2 H), 3.83 (s, 1 H), 7.07–7.47 (m, 4 H); ^{13}C NMR δ 24.1, 28.0, 30.4, 34.6, 45.4, 46.3, 61.5, 124.9, 126.4, 127.5, 142.1, 143.5. This product was used directly for the next operations without further purification.

2,2-Dimethylindan-1-yl 2-Thiophenoxyethyl Sulfide (26). Under a nitrogen atmosphere a solution of thiophenol (1.0 mL, 9.10 mmol) in dimethoxyethane (10 mL) was added dropwise to a slurry containing sodium hydride (80%, 0.30 g, 10 mmol) in dimethoxyethane (20 mL). The mixture was stirred for 5 min, and **32** (1.0 g, 3.50 mmol) in dimethoxyethane (5 mL) was added over a period of 15 min. After the mixture was stirred for 1 h, water (40 mL) was added, and the mixture was washed with sodium hydroxide (10%, 50 mL). The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were dried over anhydrous magnesium sulfate and filtered, and the filtrate was evaporated in vacuo to give the residue which was chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to yield **26** (1.00 g, 91%): bp 170 °C (0.2 mm, Kugelrohr); IR (neat) ν 3069, 3020, 2956, 2927, 2864, 1585, 1477, 1461, 1439, 1363, 1196, 1025, 736, 690 cm^{-1}; ^1H

(29) Yew, F. F.-H.; Kurland, R. J.; Mair, B. J. *Anal. Chem.* **1964**, *36*, 843.

NMR δ 1.10 (s, 3 H), 1.17 (s, 3 H), 2.53–2.90 (m, 4 H), 2.93–3.27 (m, 2 H), 3.80 (s, 1 H), 7.03–7.50 (m, 9 H); ^{13}C NMR δ 24.3, 28.2, 32.1, 34.8, 45.4, 46.5, 61.4, 124.9, 125.1, 126.5, 126.6, 127.4, 129.1, 130.3, 135.7, 142.3, 143.9; accurate mass calcd for $C_{19}H_{22}S_2$ 314.1163, found 314.1161.

2,2-Dimethylindan-1-yl Vinyl Sulfide (31). A mixture of **32** (103 mg, 0.36 mmol) and *tert*-butoxide (120 mg, 1.08 mmol) in *tert*-butyl alcohol (5 mL) was refluxed for 24 h. The mixture was poured into water (10 mL) and extracted with ether. The combined organic solutions were washed with water, dried over anhydrous magnesium sulfate, and filtered, and the filtrate was evaporated in vacuo to afford the residue, which was purified by chromatography on silica gel and eluted with hexane–ethyl acetate (20:1) to yield **31** as colorless oil (45.3 mg, 62%): ^{1}H NMR δ 1.09 (s, 3 H), 1.25 (s, 3 H), 2.74 (s, 2 H), 4.09 (s, 1 H), 5.14 (d, J = 10 Hz, 1 H), 5.26 (d, J = 16 Hz, 1 H), 6.38 (dd, J = 10, 16 Hz, 1 H), 7.03–7.46 (m, 4 H). Compound **31** decomposed gradually in chloroform solution.

Reaction of *tert*-Butyl Adamantane-1-peroxycarboxylate (27) with 26. Under a nitrogen atmosphere, a mixture of **26** (326 mg, 1.04 mmol) and **27** (252 mg, 1.00 mmol) in chlorobenzene (5 mL) was refluxed for 24 h. After the mixture was cooled to room temperature, chlorobenzene was removed by vacuum distillation. The residue was then chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to give 2,2-dimethylindan-1-one (**28**) (65.6 mg, 42%) and a brown oil, which was further chromatographed on silica gel and eluted with hexane to yield diphenyl disulfide (**29**) (74.1 mg, 34%), mp 53–55 °C (lit.[30] 58–60 °C); 2,2-dimethylindan-1-yl vinyl sulfide (**31**) (16.3 mg, 8%), which exhibited same physical properties as those of the authentic sample; phenyl vinyl sulfide (**30**) (4.1 mg, 3%), ^{1}H NMR δ 5.34 (d, J = 16 Hz, 1 H), 5.35 (d, J = 10 Hz, 1 H), 6.54 (dd, J = 10, 16 Hz, 1 H), 6.90–7.50 (m, 5 H);[31] and a trace amount of **20a**. Starting material **26** (115 mg, 35%) was also recovered.

Reaction of 27 with 2,2-Dimethylindan-1-thione (20a). A mixture of **20a** (210 mg, 1.17 mmol) and **27** (295 mg, 1.17 mmol) in chlorobenzene (5 mL) was refluxed for 24 h under a nitrogen atmosphere. After the mixture was cooled to room temperature, chlorobenzene was removed by vacuum distillation. The residue was then chromatographed on silica gel and eluted with hexane–ethyl acetate (10:1) to afford 2,2-dimethylindan-1-thione (70 mg, 33%) and 2,2-dimethylindan-1-one (121 mg, 65%), which exhibited the same physical properties as those of the authentic samples.

Acknowledgment. We thank the Croucher Foundation of Hong Kong and the National Science Council of Republic of China for support. L.L.Y. thanks the Croucher Foundation for a studentship.

Registry No. **1**, 6317-10-8; **2**, 7049-31-2; **2b**, 113425-39-1; **2c**, 113425-38-0; **2d**, 113425-37-9; **2e**, 124688-04-6; **3**, 5769-02-8; **4**, 172-16-7; **5**, 124688-02-4; **6**, 42196-84-9; **7**, 5616-55-7; **8**, 19557-70-1; **9**, 41563-48-8; **10**, 632-51-9; **11a**, 746-47-4; **11b**, 27192-91-2; (*Z*)-**11c**, 113425-41-5; (*E*)-**11c**, 113425-42-6; (*Z*)-**11d**, 113425-40-4; (*E*)-**11d**, 113469-17-3; (*Z*)-**11e**, 118477-00-2; (*E*)-**11e**, 124688-05-7; (*E*)-**12**, 782-06-9; (*Z*)-**12**, 782-05-8; **13**, 24536-68-3; **14**, 124688-03-5; **15**, 91590-50-0; **16**, 103-30-0; **17**, 30541-56-1; **18**, 1483-68-7; **19a**, 124688-10-4; **19b**, 124688-11-5; **19c**, 124688-12-6; **19d**, 124688-13-7; **19e**, 124688-14-8; **19f**, 124688-15-9; **19g**, 120932-59-4; **20a**, 100991-60-4; **20b**, 124688-19-3; **20c**, 124688-20-6; **20d**, 124688-21-7; **20e**, 124688-22-8; **20g**, 124688-28-4; **21a**, 124688-18-2; **21g**, 124688-23-9; **22a**, 4773-82-4; **24**, 33735-40-9; **25**, 119-61-9; **26**, 124688-26-2; **28**, 10489-28-8; **29**, 882-33-7; **31**, 124688-27-3; **32**, 124688-25-1; **36**, 124688-17-1; $W(CO)_6$, 14040-11-0; 9-fluorenone-2-carboxylic acid, 784-50-9; 9,9-(ethylenedithio)-fluorene-2-carboxylic acid, 118476-91-8; 2,2-dimethylindan-1-one, 10489-28-8; 2,2-dimethyl-5-methoxyindan-1-one, 124688-06-8; 2,2-dimethyl-6-methoxyindan-1-one, 124688-07-9; 2,2,5-trimethylindan-1-one, 124688-08-0; 2,2,6-trimethylindan-1-one, 57145-24-1; 5-cyano-2,2-dimethylindan-1-one, 124688-09-1; 2,2-dimethyl-1-tetralone, 2977-45-9; 4-bromo-2,2-dimethyl-1-tetralone, 124688-16-0; 2,2-dimethyl-1,2-dihydronaphthalen-1-one, 16020-15-8; 1,2-dimethylnaphthalene, 573-98-8; 2,2-dimethylindan-1-thiol, 124688-24-0.

Supplementary Material Available: 250-MHz ^{1}H NMR spectra of thiones **20a–e** and **20g** (6 pages). Ordering information is given on any current masthead page.

(30) Boykin, D. W. *J. Org. Chem.* **1979**, *44*, 424.
(31) Cookson, R. C.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1976**, 990.

(*Z*)-2,2′-Disubstituted Bifluorenylidenes by Intramolecular Desulfurdimerization Reactions[1]

Yu Chi Yip,[2a] Xiao-jun Wang,[2a,3a] Dennis K. P. Ng,[2a,3b] Thomas C. W. Mak,[2a,4] Ping Chiang,[2b] and Tien-Yau Luh*[,2a-c]

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, and Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

Received July 18, 1989

$W(CO)_6$-mediated intramolecular desulfurdimerization reactions have been used in the syntheses of bridged 2,2′-disubstituted bifluorenylidenes in satisfactory yields. Ring sizes from 12 to 24 can be synthesized by this reaction. The extension of this reaction for the synthesis of bifluorenylidene-hinged crown ethers is described. The X-ray structure of **6i** has been determined. The two fluorenylidene moieties are each planar, making a dihedral angle of 44.9°. The first optically active bifluorenylidenes were unequivocally synthesized, and the barriers for the racemization of two such molecules have been determined (12 kcal/mol). The racemization process may arise from the pyramidalization at C_9 and/or $C_{9'}$ followed by rapid twisting along the C_9–$C_{9'}$ bond.

Bifluorenylidene **1** is nonplanar with a twist angle about the C_9–$C_{9'}$ double bond of 43°.[5-7] Accordingly, **1** can be chiral and, indeed, was accidentally obtained in optically pure form, but the absolute configuration is yet unknown.[7] Various attempts to resolve bifluorenylidenes into enantiomeric pure forms have been unsuccessful.[8,9] The

(1) Part 29 of the series "Transition Metal Promoted Reactions".
(2) (a) The Chinese University of Hong Kong. (b) National Taiwan University. (c) To whom correspondence should be addressed at NTU.
(3) (a) On leave from the Institute of Chemistry, Academia Sinica, Beijing. (b) Recipient of the Croucher Foundation studentship, 1988–90.
(4) To whom correspondence should be addressed concerning the X-ray structure of **6i**.
(5) (a) Bailey, N. A.; Hull, S. E. *Acta Crystallogr.* **1978**, *B34*, 3289. (b) Bailey, N. A.; Hull, S. E. *J. Chem. Soc., Chem. Commun.* **1971**, 960.
(6) Costain, C. C.; Stoicheff, B. P. *J. Chem. Phys.* **1959**, *30*, 777.
(7) Nyburg, S. C.; Lee, J. S. *Acta Crystallogr.* **1985**, *C41*, 560.

0022-3263/90/1955-1881$02.50/0