tion for the Grant-in-Aid for Scientific Research (No. 60750803) for support of this work. We also thank Dr. K. Hirotsu, Osaka City University for X-ray analysis of the spiro compound.

**Registry No.** **2**, 109704-12-3; **3**, 109735-36-6; **4**, 113924-34-8; **5**, 108967-79-9; **6**, 92898-23-2; **7**, 91969-81-2; **8**, 109704-11-2; **9**, 76327-74-7; **10a**, 113893-91-7; **10b**, 113893-92-8; **11a**, 113924-35-9; **11b**, 113924-36-0; **14**, 113924-37-1; **15**, 113893-93-9; **16**, 113893-94-0; **17**, 113893-95-1; **18**, 113893-96-2; **19**, 113974-17-7; **20**, 113893-97-3; **21**, 113893-98-4; **22**, 113893-99-5; **23**, 113894-00-1; **24**, 113924-38-2; **25**, 113894-01-2; **26**, 113894-02-3; $CH_2{=}CR_1R_2$ ($R_1$ = H, $R_2$ = Ph), 100-42-5; $CH_2{=}CR_1R_2$ ($R_1$ = H, $R_2$ = $CH_2SiMe_3$), 762-72-1; $CH_2{=}CR_1R_2$ ($R_1$ = H, $R_2$ = $C_8H_{17}$), 872-05-9; $CH_2{=}CR_1R_2$ ($R_1$ = Me, $R_2$ = OMe), 116-11-0; $CH_2{=}CR_1R_2$ ($R_1$ = Me, $R_2$ = OAc), 108-22-5; $CH_2{=}CR_1R_2$ ($R_1$ = H, $R_2$ = CN), 107-13-1; $CH_2{=}CR_1R_2$ ($R_1$ = H, $R_2$ = $CO_2Et$), 140-88-5; $CH_2{=}CR_1R_2$ ($R_1$ = H, $R_2$ = $COCH_3$), 78-94-4; $CH_2{=}CR_1R_2$ ($R_1$ = H, $R_2$ = $C(CH_3){=}CH_2$), 78-79-5; $CH_2{=}CR_1R_2$ ($R_1$ = H, $R_2$ = OEt), 109-92-2; $CH_2{=}CR_1R_2$ ($R_1$ = Me, $R_2$ = SPh), 7594-43-6; MeOH, 67-56-1; MeCN, 75-05-8; DMF, 68-12-2; $Bu_4NBF_4$, 429-42-5; $Bu_4NClO_4$, 1923-70-2; $LiClO_4$, 7791-03-9; 5,5-dimethyl-1,3-cyclohexanedione, 126-81-8; 1,3-cyclohexanedione, 504-02-9; 4-methyl-1,3-cyclohexanedione, 14203-46-4; 1,3-cyclopentanedione, 3859-41-4; 2,4-pentanedione, 123-54-6; 2-methyl-1,3-cyclohexanedione, 1193-55-1; 2-methyl-1,3-pentanedione, 14848-68-1; 2-carbomethoxycyclohexanone, 41302-34-5; dihydrofuran, 36312-17-1; tetraethylammonium *p*-toluenesulfonate, 733-44-8.

# Free-Radical Additions of Diselenides to Dimethyl Acetylenedicarboxylate, Methyl Propiolate, and Dimethyl Maleate[1]

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The photolysis of diphenyl or dimesityl diselenide with dimethyl acetylenedicarboxylate or methyl propiolate resulted principally in the formation of the corresponding vicinal bisselenides **1a,b**, **2a,b**, and **6a,b** via a free-radical chain addition mechanism. Dimethyl maleate underwent a selenyl radical mediated isomerization to dimethyl fumarate when similarly photolyzed with diphenyl diselenide.

The 1,2-additions of many kinds of reagents to multiple bonds are known to proceed via free-radical chain mechanisms.[2,3] Despite growing interest in the radical reactions of selenium compounds,[4] only a few types such as selenosulfonates[5] ($ArSO_2SePh$) and selenenyl thiocarboxylates[6] (PhC(=O)SSePh) have been reported to undergo free-radical 1,2-additions to olefins or acetylenes. To our knowledge, similar addition reactions of the more common diselenides have not yet been documented.

The phenylselenyl radical (PhSe•) can be conveniently generated by photolysis of the corresponding diselenide[7] (eq 1). Ito[8] recently reported that this species adds reversibly to olefins containing substituents that stabilize the resulting alkyl radicals (eq 2). Although the latter

$$PhSeSePh \overset{h\nu}{\rightleftharpoons} 2\ PhSe\bullet \qquad (1)$$

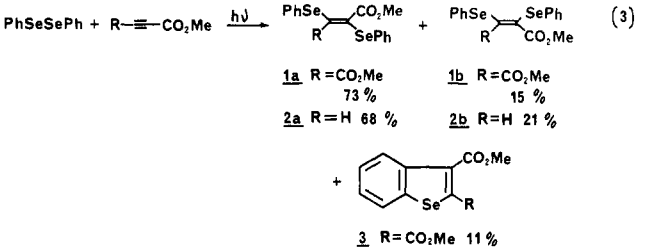
$$PhSe\bullet + RCH{=}CH_2 \rightleftharpoons R\dot{C}HCH_2SePh \qquad (2)$$

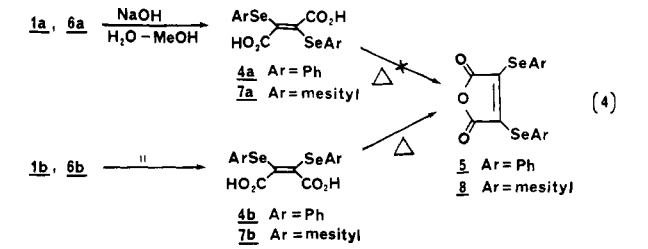
$$R\dot{C}HCH_2SePh + PhSeSePh \rightarrow PhSeCH(R)CH_2SePh + PhSe\bullet$$

intermediates could be trapped with oxygen, they did not undergo chain transfer to a second molecule of the diselenide to afford the corresponding vicinal bisselenides. We are unaware of any comparable studies with activated acetylenes.

We report that the photochemical reaction of diphenyl or dimesityl diselenide with dimethyl acetylenedicarboxylate (DMAD) or methyl propiolate resulted in the first examples of the free-radical addition of a diselenide to an acetylene. We also observed a selenyl radical mediated isomerization of dimethyl maleate to dimethyl fumarate under similar conditions.

When diphenyl diselenide was photolyzed with UV light in the presence of an equimolar amount of DMAD or methyl propiolate in benzene for 24 h, the bisselenides **1** and **2** were produced in high yield as separable mixtures of *E* and *Z* isomers in which the *E* isomers **1a** and **2a** predominated (eq 3). The minor isomer **1b** was assigned the *Z* configuration on the basis of its conversion to the corresponding cyclic anhydride **5** by saponification and dehydration of the diacid **4b** (eq 4). The isomers **2a** and




**2b** were assigned the *E* and *Z* configurations, respectively, on the basis of the lower field NMR absorption of the

(1) We gratefully acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada.

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(5) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249. Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1983**, *48*, 3077. Gancarz, R. A.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899. Miura, T.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1982**, 438.
(6) Toru, T.; Seko, T.; Maekawa, E. *Tetrahedron Lett.* **1985**, *26*, 3263.
(7) Schmidt, U.; Müller, A.; Markau, K. *Chem. Ber.* **1964**, *97*, 405. Franzi, R.; Geoffroy, M. *J. Organomet. Chem.* **1981**, *218*, 321.
(8) Ito, O. *J. Am. Chem. Soc.* **1983**, *105*, 850.

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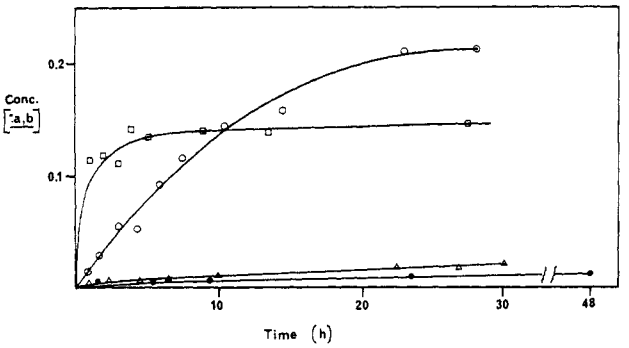
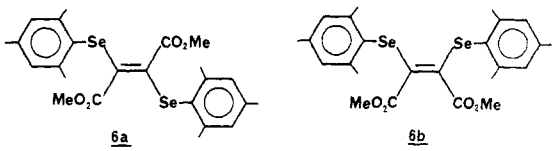



**Figure 1.** Rate of formation of products from the reaction of PhSeSePh and DMAD. All reactions were performed by treating a benzene solution of PhSeSePh (0.25 M) and DMAD (0.25 M) under nitrogen under the indicated conditions: ○ = irradiation with UV light at room temperature; □ = reflux with 2 mol % of AIBN; △ = reflux without AIBN in the dark; ● = reflux in the dark with 10 mol % of 2,6-di-*tert*-butyl-4-cresol. Product concentrations were determined by GC analysis with an internal standard (see Experimental Section); total molar concentrations of **1a** + **1b** are shown.

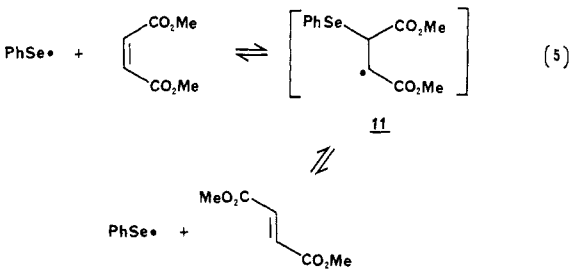
vinylic proton of **2b** where it is cis to the ester group (**2a**, δ 7.91; **2b**, δ 8.91).[9] A small amount (11%) of the benzoselenophene **3** was also formed in the reaction with DMAD. Unactivated acetylenes such as 1-decyne failed to react under these conditions. The more hindered dimesityl diselenide reacted similarly to the diphenyl derivative with DMAD to afford the *E* and *Z* adducts **6a** and **6b** in 81% and 11% yields, respectively. Only product **6b** could be converted to the cyclic anhydride **8** via the diacid **7b** (eq 4).




The products **1a**, **1b**, and **3** were obtained in comparable yields when diphenyl diselenide and DMAD were refluxed in benzene in the presence of 2 mol % of the radical initiator azobisisobutyronitrile (AIBN). Furthermore, the reaction failed completely at room temperature in the dark and proceeded very slowly in refluxing benzene in the absence of AIBN, and even more slowly in the presence of the radical inhibitor 2,6-di-*tert*-butyl-4-cresol, as shown in Figure 1. The rapid initial formation of the products with AIBN, their relatively steady production upon photolysis, and their suppressed formation with added inhibitor all support the free-radical chain mechanism shown in Scheme I.

The lack of stereospecificity in the formation of **1** and **2** suggests that the intermediate vinyl radicals **9a** and **9b** are able to equilibrate prior to the chain-transfer step or, less probably, that the radical center is sp-hybridized and linear.[10] The competing formation of selenophene **3** from DMAD can be rationalized by an intramolecular attack by the vinylic radical center in **9b** at the ortho position of the arylseleno moiety, followed by hydrogen abstraction from the intermediate **10**.[11]

The photolysis of diphenyl diselenide with dimethyl maleate in benzene resulted in the isomerization of the olefin to the corresponding fumarate, instead of in 1,2-addition (eq 5). The maleate was recovered intact when similarly irradiated in the absence of the diselenide. This

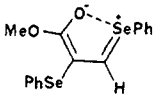



(5)

can be rationalized by assuming the reversible addition of the selenyl radical to the double bond (in accord with the kinetics-based conclusions of Ito[8]), followed by free rotation in the alkyl radical intermediate **11**, and reversion to the more stable trans olefin.[12] The failure of dimethyl maleate to undergo 1,2-addition, in contrast to the behavior of DMAD and methyl propiolate, is attributed either to a more facile reversion in the addition of the selenyl radical to the olefin or to more rapid chain transfer in the vinyl radical **9** compared to the alkyl radical **11**.

It is also worthy of note that alkenes containing geminal selenium residues and electron-withdrawing groups are of interest as capto-dative olefins,[13] and so compounds such as **1**, **2**, and **6** may be of value in this context.

Finally, we observed an interesting phenomenon in recording the IR spectrum of **2a**, which has an unexpectedly low frequency of 1683 $cm^{-1}$ for the ester carbonyl group, indicating a remarkably low bond order. Since this effect is much less pronounced in **2b**, where the ester and phenylseleno moiety are trans, we conclude that there is a substantial interaction between the carbonyl oxygen and the cis selenium atom of **2a**, perhaps via the resonance structure **12**. Presumably the opposing effects of the two ester groups in the more symmetrical compounds **1** and **6** suppress this interaction and result in more normal absorptions of 1714–1725 $cm^{-1}$.




12

## Experimental Section

Melting points were obtained on an A. H. Thomas hot-stage apparatus and are uncorrected. IR and $^1H$ NMR spectra were recorded on a Nicolet 5DX and a Varian XL200 instrument, respectively. All NMR spectra were obtained in $CDCl_3$ solution unless otherwise indicated and are reported in parts per million downfield from internal tetramethylsilane standard. Mass spectra were recorded on a Kratos M80 instrument, and GC analyses were performed on a Varian 3700 chromatograph equipped with a Varian CDS111C integrator and a flame-ionization detector, using a 15-m Megabore DB-17 column (J and W Scientific Co.). All quantitative determinations (Figure 1) were made by using cy-

(9) Olefinic hydrogens that are cis to ester groups are known to absorb downfield from their trans counterparts: Jackman, L. M.; Wiley, R. H. *J. Chem. Soc.* **1960**, 2881 and 2886. For a list of examples, see: Jackman, L. M.; Sternhell, S. In *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed., Pergamon: Oxford, 1969; p 187.

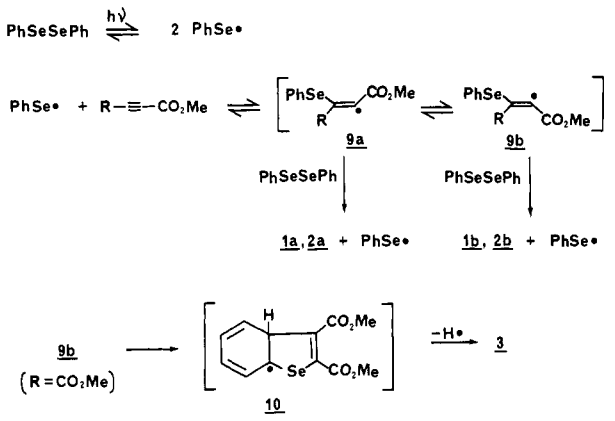
(10) For a discussion of the shapes of vinylic radicals, see: ref 3, Chapter 4, pp 90–92.

(11) The reaction of PhSSPh with DMAD under similar conditions produced the benzothiophene analogue of **3** as the principal product.

(12) Similar thiyl-mediated isomerizations of olefins are well-known: Sivertz, C. *J. Phys. Chem.* **1959**, *63*, 34. Graham, D. M.; Mieville, R. L.; Sivertz, C. *Can. J. Chem.* **1964**, *42*, 2239.

(13) Piettre, S.; Janousek, Z.; Merenyi, R.; Viehe, H. G. *Tetrahedron* **1985**, *41*, 2527. Janousek, Z.; Piettre, S.; Gorissen-Hervens, F.; Viehe, H. G. *J. Organomet. Chem.* **1983**, *250*, 197.

**Scheme I**



clododecanone as an internal standard. Preparative TLC was carried out by using Analtech 20 × 20 cm glass plates coated with 1 mm of silica gel GF. Elemental analyses were obtained by Drs. R. Yamdagni and W. S. Lin. Photolyses were performed in a Rayonet RMR-500 reactor equipped with four 254-nm lamps.[14] Dimesityl diselenide was prepared by a literature method.[15] All other chemicals were commercially available and used without further purification.

**Photolysis of Diphenyl Diselenide with DMAD.** Diphenyl diselenide (156 mg, 0.50 mmol) and DMAD (62 μL, 0.50 mmol) were photolyzed for 24 h in 2 mL of benzene. The solvent was then evaporated and the residue separated by preparative TLC in benzene to afford three fractions A–C. Fraction A ($R_f$ 0.58) contained 165 mg (73%) of dimethyl (*E*)-2,3-bis(phenylseleno)-2-butenedioate (**1a**) as a pale yellow solid: mp 109.5–110 °C (from chloroform–hexane); IR (KBr) 1724, 1685, 1439, 1428, 1250, 1018, 741, 692 cm$^{-1}$; $^1$H NMR 7.6 (m, 2 H), 7.3 (m, 3 H), 3.45 (s, 3 H); mass spectrum, *m/e* (relative intensity) 456 ($M^+$, $^{80}$Se, 12), 157 ($Ph^{80}Se^+$, 88), 77 ($Ph^+$, 100). Anal. Calcd for $C_{18}H_{16}O_4Se_2$: C, 47.58; H, 3.56. Found: C, 47.36; H, 3.26.

Fraction B ($R_f$ 0.20) contained 33 mg (15%) of the corresponding *Z* isomer **1b** as a bright yellow solid: mp 117–118.5 °C (from chloroform–hexane); IR (KBr) 1725, 1698, 1541, 1436, 1243, 748 cm$^{-1}$; $^1$H NMR 7.6 (m, 2 H), 7.3 (m, 3 H), 3.42 (s, 3 H); mass spectrum, *m/e* (relative intensity) 456 ($M^+$, $^{80}$Se, 16), 157 ($Ph^{80}Se^+$, 84), 77 ($Ph^+$, 100). Anal. Calcd for $C_{18}H_{16}O_4Se_2$: C, 47.58; H, 3.56. Found: C, 47.69; H, 3.58.

Fraction C ($R_f$ 0.32) contained 17 mg (11%) of 2,3-dicarbomethoxybenzoselenophene (**3**) as a viscous oil (GC purity >99%): IR (film) 1732, 1562, 1533, 1435, 1274, 1245, 1224, 1083, 756 cm$^{-1}$; $^1$H NMR 7.9 (m, 2 H), 7.5 (m, 2 H), 4.04 (s, 3 H), 3.93 (s, 3 H); mass spectrum, *m/e* (relative intensity) 298 ($M^+$, $^{80}$Se, 73), 267 ($M^+$ – OMe, $^{80}$Se, 100); exact mass calcd for $C_{12}H_{10}O_4Se$ 297.97443, found 297.9735.

**Thermolysis of Diphenyl Diselenide with DMAD.** Diphenyl diselenide (1.25 g, 4.0 mmol), DMAD (492 μL, 4.00 mmol), and AIBN (13 mg, 0.08 mmol) were refluxed in 8 mL of benzene under nitrogen in the dark for 20 h. Flash chromatography over silica gel then furnished 1.125 g (62%) of the *E* isomer **1a** (elution with 60% dichloromethane–hexane), 0.17 g (14%) of benzoselenophene **3** (elution with 60% dichloromethane–hexane), and 0.23 g (13%) of the *Z* isomer **1b** (elution with dichloromethane). All products were identical with those obtained in the preceding photolysis experiment.

For a comparison of reaction rates in the absence of AIBN, and in the presence of 2,6-di-*tert*-butyl-4-cresol, see Figure 1.

**Photolysis of Diphenyl Diselenide with Methyl Propiolate.** Diphenyl diselenide (156 mg, 0.50 mmol) and methyl propiolate (45 μL, 0.50 mmol) were photolyzed and worked up as in the photolysis with DMAD (vide supra) to afford two fractions A and B. Fraction A ($R_f$ 0.68) contained 135 mg (68%) of methyl (*E*)-2,3-bis(phenylseleno)propenoate (**2a**) as a viscous, pale yellow oil (GC purity >96%): IR (film) 1683, 1477, 1437, 1285, 1214, 738, 691 cm$^{-1}$; $^1$H NMR 7.91 (s, 1 H), 7.5 (m, 4 H), 7.3 (m, 6 H), 3.82 (s, 3 H); mass spectrum, *m/e* (relative intensity) 398 ($M^+$, $^{80}$Se, 17), 157 ($Ph^{80}Se^+$, 84), 77 ($Ph^+$, 100); exact mass calcd for $C_{16}H_{14}O_2Se_2$ 397.93242, found 397.9322.

Fraction B ($R_f$ 0.48) contained 42 mg (21%) of the corresponding *Z* isomer **2b** as a pale yellow oil (GC purity >99%): IR (film) 1714, 1533, 1477, 1438, 1245, 1202, 1036, 1021, 736, 690 cm$^{-1}$; $^1$H NMR 8.91 (s, 1 H), 7.7–7.3 (complex, 10 H) 3.71 (s, 3 H); mass spectrum, *m/e* (relative intensity) 398 ($M^+$, $^{80}$Se, 16), 157 ($Ph^{80}Se^+$, 72), 77 ($Ph^+$, 100); exact mass calcd for $C_{16}H_{14}O_2Se_2$ 397.93242, found 397.9343.

**Photolysis of Dimesityl Diselenide with DMAD.** Dimesityl diselenide (396 mg, 1.00 mmol) and DMAD (123 μL, 1.00 mmol) were photolyzed for 24 h in 6 mL of benzene. The product was flash chromatographed over silica gel to afford two fractions A and B. Fraction A eluted with 50% dichloromethane–hexane and contained 437 mg (81%) of dimethyl (*E*)-2,3-bis(mesitylseleno)-2-butenedioate (**6a**) as a yellow solid: mp 200–201.5 °C (from chloroform–hexane); IR (Nujol) 1714, 1699, 1249, 1026 cm$^{-1}$; $^1$H NMR 6.89 (s, 2 H), 3.29 (s, 3 H), 2.45 (s, 6 H), 2.24 (s, 3 H); mass spectrum, *m/e* (relative intensity) 540 ($M^+$, $^{80}$Se, 13), 119 ($Ar^+$, 100). Anal. Calcd for $C_{24}H_{28}O_4Se_2$: C, 53.54; H, 5.24. Found: C, 53.36; H, 5.07.

Fraction B eluted with dichloromethane and contained 58 mg (11%) of the corresponding *Z* isomer as a yellow solid: mp 129–132 °C (from chloroform–hexane); IR (KBr) 1720, 1698, 1540, 1429, 1239, 1005 cm$^{-1}$; $^1$H NMR 6.94 (s, 2 H), 3.29 (s, 3 H), 2.51 (s, 6 H), 2.26 (s, 3 H); mass spectrum, *m/e* (relative intensity) 540 ($M^+$, $^{80}$Se, 4), 119 ($Ar^+$, 100). Anal. Calcd for $C_{24}H_{28}O_4Se_2$: C, 53.54; H, 5.24. Found: C, 53.26; H, 5.29.

**(*E*)- and (*Z*)-2,3-Bis(phenylseleno)-2-butenedioic Acids (4a) and (4b).** Diester **1a** (55 mg, 0.12 mmol) was refluxed with 0.24 mmol of NaOH in 3 mL of 25% methanol–water for 2.5 h. The mixture was evaporated, triturated with water, and acidified with HCl, and the precipitated pale yellow solid was filtered and recrystallized (acetone–hexane) to afford 48 mg (94%) of the *E* diacid **4a**: mp 240–246 °C; IR (KBr) 3500–2300, 1687, 1576, 1529, 1477, 1439, 1407, 1262, 740, 691 cm$^{-1}$; $^1$H NMR ($CDCl_3$–acetone-$d_6$) 13.00 (s, 1 H), 7.6 (m, 2 H), 7.5 (m, 3 H); mass spectrum, *m/e* (relative intensity) 428 ($M^+$, $^{80}$Se, <1), 157 ($Ph^{80}Se^+$, 47), 102 (61), 78 (89), 77 (100). Anal. Calcd for $C_{16}H_{12}O_4Se_2$: C, 45.08; H, 2.84. Found: C, 45.16; H, 2.58.

Diester **1b** (55 mg, 0.12) was treated in the same manner to produce 49 mg (96%) of the *Z* diacid **4b** as a bright yellow solid: mp 169–172 °C; IR (KBr) 3500–2300, 1699, 1545, 1404, 1268, 742, 734, 691 cm$^{-1}$; $^1$H NMR (acetone-$d_6$) 13.0 (s, 1 H), 7.6 (m, 2 H), 7.4 (m, 3 H); mass spectrum nearly identical with that of anhydride **5** (vide infra), possibly due to thermal dehydration in the inlet. Anal. Calcd for $C_{16}H_{12}O_4Se_2$: C, 45.08; H, 2.84. Found: C, 45.34; H, 2.78.

**2,3-Bis(phenylseleno)-2-butenedioic Anhydride (5) and 2,3-Bis(mesitylseleno)-2-butenedioic Anhydride (8).** The *Z* diacid **4b** (10 mg) was suspended in 25 mL of toluene, and the toluene was slowly removed by distillation. The diacid gradually dissolved. The last traces of solvent were removed in vacuo, leaving **5** as a bright yellow, homogeneous (GC) gum: IR (film) 1843, 1763 cm$^{-1}$; $^1$H NMR 7.6–7.2 (complex); mass spectrum, *m/e* (relative intensity) 410 ($M^+$, $^{80}$Se, 19), 209 (24), 181 (67), 157 ($Ph^{80}Se^+$, 35), 129 (64), 77 (100); exact mass calcd for $C_{16}H_{10}O_3Se_2$ 409.89603, found 409.8961.

When the *E* diacid **4a** was similarly treated, it was recovered intact.

The saponification and dehydration of diester **6b** was carried out as in the case of diester **1b** to afford the cyclic anhydride **8**, as evidenced by IR absorptions at 1840 and 1759 cm$^{-1}$. The product was not further characterized.

**Photolysis of Diphenyl Diselenide with Dimethyl Maleate.** Diphenyl diselenide (78 mg, 0.25 mmol) and dimethyl maleate (31 μL, 0.25 mmol) were photolyzed for 24 h in 2 mL of benzene. Flash chromatography over silica gel then afforded 76 mg (96% recovery) of diphenyl diselenide (elution with hexane), identical with an authentic sample (mp, NMR), and 30 mg (83%) of dimethyl fumarate (elution with dichloromethane), identical with an authentic sample (mp, NMR).

(14) Diselenides absorb strongly near this wavelength (see: Kuder, J. E. In *Organic Selenium Compounds: Their Chemistry and Biology*; Klayman, D. L., Gunther, W. H. H., Eds.; Wiley: New York, 1973; pp 871–872.), whereas the olefins and acetylenes in this study do not.

(15) Kuwajima, I.; Shimizu, M.; Urabe, H. *J. Org. Chem.* **1982**, *47*, 837.

In a control experiment, dimethyl maleate was irradiated as above in the absence of diphenyl diselenide. It was recovered unchanged in 90% yield.

**Registry No.** **1a**, 114221-61-3; **1b**, 114221-62-4; **2a**, 114221-64-6; **2b**, 114221-65-7; **3**, 114221-63-5; **4a**, 114221-67-9; **4b**, 114221-68-0; **5**, 114221-69-1; **6a**, 114221-66-8; **6b**, 114249-90-0; **7b**, 114221-70-4; **8**, 114221-71-5; DMAD, 762-42-5; PhSeSePh, 1666-13-3; methyl propiolate, 922-67-8; dimesityl diselenide, 71518-92-8; dimethyl maleate, 624-48-6; dimethyl fumarate, 624-49-7.

# $W(CO)_6$ Mediated C–S Bond Cleavage Reactions[1]

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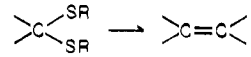
$W(CO)_6$-mediated reactions of thioethers in refluxing chlorobenzene yield mainly the corresponding dimers. Optically active thioethers give the respective racemic products. Mercaptans, on the other hand, predominantly afford the corresponding reduced products. A deuterium labeling experiment suggests that the SH group is the hydrogen source in the latter reduction reactions. A free-radical mechanism is suggested.

The reductive cleavage of the carbon–sulfur bond is important in organic synthesis[3] as well as in the hydrodesulfurization process of fossil fuels.[4] Homogeneous organometallic reagents have been investigated extensively in these applications.[5-7] Metal carbonyls have been shown to be useful to promote cleavage reactions of the carbon–sulfur bond.[5,6] Group 6 metal carbonyls are particularly thiophilic, and certain reactive C–S bonds in mercaptans and thioethers are selectively reduced with $Mo(CO)_6$ in ethereal solvents such as THF[5l] or dioxane.[5m] Although the actual mode of these reactions is not clear, it has been envisaged that the latter reactions may proceed via a radical mechanism.[5l] Accordingly, active hydrogen(s) in solvent molecules or in the substrates may be the hydrogen source for the radical abstraction reaction. Indeed, when chlorobenzene was employed as the solvent, dithioacetals underwent desulfurdimerization upon treatment with $Mo(CO)_6$ or $W(CO)_6$ (eq 1).[6] We felt that the extension



(1)

of this latter reaction to mercaptans as well as thioethers would be useful in synthesis and in understanding the mechanism of the metal carbonyl mediated C–S cleavage reactions and now wish to report our results.

**Table I. $W(CO)_6$ Mediated Reaction of Thioethers**

| substrate | product (% yield) |
|---|---|
| methyl 2-naphthylmethyl sulfide (**1**) | 1,2-di(2-naphthyl)ethane (**8**) (50)<br>2-methylnaphthalene (**9**) (34) |
| bis(2-naphthylmethyl) sulfide (**2**) | **8** (54)<br>**9** (15) |
| 1-naphthylmethyl phenyl sulfide (**3**) | 1,2-di(1-naphthyl)ethane (**10**) (53)<br>1-methylnaphthalene (**11**) (5) |
| dibenzyl sulfide (**4**) | bibenzyl (**12**) (42)[a] |
| 4-bromobenzyl phenyl sulfide (**5**) | 1,2-bis(4-bromophenyl)ethane (**13**) (48)<br>4-bromotoluene (**14**) (4) |
| 4-methoxybenzyl phenyl sulfide (**6**) | 1,2-bis(4-methoxyphenyl)-ethane (**15**) (48)<br>4-methylanisole (**16**) (4) |
| methyl 2-phenyl-2-(phenylthio)-acetate (**7**) | dimethyl 2,3-diphenylsuccinate (**17**) (47)<br>methyl phenylacetate (**18**) (3) |

[a] The yield of toluene in this reaction was not determined.

## Results and Discussion

**Desulfurdimerization of Thioethers.** A chlorobenzene solution[8] of thioether and 1 equiv of $W(CO)_6$ was heated under reflux for 24–72 h, and after workup, the corresponding product(s) was (were) obtained. The results are outlined in Table I.

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(8) Chlorobenzene was used as the solvent throughout this study for two reasons. First, it has no "active" hydrogen for the abstraction reactions. Secondly, the aromatic rings are deactivated and it is noteworthy that direct thermolysis of $W(CO)_6$ with aromatic compounds in general affords the cooresponding arene complexes in very low yield. Cf.: Davis, R.; Kane-McGuire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, p 1321.

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