is mainly controlled by a conformational dependence, already found in the starting molecule. It can be anticipated that upon an increase of the temperature the selectivity will decrease due to the leveling of the various conformer populations. At any rate, the cleavage of these bonds will remain preferential due to the greater stability of the final system.

We have seen in Figures 9 and 10 that in all cases energy barriers are found along the low-energy excited-state PES's. We thus conceive that the ring cleavage might compete with other reactive processes of the excited carbonyl, more especially with Norrish type II reactions for open-chain aliphatic compounds and Norrish type I for alicyclic compounds.[10] It is noteworthy that calculated energies of these reactions obtained by a similar method[26,31,32] lie in the same energetic range.

The case of [3.1.0] and [4.1.0] derivatives deserves some comment, and we will use the nomenclature of Dauben et al.[11] shown in Figure 1 in the following discussion.

(a) [3.1.0] Derivatives. In Figure 10 we have seen that for $\theta = 30°$, in our strain-free model, the Y rupture is preferred to the Z rupture by 13 kcal mol^{-1}. The presence of a noticeable ring strain might be of the same order of magnitude and might decrease the activation energy of the Z rupture. The reaction products will result from a competition between X, Y, and Z ruptures, and the relative stability of the various open intermediates is likely to rule the final product distribution.

(b) [4.1.0] Derivatives. The situation is clearer than for the preceding series for now the system might be considered as strain free. As can be seen in Figure 10, the Y (C_1C_2) rupture is the easiest for realistic values of θ and the product distribution will be ruled by the competition between the Y and the Norrish type I cleavages.

Acknowledgment. This study was initially suggested by Professor J. P. Pete, Reims University. We are greatly indebted to Professor J. P. Pete and Dr. J. Muzard for many stimulating discussions we had during the course of this work.

(32) H. Cardy, E. Poquet, M. Chaillet, and A. Dargelos, *Nouv. J. Chim.*, 2, 603-608 (1978).

Preparation and Diels-Alder Reactions of 1,1-Dicarbonylalkenes

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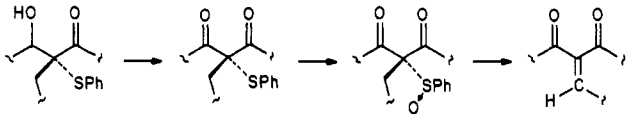
1,1-Dicarbonyl- (ester, ketone, lactone) substituted alkenes are prepared from the corresponding saturated 1-phenylsulfinyl derivatives. These are formed from precursor sulfides, which can be efficiently prepared either by oxidation of β-hydroxy-α-phenylsulfenylcarbonyl compounds or direct acylation of α-phenylsulfenyl enolate anions with acid chlorides. Some of the title compounds can be isolated and then reacted while others are generated and reacted in situ in a Diels-Alder fashion with cyclopentadiene. Endo-exo selectivities are discussed.

In a current study in our laboratory the intramolecular Diels-Alder chemistry of dienophilic 1-carbomethoxy-1-ketoalkenes is being investigated. In connection with this work, methods for the preparation of these dienophiles and their precursor sulfoxides[1] have been developed, and some intermolecular Diels-Alder reactions[2] of the title compounds have been examined. Those observations are described here.

A synthesis of the 1,1-dicarbonyl-substituted alkenes (**1**) by thermolysis of a 1-sulfinyl precursors **2** seemed advantageous since it would allow generation of **1**, a molecule potentially prone to polymerization, in the presence of Diels-Alder dienes. It would also allow for the construction of these precursors via carbon-carbon bond-forming reactions. For example, we recently reported[3] a zinc chloride assisted aldol reaction of α-phenylthio ester enolate anions with aldehydes to generate β-hydroxy-α-phenylthio esters (**3**). Successful oxidation of the alcohols **3** to ketones **4** would enable the application of this chemistry to our needs



3 **4** **2** **1**

since **4** could, of course, yield **2** and **1** upon oxidation and elimination of the sulfur. This scheme was reduced to practice as outlined in Table I. The β-hydroxy lactones **3a-d** and ester **3e** were prepared by the previous method.[3] Oxidation to the keto sulfides **4a-c** and **4e** could be effected either with dimethyl sulfoxide/trifluoroacetic anhydride[4] or Me_2SO/oxalyl chloride[5] without interference by sulfur oxidation.[6] An alternative method for prepa-

(1) The preparation and Michael reactions of di-*tert*-butyl methylenemalonate and *tert*-butyl 2-acetylacrylate were recently described: Baar, M. R.; Roberts, B. W. "Abstracts of Papers", 181st National Meeting of the American Chemical Society, Atlanta, GA, March 1981; American Chemical Society: Washington, D.C., 1981; ORGN 83.

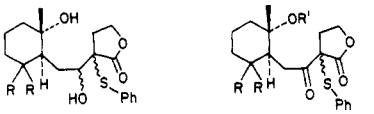
(2) Both the Diels-Alder reactivity and facile preparation of some cyclic, unsaturated β-dicarbonyl compounds have been recently described: Liotta, D.; Saindane, M.; Barnum, C. *J. Am. Chem. Soc.* **1981**, *103* 3224. Liotta, D.; Barnum, C.; Puleo, R.; Zima, G.; Bayer, C.; Kezer, H. S., III *J. Org. Chem.* **1981**, *46*, 2920. Liotta, D.; Saindane, M.; Barnum, C.; Ensley, H.; Balakrishnan, P. *Tetrahedron Lett.* **1981**, 3043.

(3) Hoye, T. R.; Kurth, M. J. *J. Org. Chem.* **1980**, *45*, 3549.

(4) Huang, S. L.; Omura, K.; Swern, D. *J. Org. Chem.* **1976**, *41*, 3329.

(5) Mancuso, A. J.; Brownfain, D. S.; Swern, D. *J. Org. Chem.* **1979**, *44*, 4148.

(6) In several related reactions it is worth noting that oxidation of lactone i with Me_2SO/TFAA[4] or with NCS/DMS[7] resulted in competing methylthiomethylation of the tertiary alcohol since mixtures of ii and iii were obtained. This problem could be circumvented by the use of pyridinium dichromate,[8] which gave only iv from v.



i R=H ii R=H, R'=H

v R=CH_3 iii R=H, R'=CH_2SCH_3

iv R=CH_3, R'=H

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Table I. Preparation of Sulfides 4, 1,1-Dicarbonylalkenes 1, and Diels-Alder Adducts 7

entry	R		yield[a]	α-sulfenyl β-dicarbonyl	enedicarbonyl	yield[a] from 4	Diels-Alder adduct ratio exo[b]		endo[b]
a	R=CH_3	3a[c]	85%	4a	(1a)	62%	7ax	1:2	7an
b	R=Ph	3b[c]	81%	4b	1b	73%	7bx	1:5	7bn
c	R=iPr	3c	91%	4c	(1c)	59%	7cx	1:3	7cn
d	R=tBu	3d		4d	(1d)	77%	7dx	0:1	7dn
e	R=Ph	3e	96%	4e	1e[d]	44%	7ex	1:3.5	7en
e'	R=Ph	5	84%	4e					
f	R=CH_3	5	84%	4f	(1f)	53%	7fx	1:3	7fn
g	R=Ph	6	58%	4g	1g	45%[e]			
h	R=$EtO_2C(CH_2)_8$	6	66%	4h	1h	65%[e]			

[a] All yields refer to chromatographed material. [b] Exo and endo are defined by the relationship of the acyl group to the bicyclo[2.2.1] system. [c] See ref 3. [d] See ref 11. [e] Yields of isolated 1g and 1h since the Diels-Alder reaction was not effected.

ration of keto sulfides 4 was found in the direct acylation of α-phenylthio ester enolate ions with acid chlorides. The success of this approach rests in the use of lithium hexamethyldisilazide as base rather than lithium diisopropylamide. The conjugate acid of the latter, less hindered base reacts faster with acid chlorides than the sulfur-stabilized ester enolate anions, thereby generating a proton source that quenches the carbanion.[9] Compounds **4e–h** were prepared in this fashion. Notice that the acylation conditions are compatible with additional ester functionality in both the acid chloride (entry h, in which the acid chloride was prepared from monoethyl sebacate and oxalyl chloride) and the α-phenylthio ester enolate anion (entries g and h, in which the diester **6** was prepared from dimethyl 2-bromoglutarate). A limitation to the method was found when pivaloyl chloride failed to react with the anion of methyl 2-(phenylthio)propanoate (**5**).[10]

With precursors **4** to enedicarbonyl compounds **1** in hand, their oxidations to sulfoxides **2** with MCPBA or CH_3CO_3H, thermolysis, and Diels–Alder reaction were studied. The thermal extrusion of benzenesulfenic acid from the α-sulfinyl-β-dicarbonyl compounds was generally facile, proceeding perceptably at room temperature and to completion within minutes at 80 °C. In most cases (the exceptions being **1b** and **1e**[11]) nonenolized enedicarbonyl

(7) Corey, E. J.; Kim, C. V. *J. Am. Chem. Soc.* **1972**, *94*, 7586.
(8) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.
(9) Not unexpectedly, *N,N*-diisopropylacetamide is formed exclusively (by ^1H NMR analysis) when a 1:1 mixture of *i*-Pr_2NH and $(Me_3Si)_2NH$ is treated with a deficiency of AcCl in $CDCl_3$ at room temperature.

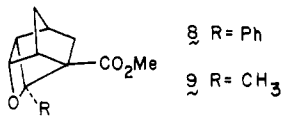
(10) Prior to discovering this acylation of the lithium enolate of **5**, we observed an interesting transformation of the sodium enolate of the sulfoxide analogue vi. Its reaction with benzoyl chloride in DMF led to the α-benzoyloxy ester vii in what can be envisioned as a Pummerer rearrangement of the kinetically formed zwitterion viii. Pyrolysis of vii in refluxing toluene gave methyl 2-phenylthiopropenoate.

vi viii vii

(11) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Org. Chem.* **1974**, *39*, 2133.

compounds 1 were unstable when concentrated and were therefore characterized only by NMR spectroscopy of the solution in which they were generated. Subsequent addition of a 1,3-diene and heating (or thermolysis of a solution containing precursor sulfoxide **2** and the 1,3-diene to trap the generated 1 in situ) provided the exo and endo Diels–Alder adducts **7a(x,n)–7f(x,n)** (see table) from cyclopentadiene.[12]

The exo or endo relationship of the ketone to the bicyclo[2.2.1] system for compounds **7a–d** derived from 2-acylbutenolides **1a–d** was determined on the basis of the absence or presence respectively of long-range ^1H–^1H coupling (2–3 Hz) between the anti proton of the bridging methylene group (H_a in Table I) and the endo proton common to the lactone and the [2.2.1] rings (H_n in Table I).[13] This method of analysis was obviously not suited for distinction of the exo/endo isomers of **7e** and **7f**. Therefore, these compounds were irradiated (**7ex** and **7en**, as a mixture, at 300 nm through Pyrex; **7fx** and **7fn**, independently, with a 450-W Hanovia lamp through Vycor) to effect Paterno–Büchi[14] reaction between the endo ketone and olefin. By analogy with previous work,[15] structures **8** and **9** were assigned to the oxetanes arising from **7en** and



8 R = Ph

9 R = CH_3

7fn. Finally, confirmation of the stereochemical assignments given to the endo isomers of lactones **7an–cn** on the basis of NMR analysis was obtained by irradiation of deuteriobenzene solutions of each at 300 nm, but the derived oxetanes were not further characterized.

The exo/endo ratios for the cyclopentadiene Diels–Alder adducts are recorded in Table I and indicate a preference in all cases for the endo orientation of the ketone group regardless of whether the ester carbonyl is held in a coplanar s-trans arrangement as in the butenolides **1a–d** or is free to attain other conformations as in the methyl esters **1e** and **1f**. The importance of steric bulk in the alkyl portion of the acyl group is demonstrated by the increased endo selectivity[16] in the series methyl ketone (entry a), isopropyl ketone (entry c), and *tert*-butyl ketone (entry d). In the last instance no trace of exo isomer was observed in the NMR spectrum of the crude reaction product. Although the origin of the effect is unclear,[17] it appears for predictive purposes that one can expect ketones to be better endo directors when in direct competition with geminal ester groups.

Finally, the chemistry of the α-phenylsulfenyl 1,5-diesters **4g** and **4h** was examined. Upon oxidation and elimination of PhSOH an enedicarbonyl compound could be observed transiently by NMR analysis of the reaction mixture but rapidly tautomerized to the stable, chromatographable dienol **1g** or **1h**. Each of these was unreactive with cyclopentadiene at 100 °C. However, the less stable enedicarbonyl tautomer has been trapped in an intramolecular Diels–Alder reaction in substrates similar to **1g** or **1h**, in which the R group contains a conjugated diene. Details of this process will be presented elsewhere.

Experimental Section

General. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer, proton magnetic resonance spectra on a Varian HFT-80 instrument, and mass spectra on AEI MS-30 (electron impact, EI) and Finnigan 4000 (chemical ionization, CI) instruments. Medium-pressure chromatography was performed on EM Lobar columns packed with LiChroprep Si 60 (40–63 μm).

Lactone Alcohols 3c and 3d. The alcohol substrates **3c** and **3d** were prepared as single isomers of undetermined stereochemistry by the method reported for **3a**, **3b**, and **3e**.[3] The isopropyl derivative **3c** was isolated in crude yield of 94% as off-white crystals. Recrystallization (3×, hexanes/EtOAc) gave an analytical sample: mp 88.5–90 °C; ^1H NMR ($CDCl_3$) δ 0.94 (d, J = 7 Hz, 3 H), 1.07 (d, J = 7 Hz, 3 H), 2.00 (d, J = 5 Hz, 1 H, OH), 2.05 (ddd, J = 3, 5, 14 Hz, 1 H), 2.68 (d of septets, J = 2, 7 Hz, 1 H), 3.02 (dd, J = 9, 14 Hz, 1 H), 3.83 (dd, J = 2, 5 Hz, 1 H), 4.22 (m, 2 H), 7.4 (m, 5 H); IR (KBr) 1740 cm^{-1}; MS (CI, NH_3, pos) 284 ($M + NH_4^+$), 267 ($M + H^+$), 249 ($M + H^+ - H_2O$), 212 ($M + NH_4^+ - C_4H_8O$); (NH_3, neg) 266 ($M + e^-$), 109 (PhS^-). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81. Found: C, 63.44; H, 6.90. The *tert*-butyl derivative **3d** was obtained in crude yield of 80% as a yellow crystalline mass. Recrystallization (4×, hexanes:EtOAc) provided an analytical sample: mp 131–134 °C; ^1H NMR ($CDCl_3$) δ 1.19 (s, 9 H), 2.25 (ddd, J = 2, 6, 14 Hz, 1 H), 3.05 (m, 1 H), 3.7–4.3 (m, 3 H), 7.36 and 7.60 (m, 5 H); IR (KBr) 1750 cm^{-1}; MS (CI, NH_3, pos) 298 ($M + NH_4^+$), 281 ($M + H^+$), 263 ($M + H^+ - H_2O$), 212 ($M + NH_4^+ - C_5H_{10}O$); (NH_3, neg) 280 ($M + e^-$), 109 (PhS^-). Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19. Found: C, 64.32; H, 7.14.

Oxidation of Alcohols 3a–e to Ketones 4a–e. To a stirred solution of Me_2SO (2.0 equiv) in CH_2Cl_2 (0.5 M) under N_2 at −78 °C was added neat trifluoroacetic anhydride or oxalyl chloride (1.5 equiv) to produce a viscous suspension or homogeneous solution, respectively. After 25 min a solution of alcohol **3** in CH_2Cl_2 (0.25 M) was added, stirring was continued at −78 °C for 10 min, and neat Et_3N (3.0 equiv) was added. The solution was allowed to warm to room temperature, quenched with 10% H_2SO_4 solution, and extracted into Et_2O. The organic layer was washed (10% H_2SO_4, H_2O, saturated $NaHCO_3$, brine), dried ($MgSO_4$), and concentrated to afford ketone **4**, which was chromatographed (3:1 hexanes/EtOAc) on SiO_2. **4a**: colorless oil; 85% yield; ^1H NMR ($CDCl_3$) δ 2.20 (ddd, J = 2, 7, 14 Hz, 1 H), 2.58 (s, 3 H), 2.84 (ddd, J = 8, 8, 14 Hz, 1 H), 4.25 (m, 2 H), 7.36 (br s, 5 H); IR (neat) 1770, 1710 cm^{-1}; MS (EI) 236, 195, 194, 161, 149, 121, 117, 110, 109, 91, 78, 77, 43. Anal. Calcd for $C_{12}H_{12}O_3S$: C, 61.00; H, 5.12. Found: C, 61.32; H, 5.26. **4b**: clear brown oil after chromatography; 81% yield; ^1H NMR ($CDCl_3$) δ 2.49 (ddd, J = 8, 8, 14 Hz, 1 H), 3.11 (ddd, J = 6, 6, 14 Hz, 1 H), 4.23 (m, 2 H), 7.45 (m, 8 H), 8.30 (dd, J = 2, 9 Hz, 2 H); IR (CCl_4) 1780, 1670 cm^{-1}; MS (EI) 298, 194, 110, 109, 106, 105, 78, 77. Anal. Calcd for $C_{17}H_{14}O_3S$: 298.0659. Found: 298.0655. **4c**: clear brown oil after chromatography; 91% yield; ^1H NMR ($CDCl_3$) δ 1.06 (d, J = 7 Hz, 3 H), 1.27 (d, J = 7 Hz, 3 H), 2.22 (ddd, J = 7, 8, 14 Hz, 1 H), 2.84 (ddd, J = 6, 7, 14 Hz, 1 H), 3.67 (septet, J = 7 Hz, 1 H), 4.20 (m, 2 H), 7.43 (m, 5 H); IR (CCl_4) 1775, 1710 cm^{-1}; MS (EI) 264, 196, 195, 194, 161, 149, 121, 110, 109, 77, 71. Anal. Calcd for $C_{14}H_{16}O_3S$: 264.0814. Found: 264.0817. **4d**: brown oil, 100% crude yield;

(12) Dienophile **1e** was also reacted with butadiene (85 °C, 3 h) to give the Diels–Alder adduct in 67% yield.

(13) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon: New York, 1969; p 334.

(14) For a recent review see: Jones, G., II. In "Organic Photochemistry"; Padwa, A., Ed.; Marcell Dekker: New York, 1981; Vol. 5, Chapter 1.

(15) (a) Sauers, R. R.; Henderson, T. R. *J. Org. Chem.* **1974**, *39*, 1850. (b) Sauers, R. R.; *J. Am. Chem. Soc.* **1975**, *97*, 4947. (c) Smith, A. B., III; Dieter, R. K. *Tetrahedron Lett.* **1976**, 327.

(16) For other examples in which steric interactions between dienophile substituents and the methylene group of cyclopentadiene perturb endo/exo ratios (e.g., endo/exo = 2.8 for methyl acrylate and 0.4 for methyl methacrylate)[16c] see: (a) Konovalov, A. I.; Kamasheva, G. I.; Loskutov, M. P. *Dokl. Chem. (Engl. Transl.)* **1971**, *201*, 363. (b) Konovalov, A. I.; Vereshchagin, A. N.; Kamasheva, G. I. *Ibid.* **1969**, *185*, 597. (c) Konovalov, A. I.; Kamasheva, G. I. *J. Org. Chem. USSR (Engl. Transl.)* **1972**, *8*, 1471. (d) Berson, J. A.; Hamlet, Z.; Mueller, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 297.

(17) PRDDO calculations (carried out by P. K. Trumper in consultation with Professor D. A. Dixon) on methyl 2-acetylpropenoate showed surprisingly little difference between the two carbonyl LUMO coefficients within each molecule. Thus it is difficult (although tempting) to ascribe the greater endo selectivity of ketone over ester to an enhanced secondary orbital interaction of the former functionality with the diene in the transition state.

^{1}H NMR ($CDCl_3$) δ 1.34 (s, 9 H), 2.37 (ddd, J = 7, 8, 14 Hz, 1 H), 2.80 (ddd, J = 6, 8, 14 Hz, 1 H), 4.07 (m, 2 H), 7.42 (m, 5 H); IR (CCl_4) 1775, 1690 cm^{-1}; MS (EI) 278, 196, 195, 194, 185, 161, 149, 120, 112, 109, 65, 57. Anal. Calcd for $C_{15}H_{18}O_3S$: 278.0976. Found: 278.0977.

Procedure for the Acylation α-Phenylthio Esters 5 and 6. To a solution of hexamethyldisilazane (1.1 mL) in dry THF (5 mL) at −78 °C under N_2 was added *n*-BuLi (2.4 M in hexanes, 2.2 mL). After 20 min a solution of sulfide **5** (1.0 g) in THF (5 mL) was added dropwise at −78 °C. The solution was then stirred for 30 min in a 0 °C bath, recooled to −78 °C, and added via cannula to a stirred solution of PhCOCl (0.6 mL) in THF (5 mL) at −78 °C. The resulting mixture was again stirred for 30 min at 0 °C, quenched with saturated NH_4Cl, and extracted with Et_2O. The Et_2O layers were washed (H_2O, $NaHCO_3$, and brine), dried ($MgSO_4$), and concentrated to leave a crude oil (1.5 g), which was chromatographed by MPLC (45 g SiO_2; 9:1 hexanes/EtOAc) to give **4e** as a low-melting (44–46 °C) solid (1.28 g, 84%). A center cut from chromatography gave the analytical sample: ^{1}H NMR ($CDCl_3$) δ 1.70 (s, 3 H), 3.64 (s, 3 H), 7.2–7.5 (m, 8 H), 8.02 (dd, J = 2, 8 Hz, 2 H); IR (neat) 1735, 1680 cm^{-1}; MS (EI) 300, 241, 195, 164, 105, 91, 77, 51. Anal. Calcd for $C_{17}H_{16}O_3S$: 300.0820; C, 67.98; H, 5.37; S, 10.67. Found: 300.0811; C, 67.76; H, 5.47; S, 10.46. **4f**: A colorless oil after chromatography (9:1 hexanes/EtOAc), 80% yield; ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 3 H), 2.35 (s, 3 H), 3.77 (s, 3 H), 7.3–7.5 (m, 5 H); IR (neat) 1740, 1710 cm^{-1}; MS (EI) 238, 196, 195, 177, 164, 163, 135, 105, 91, 77, 65, 59, 43. Anal. Calcd for $C_{12}H_{14}O_3S$: 238.0691; C, 60.48; H, 5.92; S, 13.45. Found: 238.0677; C, 60.38; H, 5.83; S, 13.24. **4g** was synthesized from **6** and PhCOCl, chromatographed (3:1 hexanes/EtOAc) to give a 58% yield, and recrystallized (hexanes) to give the analytical sample: mp 106.5–107 °C; ^{1}H NMR ($CDCl_3$) δ 2.2–2.8 (m, 4 H), 3.62 (s, 3 H), 3.65 (s, 3 H), 7.2–7.6 (m, 8 H), 8.02 (dd, J = 2, 8 Hz, 2 H); IR (KBr) 1735, 1680 cm^{-1}; MS (EI) 372, 313, 236, 204, 179, 105, 77. Anal. Calcd for $C_{20}H_{20}O_5S$: C, 64.50; H, 5.41; S, 8.61. Found: C, 64.58; H, 5.50; S, 8.67. **4h** was prepared from **6** and monoethyl sebacoyl chloride (prepared from the half acid and oxalyl chloride in CH_2Cl_2 followed by concentration from several portions of dry benzene) and chromatographed (6:1 hexanes/EtOAc) to give 66% of a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.23 (t, J = 7 Hz, 3 H), 1.29 (br s, 8 H), 1.7 (m, 4 H), 2.2–3.0 (m, 8 H), 3.64 (s, 3 H), 3.75 (s, 3 H), 4.10 (q, J = 7 Hz, 2 H), 7.32 (s, 5 H); IR (neat) 1735, 1710 cm^{-1}; MS (EI) 481, 435, 268, 236, 213, 204, 139, 121, 97, 69. Anal. Calcd for $C_{25}H_{36}O_7S$: C, 62.48; H, 7.55; S, 6.67. Found: C, 62.51; H, 7.66; S, 6.82.

Oxidation of Sulfides 4a–h. Elimination to Enedicarbonyls 1a–h, and Diels–Alder Reaction with Cyclopentadiene To Give 7. Keto lactones **4a–d** in CH_2Cl_2 (0.2 M) at 0 °C were treated with 40% peracetic acid (1.15 equiv), and the mixture was stirred for ~1 h. If desired the reaction could be quenched with cold saturated $NaHCO_3$ and extracted with CH_2Cl_2. The extracts could be washed (cold saturated $NaHCO_3$, cold brine), dried ($MgSO_4$), and concentrated to afford crude sulfoxides, which were immediately dissolved in $CDCl_3$ and warmed at 60 °C for 5 min to provide solutions of enedicarbonyl compounds **1a–d**: ^{1}H NMR ($CDCl_3$) (**1a**) δ 2.60 (s, 3 H), 4.91 (d, J = 2 Hz, 2 H), 8.23 (t, J = 2 Hz , 1 H); (**1b**) δ 5.07 (d, J = 3 Hz, 2 H), 7.3–8.1 (m, 6 H); (**1c**) δ 1.17 (d, J = 7 Hz, 6 H), 3.52 (septet, J = 7 Hz, 1 H), 4.94 (d, J = 2 Hz, 2 H), 8.25 (t, J = 2 Hz, 1 H); (**1d**) δ 1.26 (s, 9 H), 4.92 (d, J = 2 Hz, 2 H), 7.72 (t, J = 2 Hz, 1 H). These solutions could then be treated with cyclopentadiene to effect Diels–Alder addition (room temperature, several hours), but the yields were superior if the generation of **1** was performed in the presence of the diene. Thus, the initial treatment with CH_3CO_3H was followed after 45 min by the addition of Me_2S (1 equiv), benzene was added, and the solution was concentrated. Redissolution in CH_2Cl_2, addition of cyclopentadiene, and stirring at room temperature for ~3 h effected elimination and cycloaddition to provide the adducts **7ax** and **7an**, chromatographed in 9:1 hexanes/EtOAc, in a 1:2 ratio, 62% yield. Careful screening of column fractions gave pure **7ax** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.57 (m, 2 H), 2.45 (s, 3 H), 3.10 (br s, 1 H), 3.42 (br s, 1 H), 3.47 (br dd, J = 3, 10 Hz, 1 H), 3.78 (dd, J = 3, 10 Hz, 1 H), 4.29 (dd, J = 10, 10 Hz, 1 H), 6.38 (br t, J = 3 Hz, 2 H); IR ($CHCl_3$) 1755, 1705 cm^{-1}; MS (EI) 192 (1), 174 (1), 149 (5), 127 (58), 126 (9), 111 (8), 105 (10), 98 (6), 83 (13), 66 (100). Anal. Calcd for $C_{11}H_{12}O_3$: 192.0781. Found: 192.0784. One recrystallization of pure **7an** (hexanes/EtOAc) gave the analytical sample (as a white solid): mp 72–73 °C; ^{1}H NMR ($CDCl_3$) δ 1.55 (br s, 2 H), 2.39 (s, 3 H), 2.94 (br s, 1 H), 3.11 (br dd, J = 4, 10 Hz, 1 H), 3.53 (br s, 1 H), 3.98 (dd, J = 4, 10 Hz, 1 H), 4.60 (dd, J = 10, 10 Hz, 1 H), 6.06 (dd, J = 3, 6 Hz, 1 H), 6.23 (dd, J = 3, 6 Hz, 1 H); IR (KBr) 1745, 1705 cm^{-1}; MS (CI, NH_3, pos) 210 (M + NH_4^+), 193 (M + H^+), 144 (M + NH_4^+ − C_5H_6); (NH_3, neg) 192 (M + e^-), 191 (M − H^+), 165 (M + NH_2^- − CH_3CO), 126 (M + e^- − C_5H_6), 125 (M − H^+ − C_5H_6). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.98; H, 6.40. **7bx** and **7bn** were chromatographed in 9:1 hexanes/EtOAc in a 1:5 ratio; 73% yield. **7bx** was the more polar, colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.49 (br d, J = 9 Hz, 1 H), 1.72 (br d, J = 9 Hz, 1 H), 3.10 (m, 1 H), 3.50 (ddd, J = 3, 4, 10 Hz, 1 H), 3.85 (br s, 1 H), 3.93 (dd, J = 3, 10 Hz, 1 H), 4.51 (dd, J = 10, 10 Hz, 1 H), 6.45 (br s, 2 H), 7.5 (m, 3 H), 8.03 (dd, J = 2, 8 Hz, 2 H); IR ($CHCl_3$) 1760, 1670 cm^{-1}; MS (EI) 254, 196, 189, 106, 105, 77, 11. Anal. Calcd for $C_{16}H_{14}O_3$: 254.0951. Found: 254.0947. **7bn** was the less polar, crystalline solid (from hexanes/EtOAc): mp 107–120 °C; ^{1}H NMR ($CDCl_3$) δ 1.70 (m, 2 H), 2.94 (br s, 1 H), 3.15 (br d, J = 10 Hz, 1 H), 3.77 (br s, 1 H), 4.12 (dd, J = 4, 10 Hz, 1 H), 4.70 (dd, J = 10, 10 Hz, 1 H), 5.86 (dd, J = 4, 7 Hz, 1 H), 6.11 (dd, J = 4, 7 Hz, 1 H), 7.45 (m, 3 H), 8.05 (dd, J = 2, 7 Hz, 2 H); IR (KBr) 1750, 1670 cm^{-1}; MS (CI, NH_3, pos) 272 (M + NH_4^+), 206 (M + NH_4^+ − C_5H_6); (NH_3, neg) 254 (M + e^-), 188 (M + e^- − C_5H_6), 187 (M − H^+ − C_5H_6). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.80; H, 5.60. **7cx** and **7cn** were chromatographed in 9:1 hexanes/EtOAc in a 1:3 ratio, 59% yield. Careful screening of the chromatographic fractions allowed isolation of pure **7cn** as white crystals (2× from hexanes): mp 56–58 °C; ^{1}H NMR ($CDCl_3$) δ 1.06 (d, J = 7 Hz, 6 H), 1.62 (m, 2 H), 2.94 (m, 2 H), 3.37 (septet, J = 7 Hz, 1 H), 3.54 (br s, 1 H), 4.03 (dd, J = 3, 10 Hz, 1 H), 4.51 (dd, J = 10, 10 Hz, 1 H), 6.04 (dd, J = 3, 7 Hz, 1 H), 6.27 (dd, J = 3, 7 Hz, 1 H); IR (KBr), 1760, 1710 cm^{-1}; MS (EI) 220, 202, 196, 177, 155, 150, 149, 136, 110, 105, 66, 43. Anal. Calcd for $C_{13}H_{16}O$: 220.1107. Found: 220.1103. The minor isomer, **7cx**, could not be isolated free of **7cn** and its structural assignment rests only on analogy with the NMR spectral data of **7ax** and **7bx**. **7dn** chromatographed in 3:1 hexanes/EtOAc, 77% yield: mp 100–102 °C; ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 9 H), 1.52 (m, 2 H), 2.91 (br s, 1 H), 2.96 (br dd, J = 3, 10 Hz, 1 H), 3.55 (br s, 1 H), 4.08 (dd, J = 3, 10 Hz, 1 H), 4.68 (dd, J = 10, 10 Hz, 1 H), 6.09 (dd, J = 3, 6 Hz, 1 H), 6.30 (dd, J = 3, 6 Hz, 1 H); MS (CI, NH_3, pos) 252 (M + NH_4^+), 235 (M + H^+), 186 (M + NH_4^+ − C_5H_6); (NH_3, neg) 233 (N − H^+), 168 (M + e^- − C_5H_6).

The oxidations of **4e–h** were done by the following general procedure. Sulfide **4** in CH_2Cl_2 (0.25 M) at 0 °C was treated with solid MCPBA (1.0 equiv) for 0.5 h. The mixture was diluted with CH_2Cl_2, washed (saturated $NaHCO_3$, brine), dried ($MgSO_4$), and concentrated at room temperature to leave crude sulfoxide. A solution of this sulfoxide in dry benzene (0.8 M) was refluxed for 0.5 h. The crude enedicarbonyl compound **1e** was isolated by concentration as a readily polymerized (as upon attempted SiO_2 chromatography) oil contaminated with products originating from PhSOH: ^{1}H NMR ($CDCl_3$) δ 3.76 (s, 3 H), 6.06 (d, J = 1 Hz, 1 H), 6.72 (d, J = 1 Hz, 1 H), 7.3–7.7 (m, 3 H), 7.87 (dd, J = 2, 8 Hz, 2 H). The acetyl analogue **1f** polymerized even more readily and was not isolated. The dienol **1g** was isolated after chromatography (6:1 hexanes/EtOAc) in 45% yield (from **4g**) as a white solid: mp 75–80 °C; ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 3 H), 3.92 (s, 3 H), 6.27 (d, J = 16 Hz, 1 H), 7.3–7.7 (m, 6 H), 8.97 (s, 1 H, OH); IR (KBr) 1740–1630 (br), 1590, 1430 cm^{-1}; MS (EI) 262, 230, 203, 202, 199, 171, 170, 157, 153, 105, 77, 59, 44. Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 63.82; H, 5.50. The dienol **1h** was obtained after chromatography (6:1 hexanes/EtOAc) in 65% yield (from **4h**) as a purple oil: ^{1}H NMR ($CDCl_3$) δ 1.23 (t, J = 7 Hz, 3 H), 1.2 (br s, 8 H), 1.55 (br m, 4 H), 2.26 (br t, J = 7 Hz, 2 H), 2.55 (br t, J = 7 Hz, 2 H), 3.74 (s, 3 H), 3.86 (s, 3 H), 4.08 (q, J = 7 Hz, 2 H), 6.17 (d, J = 16 Hz, 1 H), 7.51 (d, J = 16 Hz, 1 H), 8.02 (s, 1 H, OH); IR (neat) 3100–2500, 1730, 1635, 1580 cm^{-1}; MS (EI) 370, 293, 292, 213, 200, 168, 153, 139, 136, 127, 121, 97, 69, 44. Anal. Calcd for $C_{19}H_{30}O_7$: C, 61.61; H, 8.16. Found: C, 61.62; H, 8.16. The benzene solutions of in situ generated enedicarbonyls **1e** and **1f** were treated with cyclopentadiene (2 equiv) at room temperature for 15 min. The mixture was diluted

with Et_2O, washed (saturated $NaHCO_3$, brine), dried ($MgSO_4$), and concentrated to give **7ex** and **7en** chromatographed in 19:1 hexanes/EtOAc, 44% yield in a 1:3.5 ratio. The minor isomer **7ex** was obtained as pure only after chromatography of an irradiated solution of both **7ex** and **7en**, which converted **7en** into the oxetane **8**. **7ex**: mp 74–76 °C; ^1H NMR ($CDCl_3$) δ 1.53 (br s, 2 H), 1.99 (dd, J = 4, 12 Hz, 1 H), 2.41 (br d, J = 12 Hz, 1 H), 2.94 (br s, 1 H), 3.50 (s, 3 H), 3.65 (br s, 1 H), 5.93 (dd, J = 3, 6 Hz, 1 H), 6.37 (dd, J = 3, 6 Hz, 1 H), 7.45 (m, 3 H), 7.91 (dd, J = 2, 8 Hz, 2 H); IR (CCl_4) 1745, 1685 cm^{-1}; MS (EI) 256, 225, 224, 191, 159, 120, 105, 91, 77, 66. Anal. Calcd for $C_{16}H_{16}O_3$: 256.1098. Found: 256.1089. **7en**: ^1H NMR ($CDCl_3$) δ 1.45 (br d, J = 9 Hz, 1 H), 1.79 (br d, J = 9 Hz, 1 H), 2.04 (dd, J = 3, 12 Hz, 1 H), 2.48 (dd, J = 4, 12 Hz, 1 H), 2.94 (br s, 1 H), 3.62 (s, 3 H), 3.6 (br s, 1 H), 5.96 (dd, J = 3, 6 Hz, 1 H), 6.11 (dd, J = 3, 6 Hz, 1 H), 7.45 (m, 3 H), 7.83 (dd, J = 2, 8 Hz, 2 H); IR (CCl_4) 1735, 1690 cm^{-1}. This major adduct was further characterized as its oxetane **8**. **7fx** and **7fn** were chromatographed in 19:1 hexanes/EtOAc; 53% yield. **7fx**: ^1H NMR ($CDCl_3$) δ 1.44 (m, 2 H), 1.98 (m, 2 H), 2.18 (s, 3 H), 2.87 (br s, 1 H), 3.34 (br s, 1 H), 3.66 (s, 3 H), 5.99 (dd, J = 3, 6 Hz, 1 H), 6.26 (dd, J = 3, 6 Hz, 1 H); IR (neat) 1740, 1710 cm^{-1}; MS (EI) 194, 162, 128, 113, 97, 91, 66, 43. Anal. Calcd for $C_{11}H_{14}O_3$: 194.0942; C, 68.02; H, 7.26. Found: 194.0940; C, 67.79; H, 7.41. **7fn**: ^1H NMR ($CDCl_3$) δ 1.60 (m, 2 H), 2.03 (s, 2 H), 2.10 (s, 3 H), 2.87 (br s, 1 H), 3.42 (br s, 1 H), 3.70 (s, 3 H), 5.90 (dd, J = 3, 6 Hz, 1 H), 6.20 (dd, J = 3, 6 Hz, 1 H); IR (neat) 1735, 1715 cm^{-1}; MS (EI) 194, 162, 129, 128, 113, 97, 93, 91, 66, 55, 43; UV (95% EtOH) λ 285 (sh, ϵ 40). Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 67.99; H, 7.21.

Preparation of Dimethyl 2-(Phenylthio)glutarate (6). From use of the procedure of Schwenk and Papa[18] monomethyl glutarate (20 g) was refluxed in $SOCl_2$ (40 mL) for 2 h. Bromine (7.4 mL, 1.05 equiv) was then added dropwise to the gently refluxing mixture over 1 h, and this was allowed to stand at room temperature for 12 h. The mixture was cautiously poured into MeOH (70 mL) at 0 °C. After 3 h at room temperature this mixture was partitioned between water and Et_2O. A standard workup and vacuum distillation provided a forerun of dimethyl glutarate (7.4 g) and dimethyl 2-bromoglutarate [bp 50–60 °C (0.5 mmHg), 6.2 g, 19%]: ^1H NMR ($CDCl_3$) δ 2.1–2.6 (m, 4 H), 3.65 (s, 3 H), 3.75 (s, 3 H), 4.32 (t, J = 7 Hz, 1 H); IR (neat) 1730 cm^{-1}. Sodium (0.66 g) was dissolved in absolute MeOH (30 mL) at room temperature and benzenethiol (3.2 mL) was added. After 15 min the bromo ester (6.2 g) was added dropwise to the PhSNa solution at 0 °C. This mixture was then refluxed for 1 h, concentrated under reduced pressure, and partitioned between water and Et_2O. A normal workup gave a crude oil, which was chromatographed (3:1 hexanes/EtOAc) to give **6** (6.2 g, 90%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 2.1 (m, 2 H), 2.5 (br t, J = 7 Hz, 2 H), 3.63 (s, 3 H), 3.65 (s, 3 H), 3.6 (m, 1 H), 7.3 (m, 5 H); IR (neat) 1730 cm^{-1}; MS (EI) 268, 236, 204, 194, 149, 131, 110, 109, 105, 91, 77, 65. Anal. Calcd for $C_{13}H_{16}O_4S$: 268.0769; C, 58.19; H, 6.01. Found: 268.0767; C, 58.27; H, 6.03.

Preparation of Oxetanes 8 and 9. A mixture of Diels–Alder adducts **7ex** and **7en** (247 mg, ratio 1:3.5) was dissolved in benzene (0.4 M) in a Pyrex tube, which was then flushed with argon and irradiated at 300 nm (Rayonet) for 10 h. The NMR spectrum of the crude reaction mixture indicated complete consumption of the major isomer **7en**. The mixture was chromatographed (3:1 hexanes/EtOAc) to give the less polar, recovered **7ex** (26 mg, 11%) and more polar oxetane **8** (124 mg, 50%) as a white solid: mp 82–85 °C (from hexanes); ^1H NMR ($CDCl_3$) δ 1.82 (m, 2 H), 1.84 (d, J = 10 Hz, 1 H), 2.18 (br s, 1 H), 2.26 (br d, J = 10 Hz, 1 H), 3.19 (br dd, J = 2, 4 Hz, 1 H), 3.45 (m, 1 H), 3.63 (s, 3 H), 4.78 (dd, J = 3, 5 Hz, 1 H), 7.3 (m, 5 H); IR (CCl_4) 1740 cm^{-1}; MS (EI) 256, 224, 200, 191, 179, 159, 151, 141, 115, 105, 91, 77, 66, 59, 51. Anal. Calcd for $C_{16}H_{16}O_3$: 256.1099; C, 74.98; H, 6.29. Found: 256.1101; C, 74.61; H, 6.38. By a similar procedure (quartz tube, Vycor filter, Hanovia 450-W lamp, 11 h) pure **7fn** gave oxetane **9** after chromatography (3:1 hexanes/EtOAc) in 68% yield: ^1H NMR ($CDCl_3$) δ 1.45 (s, 3 H), 1.72 (m, 2 H), 1.7–2.2 (m, 3 H), 3.0 (m, 2 H), 3.71 (s, 3 H), 4.64 (dd, J = 3, 4 Hz, 1 H); IR (neat) 1730 cm^{-1}; MS (EI) 194, 179, 176, 162, 138, 129, 119, 105, 91, 79, 66, 59, 55, 43. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 67.89; H, 7.27. When pure **7fx** was irradiated under identical conditions for the same time, decomposition to a multitude of products (^1H NMR, HPLC), which did not include oxetane **9**, was observed.

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Registry No. 1a, 80436-91-5; **1b**, 82111-75-9; **1c**, 82111-76-0; **1d**, 82111-77-1; **1e**, 82111-78-2; **1f**, 22415-00-5; **1g**, 82111-79-3; **1h**, 82111-80-6; **3a**, 82111-61-3; **3b**, 82111-62-4; **3c**, 82111-63-5; **3d**, 82111-64-6; **3e**, 82111-65-7; **4a**, 82111-67-9; **4b**, 82111-68-0; **4c**, 82111-69-1; **4d**, 82111-70-4; **4e**, 82111-71-5; **4f**, 82111-72-6; **4g**, 82111-73-7; **4h**, 82111-74-8; **5**, 21673-18-7; **6**, 82111-66-8; **7ax**, 82111-81-7; **7an**, 82166-36-7; **7bx**, 82111-82-8; **7bn**, 82166-37-8; **7cx**, 82111-83-9; **7cn**, 82166-38-9; **7dx**, 82111-84-0; **7dn**, 82166-39-0; **7ex**, 82111-85-1; **7en**, 82111-87-3; **7fx**, 82111-86-2; **7fn**, 82111-88-4; **8**, 82111-89-5; **9**, 82111-90-8; i, 82111-91-9; ii, 82111-92-0; iii, 82134-48-3; iv, 82111-93-1; v, 76232-18-3; vi, 82111-94-2; vii, 82111-95-3; acetyl chloride, 75-36-5; monoethyl sebacoyl chloride, 6946-46-9; 1,3-cyclopentadiene, 542-92-7; benzoyl chloride, 98-88-4; monomethyl glutarate, 1501-27-5; dimethyl glutarate, 1119-40-0; dimethyl 2-bromoglutarate, 760-94-1; sodium thiophenoxide, 930-69-8; butadiene, 106-99-0.

(18) Schwenk, E.; Papa, D. *J. Am. Chem. Soc.* **1948**, *70*, 3626.