Reaction of thioketones with propiolic acids

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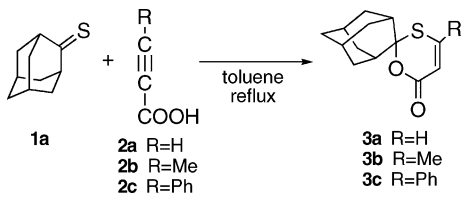
The reaction of adamantane-2-thione with propiolic acid afforded a novel type of cycloadduct, spiro[adamantane-2,2′-6′*H*-[1,3]-oxathiin]-6′-one (**3a**), in quantitative yield. The reaction of thiobenzophenone with propiolic acid gave 2,2-diphenyl-6′*H*-[1,3]-oxathiin]-6′-one and 4-phenyl-3-thia-3,4-dihydronaphthoic acid in 34% and 35% yields, respectively. The reaction might proceed through a concerted process, as confirmed by kinetics. The reaction of adamantane-2-thione with 2-butynoic acid or phenylpropiolic acid gave the corresponding adducts regioselectively. Interestingly, only one isomer was obtained by the reaction of thiofenchone with propiolic acid, suggesting that the reaction proceeded diastereospecifically. Oxidation of adducts **3** by dimethyldioxirane or *m*-chloroperoxybenzoic acid gave the corresponding sulfoxides and sulfones. The sulfoxides were thermally decomposed to give disulfide or another type of 1,3-oxathiin-6-one.

Introduction

Thioketones (**1**) are known to react with dienes to give the corresponding Diels–Alder adducts.[1] α,β-Unsaturated thioketones readily dimerize, and these dimers are employed as sources of the monomers by the retro Diels–Alder reaction. The monomers react with dienophiles to give the corresponding adducts.[2] On the other hand, dihydrobenzothiopyrans have been synthesized by the reaction of aromatic thioketones with dimethyl acetylenedicarboxylate.[3] Photoreaction of 9-xanthenethione with acetylenes initially formed [2 + 2] cycloadducts, which further reacted with acetylenes to give spiro adducts.[4] We have also reported the reaction of monomeric thioketones **1** with benzyne to give the corresponding four-membered benzothietes in good yields.[5] The reaction of 3-thiooxoandrosta-1,4-diene-17-one with propiolic acid (**2a**) reported by Weiss *et al.* afforded the corresponding 1,3-oxathiin-6-ones **3** (thiodioxenone), the first example of monomeric thioketones **1** with acetylenic acids.[6] Recently, we have communicated the synthesis of **3** by the reaction of several types of isolable monomeric thioketones with acetylenic acid.[7] The photoreaction of thiodioxenones **3** has been carried out by Schmidt and Margaretha.[8] Herein, we report the full details of the cycloaddition reaction of thioketones with propiolic acid and the oxidation of the cycloadducts.

Results and discussion

Treatment of adamantane-2-thione (**1a**) with propiolic acid (**2a**) in refluxing toluene resulted in the formation of spiro[adamantane-2,2′-6′*H*-[1,3]-oxathiin]-6′-one (**3a**), in quantitative yield (Scheme 1). The structure of **3a** was determined by spectroscopic analysis. Its ^{1}H NMR spectrum featured two doublet signals at 6.11 and 7.36 ppm, which clearly indicated the existence of two olefinic protons.



Scheme 1

Similarly, 2-butynoic acid (**2b**) and phenylpropiolic acid (**2c**) reacted with **1a** to give the corresponding 6*H*-1,3-oxathiin-6-ones **3b**, **3c**, which are the thio analogues of 6*H*-1,3-dioxin-6-ones (Table 1). 6*H*-1,3-Dioxin-6-ones, which are produced by the cycloaddition reaction of ketones with Meldrum's acid,[9] are well known as the precursors of many natural products.

Since propiolic acid easily reacts with adamantane-2-thione, we next attempted the one-pot synthesis of **3a** from 2-adamantanone (**4**). Treatment of **4** with tetraphosphorus decasulfide, followed by the addition of propiolic acid, gave **3a** in 65% yield (Scheme 2).

Ohno *et al.*[3a,10] and Gotthardt *et al.*[4,11] reported that the cycloaddition and photoreaction of thiobenzophenone (**1b**) with dimethyl

Table 1 Reaction of **1a** with acetylenic acids **2**

Acid		Conditions		Product	
2	Mol equiv.	Solvent	Time/h	**3**	Yield (%)
2a	3	Toluene	3	**3a**	86
2a	3	Toluene	6	**3a**	100
2a	4	Benzene	12	**3a**	85
2a	3	Chloroform	12	**3a**	100
2a	3	Acetone	12	**3a**	0
2b	3	Toluene	96	**3b**	81
2c	3	Toluene	96	**3c**	78

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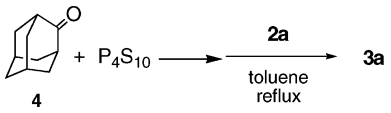
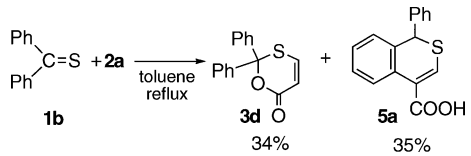


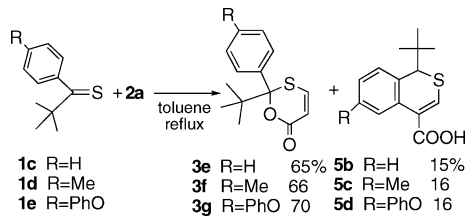
Scheme 2

acetylenedicarboxylate (DMAD) gave methyl 2-carbomethoxy-4-phenyl-3-thia-3,4-dihydronaphthoate in good yield. Instead of DMAD, **2a** gave the same result.[10,11] Since the above result suggested the possibility of the formation of 6*H*-1,3-oxathiin-6-one **3**, we reinvestigated the present reaction. When a concentrated solution (0.5 mol L^{-1}) of **1b** and **2a** in toluene was refluxed for 8 h, 2,2-diphenyl-6*H*-1,3-oxathiin-6-one (**3d**) was obtained in 34% yield along with naphthoic acid (**5a**) (35%) (Scheme 3).



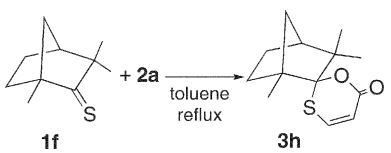
Scheme 3

When thiopivalophenone (**1c**), one of the aromatic thioketones, was chosen as the substrate, 2-*tert*-butyl-2-phenyl-6*H*-1,3-oxathiin-6-one (**3e**) was obtained in 65% yield (Scheme 4). Less than 15% of normal cycloadduct **5b** was obtained as a side product, suggesting that the formation rate of **3d** was higher than that of **5b**. Thus, even in the case of unsaturated thioketones, thiodioxenones **3** were obtained in moderate yields.



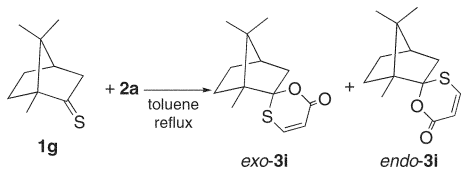
Scheme 4

Weiss *et al.* reported that the reaction of 3-thiooxoandrosta-1,4-diene-17-one with **2a** gave the corresponding 6*H*-1,3-oxathiin-6-one.[6] They suggested that the reaction might proceed through an ionic intermediate, however no confirmation was observed. To check the exact reaction mechanism, we have tried the reaction of thiofenchone (**1f**) with **2a**. If the reaction proceeds through an ionic intermediate, both isomers (*exo*- and *endo*-cycloadducts) will be formed in a nearly 1 : 1 ratio. When a solution of **1f** and **2a** in toluene was refluxed for 5 h, only one cycloadduct (*exo*-**3h**) (83%) was obtained, suggesting that the reaction proceeded diastereospecifically (Scheme 5). The structure of **3h** was confirmed by its X-ray crystallographic analysis.[7]



Scheme 5

We then tried the reaction of thiocamphor (**1g**) with **2a**. A thioketone with less bulky substituting groups, such as **1g**, will afford both isomers even in a concerted process. Additionally, thiocamphor **1g** isomerizes to the corresponding enethiol, which may afford the ene reaction product. Treatment of **1g** with **2a** in refluxing toluene resulted in the formation of the corresponding *exo–endo* adducts (*exo* : *endo* = 5 : 1) **3i** in 66% yield (Scheme 6) along with unidentified products. Although it is not clear whether ene-reaction products were formed or not, yields of those products were less than 5%. Since the exact structure of main product **3i** is not clear, we then tried the X-ray crystallographic analysis of major product of **3i**. Fig. 1 shows an ORTEP drawing of *exo*-**3i**.



Scheme 6

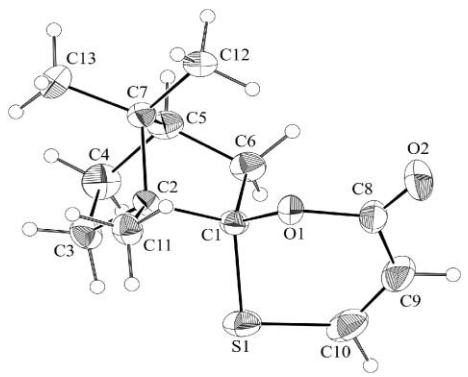
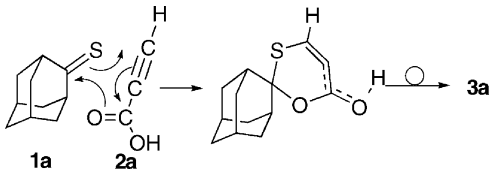


Fig. 1 ORTEP drawing of compound **3i**. Selected data for *exo*-**3i**: bond lengths: C_1–S_1 = 1.835(2) Å, C_1–O_1 = 1.435(3) Å, C_{10}–S_1 = 1.719(4) Å, C_8–O_1 = 1.366(3) Å, bond angles: O_1–C_1–S_1 = 108.0(2)°, C_1–S_1–C_{10} = 96.48(14)°, C_1–O_1–C_8 = 119.1(2)°.

Since the present reaction might proceed through the cycloaddition mechanism, we then carried out kinetic analysis. The formation of **3a** from thioketone **1a** and **2a** could be conveniently and accurately monitored by ^{1}H NMR spectroscopy. A second-order reaction was observed by this technique. The rate constant of 2.89×10^{-2} mol^{-1} dm^3 min^{-1} at 353 K was obtained, which was slightly dependent on the solvent used (relative rate; toluene : benzene = 1 : 1.78 at 353 K, chloroform : toluene = 1.23 : 1 at 333 K). The reaction did not proceed in polar solvents, such as DMSO, acetonitrile, and methanol. Variable temperature NMR spectroscopy over the range of 60 to 110 °C with toluene as solvent was used to obtain the activation parameters of $\Delta H^{\ddagger} = 44$ kJ mol^{-1} and $\Delta S^{\ddagger} = -184$ J K^{-1}.

The observations of second-order reaction kinetics and a highly stereoselective addition suggest a cycloaddition mechanism for the thermal addition (Scheme 7). The large, negative entropy of activation is consistent with the rigid cyclic transition state, which indicates the relative independence of the reaction rate from the solvent. The solvation of **2a** by polar solvents might prevent the initial addition of this cycloaddition.

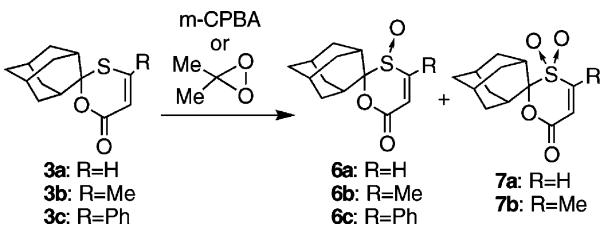


Scheme 7

The photocycloaddition reaction of thione **1b** with olefins afforded thietanes and 1,4-dithianes *via* radical intermediates.[12] The benzo derivative of this type of compound was synthesized by Dittmer *et al.*[13] They reacted benzenediazonium 2-carboxylate with **1b** to afford benzo-1,3-oxathian-2-one. Krische *et al.* also synthesized benzo-1,3-oxathiin-2-ones by a three step reaction from 2-iodobenzoic acids.[14]

Oxidation of 6*H*-1,3-oxathiin-6-one

The photoreaction of thiodioxenones **3a** was recently carried out by Schmidt and Margaretha.[8] They suggested the formation of adamantine-2-one *via* [4 + 2] cycloreversion. We first tried the thermolysis of **3a**. Attempted thermolysis of **3a** in refluxing xylene led to the recovery of starting **3a** quantitatively, whose reactivity is quite different from that of dioxenones. Dioxenones are usually afforded the [4 + 2] cycloreversion products in refluxing toluene.[9,15] Thus, we then tried the oxidation of thiodioxenones in the hope of obtaining the more reactive sulfoxides **6**. The oxidation of **3a** with dimethyldioxirane (DMD) (1.2 mol equiv.) gave the corresponding sulfoxide **6a** (80%) and sulfone **7a** (12%), whereas the oxidation of **3a** with *m*-CPBA (1.5 mol. equiv.) resulted in the formation of **6a** (55%) and **7a** (15%) along with 2-adamantanone (12%), which might be formed by acid hydrolysis (Scheme 8). When excess of *m*-CPBA (4 mol equiv.) was used, only **7a** was obtained in 85% yield. Other sulfoxides were obtained in a similar manner. The results are shown in Table 2.

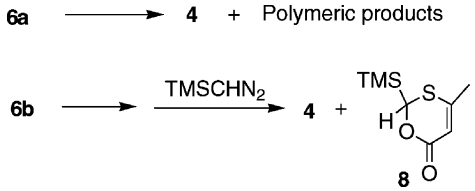


Scheme 8

Thus, selective oxidation gave the corresponding sulfoxides **6a–c** in good yields.

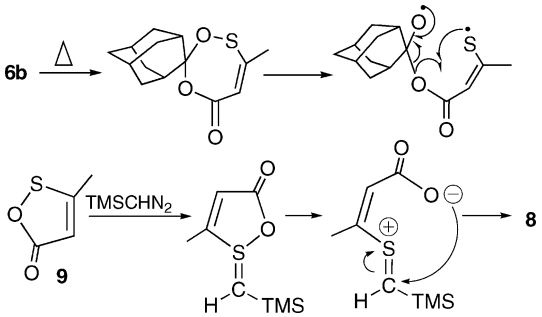
Thermolysis of sulfoxide 6

Since sulfoxides are generally converted into sulfenates on heating,[16] we next attempted the thermolysis of 6*H*-1,3-oxathiin-6-one *S*-oxides **6**. A recent study concerning thiosulfinates is applied to the DNA cleavage.[17] Treatment of **6a** in refluxing toluene resulted in polymeric products, whereas the thermolysis of **6b** afforded unstable olefinic products, which could not be isolated due to the tendency of polymerization. When the reaction was carried out in the presence of trimethylsilyldiazomethane ($TMSCHN_2$), 4-methyl-2-trimethylsilyl-6*H*-1,3-oxathiin-6-one (**8**), was obtained (Scheme 9).



Scheme 9

According to Krische and Walter, thermolysis of 4*H*-3,1-benzooxanthiin-4-one *S*-oxide gave ring contraction product, 3*H*-2,1-benzooxathiol-3-one.[18] Thus, the reaction is surmised to proceed as follows. Sulfoxide **6b** was rearranged to sulfenate, which was cleaved to give a biradical and adamantanone. The biradical was further cyclized to afford 5-methyl-3*H*-2,1-oxathiol-3-one (**9**), which was attacked by $TMSCHN_2$ to give **8** *via* Pummerer rearrangement (Scheme 10).[19]

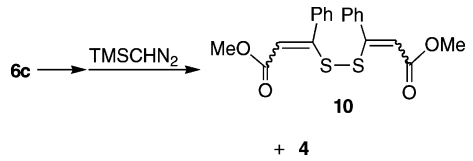


Scheme 10

When **6c** was treated with $TMSCHN_2$ in refluxing toluene, disulfide **10** was obtained. In this case, the phenyl group stabilized the biradical intermediate, preventing the cyclization, and further reaction with $TMSCHN_2$ gave disulfide **10** (Scheme 11).

Table 2 Oxidation of 6*H*-1,3-oxathiin-6-ones **3a–c**

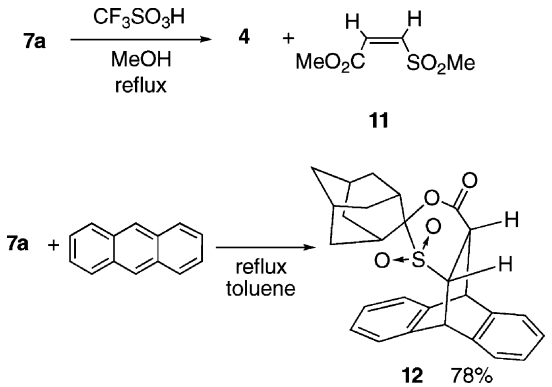
Compound **3a–c**	Oxidant	Mol equiv.	Solvent	**6**	Yield (%)	**7**	Yield (%)
3a	*m*-CPBA	1.5	CH_2Cl_2	**6a**	55	**7a**	15
3a	DMD	1.5	Acetone	**6a**	80	**7a**	12
3a	*m*-CPBA	4.0	Acetone	**6a**	0	**7a**	85
3b	DMD	1.5	Acetone	**6b**	75	**7b**	6
3b	*m*-CPBA	3.5	Acetone	**6b**	0	**7b**	86
3c	DMD	1.5	Acetone	**6c**	78	**7c**	—



Scheme 11

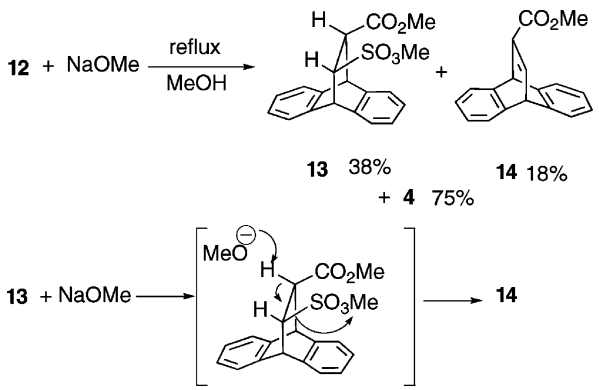
Reaction of sulfone 7a with anthracene

In contrast with **3a** and **6a**, sulfone **7a** was alcoholyzed to give the corresponding ester (**11**) in 68% yield. We then tried the reaction of these compounds with anthracene in the hope of obtaining the corresponding Diels–Alder adducts. **7a** reacted with anthracene to afford the Diels–Alder adducts in 78% yield, whereas **3a–c** did not afford the corresponding adducts. (Scheme 12). Thus, **7a** is found to be a good dienophile.



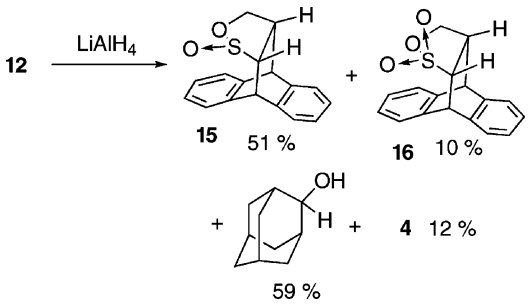
Scheme 12

Basic alcoholysis of **12** in methanol afforded the sulfonate (38%) (**13**) and unsaturated (18%) ester (**14**) along with **4** (75%) (Scheme 13). Ester **14** might be formed by basic abstraction of **13**. Structure of **14** was confirmed by the independent synthesis of anthracene with methyl propiolate.



Scheme 13

Reduction of **12** by $LiAlH_4$ in THF afforded two products, cyclic sulfinate (**15**) and sulfonate (**16**), along with adamantanol and **4**. When excess of $LiAlH_4$ was used, the cyclic sulfinate was obtained in 60% yield (Scheme 14). Although the syntheses of cyclic sulfinates are well known, the present method provides a new type of synthesis of tetracyclic sulfinates.[20]



Scheme 14

In conclusion, we have synthesized novel cyclic 6*H*-1,3-oxathiin-6-ones **3** by reacting thioketones with propiolic acid derivatives, the oxidation of which afforded the corresponding sulfoxides **6** and sulfones **7**. Thermolysis of sulfoxides gave another type of 6*H*-1,3-oxathiin-6-one **8** and disulfide **10**. Reaction of **7** with anthracene gave the corresponding adduct **12**, which was reduced by LAH to afford a new type of sultine **15**.

Experimental

General

All chemicals were obtained from commercial suppliers and were used without further purification. Analytical TLC was carried out on precoated plates (Merck silica gel 60, F254) and flash column chromatography was performed with silica (Merck, 70–230 mesh). NMR spectra (^{1}H at 400 MHz; ^{13}C at 100 MHz) were recorded in $CDCl_3$ solvent, and the chemical shifts were expressed in ppm relative to internal TMS. The melting points were uncorrected.

Materials

Thiones were synthesized by the reaction of ketones with tetraphosphorus decasulfide according to the reported methods.[21]

Reaction of adamantane-2-thione (1a) with propiolic acid (2a)

To a solution of **1a** (332 mg, 2.0 mmol) in toluene (15 mL) was added **2a** (422 mg, 6.0 mmol) in one portion. After being refluxed for 5 h, the reaction mixture was evaporated to give pale yellow crystals of spiro[adamantane-2,2′-6*H*′-[1,3]-oxathiin]-6′-one (**3a**), which was almost pure (470 mg, 1.99 mmol). Recrystallization from hexane gave pure adduct **3a**. **3a**: colorless crystals; mp 141–142 °C. ^{1}H NMR ($CDCl_3$) δ = 1.65 (d, 2H, J = 13 Hz, CH_2), 1.75 (s, 2H, CH_2), 1.83 (d, 2H, J = 14 Hz, CH), 1.88 (s, 2H, CH_2), 2.05 (d, 2H, J = 14 Hz, CH), 2.37 (d, 2H, J = 13 Hz, CH_2), 2.53 (s, 2H, CH), 6.12 (d, 1H, J = 10 Hz, =CH), 7.34 (d, 1H, J = 10 Hz, =CH). ^{13}C NMR ($CDCl_3$) δ = 26.51, 26.68, 32.26, 34.75, 36.55, 37.53, 95.53 (S-C-O), 113.57 (=CH), 142.08 (=CH-S), 161.94 (C=O). MS: Found: 236 (M^+), Calcd for $C_{13}H_{16}O_2S$: 236. Anal. Found: C, 65.96; H, 6.78%. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82%.

4′-Methylspiro[adamantane-2,2′-6*H*′-[1,3]-oxathiin]-6′-one (3b). 81%, mp 91–92 °C. ^{1}H NMR ($CDCl_3$) δ = 1.64 (d, 2H, J = 12 Hz, CH_2), 1.74 (s, 2H, CH_2), 1.81 (d, 2H, J = 12 Hz, CH_2), 1.82 (s, 2H, CH), 2.06 (d, 2H, J = 12 Hz, CH_2), 2.15 (d, 3H, J = 1 Hz, CH_3), 2.35 (d, 2H, J = 12 Hz, CH_2), 2.47 (s, 2H, CH), 5.95 (d, 1H,

$J = 1$ Hz, =CH). ^{13}C NMR ($CDCl_3$) $\delta = 23.67$ (CH_3), 26.46, 26.71, 32.43, 34.73, 36.66, 37.54, 94.77 (S-C-O), 111.03 (=CH), 154.99 (=CCH_3), 162.90 (C=O). Anal. Found: C, 66.94; H, 7.25%. Calcd for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25%.

4′-Phenylspiro[adamantane-2,2′-6*H*′-[1,3]-oxathiin]-6′-one (3c). 78%, mp 129–130 °C. ^{1}H NMR ($CDCl_3$) $\delta = 1.70$ (d, 2H, $J =$ 12 Hz, CH_2), 1.78 (s, 2H, CH_2), 1.87 (d, 2H, $J = 12$ Hz, CH), 1.93 (s, 2H, CH_2), 2.20 (d, 2H, $J = 13$ Hz, CH), 2.41 (d, 2H, $J = 12$ Hz, CH_2), 2.58 (s, 2H, CH), 6.40 (s, 1H, =CH), 7.42–7.51 (m, 3H, Ph), 7.64–7.67 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$) $\delta = 26.47$, 26.50, 32.28, 34.90, 36.43, 37.53, 94.69 (S-C-O), 109.52 (=CH), 127.33, 128.82, 131.33, 135.68, 155.26 (=C-S), 163.57 (C=O). Anal. Found: C, 65.96; H, 6.78%. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82%.

Reaction of adamantanone (4) with tetraphosphorus decasulfide followed by the addition of 2a

To a solution of **4** (750 mg, 5.0 mmol) in toluene (25 mL) was added tetraphosphorus decasulfide (890 mg, 2.0 mmol) in one portion. After being refluxed for 1 h, **2a** (1.05 g, 15 mmol) was added and further refluxed for 10 h. The reaction mixture was washed with water, separated, dried over magnesium sulfate, and filtered. The filtrate was evaporated to give a brown oil, which was chromatographed over silica gel by elution with hexane–dichloromethane (1 : 1) to afford colorless crystals of **3a** (767 mg, 3.25 mmol, 65%).

Reaction of thiobenzophenone (1b) with 2a

To a solution of **1b** (198 mg, 1.0 mmol) in toluene (2 mL) was added **2a** (210 mg, 3.0 mmol) in one portion. After refluxing for 7 h, the reaction mixture was evaporated to give a pale yellow oil, which was chromatographed over silica gel by elution with hexane–dichloromethane (1 : 1) to afford 2,2-diphenyl-6*H*-1,3-oxathiin-6-one (**3d**) (91 mg, 0.34 mmol, 34%). **3d**: mp 126–127 °C. ^{1}H NMR ($CDCl_3$) $\delta = 6.07$ (d, 1H, $J = 10.8$ Hz, =CH), 7.32–7.37 (m, 7H, =CH and Ph), 7.54–7.59 (br d, 4H, Ph). ^{13}C NMR ($CDCl_3$) $\delta =$ 94.11 (S-C-O), 116.74 (=CH), 126.86 (Ph), 128.45 (Ph), 129.06 (Ph), 140.20 (=CH), 142.54 (Ph), 162.05 (COO). Anal. Found: C, 71.73; H, 4.57%. Calcd for $C_{16}H_{12}O_2S$: C, 71.62; H, 4.51%. Further elution with dichloromethane afforded 4-phenyl-3-thia-3,4-dihydronaphthoic acid (**5a**) (94 mg, 0.35 mmol, 35%). **5a**: mp 172–173 °C (Lit.[10] mp 164–165 °C). ^{1}H NMR ($CDCl_3$) $\delta = 5.16$ (s, 1H, CH), 7.02 (d, 1H, $J = 7.2$ Hz, Ar), 7.16–7.43 (m, 7H, Ar), 7.94 (s, 1H, =CH), 8.09 (d, 1H, J = 7.2 Hz, Ar). ^{13}C NMR ($CDCl_3$) $\delta = 47.18$ (CH), 125.76, 127.20, 127.26, 127.81, 127.83, 128.17, 128.59, 128.86, 130.40, 131.00, 138.84, 139.57, 169.76 (COO). Anal. Found: C, 71.39; H, 4.56%. Calcd for $C_{16}H_{12}O_2S$: C, 71.62; H, 4.51%.

Reaction of thiopivalophenone (1c) with 2a

To a solution of **1c** (534 mg, 3.0 mmol) in toluene (15 mL) was added **2a** in one portion. After being refluxed for 8 h, the reaction mixture was evaporated to give pale yellow crystals, which were chromatographed over silica gel by elution with dichloromethane–hexane (1 : 1) to afford 2-*tert*-butyl-2-phenyl-6*H*-1,3-oxathiin-6-one (**3e**) (484 mg, 1.95 mmol, 65%). **3e**: mp 124–125 °C. ^{1}H NMR ($CDCl_3$) $\delta = 1.09$ (s, 9H, *tert*-Bu), 5.91 (d, 1H, $J = 10$ Hz), 7.22 (d, 1H, $J = 10$ Hz, =CH), 7.22–7.35 (m, 3 H, Ph), 7.57–7.61 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$) $\delta = 25.99$ (*tert*-butyl), 40.43 (*tert*-butyl), 101.46 (S-C-O), 114.96 (=CH), 127.01, 128.51, 128.66, 138.30, 141.91 (=CH), 162.78 (C=O). Anal. Found: C, 67.47; H, 6.59%. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49%.

4-*tert*-Butyl-3-thia-3,4-dihydronaphthoic acid (5b). (112 mg, 0.45 mmol, 15%): mp 189–190 °C. ^{1}H NMR ($CDCl_3$) $\delta = 0.94$ (s, 9H, *tert*-butyl), 3.71 (d, 1H, $J = 2$ Hz, CH), 7.10 (br d, 1H, $J =$ 7 Hz, Ph), 7.28–7.36 (m, 2H, Ph), 7.97 (d, 1H, $J = 2$ Hz, =CH), 8.04 (br d, 1H, $J = 6$ Hz, Ph). ^{13}C NMR ($CDCl_3$) $\delta = 26.72$ (*tert*-butyl), 39.14 (*tert*-butyl), 54.17 (S-CH), 125.53, 126.84, 127.63, 127.74, 128.49, 130.35, 130.54, 140.56 (=CH), 169.37 (C=O). Anal. Found: C, 63.46; H, 6.85%. Calcd for $C_{14}H_{16}O_2S + H_2O$: C, 63.14; H, 6.81%.

Other reactions were carried out in a similar manner by using 3.0 mmol of thiopivalophenone.

2-*tert*-Butyl-2-*p*-tolyl-6*H*-1,3-oxathiin-6-one (3f). (519 mg, 1.98 mmol, 66%): mp 104–105 °C. ^{1}H NMR ($CDCl_3$) $\delta = 1.09$ (s, 9H, *tert*-butyl), 2.34 (s, 3H, CH_3), 5.92 (d, 1H, $J = 10$ Hz, =CH), 7.08 (d, 2H, $J = 9$ Hz, *p*-Tol), 7.21 (d, 1H, $J = 10$ Hz, =CH), 7.46 (d, 2H, $J = 9$ Hz, *p*-Tol). ^{13}C NMR ($CDCl_3$) $\delta =$ 20.96 (*tert*-butyl), 25.96 (CH_3), 40.42 (*tert*-butyl), 101.54, 114.90 (=CH), 127.70, 128.39, 135.22, 138.55, 141.99 (=CH), 162.85 (COO). Anal. Found: C, 69.00; H, 6.78%. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92%.

4-*tert*-Butyl-7-methyl-3-thia-3,4-dihydronaphthoic acid (5c). (126 mg, 0.48 mmol, 16%): mp 192–193 °C. ^{1}H NMR ($CDCl_3$) $\delta = 0.92$ (s, 9H, *tert*-butyl), 2.38 (s, 3H, Tol-CH_3), 3.68 (s, 1H, CH), 6.98 (d, 1H, $J = 8$ Hz, Ar), 7.11 (br d, 1H, $J = 8$ Hz, Ar), 7.83 (br s, 1H, Ar), 7.94 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$) $\delta =$ 21.55 (CH_3), 26.81 (*tert*-butyl), 39.18 (*tert*-butyl), 54.09 (S-CH), 125.34, 125.59, 127.12, 128.37, 130.06, 137.11, 140.67 (=CH), 156.44, 169.71 (COO). Anal. Found: C, 68.33; H, 6.58%. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92%.

2-*tert*-Butyl-2-*p*-phenoxyphenyl-6*H*-1,3-oxathiin-6-one (3g). (681 mg, 2.1 mmol, 70%): mp 116–117 °C. ^{1}H NMR ($CDCl_3$) $\delta =$ 1.09 (s, 9H, *tert*-butyl), 5.95 (d, 1H, $J = 10$ Hz, =CH), 6.89 (d, 2H, $J = 9$ Hz, Ar), 7.03 (d, 2H, $J = 10$ Hz, Ar), 7.15 (m, 1H, Ar), 7.24 (d, 1H, $J = 10$ Hz, =CH), 7.35 (m, 2H, Ar), 7.53 (d, 2H, $J = 9$ Hz, Ar). ^{13}C NMR ($CDCl_3$) $\delta = 25.89$ (*tert*-butyl), 40.49 (*tert*-butyl), 101.22 (S-C-O), 114.85 (=CH), 116.24, 119.51, 123.88, 129.76, 132.35, 141.96 (=CH), 155.98, 157.79, 162.63 (COO). Anal. Found: C, 70.30; H, 6.00%. Calcd for $C_{14}H_{16}O_2S$: C, 70.56; H, 5.92%.

4-*tert*-Butyl-7-phenoxy-3-thia-3,4-dihydronaphthoic acid (5d). (156 mg, 0.48 mmol, 16%): mp 205–206 °C. ^{1}H NMR ($CDCl_3$) $\delta =$ 0.93 (s, 9H, *tert*-butyl), 3.70 (br s, 1H, CH), 6.92 (dd, 1H, $J = 2$ and 8 Hz, Ar), 7.02–7.05 (m, 3H, Ar and PhO), 7.11 (m, 1H, PhO), 7.33 (m, 2H, PhO), 7.90 (br s, 1H, =CH), 7.99 (br s, 1H, Ar). ^{13}C NMR ($CDCl_3$) $\delta = 26.63$ (*tert*-butyl), 39.17 (*tert*-butyl), 53.72 (SCH), 117.44, 117.78, 118.82, 123.24, 123.35, 125.04, 129.69, 131.41, 131.86, 141.55, 156.36, 156.96, 169.85 (COO). Anal. Found: C, 70.63; H, 6.01%. Calcd for $C_{14}H_{16}O_2S$: C, 70.56; H, 5.92%.

Reaction of thiofenchone (1f) with 2a

To a solution of **1f** (337 mg, 2.0 mmol) in toluene (15 mL) was added **2a** (422 mg, 6.0 mmol) in one portion. After being refluxed for 5 h, the reaction mixture was evaporated to give pale yellow crystals of 1,3-oxathiine-6-one **3h**. Recrystallization from hexane gave pure adduct **3h** (395 mg, 1.66 mmol, 83%). Spiro[fenchane-2,2′-[1,3]-oxathiin]-6′-one (**3h**): mp 151.5–153 °C. ^{1}H NMR ($CDCl_3$) $\delta = 1.19$ (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.27–1.77 (m, 6H, CH_2), 2.19 (d, 1H, $J = 10$ Hz, CH), 6.04 (d, 1H, $J = 10$ Hz, =CH), 7.38 (d, 1H, $J = 10$ Hz, =CH). ^{13}C NMR ($CDCl_3$) $\delta = 17.83$ (CH_3), 25.00 (CH_3), 25.99 (CH_3), 30.06, 30.44, 40.28, 49.78, 51.44, 54.85, 103.67 (S-C-O), 114.57, 142.86, 163.15 (COO). Anal. Found: C, 65.51; H, 7.58%. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61%.

Reaction of thiocamphor (1g) with 2a

To a solution of **1g** (304 mg, 2.0 mmol) in toluene (15 mL) was added **2a** (422 mg, 4.0 mmol) in one portion. After being refluxed for 13 h, the reaction mixture was evaporated to give a pale yellow oil, which was chromatographed over silica gel by elution from hexane–dichloromethane (1 : 1) to afford a mixture of *endo*- and *exo*-thiodioxenone (315 g, 1.32 mmol, 66%). Recrystallization from hexane gave pure *exo*-adduct **3i** (158 mg, 0.66 mmol, 33%). Another isomer, *endo*-**3i**, could not be isolated in pure form. *exo*-Spiro[camphane-2,2′-[1,3]-oxathiin]-6′-one **3i**: mp 144–145 °C. ^{1}H NMR ($CDCl_3$) $\delta = 0.94$ (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 1.20 (m, 1H, CH_2), 1.64 (m, 2H, CH_2), 1.78 (m, 1H, CH_2), 1.92 (m, 1H, CH_2), 2.08 (d, 1H, $J = 14$ Hz, CH_2), 2.90 (m, 1H, CH), 6.13 (d, 1H, $J = 10$ Hz, =CH), 7.48 (d, 1H, $J = 10$ Hz, =CH). ^{13}C NMR ($CDCl_3$) $\delta = 11.52$ (CH_3), 20.84 (CH_3), 21.29 (CH_3), 26.13 (CH_2), 30.44, 40.28, 49.78, 51.44, 54.85, 103.67, (S-C-O), 114.57, 142.86, 163.15 (COO). Anal. Found: C, 65.29; H 7.61%. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61%.

Crystal data for *exo*-**3i**: Crystal data for $C_{13}H_{18}O_2S$. Crystallized from hexane. Mo-Kα radiation. $M = 238.35$, $a = 7.69(5)$, $b = 9.26(5)$, $c = 17.15(5)$ Å, $V = 1221.11$ Å^3, $T = 298$ K, orthorhombic, space group = $P2_12_12_1$, $Z = 4$. $n = 0.248$ mm^{-1}, 4013 measured reflections, 2044 independent reflections, $R_{int} = 0.033$, Final $R = 0.0485$ for 1458 observed reflections ($I > 2\sigma(I)$), $R = 0.0781$ for all reflections.†

Oxidation of 3a using *m*-CPBA

To a solution of **3a** (236 mg, 1.0 mmol) in dichloromethane (5 mL) was added a solution of *m*-CPBA (259 mg, 1.5 mmol) in dichloromethane (10 mL). After being stirred for 5 h, a colorless solid of *m*-chlorobenzoic acid was precipitated, which was filtered off. The filtrate was washed with 5% aqueous sodium carbonate (10 ml) twice and dried over magnesium sulfate, filtered and evaporated to give pale yellow oil, which was chromatographed over silica gel by elution with dichloromethane–hexane (1 : 1) to afford spiro[adamantine-2,2′-[1,3]oxathiin]-6′-one 3′-oxide (**6a**) (139 mg, 0.55 mmol, 55%). **6a**: colorless crystals; mp 70 °C (decomp.). ^{1}H NMR ($CDCl_3$) $\delta = 1.68$ (d, 2H, $J = 13$ Hz, CH), 1.78–1.86 (m, 4H, CH_2), 1.94–2.06 (m, 4H, CH_2), 2.13 (s, 1H, CH), 2.19 (d, 1H, $J = 13$ Hz, C*H*H), 2.34 (d, 1H, $J = 14$ Hz, C*H*H), 2.46 (d, 1H, $J = 13$ Hz, C*H*H), 2.72 (s, 1H, CH), 6.60 (d, 1H, $J = 10$ Hz, =CH), 7.61 (d, 1H, $J = 10$ Hz, =CH). ^{13}C NMR ($CDCl_3$) $\delta = 26.36$, 26.75, 31.50, 31.92, 33.23, 33.33, 34.32, 35.60, 37.40, 101.36 (S-C-O), 126.31 (=CH), 140.27 (=CH-S), 159.13 (C=O). IR (neat) ν_{max}/cm^{-1} = 3060, 2977, 2899, 2866, 1737, 1618, 1455, 1312. 1276, 1243, 1226, 1149, 1098, 1069, 1038, 1011 (S=O), 860, 799, 750, 663. Anal. Found: C, 62.15; H, 6.46%. Calcd for $C_{13}H_{16}O_3S$. C, 61.88; H, 6.39%. Further elution with dichloromethane gave spiro[adamantane-2,2′-[1,3]oxathiin]-6′-one 3′,3′-dioxide (**7a**) (38 mg, 0.15 mmol, 15%) and adamantanone **4** (18 mg, 0.12 mmol, 12%). Sulfone **7a**: colorless crystals; mp 178–179 °C. ^{1}H NMR ($CDCl_3$) $\delta = 1.75$ (d, 2H, $J = 13$ Hz, CH_2), 1.79 (s, 2H, CH_2), 1.84 (d, 2H, $J = 14$ Hz, CH), 1.96 (m, 2H, CH_2), 2.31 (d, 2H, $J = 14$ Hz, CH), 2.54 (d, 2H, $J = 14$ Hz, CH_2), 2.67 (s, 2H, CH), 6.51 (d, 1H, $J = 15$ Hz, =CH), 7.05 (d, 1H, $J = 15$ Hz, =CH). ^{13}C NMR ($CDCl_3$) $\delta =$ 26.02, 26.37, 33.16, 33.25, 33.41, 37.43, 101.53 (S-C-O), 127.44 (=CH), 140.46 (=CH-S), 158.33 (C=O). Anal. Found. C, 58.40; H, 6.02%. Calcd for $C_{13}H_{16}O_4S$. C, 58.19; H, 6.01%.

When excess of *m*-CPBA (4 mol equiv., 0.69 g) was used in acetone, only sulfone **7a** was isolated in 85% yield (0.227 g, 0.85 mmol).

Oxidation of 3b using DMD

To a solution of **3b** (250 mg, 1.0 mmol) in acetone (15 mL) was added a solution of DMD (0.083 M in acetone, 18 mL, 1.5 mmol). After being stirred for 5 h, the reaction mixture was evaporated to give colorless crystals, which were chromatographed over silica gel by elution with dichloromethane–hexane (1 : 1) to afford 4′-methylspiro[adamantane-2,2′-[1,3]oxathiin]-6′-one 3′-oxide (**6b**) (200 mg, 0.75 mmol, 75%). **6b**: colorless crystals; mp 113–114 °C. ^{1}H NMR ($CDCl_3$) $\delta = 1.66$ (br d, 1H, $J = 13$ Hz, CH), 1.75–1.86 (m, 4H, CH_2), 1.92–2.26 (m, 6H, CH_2), 2.36 (d, 1H, $J = 14$ Hz, C*H*H), 2.43 (s, 3H, CH_3), 2.46 (br, 1H, C*H*H), 2.73 (s, 1H, CH), 6.28 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$) $\delta = 21.37$ (CH_3), 26.72, 27.06, 31.77, 32.50, 33.37, 33.60, 34.55, 35.73, 37.68, 100.42 (S-C-O), 120.63 (=CH), 154.04 (=CH-S), 159.65 (C=O). IR (neat) ν_{max}/cm^{-1} = 3006, 2919, 2899, 2862, 1716, 1633, 1445, 1380, 1360, 1284, 1254, 1221, 1099, 1081, 1046 (S=O), 1015, 964, 947, 916, 897, 879, 835, 747, 724, 645. Anal. Found: C, 63.20; H, 6.74%. Calcd for $C_{14}H_{19}O_3S$: C, 63.13; H, 6.81%.

4′-Methylspiro[adamantane-2,2′-[1,3]-oxathiin]-6′-one 3′,3′-dioxide (**7b**) (17 mg, 0.06 mmol, 6%): colorless crystals; mp 122–123 °C. ^{1}H NMR ($CDCl_3$) $\delta = 1.74$ (d, 2H, $J = 13$ Hz, CH_2), 1.79 (s, 2H, CH_2), 1.82 (d, 2H, $J = 14$ Hz, CH), 1.95 (d, 2H, $J =$ 14 Hz, CH), 2.27 (s, 3H, CH_3), 2.31 (d, 2H, $J = 13$ Hz, CH), 2.54 (d, 2H, $J = 14$ Hz, CH_2), 2.65 (s, 2H, CH), 6.26 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$) $\delta = 14.80$ (CH_3), 26.35, 26.73, 33.31, 33.55, 33.79, 37.78, 100.19 (S-C-O), 123.13 (=CH), 151.64 (=CH-S), 158.44 (C=O). IR (neat) ν_{max}/cm^{-1} = 3053, 2941, 2915, 2895, 2873, 1724, 1642, 1455, 1432, 1305 (SO_2), 1281, 1246, 1223, 1155 (SO_2), 1120, 1102, 1075, 1045, 1010, 968, 945, 903, 885, 850, 772, 742, 716, 687, 657. Anal. Found: C, 59.38; H, 6.38%. Calcd for $C_{14}H_{18}O_4S$. C, 59.55; H, 6.43%.

4′-Phenylspiro[adamantane-2,2′-[1,3]-oxathiin]-6′-one 3′-oxide (**6c**) (256 mg, 0.78 mmol, 78%): colorless crystals; mp 141–142 °C. ^{1}H NMR ($CDCl_3$) $\delta = 1.68$ (br d, 1H, $J = 13$ Hz, CH), 1.75–1.92

† CCDC reference number 604020. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605068a

(m, 4H, CH_2), 1.98–2.10 (m, 4H, CH_2), 2.21 (br s, 2H, CH_2), 2.45 (d, 1H, $J = 14$ Hz, C*H*H), 2.52 (d, 1H, $J = 14$ Hz, C*H*H), 2.79 (s, 1H, CH), 6.68 (s, 1H, =CH), 7.40–7.60 (m, 3H, Ph), 7.40 (br d, $J = 8$ Hz, Ph). IR (neat) $\nu_{max}/cm^{-1} = 3036$, 2930, 2897, 2852, 1709, 1602, 1491, 1470, 1444, 1355, 1307, 1282, 1247, 1216, 1099, 1085, 1048 (S=O), 1018, 964, 950, 886, 842, 762, 687. Anal. Found. C, 69.75; H, 6.22%. Calcd for $C_{19}H_{20}O_3S$. C, 69.48; H, 6.14%.

Thermolysis of 6b

A solution of **6b** (133 mg, 0.5 mmol) and trimethylsilyldiazomethane (2.0 M solution in hexane, 1.5 mL, 1.5 mmol) in chloroform (15 mL) was refluxed for 3 h. The reaction mixture was evaporated to give a pale yellow oil, which was chromatographed over silica gel by elution with dichloromethane–hexane (1 : 1) to give **4** and 4-methyl-2-trimethylsilyl-6*H*-1,3-oxathiin-6-one (**8**) (65 mg, 0.32 mmol, 64%). **8**: colorless crystals; mp 70–73 °C. ^{1}H NMR ($CDCl_3$) $\delta = 0.23$ (s, 9H, TMS), 2.20 (s, 3H, CH_3), 5.32 (s, 1H, CH), 5.96 (s, 1H, =CH). ^{13}C NMR ($CDCl_3$) $\delta = -4.81$ (TMS), 22.44 (CH_3), 74.25 (CH), 111.57 (=CCO), 159.25 (=CCH_3), 163.07 (C=O). Anal. Found. C, 47.09; H, 6.94%. Calcd for $C_8H_{14}O_2SSi$. C, 47.49; H, 6.97%.

Thermolysis of 6c

A solution of **6c** (165 mg, 0.5 mmol) and trimethylsilyldiazomethane (2.0 M solution in hexane, 1.5 mL, 1.5 mmol) in chloroform was refluxed for 4 h. The reaction mixture was evaporated to give a pale yellow oil, which was chromatographed over silica gel by elution with dichloromethane–hexane (1 : 1) to give **4** (45 mg, 0.60 mmol, 60%) and disulfide **10** (49 mg, 0.25 mmol, 50%). Disulfide **10**: pale yellow oil. ^{1}H NMR ($CDCl_3$) $\delta = 3.63$ (3, 6H, OCH_3), 5.89 (s, 2H, =CH), 7.10–7.22 (m, 4H, Ph), 7.32–7.42 (m, 6H, Ph). ^{13}C NMR ($CDCl_3$) $\delta = 51.86$ (OCH_3), 118.27 (=CH), 128.31 128.83, 129.24, 137.55, 160.44 (=C), 165.49 (C=O). Anal. Found: C, 59.30; H, 4.69%. Calcd for $C_{20}H_{18}O_4S_2 + H_2O$. C, 59.39; H, 4.98%.

Methanolysis of 7a

To a solution of **7a** (134 mg, 0.5 mmol) in MeOH (10 mL) was added trifluoromethanesulfonic acid (15 mg, 0.1 mmol). After refluxing for 5 h, water (25 mL) was added and extracted from dichloromethane (5 mL × 3). The combined extract was dried over magnesium sulfate, filtered, and evaporated to give a pale yellow oil, which was chromatographed over silica gel by elution with dichloromethane–hexane (1 : 1) and dichloromethane to afford 2-adamantanone (57 mg, 0.38 mmol) and methyl 2-carbomethoxyethenesulfonate (**11**) (48 mg, 0.29 mmol, 68%). Compound **11**. colorless oil. ^{1}H NMR $CDCl_3$) $\delta = 3.82$ (s, 3H, OMe), 3.84 (s, 3H, OMe), 6.35 (d, 1H, $J = 11$ Hz, =CH), 6.77 (d, 1H, $J = 11$ Hz, =CH). ^{13}C NMR ($CDCl_3$) $\delta = 52.79$ (OMe), 54.17 (OMe), 126.58 (=CH), 153.27 (=CH), 164.33 (C=O). IR: $\nu/cm^{-1} = 3039$, 2954, 1728 (C=O), 1622, 1437, 1348, 1265, 1224, 1185, 1160, 1118, 990, 819, 792, 699, 670. Anal. Found: C, 36.23; H, 4.77%. Calcd for $C_5H_8O_4S$. C, 36.58; H, 4.91%.

Reaction of 7a with anthracene

To a solution of **7a** (540 mg, 2.0 mmol) in xylene (10 mL) was added a solution of anthracene (430 mg, 2.4 mmol) in xylene (10 mL). After refluxing for 12 h, the reaction mixture was evaporated to afford pale brown crystals, which were chromatographed over silica gel by elution with dichloromethane to afford the corresponding Diels–Alder adduct (**12**) (697 mg, 1.56 mmol, 78%). Compound **12**. colorless plates; mp 280 °C (sub.). ^{1}H NMR ($CDCl_3$) $\delta = 1.55$ (d, 1H, $J =$ Hz, CH_2), 1.66–1.81 (m, 5H, CH_2), 1.86 (s, 1H, CH), 1.92 (s, 1H, CH), 2.08 (d, 1H, $J = 12.8$ Hz, CH_2), 2.22 (d, 1H, $J = 12.8$ Hz, CH_2), 2.40 (s, 2H, CH), 2.48 (d, 1H, $J = 13.2$ Hz, CH_2), 2.61 (d, 1H, $J = 12.8$ Hz, CH_2), 3.44 (dd, 1H, $J = 11.6$ and 2.0 Hz, CH), 3.77 (d, 1H, $J = 11.6$ and 2.0 Hz, CH), 5.01 (s, 2H, CH), 7.15–7.20 (m, 4H, Ar), 7.35–7.48 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) $\delta = 25.94$, 26.60, 31.09, 33.12, 33.32, 33.67, 33.95, 37.53, 42.08, 46.24, 46.76, 56.59, 98.37, 123.91, 124.78, 126.03, 126.62, 126.87, 127.06, 127.30, 127.34, 138.86, 139.85, 141.50, 165.35 (C=O). Anal. Found: C; 72.31, H; 5.85%. Calcd for $C_{27}H_{26}O_4S$: C, 72.62; H, 5.85%.

Basic alcoholysis of 12

To a solution of sodium methoxide (160 mg, 3 mmol) in methanol (10 mL) was added a solution of **12** (0.447 g, 1.0 mmol) in methanol (10 mL). After refluxing for 12 h, the reaction mixture was concentrated to 5 ml and water (15 mL) was added. The reaction mixture was extracted with dichloromethane (5 mL × 3). The combined extracts were dried over magnesium sulfate, filtered, and evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with dichloromethane to give 2-adamantanone (119 mg, 0.78 mmol), 9,10-dihydro-9,10-ethano-11-methoxycarbony-12-methoxysulfonylanthracene (**13**) (137 mg, 0.38 mmol, 38%) and 9,10-dihydro-9,10-etheno-11-methoxycarbonylanthracene (**14**) (47 mg, 0.18 mmol, 18%). Compound **13**. colorless oil. ^{1}H NMR ($CDCl_3$) $\delta = 3.19$ (d, 1H, $J =$ 10 Hz, CH), 3.39 (d, 1H, $J = 10$ Hz, CH), 3.63 (s, 3H, OMe), 3.85 (s, 3H, OMe), 4.56 (s, 1H, CH) 4.70 (s, 1H, CH), 7.15 (m, 2H, Ar), 7.18 (m, 2H, Ar), 7.22–7.38 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) $\delta =$ 45.15 (CH), 47.06 (CH), 48.18 (CH), 52.56 (OMe) 54.41 (OMe), 69.86 (CH), 124.04, 124.08, 124.45, 125.66, 126.82, 126.90, 126.97, 127.07 139.19, 140.19, 141.65, 141.83, 171.80 (COO). Anal. Found C, 63.60; H, 5.29%. Calcd for $C_{19}H_{18}O_5S$. C, 63.67; H, 5.06%.

Compound **14**. Colorless crystals; mp 179–180 °C (lit.[22] mp 177–179 °C). ^{1}H NMR ($CDCl_3$) $\delta = 3.73$ (s, 3H, OMe), 5.24 (d, 1H, $J =$ 10 Hz, CH), 5.67 (s, 1H, =CH), 6.98 (m, 4H, Ar), 7.31 (m, 2H, Ar), 7.37 (m, 2H, Ar), 7.87 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$) $\delta = 50.60$ (CH), 51.81 (OCH), 52.04 (OMe), 123.93, 125.10, 125.27, 127.75, 144.57, 144.68, 145.46 (=C), 149.85 (=CH), 165.43 (COO).

Reduction of 12

To a suspension of $LiAlH_4$ (57 mg, 1.5 mmol) in THF (10 mL) was added **12** (0.447 g, 1.0 mmol) at room temperature. After refluxing for 14 h, methanol (2 mL) and water (10 mL) were added to the reaction mixture, which was neutralized by aq. HCl, and extracted with dichloromethane (5 mL × 3). The combined extracts were dried over magnesium sulfate, filtered, and evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with dichloromethane to afford sulfinate **15** (144 mg, 0.51 mmol, 51%), and sulfonate **16** (30 mg, 0.10 mmol, 10%). 2-Adamantanol (90 mg, 0.59 mmol) and 2-adamantanone (18 mg, 0.12 mmol, 12%) were also obtained. Compound **15**: colorless

crystals; mp 243–244 °C. ^{1}H NMR ($CDCl_3$) $\delta = 3.19$ (br t, 1H, $J = 8$ Hz, CH), 3.74 (br d, 1H, $J = 8$ Hz, CH), 4.28 (br s, 1H, ArCH), 4.42 (br d, 1H, $J = 10$ Hz, C*H*H), 4.85–4.90 (m, 2H, CH*H* and ArCH), 7.12–7.25 (m, 4H, Ar), 7.26–7.37 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) $\delta = 44.15$ (CH), 45.15 (CH), 48.32 (CH), 77.63 (CH_2), 80.32 (CH), 124.07, 124.23, 124.85, 125.36, 126.85, 126.96, 127.00, 127.35, 138.36, 139.57, 140.95, 142.84. MS: Found: 282 (M^+), Calcd for $C_{17}H_{14}O_2S$: 282. Anal. Found: C, 71.98; H, 5.13%. Calcd for $C_{17}H_{14}O_2S$. C, 72.31; H, 5.00%. Compound **16**. colorless crystals; mp 246–247 °C. ^{1}H NMR ($CDCl_3$) $\delta = 3.14$ (br dd, 1H, $J = 11$ and 9 Hz, CH), 3.64 (d, 1H, $J = 11$ Hz, CH), 3.90 (t, 1H, $J = 9$ Hz, C*H*H), 4.32 (br s, 1H, ArCH), 4.52 (t, 1H, $J = 9$ Hz, CH*H*), 4.63 (br s, 1H, ArCH), 7.07–7.16. Anal. Found: C, 68.75; H, 4.91%. Calcd for $C_{17}H_{14}O_3S$. C, 68.44; H, 4.73%.

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