Notes

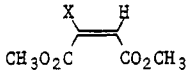
Preparation of Dimethyl 2-(Phenylthio)maleate, Dimethyl 2-(Phenylthio)fumarate, and Their Sulfoxides

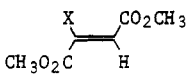
Janet A. Kaydos and Douglas L. Smith*

Department of Chemistry, Allegheny College, Meadville, Pennsylvania 16335

Received September 20, 1982

In conjunction with ongoing research we required selective high-yield preparations of the isomeric dimethyl 2-(phenylsulfinyl)-2-butene-1,4-dicarboxylates **1b** and **2b**.





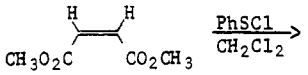
1 a (X=SPh); b (X=SPh, O)

2 a (X=SPh); b (X=SPh, O)

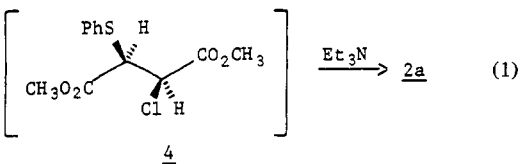
A reasonable approach to these isomers is oxidation of the corresponding sulfides **1a** and **2a**. The *Z* sulfide **2a** has been prepared from dimethyl acetylenedicarboxylate,[1] but pure *E* isomer **1a** is not known. We now report the synthesis of the *E* olefin **1a** as well as two additional means for the preparation of **2a**.

Newton et al.[1] have already demonstrated that nucleophilic addition of 1 equiv of benzenethiol to dimethyl acetylenedicarboxylate results in an 85:15 mixture of **2a**/**1a**, as determined by NMR. Although this mixture is unseparable both by distillation (thermal isomerization to a 1:1 mixture occurs) and by column chromatography, saponification of the mixed esters followed by purification of the *Z* diacid and reesterification does yield **2a** free of any contaminating **1a**.[1]

Surprisingly, dimethyl maleate (**3**) adds benzenesulfenyl chloride (generated in situ by the procedure of Hopkins and Fuchs[2]) in a stereospecific manner at room temperature, and as indicated in eq 1 subsequent elimination with



3

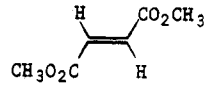


4

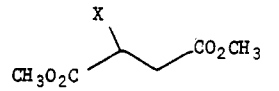
(1)

triethylamine from the unisolated intermediate **4** yields the *Z* sulfide **2a** (74%). Unfortunately, dimethyl fumarate (**5**) reacts with benzenesulfenyl chloride much less readily, and this sequence could not be adjusted so as to produce a comparable yield of **1a**.

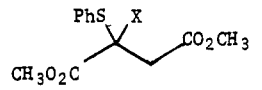
As an alternative approach we have investigated a few eliminations (both syn and anti in nature) from compounds of the general structure **7**. These would not be expected



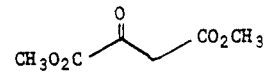
5



6 a (X=SPh); b (X=SPh, O)



7 a (X=Cl); b (X=OCCH$_3$, O); c (X=SPh); d (X=SPh, O)



8

to be as stereoselective as the process outlined in eq 1, and indeed they were not. Nucleophilic addition of benzenethiol to either dimethyl maleate (**3**) or dimethyl fumarate (**5**) affords the sulfide **6a**,[3] which may be chlorinated easily by the method of Tuleen and Marcum[4] to give **7a**. Elimination with triethylamine then produces an 88:12 mixture of **1a**/**2a** (as indicated by NMR), which can be separated by extensive chromatography. By this means a 66% yield of pure **1a** is finally obtained.

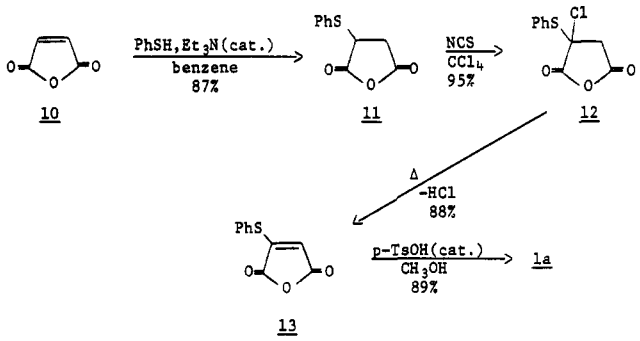
Neither treatment of **6a** with lead tetraacetate[5a] nor electrolysis of **6a** in sodium acetate–moist acetic acid[5b] results in formation of the intermediate **7b**. However, the sulfoxide **6b**, formed by oxidation of **6a**, does undergo Pummerer rearrangement–elimination without isolation of intermediate **7b** (if it is in fact involved in the reaction) when treated with acetic anhydride–methanesulfonic acid.[6] Unfortunately, although some **1a**/**2a** (approximately 60:40) is formed in this manner, the major product is dimethyl fumarate (**5**). Since the sulfoxide **6b** slowly eliminates the elements of PhSOH at room temperature to yield **5**,[7] such an elimination apparently competes favorably with the action of acetic anhydride on **6b**.

The dithoketal **7c** is easily obtained from dimethyl oxalacetate (**8**) by treatment with benzenethiol and $BF_3 \cdot Et_2O$.[8] Oxidation to the monosulfoxide **7d** followed, without isolation, by pyrolysis in refluxing toluene results in a 60:40 ratio of **1a**/**2a**. Consequently, syn elimination from **7d** is even less effective than anti elimination from **7a** as a means of producing **1a** (i.e., 60% **1a** vs. 88% **1a**).

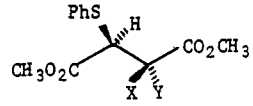
(1) McDonald, J. W.; Corbin, J. L.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2056.
(2) Hopkins, P. B.; Fuchs, P. L. *J. Org. Chem.* **1978**, *43*, 1208.
(3) Bossert, F. *Justus Liebigs Ann. Chem.* **1964**, *680*, 40.
(4) Tuleen, D. L.; Marcum, V. C. *J. Org. Chem.* **1967**, *32*, 204.
(5) (a) Trost, B. M.; Massiot, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 4405. (b) Nokami, J.; Hatate, M.; Wakabayashi, S.; Okawara, R. *Tetrahedron Lett.* **1980**, *21*, 2557.
(6) Monteiro, H. J.; Gemal, A. L. *Synthesis* **1975**, 437.
(7) Givens, J. W., III; Smith, D. L., unpublished results.
(8) We thank Patricia M. Valone for preparing compound **7c**.

0022-3263/83/1948-1096$01.50/0

Scheme I



The mixtures of **1a**/**2a** can be resolved into pure **1a** and pure **2a** in an interesting fashion. Nucleophilic addition of benzenethiol to such a mixture produces an 89:11 mixture of the bis sulfides **9a** and **9c**, which is easily separable by fractional crystallization.[1] Subsequent oxidation of meso isomer **9a** to the monosulfoxide **9b** followed, without isolation, by pyrolysis gives **2a** in an 84% yield, while similar treatment of **9c** produces **1a** in a 98% yield via the intermediacy of **9d**.



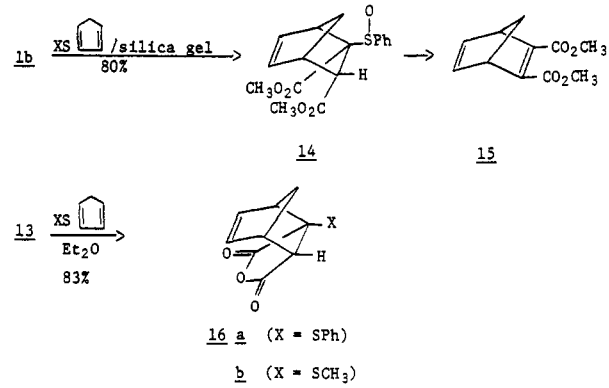
9 **a** (X=H, Y=SPh)
b (X=H, Y=SPh, O)
c (X=SPh, Y=H)
d (X=SPh, Y=H, O)

Pure **1a**, pure **2a**, or any mixture of the two results in a similar proportion of **9a** and **9c** when treated with benzenethiol. This is also the case if dimethyl acetylenedicarboxylate is treated with two or more equivalents of benzenethiol.[1] As pointed out by Newton et al.[1] the first addition of thiol to the alkyne is predominantly trans in stereochemistry, but our results do not support their contention that the second addition of the thiol to the resulting olefins is stereospecifically cis. Instead, an alternative interpretation of the data is that, regardless of the stereochemistry of the second addition of thiol, the product mixture containing **9a** and **9c** isomerizes (equilibrates?) to the observed product ratio. We have demonstrated that this may in fact be the case by monitoring this isomerization with the use of NMR. A benzene solution of either **9a** or **9c** also containing small amounts of both benzenethiol and triethylamine isomerizes to a mixture of **9a** and **9c** rich in the meso isomer over a period of about 18 h at room temperature. We did not attempt to measure the position of equilibrium.

Neither the approach utilizing intermediate **7a** nor that starting from **9c** is adequate for the preparation of **1a**. The former involves a tedious chromatographic separation, while the latter suffers from the fact that the required precursor **9c** is always the minor product of those reactions in which it is formed. However, **1a** may be prepared conveniently by the sequence shown in Scheme I.

Nucleophilic addition of benzenethiol to maleic anhydride (**10**) forms the sulfide **11**,[9] which is then chlorinated to **12**.[4] Elimination to the unsaturated sulfide **13** can be achieved with triethylamine, but is more conveniently accomplished by thermal elimination of HCl.[10] The anhydride **13** then easily opens to **1a** when treated with acidic methanol.

Scheme II



Oxidation of pure **1a** or pure **2a** with *m*-chloroperbenzoic acid at 0 °C affords the desired sulfoxides **1b** and **2b**, respectively. As shown in Scheme II sulfoxide **1b** is synthetically equivalent to dimethyl acetylenedicarboxylate in the Diels–Alder reaction with cyclopentadiene, a reaction which occurs at room temperature on silica gel. Initial adduct **14** was not isolated, and thus the stereochemistry is undetermined; instead **15** is the observed product. Apparently pyrolytic elimination of the elements of PhSOH occurs either at room temperature or upon work up.

The anhydride **13** is also a good dienophile, giving **16a** upon reaction with cyclopentadiene. Once again the stereochemistry of this adduct could not be determined unambiguously but is assigned as shown on the basis of that found for **16b**, which was prepared analogously by Trost.[11]

Experimental Section

All reagents were purchased from Aldrich Chemical Co. and were used as obtained. Melting points were recorded in open capillaries on a Mel-Temp apparatus and are uncorrected. Likewise, boiling points are uncorrected. For those distillations involving a Kugelrohr apparatus the temperatures given are of the hot air bath and do not represent true boiling points. Column chromatography was conducted on 60–200-mesh silica gel supplied by Sargent-Welch, while Baker's silica gel was used for flash chromatography. The support in some of the Diels–Alder reactions as well as the adsorbent for preparative TLC was EM silica gel 60 PF-254. The NMR spectra were obtained in solutions in either CCl_4 or $CDCl_3$ on a Perkin-Elmer R12A instrument and are reported in δ units downfield from $(CH_3)_4Si$. The IR spectra were recorded as neat films or as KBr pellets on either a Perkin-Elmer 700 or a Perkin-Elmer 1310 infrared spectrometer and were calibrated with polystyrene. All elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Dimethyl 2-(Phenylthio)fumarate (2a) from 3 and Benzenesulfenyl Chloride. A solution of 7.23 g (50.0 mmol) of PhSCl in 50 mL of CH_2Cl_2 was prepared according to the method of Fuchs.[2] This solution was freed of precipitate by filtration under a stream of nitrogen, and 6.2 mL (7.2 g, 50 mmol) of dimethyl maleate was added to the red filtrate. The solution was allowed to stir for 36 h at ambient temperature under the protection of a drying tube, during which time the color changed to yellow.

The mixture was cooled to 0 °C, and a solution of 8.0 mL (excess) of triethylamine in 20 mL of CH_2Cl_2 was added dropwise. After being stirred an additional 0.5 h at room temperature, the

(9) Zienty, F. B.; Vineyard, B. D.; Schleppnik, A. A. *J. Org. Chem.* **1962**, *27*, 3140.

(10) This method for preparation of compound **13** should be contrasted with that used by Trost and Lunn[11] in the preparation of 2-(methylthio)maleic anhydride.

(11) Trost, B. M.; Lunn, G. *J. Am. Chem. Soc.* **1977**, *99*, 7079.

solution was extracted with 50 mL of water, the organic layer dried over anhydrous $MgSO_4$, and the spent drying agent was removed by filtration. Evaporation of the solvent from the filtrate left 11.40 g of a yellow oil. Chromatography ($CHCl_3$) returned 9.32 g (74% yield) of pure **2a**: NMR (CCl_4) δ 7.20–7.72 (m, 5 H), 6.30 (s, 1 H), 3.75 (s, 3 H), 3.29 (s, 3 H); IR (neat) 1732, 1711, 1582 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_4S$: C, 57.13; H, 4.80. Found: C, 57.22; H, 4.73.

***meso*- and DL-Dimethyl 2,3-Bis(phenylthio)succinates (9a,c).** Compound **6a** was prepared essentially by the method of Bossert[3] by adding a solution of dimethyl maleate in benzene to one containing benzenethiol and a catalytic amount of triethylamine in benzene at room temperature. The product could be purified by distillation under vacuum [bp 135–137 °C (1.2 mm)] but was normally used without purification.

A mixture of 7.51 g (29.6 mmol) of crude **6a** and 4.21 g (31.4 mmol) of *N*-chlorosuccinimide in 75 mL of CCl_4 was heated at reflux for 14 h.[4] The yellow solution was cooled in an ice–water bath and filtered to remove the precipitate which had formed. Evaporation of the solvent from the filtrate left 8.37 g (98% yield) of crude **7a** as an orange oil: NMR (CCl_4) δ 7.20–7.80 (m, 5 H), 3.61 (s, 6 H), 3.22–3.38 (d, 2 H); IR (neat) 1742 cm^{-1}. This material decomposed to a 1:1 mixture of **1a** and **2a** upon attempted distillation. Although purification was not necessary for the next reaction, it could be achieved with chromatography ($CHCl_3$ as the eluent).

To a solution of 31.94 g (111 mmol) of crude **7a** in 280 mL of benzene was added 17.0 mL (12.4 g, 123 mmol) of triethylamine. The mixture was allowed to stir at ambient temperature for 4 days before it was filtered and the solvent evaporated from the filtrate to leave 27.75 g of a dark yellow oil, which proved by NMR analysis to be an 88:12 mixture of **1a**/**2a**. Repetitive preparative layer chromatography ($CHCl_3$) of 0.30 g of this mixture provided 0.08 g of **2a** (larger R_f) and 0.20 g of **1a** (lower R_f), each identical in all respects with samples prepared elsewhere in this report. Column chromatography proved more troublesome in separating larger batches of these isomers.

Finally, a solution of 24.80 g (98.4 mmol) of a mixture of **1a** and **2a** in 30 mL of benzene was slowly added to a solution of 10.1 mL (10.8 g, 98.2 mmol) of PhSH and 0.5 mL (catalytic) of triethylamine in 100 mL of benzene at 0 °C. The mixture was brought to room temperature and stirred overnight. Filtration and evaporation of the solvent from the filtrate left 30.73 g (86% yield) of an off-white solid.

Recystallization from methanol yielded 27.35 g of **9a**: mp 106.5–109 °C (lit.[1] mp 104–105.5 °C); NMR ($CDCl_3$) δ 7.23–7.60 (m, 10 H), 3.96 (s, 2 H), 3.67 (s, 6 H); IR (KBr) 1723 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_4S_2$: C, 59.65; H, 5.00. Found: C, 59.66; H, 5.09.

Concentration of the mother liquor, filtration, and one further recrystallization from methanol of the solid obtained yielded 3.27 g of **9c**: mp 70–72 °C; NMR ($CDCl_3$) δ 7.25–7.65 (m, 10 H), 3.85 (s, 2 H), 3.60 (s, 6 H); IR (KBr) 1720 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_4S_2$: C, 59.65; H, 5.00. Found: C, 59.67; H, 4.94.

Equilibration of 9a and 9c. These samples were prepared in NMR tubes: (a) 0.50 g of **9a** and 0.10 mL of Et_3N in 1.50 mL of benzene, (b) 0.50 g of **9c** and 0.10 mL of Et_3N in 1.50 mL of benzene, (c) 0.50 g of **9a** and 0.10 mL of PhSH in 1.50 mL of benzene, (d) 0.50 g of **9c** and 0.10 mL of PhSH in 1.50 mL of benzene, (e) 0.50 g of **9a**, 0.10 mL of Et_3N, and 0.10 mL of PhSH in 1.50 mL of benzene, (f) 0.50 g of **9c**, 0.10 mL of Et_3N, and 0.10 mL of PhSH in 1.50 mL of benzene. Samples a and b were discarded as copious quantities of precipitate formed immediately.

The other samples were stored at room temperature, and their NMR spectra were taken every 0.5 h for 18 h. Samples c and d did not change during this period, but in samples e and f the alternative isomer gradually accumulated. (The signal at δ 3.96 for **9a** and the one at δ 3.85 for **9c** were monitored.) Ultimately both samples became rich in the meso isomer **9a**, and no further alteration in composition seemed to occur with time.

2-(Phenylthio)maleic Anhydride (13). A solution consisting of 20.00 g (204 mmol) of maleic anhydride, 20.8 mL (22.4 g, 204 mmol) of PhSH, and 2.0 mL (catalytic) of triethylamine in 300 mL of benzene was allowed to stir at ambient temperature under the protection of a drying tube for 16 h. The color was initially orange but changed rapidly to dark brown as the exothermic reaction occured. Evaporation of the solvent left 41.97 g of a dark oil.[12] Flash chromatography on 70 g of silica gel with 300 mL of ethyl ether for elution yielded 37.12 g (87% yield) of **11** as a yellow oil: NMR ($CDCl_3$) δ 7.20–7.75 (m, 5 H), 4.17 (dd, 1 H, A of an ABC pattern, J_{AB} = 9 Hz, J_{AC} = 4 Hz), 3.35 (dd, 1 H, B of an ABC pattern, J_{BA} = 9 Hz, J_{BC} = 19 Hz), 2.75 (dd, 1 H, C of an ABC pattern, J_{CA} = 4 Hz, J_{CB} = 19 Hz); IR (neat) 1860, 1785 cm^{-1}.

To a solution of 21.00 g (101 mmol) of **11** in 300 mL of CCl_4 was added 13.48 g (101 mmol) of *N*-chlorosuccinimide, and the resulting solution was heated at reflux while protected by a drying tube overnight.[4] The reaction mixture was cooled in an ice–water bath and freed of precipitate by filtration. Evaporation of the solvent from the filtrate left 23.28 g (95% yield) of crude **12** as a yellow oily solid. This material decomposed partially to **13** upon attempted recrystallization, chromatography, or distillation. For the crude material: NMR ($CDCl_3$) δ 7.35–7.85 (m, 5 H), 3.55 (s, 2 H); IR (neat) 1870, 1760 cm^{-1}.

Crude **12** (17.94 g, 74.0 mmol) was placed in a large beaker. This was heated in a fume hood through the range 110–150 °C over a period of 15 min, during which time HCl was liberated and the residue became quite dark. The cooled residue was then distilled under vaccum through an air-cooled short-path condenser. Alternatively, crude **12** could be distilled directly as long as the vacuum pump used was well protected against the corrosive HCl vapors liberated. By either means 13.30 g (88% yield) of **13** distilled as a bright yellow oil which solidified on cooling. Two recrystallizations from CCl_4–pentane provided light yellow needles: bp 147–151 °C (0.8 mm); mp 59–60 °C; NMR ($CDCl_3$) δ 7.56 (m, 5 H), 5.91 (s, 1 H); IR (KBr) 1832, 1780, 1575 cm^{-1}. Anal. Calcd for $C_{10}H_6O_3S$: C, 58.24; H, 2.93. Found: C, 58.31; H, 2.95.

Dimethyl 2-(Phenylthio)maleate (1a) from 13. A solution of 3.00 g (14.6 mmol) of **13** and 0.25 g (catalytic) of *p*-toluenesulfonic acid monohydrate in 45 mL of methanol was heated at reflux overnight. The solvent was evaporated, leaving 3.84 g of a yellow oil. Chromatography ($CHCl_3$) returned 3.27 g (89%) pure **1a**: NMR (CCl_4) δ 7.25–7.60 (m, 5 H), 5.46 (s, 1 H), 3.58 (s, 6 H); IR (neat) 1728, 1608 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_4S$: C, 57.13; H, 4.80. Found: C, 57.33; H, 4.69.

In one experiment crystals formed in the crude oil. Dilution with CCl_4, filtration, and recrystallization of the solid from $CHCl_3$–pentane gave 0.19 g of white needles, which proved to be one of the two possible half ester–half acids: mp 113–119 °C dec; NMR ($CDCl_3$) δ 9.20 (s, 1 H), 7.45 (m, 5 H), 5.45 (s, 1 H), 3.62 (s, 3 H); IR (KBr) 2340–3600, 1680–1725, 1600 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_4S$: C, 55.45; H, 4.23. Found: C, 55.78; H, 4.27.

Dimethyl 2,2-Bis(phenylthio)succinate (7c).[8] Dimethyl oxalacetate (**8**, mp 73–75 °C) was prepared from oxalacetic acid according to the procedure of Fenton and Jones.[13] Then 1.48 g (9.25 mmol) of this compound was mixed with 2.0 mL (2.1 g, 19 mmol) of PhSH and 1.5 mL of $BF_3{\cdot}Et_2O$ in 30 mL of benzene. The solution was heated at reflux for 24 h, after which time the solvent was removed by evaporation. An orange oil resulted which began to crystallize upon standing. Trituration with cold ethanol resulted in the collection of 4.77 g of crude solid. Recrystallization from ethanol yielded 2.11 g (63% yield) of **7c** as white prisms: mp 103–105 °C; NMR ($CDCl_3$) δ 7.30–7.75 (m, 10 H), 3.75 and 3.67 (2 s, 6 H), 2.80 (s, 2 H); IR (KBr) 1730 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_4S_2$: C, 59.65; H, 5.00. Found: C, 59.48; H, 5.10.

Pummerer Rearrangement of 6b. A solution of 8.39 g (48.6 mmol at 85%) of *m*-chloroperbenzoic acid in 120 mL of CH_2Cl_2 was added dropwise to a solution of 10.50 g (41.3 mmol) of **6a** in 60 mL of CH_2Cl_2 at 0 °C. The mixture was allowed to stir at 0 °C overnight. Then it was diluted with 60 mL of CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ solution (2 × 40 mL). The organic layer was dried over anhydrous $MgSO_4$, and the spent drying agent was removed by filtration.

The filtrate was treated immediately with 4.5 mL (4.9 g, 48 mmol) of acetic anhydride and 5 drops (catalytic) of methanesulfonic acid, placed under an atmosphere of nitrogen, and allowed to stir at ambient temperature for 16 h.[6] During this time a yellow color developed.

(12) The crude oil could be purified by vacuum distillation as reported in ref. 9 [bp 165–170 °C (1.3 mm)]; however, flash chromatography was found to be much more convenient.

(13) Fenton, H. J. H.; Jones, H. O. *J. Chem. Soc.* **1900**, *77*, 79.

The mixture was extracted with 40 mL of saturated aqueous $NaHCO_3$ solution, the organic layer dried over anhydrous $MgSO_4$, and the spent drying agent removed by filtration. Evaporation of the solvent from the filtrate left 8.54 g of a yellow semisolid. Analysis by NMR ($CDCl_3$) indicated that this was a mixture of approximately 75% dimethyl fumarate (**5**; signal at δ 6.78) and 25% of a 60:40 mixture of **1a** and **2a** (signals at δ 5.45 and 6.30, respectively). Although no rigorous attempt was made to separate the components, preparative layer chromatography ($CHCl_3$) provided white crystals (mp 102.5–104 °C) which were identical in all respects with dimethyl fumarate (mixture melting point 102–104.5 °C), thus confirming the assignment made by NMR of the crude mixture.

Eliminations via 7d, 9b, and 9d. These reactions were conducted identically. A solution of 2.80 g (16.2 mmol at 85%) of *m*-chloroperbenzoic acid in 50 mL of CH_2Cl_2 was added dropwise to a solution of 13.8 mmol of sulfide (either **7c**, **9a**, or **9c**) in 35 mL of CH_2Cl_2 at 0 °C. The mixture was allowed to stir at 0 °C overnight. Then it was diluted with 50 mL of CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ solution (2 × 20 mL). The organic layer was dried over anhydrous $MgSO_4$, and the spent drying agent removed by filtration. The solvent was evaporated from the filtrate and replaced with 100 mL of toluene. This new solution was then heated at reflux for 2 h and cooled, and the solvent was removed by evaporation under vacuum.

From **7c**: 4.10 g of a yellow oil; NMR (CCl_4) analysis showed that in addition to other aromatic material (perhaps PhSSPh) this was a 60:40 mixture of **1a**/**2a**. No further isolation was attempted.

From **9a**: 3.73 g of a yellow oil; chromatography ($CHCl_3$) returned 2.90 g (83% yield) of an oil identical in all respects with **2a**.

From **9c**: 3.97 g of a yellow oil; chromatography ($CHCl_3$) returned 3.41 g (98% yield) of an oil identical in all respects with **1a**.

Dimethyl 2-(Phenylsulfinyl)maleate (1b) and Dimethyl 2-(Phenylsulfinyl)fumarate (2b). In each reaction 2.42 g (14.0 mmol at 85%) of *m*-chloroperbenzoic acid in 30 mL of CH_2Cl_2 was added dropwise to a solution of 3.02 g (12.0 mmol) of sulfide (either **1a** or **2a**) in 18 mL of CH_2Cl_2 at 0 °C. The solution was allowed to stir at 0 °C overnight. Then it was diluted with 40 mL of CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$ solution (2 × 20 mL). The organic layer was dried over anhydrous $MgSO_4$ and the spent drying agent removed by filtration. Evaporation of the solvent from the filtrate left a yellow oil in each case (3.34 g from **1a** and 3.19 g from **2a**). Column chromatography ($CHCl_3$) followed by Kugelrohr distillation (at 220 °C, 1.1 mm) yielded the purified materials.

1b: yellow oil; 2.61 g (82% yield); NMR (CCl_4) δ 7.55 (m, 5 H), 6.88 (s, 1 H), 3.58 and 3.76 (2 s, 6 H); IR (neat) 1723, 1645 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_5S$: C, 53.72; H, 4.51. Found: C, 53.59; H, 4.78.

2b: yellow oil; 2.57 g (81% yield): NMR (CCl_4) δ 7.50 (m, 5 H), 7.11 (s, 1 H), 3.66 and 3.81 (2 s, 6 H); IR (neat) 1723, 1635 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_5S$: C, 53.72; H, 4.51. Found: C, 53.88; H, 4.52.

Dimethyl Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (15). Compound **1b** (2.00 g, 7.50 mmol) was adsorbed onto 10 g of silica gel[14] by dissolving the sulfoxide in CH_2Cl_2, adding the silica gel to this solution, and evaporating the CH_2Cl_2 on a rotary evaporator until dry powder was obtained. Then 12 mL of freshly distilled cyclopentadiene was added, the flask stoppered, and the mixture allowed to stir at room temperature for 24 h.

At the end of this time the mixture was filtered and the silica gel washed with successive portions of CH_2Cl_2 (about 100 mL total). Evaporation of the combined washings was followed by Kugelrohr distillation under high vacuum. The cyclopentadiene dimer easily distilled first followed by 1.24 g (80% yield) of the product (distilled at 170 °C and 1.3 mm). This product was identical in every way with dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate prepared separately from cyclopentadiene and dimethyl acetylenedicarboxylate.[15]

(14) Use of silica gel in Diels–Alder reactions was adapted from: Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383.

2-(Phenylthio)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Anhydride (16a). A solution of 2.00 g (9.71 mmol) of **13** and 2.0 mL of freshly distilled cyclopentadiene in 10 mL of ethyl ether was stirred at room temperature for 30 h. During this time the initially yellow solution became colorless. Evaporation of the solvent left 2.95 g of solid which, upon recrystallization from CCl_4–pentane, gave 2.19 g (83% yield) of white crystals: mp 90–92 °C; NMR ($CDCl_3$) δ 7.35–7.85 (m, 5 H), 6.37 (m, 2 H), 3.12–3.70 (m, 3 H), 2.35 (d, 1 H, J = 9 Hz), 1.94 (d, 1 H, J = 9 Hz); IR (KBr) 1862, 1780 cm^{-1}. Anal. Calcd for $C_{15}H_{12}O_3S$: C, 66.16; H, 4.44. Found: C, 66.44; H, 4.50.

Registry No. **1a**, 59790-39-5; **1b**, 84649-35-4; **2a**, 59790-38-4; **2b**, 84649-36-5; **3**, 624-48-6; **6a**, 785-44-4; **6b**, 84649-34-3; **7a**, 84649-29-6; **7c**, 84649-33-2; **8**, 25007-54-9; **9a**, 53256-00-1; **9c**, 84649-30-9; **10**, 108-31-6; **11**, 57242-92-9; **12**, 84649-31-0; **13**, 84649-32-1; **15**, 947-57-9; **16a**, 84649-37-6; PhSCl, 931-59-9; PhSH, 108-98-5; cyclopentadiene, 542-92-7.

(15) Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1931**, *490*, 236.

5-*tert*-Butyladamantan-2-one

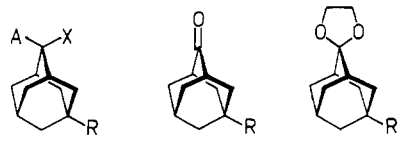
W. J. le Noble,* Sushil Srivastava, and Chiu K. Cheung

Department of Chemistry, State University of New York, Stony Brook, New York 11794

Received April 8, 1982

Studies of the stereochemistry of reactions at saturated carbon can basically be founded on the use of either chiral or geometrically isomeric substrates and products. The employment of enantiomers involves often knotty questions about their availability, optical purities, and relative configurations, but it has the advantage that only one isomer needs to be deployed since stereorandomness is defined, a priori, by the formation of a racemic product. The alternative[1] use of geometric isomers such as *E* and *Z* 4-substituted *tert*-butylcyclohexanes avoids the difficulties often associated with the use of chiral substrates but introduces another complication in that stereorandomness cannot then be equated with a 50:50 mixture of products, and hence both isomers must be studied.

1,4-Substituted adamantanes 1 offer a possible combi-



1 2 3

a, R = OH; b, R = COOMe; c, R = CMe_2OH; d, R = $CMe{=}CH_2$; e, R = $CMe(CH_2)_2$; f, R = CMe_3

nation of these advantages.[2] As both substituents A and X are simultaneously axial to one ring and equatorial to the other, there is no built-in thermodynamic prejudice toward one isomer on that account. One might seek to further reduce the possibility of a residual deviation from equal product free energies by a proper choice of the bridgehead substituent (e.g., with R = D). Two applica-

(1) See, for example: Kim, C. J.; Brown, H. C. *J. Am. Chem. Soc.* **1969**, *91*, 4286, 4287.

(2) The rigid and geometrically well-defined adamantane skeleton can obviously be used in a variety of stereochemical approaches; a brief survey of these may be found in: Nordlander, J. E.; Haky, J. E. *J. Org. Chem.* **1980**, *45*, 4782.

(3) Bone, J. A.; Pritt, J. R.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2644. Cloke, C.; Pritt, J. R.; Whiting, M. C. *Ibid.* **1972**, 2648.

0022-3263/83/1948-1099$01.50/0