6398-62-5; HS-(cyclo-C=N-N=N-N)-$CH_2COOSi(CH_3)_3$, 81589-11-9; n-$C_{12}H_{25}OSiMe_3$, 6221-88-1; $H_3C(CH_2)_3C(CH_3)_2OSiMe_3$, 81588-99-0; 2-$CH_3C_6H_4OSiMe_3$, 1009-02-5; 2,6-$[CH(CH_3)CH_2CH_3]_2C_6H_3OSiMe_3$, 61283-84-9; $C_6H_{12}O_6$(fructose)$[Si(CH_3)_3]_5$, 19126-98-8; Me_3SiO-(cyclo-N-C(O)CH_2CH_2CO), 74124-80-4; $C_6H_5SSi(CH_3)_3$, 4551-15-9; $(CH_3)_3SiS$-(cyclo-C=N-N=C(CH_3)S), 81589-00-6; $CH_3CONHSiMe_3$, 13435-12-6; $CH_3CSNHSiMe_3$, 58065-67-1; $4O_2NC_6H_4CONHSiMe_3$, 1020-48-0; $Me_3SiNHCONHSiMe_3$, 18297-63-7; $CH_3SO_2NHSiMe_3$, 999-96-2; $C_6H_5SO_2NHSiMe_3$, 17865-14-4; 4-$CH_3C_6H_4SO_2NHOSiMe_3$, 81974-63-2; 4-$CH_3C_6H_4NHSiMe_3$, 63911-83-1; $C_6H_5NHNHSiMe_3$, 13271-92-6; (cyclo-CH=CH-N=CH-N)-$SiMe_3$, 18156-74-6; o-(cyclo-C_6H_4-CO-N$(SiMe_3)$-CO), 10416-67-8; $(C_2H_5O)_2POSiMe_3$, 13716-45-5; $(C_6H_5O)_2PONHSiMe_3$, 17938-28-2; $(SiMe_3)_3PO_4$, 10497-05-9; C_6H_5C-OOH, 65-85-0; C_6H_5CSOH, 98-91-9; $C_2H_5OOCCH_2COOH$, 1071-46-1; dl-$HOCH_2CH(NH_2)COOH$, 302-84-1; $HSCH_2COOH$, 68-11-1; HS-(cyclo-C=N-N-N-N)-CH_2CO_2H, 57658-36-3; n-$C_{12}H_{25}OH$, 112-53-8; $CH_3(CH_2)_3C(CH_3)_2OH$, 2370-12-9; 2-$CH_3C_6H_4$-OH, 95-48-7; 2,6-$[CH$-$(CH_3)CH_2CH_3]_2C_6H_3OH$, 5510-99-6; $C_6H_{12}O_6$(fructose), 57-48-7; HO-(cyclo-N-C(O)CH_2CH_2CO), 6066-82-6; C_6H_5SH, 108-98-5; HS-(cyclo-C=N-N=C(CH_3)S), 29490-19-5; CH_3CONH_2, 60-35-5; CH_3C-SNH_2, 62-55-5; 4-$O_2NC_6H_4CONH_2$, 619-80-7; H_2NCONH_2, 57-13-6; $CH_3SO_2NH_2$, 3144-09-0; $C_6H_5SO_2NH_2$, 98-10-2; 4-$CH_3C_6H_4SO_2NHOH$, 1593-60-8; 4-$CH_3C_6H_4NH_2$, 106-49-0; C_6H_5NH-NH_2, 100-63-0; (cyclo-CH=CH-N=CH-NH), 288-32-4; o-(cyclo-$C_6H_4CONHCO$), 85-41-6; $(C_2H_5O)_2POH$, 868-85-9; $(C_6H_5O)_2PONH_2$, 2015-56-7; H_PO_4, 7664-38-2; 4-$CH_3C_6H_4SO_2NHPO(OC_6H_4NO_2-4)_2$, 81589-21-1; $[(C_6H_5O)_2PO]_2NH$, 3848-53-1; $Cl_3CCONHPO(OC_6H_4N$-O_2-4$)_2$, 38187-67-6; 1-hexanol, 111-27-3; 17β-hydroxy-4-androsten-2-one, 82639-21-2; 7-amino-3-[(1-methyl-1H-tetrazol-5-yl)thio]-methyl]-3-cephem-4-carboxylic acid, 24209-38-9; 1-butanol, 71-36-3; 1-[(trimethylsilyl)oxy]hexane, 17888-62-9; 17β-[(trimethylsilyl)-oxy]-4-androsten-2-one, 82639-22-3; trimethylsilyl 7-[(trimethylsilyl)amino]-3-[[1-methyl-1H-tetrazol-5-yl)thio]methyl]-3-cephem-4-carboxylate, 81589-17-5; 2-(trimethylsilyl)-1,2-benzisothiazolin-3-one 1,1-dioxide, 82639-23-4; 3-[(trimethylsilyl)oxy]-1,2-benzisothiazole 1,1-dioxide, 82639-24-5; hexamethyldisilazane, 999-97-3; saccharin, 81-07-2; sodium saccharin, 128-44-9; succinimide, 123-56-8; 3,3-dimethylglutarimide, 1194-33-8; maleimide, 541-59-3; 1,8-naphthalimide, 81-83-4; 3,4,5,6-tetrachlorophthalimide, 1571-13-7; 3,4,5,6-tetrabromophthalimide, 24407-32-7; barbituric acid, 67-52-7; 1,2-benzisothiazol-3(2H)-one, 2634-33-5; 4-(benzoyloxy)-1,2-dihydro-1-oxophthalazine, 1705-04-0; dimethyl N-(trichloroacetyl)-phosphoramidate, 1666-45-1; bis(4-nitrophenyl) N-[(dimethylamino)sulfonyl]phosphoramidate, 81589-29-9; diisopropyl N-(dichloroacetyl)phosphoramidate, 3807-94-1; bis(2-chlorophenyl) N-[(4-chlorophenyl)sulfonyl]phosphoramidate, 81589-30-2; N,N-dimethylsulfonamide, 3984-14-3; N-(1-naphthoyl)-4-toluenesulfonamide, 81589-31-3; N-(2-methoxybenzoyl)-4-toluenesulfonamide, 81589-32-4.

Supplementary Material Available: Physical constants for the products of Table I and Table IV containing 30 additional examples (3 pages). Ordering information is given on any current masthead page.

Fragmentation of Bicyclo[4.4.1]undecan-11-ones

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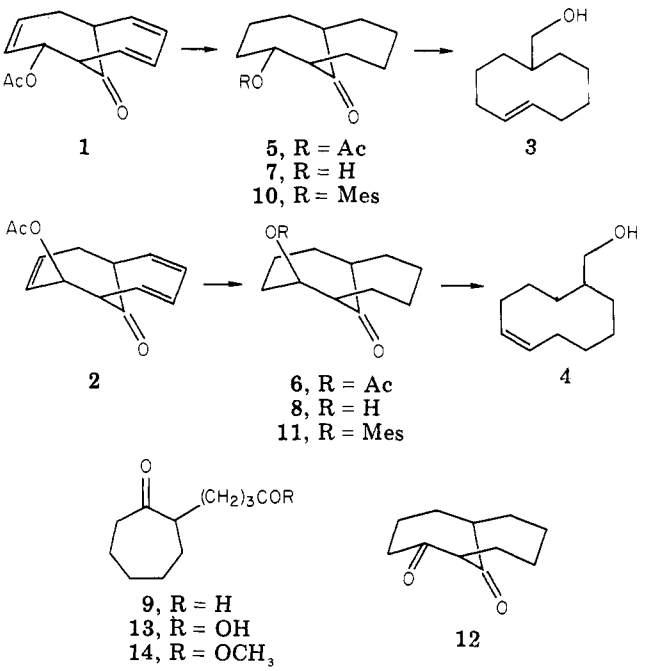
The formation of 8- to 12-membered rings remains a synthetic challenge because of entropy and enthalpy losses upon cyclization.[2] A common approach to these systems has been the fragmentation of the bicyclic structure, which requires that the bond being broken and the leaving group have an antiperiplanar relationship.[3] Bicyclo[4.4.0]decanes have been shown to fragment to yield either (*E*)- or (*Z*)-cyclodecenes.[4-6] One-carbon bridged systems have been used to generate *Z* isomers of cyclooctenes and cyclodecenes.[7] Herein we describe the fragmentation reactions of two isomeric bicyclo[4.4.1]undecanes **10** and **11** that afford (*E*)-cyclodecene **3** and (*Z*)-cyclodecene **4**, respectively, establishing that the fragmentation of an appropriate one-carbon bridge system can afford either olefin isomer.

Scheme I



The formation of bicyclo[4.4.1]undecatrienones via the [6 + 4] cycloaddition reaction of cycloheptatrienones has been examined in detail.[8] The use of stereochemically pure dienes has permitted the selective formation of 7α-acetoxybicyclo[4.4.1]undeca-2,4,8-trien-11-one (**1**) and

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7β-acetoxybicyclo[4.4.1]undeca-2,4,8-trien-11-one (2). These trienes can be converted into substrates suitable for fragmentation (Scheme I). If the stereoelectronic requirements can be met, stereoselective olefin formation is expected.[5] Bicyclo[3.3.1]nonanes,[7a-c] bicyclo[4.2.1]nonanes,[7d] bicyclo[4.3.1]decanes,[7b] and bicyclo[5.3.1]undecanes[7e] each lack the conformational mobility necessary for antiperiplanar alignment of leaving groups in both of the stereoisomers. In these instances,[7] the nonfragmenting isomer often underwent simple elimination during the reaction. Molecular models of alcohols 7 and 8 indicated that 7 possessed one low-energy conformation with a stereochemistry appropriate for fragmentation. Alcohol 8 has several conformations of comparable energy, one of which has the desired geometry for fragmentation. Therefore, transformations of 8 might be complicated by mesylate reduction.

To convert 1 and 2 into 3 and 4, we completed a short sequence of reactions. Reduction of these adducts, 1 and 2, with palladium on carbon in 95% ethanol on a Paar apparatus afforded the acetoxy ketones 5 and 6 in 84 and 95% yields, respectively.[9] We did not observe hydrogenolysis of the allylic acetate. Hydrolysis of the acetoxy ketones to give hydroxy ketones 7 and 8 proved troublesome. After surveying several reaction conditions with 5, we found that tetra-*n*-butylammonium hydroxide in tetrahydrofuran (THF) at room temperature gave 7 in 80% yield uncontaminated by keto aldehyde 9. Under other conditions, 9 became the major product; attempted realdolization of 9 with acid or base failed. Similarly, alcohol 8 was obtained in 78% yield. The mesylates 10 and 11 were prepared by the method of Servis[11] and treated directly with lithium aluminum hydride in THF. Alcohol 8 gave (*E*)-cyclodecene 3 in 78% yield, while alcohol 9 afforded (*Z*)-cyclodecene 4 in 40% yield. The identity of 3 and 4 was readily established by their respective unique infrared absorptions at 983 and 695 cm^{-1}.

We then sought to determine the stereoselectivity of the reactions of related diketone 12. We anticipated facile differentiation of the carbonyls, since 12 is highly strained and the bridgehead is slightly sterically hindered.[4] Other bicyclic diketones had been shown to undergo selective reaction with nucleophiles. Compound 12 was prepared from 7 by Jones oxidation. Treatment of 12 with 1 equiv of lithium tri-*tert*-butoxyaluminum hydride in THF at −78 °C gave four hydroxy ketones in approximately equivalent amounts. Two of these compounds were 7 and 8. We assume hydride addition occurred at both faces of both carbonyls with equal facility.[9] On the other hand, treatment of 12 with potassium hydroxide in ethanol, followed by acidification, yielded only keto acid 13, which was characterized as methyl ester 14. Clearly, regioselective addition of nucleophiles to 12 occurs when the addition is reversible.

We have shown that a bicyclo[4.4.1]undecan-11-one is a suitable precursor for either a *trans*-cyclodecene or a *cis*-cyclodecene via a fragmentation pathway. Application of this cycloaddition–fragmentation process to more complex systems is in progress.

Experimental Section

General. Infrared spectra were recorded as thin films on a Beckman IR 18-AX spectrophotometer; bands yielding structural information are reported in reciprocal centimeters, with polystyrene calibration. Ultraviolet–visible absorption spectra were recorded on a Perkin-Elmer 550 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian EM 390 at 35 °C in deuteriochloroform, and peak positions are reported in parts per million from tetramethylsilane internal standard as multiplet (m), pentet (p), quartet (q), triplet (t), doublet (d), or singlet (s). Decoupling experiments were completed on a Varian HR-220 spectrometer. ^{13}C NMR were recorded on a Varian CFT-20 spectrometer or on a Nicolet 200-MHz multinuclear, wide-bore spectrometer. Low-resolution mass spectra were obtained from an LKB 9000 at 70 eV or at 16- to 20-eV ionizing voltage or on a Finnigan 4021 GCMSDS. Relative percentages of the base peak are in parentheses. High-resolution spectra were performed at the California Institute of Technology Analytical Laboratory or at the Biomedical Mass Spectrometry Resource.

GLPC analysis was performed on a Varian 3700 gas chromatograph with FID detector outfitted with 6 ft × 0.25 in. glass column containing 3% SE 30 or 3% DEXIL on 100/120 Gas Chrom Q (Applied Science).

Reagents and Solvents. Tetrahydrofuran was distilled from sodium benzophenone immediately prior to use. We purified all aromatic solvents by distillation from fresh sodium, discarding the first 10% of the distillate. All other solvents were purchased from Mallinckrodt Chemical and used as received. All reactions were magnetically stirred under a nitrogen atmosphere. The "standard workup" involved partitioning the product between equal volumes of ether and water. The water layer was washed with ether (two times). The pooled ether layers were washed with saturated sodium chloride solution (1 × $^1/_3$ volume), dried over anhydrous sodium sulfate, and concentrated with a rotary evaporator at aspirator pressure.

7α-Acetoxybicyclo[4.4.1]undeca-2,4,8-trien-11-one (1). A solution of 1.06 g (10 mmol) of cycloheptatrienone[12] and 2.00 g (18 mmol) of (*E*)-1-acetoxy-1,3-butadiene[13] in 25 mL of xylene was heated at reflux for 12 h. Removal of the xylene and column chromatography of the residue on silica gel (hexane–ethyl acetate, 4:1) yielded an analytical sample (1.24 g, 57%) of 3: IR 1745, 1705, 1225 cm^{-1}; NMR δ 2.07 (s, 3 H), 2.56 (m, 2 H), 3.54 (br q, J = 6 Hz, 1 H), 3.67 (br t, J = 6 Hz, 1 H), 5.73 (m, 5 H), 6.10 (m, 2 H); ^{13}C NMR δ 202.9 (s), 170.2 (s), 131.6 (d), 130.6 (d), 130.0 (d), 127.6 (d), 126.2 (d), 125.3 (d), 69.6 (d), 61.2 (d), 55.4 (d), 29.2 (t), 21.0 (q); mass spectrum (70 eV), m/z 218 (2.5), 176 (4.9), 158 (11), 149 (11), 108 (9), 107 (100), 91 (9); HRMS, observed m/z 218.094; $C_{13}H_{14}O_3$ requires 218.0943. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.31; H, 6.59.

7β-Acetoxybicyclo[4.4.1]undeca-2,4,8-trien-11-one (2). A solution of 1.06 g (10 mmol) of cycloheptatrienone and 3.00 g (27 mmol) of (*Z*)-1-acetoxy-1,3-butadiene[14] in 10 mL of xylene was heated at reflux for 24 h. The xylene was removed to leave adducts and cycloheptatrienone in a 3:1 ratio. Evaporative distillation left 1.7 g of only 1:1 adducts. Filtration through 20 g of silica gel (ethyl acetate) provided 1.07 g (49%) of 1:1 adducts, from which 0.28 g (12%) of 2 was obtained by HPLC separation (hexane–ethyl acetate, 85:15): IR 3020, 2950, 1745, 1710, 1700, 1376, 1240, 1190, 1050, 1040 cm^{-1}; NMR δ 2.14 (s, 3 H), 2.31 (br d of t, $J \approx 7$ and 16 Hz, 1 H), 2.60 (m, 1 H), 3.54 (br q, $J \approx 7$ Hz, 1 H), 3.75 (br s, 1 H), 5.60 (m, 3 H), 5.90 (m, 4 H); ^{13}C NMR δ 203.3 (s), 169.8 (s), 132.6 (d), 129.7 (d), 127.2 (d), 126.8 (d), 126.3 (d), 124.3 (d), 70.6 (d), 60.8 (d), 55.5 (d), 26.5 (t), 21.1 (q); HRMS, observed m/z 218.0941; $C_{13}H_{14}O_3$ requires 218.0943. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.66; H, 6.53. The remaining material (0.75 g) was a mixture of [4 + 2] adducts.

2α-Acetoxybicyclo[4.4.1]undecan-11-one (5). A solution of 1.24 g (5.7 mmol) of 7α-acetoxybicyclo[4.4.1]undeca-2,4,8-trien-11-one (1)[8,10] and 0.2 g of 10% palladium on carbon in 100 mL of 95% ethanol was placed on a Paar apparatus under 60 psi of hydrogen and shaken for 4 h. The suspension was filtered through Celite, and the filtrate was concentrated. The oil was dissolved in 50 mL of ether and subjected to the standard workup to provide 1.07 g (84%) of 5: IR 2935, 2875, 1745, 1705, 1220 cm^{-1}; NMR

(9) Treatment of 12 with methyllithium or methylmagnesium bromide afforded complex mixtures of hydroxy ketones derived from nucleophilic addition at both carbonyl groups.

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δ 1.73 (m, 14 H), 2.02 (s, 3 H), 2.82 (p, $J \approx 7$ Hz, 2 H), 5.22 (t, $J \approx 7$ Hz, 1 H); HRMS, observed m/z 224.1410; $C_{13}H_{20}O_3$ requires 224.1411.

2β-Acetoxybicyclo[4.4.1]undecan-11-one (6). Using the above method for **5**, we obtained the desired product in >95% yield on a 0.5-mmol scale: IR 2930, 2860, 1732, 1690, 1238 cm^{-1}; NMR δ 1.6–2.1 (m, 14 H), 2.02 (s, 3 H), 2.6–3.2 (m, 2 H), 4.88 (m, 1 H); HRMS, observed m/z 224.1411; $C_{13}H_{20}O_3$ requires 224.1414.

2α-Hydroxybicyclo[4.4.1]undecan-11-one (7). A solution of 1.07 g (4.8 mmol) of **5** and 4.0 g of tetra-*n*-butylammonium hydroxide in methanol was allowed to stir for 24 h at ambient temperature. Dilution of this solution with 50 mL of water and completion of the standard workup left 0.70 g (80.5%) of alcohol **7**: 3420, 2940, 2875, 1675 cm^{-1}; NMR δ 1.80 (m, 14 H), 2.60 (s, exchanges with D_2O, 1 H), 2.85 (br m, 2 H), 4.00 (m, 1 H); mass spectrum (70 eV), m/z 182 (M^+, 5), 180 (8), 164 ($M^+ - H_2O$, 63), 112 (100); HRMS, observed m/z 182.1293; $C_{11}H_{18}O_2$ requires 182.1304.

Other hydrolysis conditions afforded substantial amounts of an additional compound assigned structure **9**: NMR (partial) δ 9.50 (s).

2β-Hydroxybicyclo[4.4.1]undecan-11-one (8). To a solution of the acetate (100 mg, 0.45 mmol) in 20 mL of methanol was added 470 mg (0.45 mmol) of a 25% solution of tetra-*n*-butylammonium hydroxide in methanol. After stirring for 20 h at room temperature, 15 mL of water was added, and the resulting solution was extracted with 4 × 15 mL of Et_2O. The combined ether layers were dried over $MgSO_4$, and the solvent was removed to leave 63 mg of the alcohol (78%) contaminated with a small amount of aldehyde (<5%): IR 3420, 2940, 2870, 1690 cm^{-1}; NMR δ 1.20–2.10 (m, 14 H), 2.40–3.10 (m, 2 H), 3.88 (m, 1 H); HRMS, observed m/z 182.1302; $C_{11}H_{18}O_2$ requires 182.1304.

(*E*)-5-Cyclodecenyl-1-methanol (3). According to the procedure of Crossland and Servis,[11] 0.101 g (0.55 mmol) of **7** was added to 0.125 mL of triethylamine in 3 mL of methylene chloride (CH_2Cl_2) at 0 °C. This mixture was then treated with 0.055 mL (0.69 mmol) of methanesulfonyl chloride over a 15-min period. The mixture was then stirred for 20 min, diluted with 10 mL of CH_2Cl_2, and washed successively with 10 mL of cold water, 10% HCl, saturated Na_2CO_3, and brine. Completion of the standard workup provided 0.148 g of mesylate **10**: NMR δ 1.80 (m, 14 H), 2.80 (m, 2 H), 3.05 (br s, 3 H), 5.10 (br m, 1 H).

A solution of 0.139 g (0.53 mmol) of this crude mesylate in 10 mL of dry THF was treated with 0.070 g of $LiAlH_4$. The resulting suspension was heated at reflux for 7 h, cooled, and processed as usual to give 0.072 g (78% yield) of **3**: IR 3350, 2900, 2850, 1458, 1030, 983 cm^{-1}; NMR δ 1.00–2.10 (m, 15 H), 2.30 (br s, exchanges with D_2O, 1 H), 3.40 (d, J = 6 Hz, 2 H), 5.47 (br m, 2 H); mass spectrum (20 eV), m/z 168 (M^+, 41), 150 (18), 137 (100), 135 (41); HRMS, observed m/z 168.151; $C_{11}H_{20}O$ requires 168.151.

(*Z*)-5-Cyclodecenyl-1-methanol (4). Using the procedure for **3**, we obtained the crude mesylate in 80% yield on a 0.3-mmol scale: IR 2965, 2860, 1685, 1355, 1170 cm^{-1}; NMR δ 1.50–2.20 (m, 14 H), 2.65 (m, 2 H), 3.00 (s, 3 H), 4.70 (m, 1 H). Crude **11** (0.105 g) afforded 0.057 g (49%) of crude **4**. An analytical sample of **4** (29% yield) was obtained by purification on silica gel: IR 3370 (br), 2940, 2850, 1630, 1450, 1030, 735, 695 cm^{-1}; NMR δ 1.10–1.70 (m, 15 H), 3.45 (m, 2 H), 5.39 (m, 2 H); HRMS, observed m/z 168.1514; $C_{11}H_{20}O$ requires 168.1512.

Bicyclo[4.4.1]undecane-2,11-dione (12). A solution of 0.30 g of **7** in 30 mL of reagent-grade acetone at 0 °C was treated with Jones reagent until the red color persisted. The suspension was stirred for 10 min, treated with 2-propanol (1 mL), and filtered through solid sodium carbonate. The filtrate was condensed, and the residue was dissolved in ether. Completion of the standard workup afforded 0.29 g (98%) of **12**: IR 1700 cm^{-1}; NMR δ 1.0–2.4 (m, 12 H), 2.45 (t, J = 6 Hz, 2 H), 2.75 (m, 1 H), 3.38 (t, J = 6 Hz, 2 H).

Methyl 4-(2-Oxo-1-cycloheptyl)butyrate (14).[15] A solution of 0.51 g of diketone **12** in 40 mL of 10% aqueous sodium hydroxide was heated at reflux for 2 h. The solution was cooled, acidified with 10% aqueous hydrochloric acid, and washed with ether (4 × 50 mL). Completion of the standard workup on the pooled ether layers afforded 0.53 g (94% yield) of a yellow oil: IR 3400–2500 (br), 2490, 2860, 1700 (br), 1450, 1250 cm^{-1}; NMR δ 1.2–1.9 (m, 12 H), 2.3 (t, J = 6 Hz, 2 H), 2.4 (m, 3 H); mass spectrum (70 eV), m/z 198 (M^+).

The keto acid (0.53 g, 2.7 mmol) was dissolved in 40 mL of anhydrous methanol and treated with freshly distilled boron trifluoride etherate (0.70 mL, 5.7 mmol). This mixture was heated at reflux for 24 h, cooled, and diluted with 20 mL of 5% aqueous sodium bicarbonate. Most of the methanol was removed with a rotary evaporator. The residue was extracted with ether (4 × 50 mL). Completion of the standard workup of the pooled ether layers provided 0.47 g (83% yield) of **14**: IR 2920, 2965, 1745, 1715, 1450, 1175 cm^{-1}; NMR δ 1.2–2.0 (m, 12 H), 2.2–2.6 (m, 5 H), 3.6 (s, 3 H); ^{13}C NMR δ 215.8, 173.9, 51.9, 51.5, 42.9, 34.0, 31.6, 31.3, 29.5, 28.6, 24.4, 22.7; mass spectrum (70 eV), m/z 212 (M^+), 112 (base); HRMS, observed m/z 212.1406; $C_{12}H_{20}O_3$ requires 212.1409.

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Registry No. **1**, 82614-26-4; **2**, 82659-79-8; **3**, 82614-27-5; **4**, 82614-28-6; **5**, 82614-29-7; **6**, 82659-80-1; **7**, 82614-30-0; **8**, 82659-81-2; **9**, 82614-34-4; **10**, 82614-31-1; **11**, 82659-82-3; **12**, 82614-32-2; **13**, 33366-38-0; **14**, 82614-33-3; (*Z*)-1-acetoxy-1,3-butadiene, 35694-19-0; (*E*)-1-acetoxy-1,3-butadiene, 35694-20-3; cycloheptatrienone, 539-80-0.

(15) We are grateful to W. McBride for obtaining some of the spectral data as a part of a rotation project, Winter Quarter, 1980.

Elimination–Addition Reactions of 3-[2-(Arylthio)ethyl]sydnones. Displacement of the Sulfide by an Ether Group

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During a metabolism study[1] of some antiinflammatory sydnones, **1**,[2] in the rat, we observed that these sydnones tended to decompose in solutions containing strong bases.[3,4] We investigated the reaction of **1** in CD_3OD containing CD_3ONa. The ^1H NMR spectrum of **1b** (at probe temperature) changed quickly and dramatically after the concentration of CD_3ONa reached about 2 N. At that point, the triplet at 4.46 ppm (CH_2N) disappeared with the simultaneous collapse of the triplet to a singlet at 3.33 ppm (CH_2S) (measured downfield from tetramethylsilane). At the same time, new singlets began to appear at 2.13, 3.63, and 3.82 ppm whose intensity grew with time. Also, the symmetrical sets of signals arising from the arene protons (AA′BB′) became diffuse, with the appearance of new lines. The reaction was about 80% complete after 2 h.

(1) To be reported elsewhere.

(2) (a) Wagner, H.; Hill, J. B. *J. Med. Chem.* **1974**, *17*, 1337–1338. (b) Hill, J. B.; Ray, R. E.; Wagner, H.; Aspinall, R. L. *Ibid.* **1974**, *18*, 50–53.

(3) During routine isolation procedures, a chloroform solution of **1** may be washed repeatedly with cold aqueous sodium hydroxide solutions without appreciately destroying any sydnone. As a matter of fact, when **1** in $CDCl_3$ is shaken repeatedly with 1.5 N NaOD in D_2O, no active methylene H–D exchange occurs.

(4) Hot aqueous sodium hydroxide hydrolyzes sydnones to the starting *N*-nitroso acids (Garret, E. R. *J. Pharm. Sci.* **1964**, *53*, 42–43).

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