New Synthetic Reactions. Dimethylsulfonium 2-Oxotetrahydrofuryl-3-ylide as an Annelating Reagent[1]

BARRY M. TROST*[2] AND HENRY C. ARNDT

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

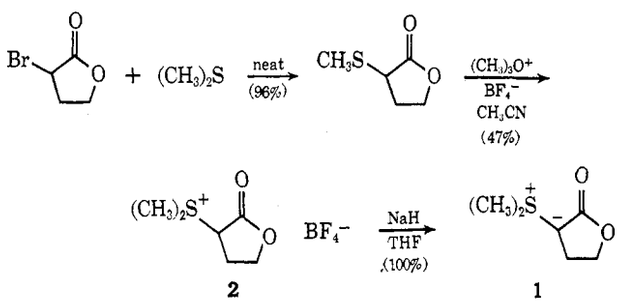
Received March 8, 1973

Alkylation of α-methylthio-γ-butyrolactone available from 2-bromo-γ-butyrolactone with trimethyloxonium fluoroborate followed by deprotonation with sodium hydride generates dimethylsulfonium 2-oxotetrahydrofuryl-3-ylide. This new annelating reagent combines with acrolein, methyl vinyl ketone, acrylonitrile, dimethyl fumarate, diethyl maleate, and benzalacetophenone to give the corresponding cyclopropanes in 25–90% yields in a highly stereoselective reaction. Nonenolizable 1,2-dicarbonyl compounds also condense to give a glycidic lactone but in low yield. Some transformations of the acrolein adduct are described. Treatment of 2-methylthio-γ-butyrolactone with lithium diisopropylamide generated the corresponding enolate as demonstrated by deuteration and methylation. Attempts to condense this enolate with cyclohexanone failed.

The utility of sulfur ylides (π sulfuranes) in synthesis has encouraged the development of new types of ylides and the exploration of their synthetic potential.[3] As a result many alkyl-substituted ylides[4] and ylides stabilized by carboxylate,[5] carboalkoxy,[6] acyl,[7] and cyano[8] groups have been developed. The existence of many geminal-substituted cyclopropanes in which the alkyl groups are differentially functionalized encouraged us to examine the synthesis and reactions of dimethylsulfonium 2-oxotetrahydrofuryl-3-ylide.[9] Use of such a reagent would introduce geminal cyclopropyl groups at the oxidation level of an alcohol and an ester.

The ylide was obtainable as a somewhat stable solid which would decompose over a period of weeks in the freezer by deprotonation of *S*,*S*-dimethyl-*S*-(2-oxotetrahydro-3-furyl)sulfonium fluoroborate (**2**) with sodium hydride (Scheme I). The latter was readily

SCHEME I
GENERATION OF YLIDE 1



available by the methylation of α-methylthio-γ-butyrolactone, the disproportionation product of dimethyl sulfide and 2-bromo-γ-butyrolactone. The ylide **1** showed an exceedingly low carbonyl stretch at 1647 cm^{-1}, indicating extensive delocalization of negative charge. The approximately 30-cm^{-1} shift from that of dimethylsulfonium carboethoxymethylide (**3**)

$$(CH_3)_2S{=}CHCO_2C_2H_5$$
3

(1620 cm^{-1})[6] is what is expected for placement of the carbonyl in a five-membered ring. The nmr spectrum exhibits two approximate triplets (J = 8 Hz) at δ 4.30 and 2.75 for the ring protons and a singlet at δ 2.68 for the *S*-methyl groups. The shift of only 0.1 ppm from the salt to the ylide for the *S*-methyl groups compares to a 0.4-ppm shift for the same change in the case of ylide **3**. The fixed cisoid configuration in the lactone ylide **1** accounts for this difference.[10] Attempts to generate the ylide with hydroxylic base led only to decomposition.

Condensation of the preformed ylide with Michael acceptors gave mixed results (see Scheme II). Good Michael systems such as acrylonitrile, benzalacetophenone, diethyl maleate, dimethyl fumarate, acrolein, and methyl vinyl ketone generated the desired cyclopropanes in yields from 12 to 90%. Synthetically, it is sometimes advantageous to prepare the ylide in the presence of the Michael acceptor. Thus, in the case of chalcone, the adduct **9** was obtained in 92% yield (based on sulfonium salt **2**) by generating the ylide *in situ* with sodium hydride, whereas with the preformed ylide, the yield of adduct was only 12% (based on ylide **1**). In order to explore this question further, the reaction of acrylonitrile was examined in more detail (see Table I). The lower yields obtainable in DMF or HMPA may be attributable to the instability of the ylide in these solvents. The stability factor also poses a problem in acetonitrile and tetrahydrofuran, as evidenced by the increase in yield as a function of increasing the ratio of trapping agent to ylide. Synthetically, the best overall yields of cyclopropanes are obtained by use of *in situ* ylide generation and of an approximately 2:1 ratio of Michael acceptor to ylide. Acetonitrile appears to be the best solvent for reactions with preformed ylide.

The structures of the adducts are clearly supported by spectroscopic data. The ir spectra had a lactone

(1) Part 12 of our series on new synthetic reactions.

(2) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient.

(3) For some reviews see C. Agami, *Bull. Soc. Chim. Fr.*, 1021 (1965); J. C. Bloch, *Ann. Chim. (Paris)*, **10**, 419 (1965); A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966; P. A. Lowe, *Chem. Ind. (London)*, 1070 (1970). For the fundamental papers in synthetic applications see E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965), and V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961).

(4) For example see E. J. Corey and W. Oppolzer, *J. Amer. Chem. Soc.*, **86**, 1899 (1964); E. J. Corey, M. Jautelat, and W. Oppolzer, *Tetrahedron Lett.*, 2325 (1967); A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Amer. Chem. Soc.*, **86**, 918 (1964); R. W. LaRochelle, B. M. Trost, and L. Krepski, *J. Org. Chem.*, **36**, 1126 (1971).

(5) J. Adams, L. Hoffman, Jr., and B. M. Trost, *J. Org. Chem.*, **35**, 1600 (1970).

(6) K. W. Ratts and A. N. Yao, *ibid.*, **31**, 1185 (1966); G. B. Payne, *ibid.*, **32**, 3351 (1967).

(7) B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 138 (1967); H. Nozaki, M. Takaku, and K. Kondo, *Tetrahedron*, **22**, 2145 (1966); T. Mukaiyama and M. Higo, *Tetrahedron Lett.*, 5297 (1970); M. Higo, T. Sakashita, M. Toyoda, and T. Mukaiyama, *Bull. Chem. Soc. Jap.*, **45**, 250 (1972).

(8) D. Jeckel and J. Gosselck, *Tetrahedron Lett.*, 2101 (1972); B. M. Trost and L. S. Melvin, Jr., unpublished work.

(9) *Cf.* H. Nozaki, D. Tunemoto, S. Matubara, and K. Kondo, *Tetrahedron*, **23**, 545 (1967).

(10) J. Casanova and D. A. Rutolo, *Chem. Commun.*, 1224 (1967).

SCHEME II

MICHAEL REACTIONS OF YLIDE 1

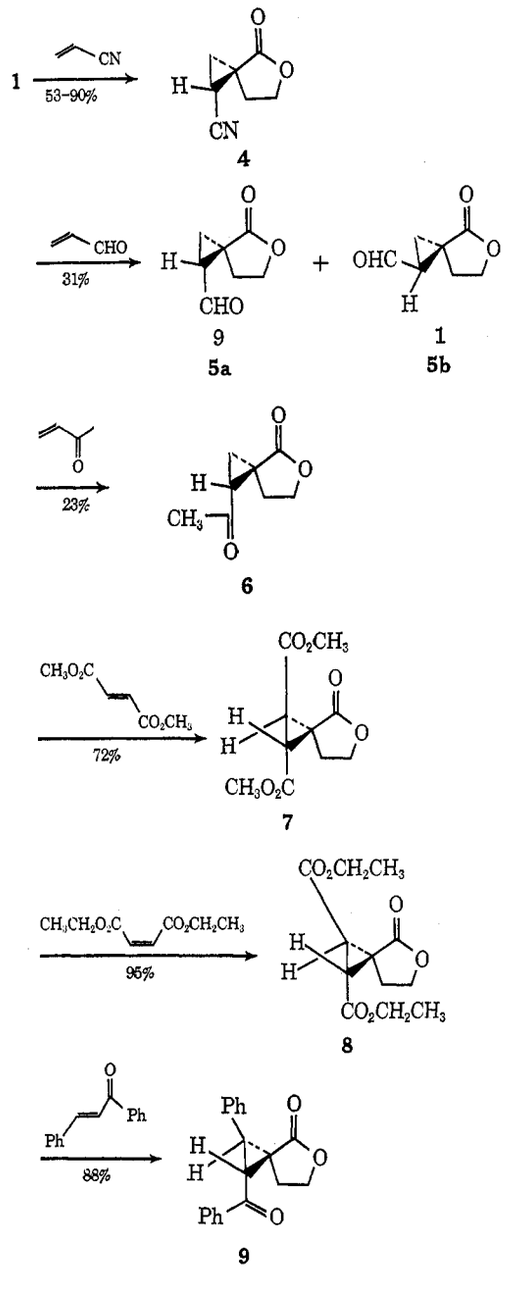


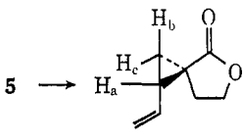
TABLE I

YIELD DATA FOR ADDUCT 4[a]

Mode of ylide generation	Ratio ylide: acrylonitrile	Solvent	Time, hr	Yield, %
1, Preformed	1:1	CH_3CN	8	58[b]
2, *In situ*	1:1	THF	8	64[c]
3, *In situ*	1:2	THF	8	75[c]
4, *In situ*	1:4	THF	8	84[c]
5, *In situ*	1:1	DMF	8	17[c]
6, *In situ*	1:1	HMPA	6	21[c]

[a] All runs carried out at room temperature and all yields are of isolated product. [b] Yield based on starting ylide **1**. [c] Yield based on starting salt **2**.

carbonyl at 1770–1775 cm^{-1}. The rest of the spectral data is summarized in the Experimental Section. In each case examined, condensation generated one major cyclopropane isomer whose stereochemistry is assigned in structures **4**–**9**. The stereochemistry of adduct **5** was most thoroughly investigated. Its nmr spectrum showed two aldehyde proton absorptions at δ 9.62 and 9.28 in the ratio of 9:1. Since the carboxaldehydo group of **5b** lies directly in the shielding cone of the lactone carbonyl, the higher field absorption was assigned to this isomer. Treatment of the aldehyde with triphenylphosphonium methylene produced the olefin **10** as an essentially single isomer after chromato-



10

graphic separation. The cyclopropane protons appear at δ 2.02 (ddd, J = 8.9, 6.4, 5.1 Hz), 1.50 (dd, J = 8.9, 4.5 Hz), and 0.90 (dd, J = 6.4, 4.5 Hz) assignable to H_a, H_b, and H_c, respectively, on the basis of relative chemical shifts, cyclopropyl cis coupling being larger than trans coupling,[11] and pseudocontact shift data.[12] Upon addition of 20 mol % of Eu(fod)$_3$ the absorptions at δ 1.50 and 0.90 shift to δ 2.40 and 1.40, respectively, indicating that H_b is cis to the lactone carbonyl and H_c trans. The shift of H_a from δ 2.02 to 3.10, combined with the coupling constants, demands that it is cis to the lactone carbonyl.

For adduct **6**, the protons of the cyclopropyl methylene group appear as a simple doublet at δ 1.4 (J = 7.2 Hz) in the nmr spectrum, indicating that each is in the same magnetic environment, *i.e.*, cis to a carbonyl group as in structure **6**. Such accidental equivalence would not be explicable on the basis of the alternative isomer. Similarly, adducts **7** and **8** show nonequivalent ester groups in their nmr spectra (see Experimental Section) demanding the trans isomers. The stereochemistry of the remaining adducts are assigned on the basis of analogy to the above and earlier work.[5–8]

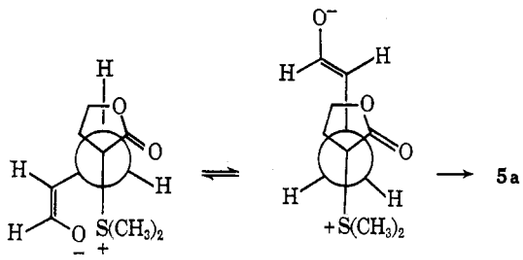
Stabilized ylides add reversibly to α,β-unsaturated systems to generate intermediate enolates, thus the loss of olefin stereochemistry in the product.[5–9] The stereochemical preferences seen normally reflect the thermodynamic stability of these intermediates. In considering the conformers for the precursors of **5a** and **5b** (**11a** and **11b**, respectively), clearly steric and unfavorable dipole–dipole interactions are minimized in **11a** compared to **11b**, thus accounting for the stereoselectivity observed.

Less reactive Michael acceptors such as ethyl 3-methyl-2-butenoate, carvone, and methyl sorbate failed to react. Carbonyl condensations with cyclohexanone and benzaldehyde were also unsuccessful. 1,2-Dicarbonyl systems gave mixed results. Biacetyl and methyl pyruvate failed to condense, presumably because of enolization under the reaction conditions. Benzil, which cannot enolize, did condense, although in low yields, to produce adduct **12**.[13] Its infrared spectrum showed carbonyl absorptions at 1785 and 1670 cm^{-1}. The nmr spectrum showed only the typical pattern for the CH_2CH_2 unit of the lactone ring in

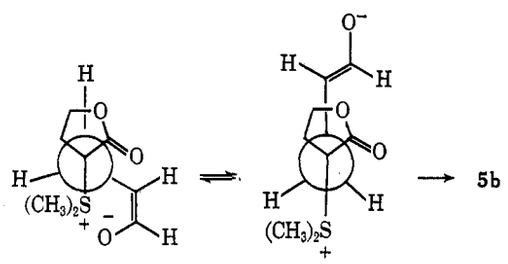
(11) J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, **84**, 2249 (1962); A. Bothner-by, *Advan. Magn. Resonance*, **1**, 195 (1965).

(12) P. E. Manni, G. A. Howie, B. Katz, and J. M. Cassady, *J. Org. Chem.*, **37**, 2769 (1972).

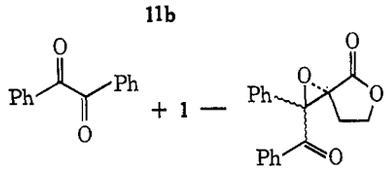
(13) For a glycidic lactone see J. D. White, J. B. Bremner, M. J. Dimsdale, and R. L. Garcea, *J. Amer. Chem. Soc.*, **93**, 7398 (1971).



11a



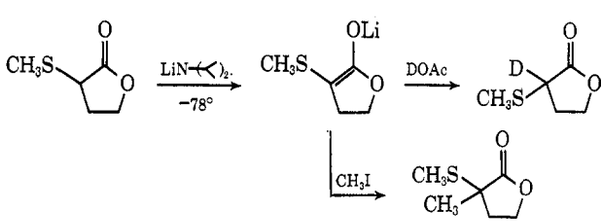
11b



12

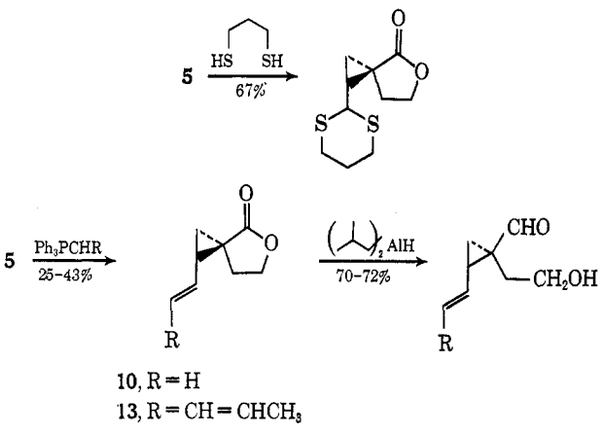
addition to aromatic absorptions but did suggest that the adduct was essentially stereohomogeneous.

To overcome this unreactivity, a brief investigation centered on the generation and properties of the anion of α-methylthio-γ-butyrolactone.[14] Dropwise addition of the sulfide to a −78° solution of lithium diisopropylamide in THF followed by quenching with DOAc generated the corresponding 2-deuterio-2-methylthio-γ-butyrolactone, which was 65% d_1, by nmr and mass spectral analysis.[15] Addition of 1 equiv of methyl



iodide to the anion generated the methylated compound in 37% yield. However, attempts to condense cyclohexanone with the lactone enolate led to essentially quantitative recovery of starting materials. Its failure to undergo ketone condensation may be due to enolization.

In ancillary experiments, some transformations of the cyclopropane adducts were investigated. Adduct **5** formed a dithiane derivative quite smoothly, although attempts to desulfurize this adduct failed. The aldehyde underwent Wittig condensation with triphenylphosphonium methylide and crotylide to give olefin lactones **10** and **13**. Reduction of the lactone to



10, R = H
13, R = CH=CHCH$_3$

the lactol proceeded smoothly with diisobutylaluminum hydride. It is interesting to note that the product exists solely in the hydroxyaldehyde form as evidenced by the carbonyl stretching frequency at 1700 cm^{-1} in the infrared spectrum and the aldehyde proton at δ 8.80–9.06. Such products would be valuable intermediates to the dictyopterenes.[16]

Experimental Section

General.—Melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Model 11 and Model 15 spectrophotometers. Nmr spectra were determined on Varian Associates Model A-60A, HA-100, or XL100 spectrometers fitted with a variable-temperature probe. Chemical shifts are given in parts per million relative to TMS as an internal standard. Abbreviations for multiplicity are s, singlet; d, doublet; app t, apparent triplet; t, triplet; and m, multiplet. Mass spectra were taken on a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 V. Analyses were performed by Spang Microanalytical Laboratory. Vpc analyses were performed on an Aerograph Model 90P instrument. Tlc separations were achieved on Merck (Darmstadt) silica gel PF-254. All reactions were carried out under an atmosphere of nitrogen.

Preparation of α-Methylthio-γ-butyrolactone.—A mixture of 58.2 g (0.35 mol) of α-bromo-γ-butyrolactone and 85 g (100 ml, 1.37 mol) of dimethyl sulfide was refluxed for 20 hr under a nitrogen atmosphere. After the mixture was allowed to cool, filtration removed the precipitated trimethylsulfonium bromide, which was washed thoroughly with ether. The ether washes were combined with the original filtrate and the solvent was removed *in vacuo*, leaving a pale yellow oil. Distillation under reduced pressure yielded 44.6 g (96%) of α-methylthio-γ-butyrolactone: bp 82–86° (0.5 mm); ir (CCl_4) 1779 cm^{-1}; nmr (CCl_4) δ 2.25 (3 H, s), 2.3–3.0 (2 H, m), 3.24 (1 H, dd, J = 8.2, 5.4 Hz), and 4.34 (app t, J = 7.2 Hz); mass spectrum m/e (rel intensity) 132 (59), 122 (5), 120 (4), 86 (100), 73 (45), and 55 (44).

Anal. Calcd for $C_5H_8O_2S$: 132.02450. Found: 132.02457.

Preparation of Dimethyl(2-oxotetrahydro-3-furyl)sulfonium Fluoroborate (3).—α-Methylthio-γ-butyrolactone (30 g, 0.23 mol) was dissolved in 750 ml of dry (freshly distilled from calcium hydride) acetonitrile under nitrogen. Trimethyloxonium fluoroborate (33.6 g, 0.23 mol) was added in one portion. After the mixture was stirred for 1.5 hr at room temperature, the solvent was removed *in vacuo* and the residual oil was swirled with ether. After the ether washes were decanted, the residue was dissolved

(14) For other studies on enolates derived from lactones see A. E. Greene, J. C. Müller, and G. Ourisson, *Tetrahedron Lett.*, 2489 (1972); P. A. Grieco and K. Hiroi, *J. Chem. Soc., Chem. Commun.*, 1317 (1972); G. H. Posner and G. L. Loomis, *ibid.*, 892 (1972).

(15) The less than 100% deuterium incorporation is presumably due to isotope dilution because of the presence of protonic diisopropylamine. A similar effect has been found in quenching enolates of esters generated in similar fashion. See M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, **93**, 2318 (1971).

(16) For a leading reference see J. A. Pettus and R. E. Moore, *J. Amer. Chem. Soc.*, **93**, 3087 (1971).

in 20 ml of dry acetonitrile and absolute ethanol was added to precipitate the sulfonium salt. The resultant solid was recrystallized twice from ethanol–acetonitrile to give 25 g (47%) of sulfonium salt: mp 81.5–82.5°; ir (Nujol) 1748 cm^{-1}; nmr (CO_3CN) δ 2.1–3.0 (2 H, m), 3.02 (3 H, s), 3.05 (3 H, s), and 4.3–4.8 (3 H, m).

Anal. Calcd for $C_6H_{11}O_2SBF_4$: C, 30.75; H, 4.74; S 13.66; F, 32.47. Found: C, 30.86; H, 4.55; S, 13.82; F, 32.60.

Preparation of Dimethylsulfonium 2-Oxotetrahydrofuryl-3-ylide (1).—Sodium hydride (257 mg, 6.00 mmol, of a 56% dispersion in mineral oil) was washed free of mineral oil with pentane under a nitrogen atmosphere. Subsequently, 50 ml of dry tetrahydrofuran (distilled from sodium benzophenone ketyl) and then 1.50 g (6.4 mmol) of salt **2** were added. Stirring continued at room temperature until evolution of hydrogen ceased. The solution was decanted from a solid residue. The latter was washed with chloroform and the chloroform layer was combined with the tetrahydrofuran solution. Evaporation *in vacuo* produced a gum which was induced to crystallize by dissolving in ethanol and adding ether. In this way, 880 mg (quantitative yield) of ylide **1** was obtained. For infrared and nmr spectral data see results and discussion section. **1** had uv (CH_3CN) λ_{max} 263 nm (ϵ 107); mass spectrum *m/e* (rel intensity) 146 (7), 132 (59), 100 (42), 98 (62), 86 (100), and 73 (45).

Anal. Calcd for $C_6H_{10}O_2S$: 146.04015. Found: 146.04055.

Reaction of π Sulfurane 1 with Acrylonitrile. Method A (*in Situ* Generation).—A suspension of 192 mg (4.5 mmol of a 56% mineral oil dispersion) of sodium hydride, 1.10 g (4.70 mmol) of dimethyl(2-oxotetrahydro-3-furyl)sulfonium fluoroborate, and 984 mg (18.6 mmol) of acrylonitrile in 25 ml of dry tetrahydrofuran was prepared under nitrogen. This mixture was stirred for 8 hr at room temperature. The mixture was then poured into water and extracted with ethyl acetate. After drying over anhydrous magnesium sulfate and removal of solvent *in vacuo*, a nearly colorless oil remained. Chromatographic separation by tlc eluting with chloroform and washing the product off the silica gel with ether gave 544 mg (84%) of cyclopropane **4**: ir ($CHCl_3$) 2250 and 1768 cm^{-1}; nmr ($CDCl_3$) δ 4.48 (2 H, app t, J = 7 Hz), 2.50 (2 H, app t, J = 7 Hz), 2.05 (1 H, dd, J = 8.5, 6.7 Hz), 1.52 (1 H, dd, J = 8.5, 4.5 Hz), and 1.46 (1 H, dd, J = 6.7, 4.5 Hz); mass spectrum *m/e* (rel intensity) 137 (7), 136 (4), 119 (5), 109 (12), 84 (39), 56 (100), and 55 (59).

Anal. Calcd for $C_7H_7O_2N$: 137.04767. Found: 137.04762.

Method B (Preformed).—Dimethylsulfonium 2-oxotetrahydrofuryl-3-ylide (385 mg, 2.64 mmol) was dissolved in 25 ml of dry acetonitrile (distilled from calcium hydride) under nitrogen. Acrylonitrile (152 mg, 2.87 mmol) was added in one portion and the solution was stirred for 8 hr at room temperature. The reaction mixture was evaporated *in vacuo* and the crude product was chromatographed on silica gel utilizing chloroform as the eluting solvent. In this way 209 mg (58%) of cyclopropane **4** identical with the material previously characterized was obtained.

Reaction of π Sulfurane 1 with Benzalacetophenone.—As described above for the *in situ* method (method A), 1.00 g (4.3 mmol) of salt **2**, 182 mg (4.3 mmol) of a 56% mineral oil dispersion of sodium hydride, and 930 mg (4.4 mmol) of benzalacetophenone in 30 ml of THF was converted to 1.1 g (88%) of crystalline product **9**, mp 106.5–107°, after tlc purification utilizing benzene as the eluting solvent: uv (C_2H_5OH) λ_{max} 248 nm (ϵ 10,700); nmr ($CDCl_3$) δ 8.1 (2 H, m), 7.72 (3 H, m), 7.4 (5 H, pseudosinglet), 4.47 (2 H, app t, J = 7.7 Hz), 3.98 (1 H, d, J = 7 Hz), 3.47 (1 H, d, J = 7 Hz), 2.52 (2 H, app t, J = 7.7 Hz); mass spectrum *m/e* (rel intensity) 292 (3), 187 (5), 128 (3), 105 (100), and 77 (17).

Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.05; H, 5.86; mol wt, 292.10994. Found: C, 77.70; H, 5.59; mol wt, 292.10886.

Reaction of π Sulfurane 1 with Diethyl Maleate.—As described above for method B, 137 mg (0.94 mmol) of π sulfurane **1** and 147 mg (0.85 mmol) of freshly distilled diethyl maleate in 25 ml of dry acetonitrile generated 209 mg (95%) of **8** after tlc isolation utilizing chloroform as the eluting solvent: ir ($CHCl_3$) 1775 and 1725 cm^{-1}; nmr ($CDCl_3$) δ 4.43 (2 H, app t, J = 7.2 Hz), 4.18 (2 H, q, J = 7 Hz), 4.15 (2 H, q, J = 7 Hz), 2.2–3.0 (4 H, m), 1.28 (3 H, t, J = 7 Hz), and 1.23 (3 H, t, J = 7 Hz); mass spectrum *m/e* (rel intensity) 256 (1), 186 (32), 185 (26), 177 (12), 144 (100), 132 (32), 129 (51), 115 (22), 86 (48), 84 (70), 73 (24), and 55 (30).

Anal. Calcd for $C_{12}H_{16}O_6$: 256.09468. Found: 256.09503.

Reaction of π Sulfurane 1 with Dimethyl Fumarate.—By method B, 350 mg (2.4 mmol) of π sulfurane **1** and 376 mg (2.6 mmol) in 20 ml of acetonitrile gave 390 mg (72%) of crystalline **7**, mp 93.5–94.0°, after tlc purification utilizing chloroform as the eluting solvent: ir ($CHCl_3$) 1772 and 1726 cm^{-1}; nmr ($CDCl_3$) δ 4.48 (2 H, app t, J = 7.2 Hz), 4.12 (3 H, s), 4.05 (3 H, s), 2.90 (1 H, d, J = 6.8 Hz), 2.68 (1 H, d, J = 6.8 Hz), and 2.50 (2 H, app t, J = 7.2 Hz).

Reaction of π Sulfurane 1 with Methyl Vinyl Ketone.—Preformed dimethylsulfonium 2-oxotetrahydrofuryl-3-ylide (251 mg, 1.72 mmol) was dissolved in 25 ml of dimethylformamide (freshly distilled from calcium hydride) at room temperature. In one portion, 131 mg (1.87 mmol) of methyl vinyl ketone was added and the solution was stirred for 7 hr at room temperature. It was then poured into 150 ml of water and extracted with 3 × 25 ml of ethyl acetate. The ethyl acetate extracts were washed with 3 × 50 ml of water to remove dimethylformamide. After the extracts were dried over anhydrous potassium carbonate and the solvent was removed *in vacuo*, the product was purified by tlc utilizing chloroform as the eluting solvent to give 62 mg (23%) of **6** as an oil: ir ($CHCl_3$) 1769 and 1705 cm^{-1}; nmr ($CDCl_3$) δ 4.28 (2 H, app t, J = 7.5 Hz), 2.47 (1 H, t, J = 7.2 Hz), 2.25 (3 H, 3), 2.22 (2 H, app t, J = 7.5 Hz), and 1.40 (2 H, d, J = 7.2 Hz); mass spectrum *m/e* (rel intensity) 154 (6), 139 (23), 136 (100), 112 (58), 111 (82), 108 (75), 95 (58), 83 (43), 67 (93), and 53 (53).

Anal. Calcd for $C_8H_{10}O_3$: 154.06299. Found: 154.06359.

Reaction of π Sulfurane 1 with Acrolein.—By method A, 10 g (42.7 mmol) of salt **2**, 1.83 g (38.0 mmol) of 56% mineral oil dispersion of sodium hydride, and 2.39 g (42.7 mmol) of acrolein in 250 ml of dry tetrahydrofuran produced 1.65 g (31%) of cyclopropane **5** as a colorless oil after silica gel chromatography utilizing chloroform as the eluting solvent: ir ($CHCl_3$) 2730, 1772, and 1705 cm^{-1}; nmr ($CDCl_3$) δ 9.62 (1 H, d, J = 3 Hz), 4.45 (2 H, app t, J = 7.1 Hz), 2.55 (1 H, ddd, J = 10.1, 7.1, 3.0 Hz), 2.43 (2 H, app t, J = 7.1 Hz), and 1.40–2.1 (2 H, m); mass spectrum *m/e* (rel intensity) 140 (8), 122 (14), 109 (74), 91 (54), 86 (58), 79 (100), 77 (68), and 71 (98). In the nmr spectrum a doublet also appeared at δ 9.28 (J = 6 Hz). Utilizing the relative intensity of this signal to the one at δ 9.62 gave an isomer ratio of 1:9.

Anal. Calcd for $C_7H_8O_3$: 140.08372. Found: 140.08314.

Preparation of Glycidic Lactone 12.—To a solution of 267 mg (1.83 mmol) of ylide **1** in 20 ml of dry acetonitrile was added 418 mg (2.0 mmol) of benzil at room temperature. The mixture was stirred for 2.5 hr at room temperature and 2 hr at 84°. After cooling and evaporation of solvent, the crude material was chromatographed on silica gel utilizing chloroform as the eluting solvent. In this way, 76 mg (14% yield) of glycidic lactone, mp 139–140°, was obtained in addition to a recovery of 260 mg (62%) of benzil: ir ($CHCl_3$) 1785, 1670, 1590, and 1580 cm^{-1}; nmr ($CDCl_3$) δ 8.0 (2 H, m), 7.1–7.8 (8 H, m), 4.46 (2 H, app t, J = 7.0 Hz), and 2.47 (2 H, app t, J = 7.0 Hz); uv (C_2H_5OH) 254 nm (ϵ 8200); mass spectrum *m/e* (rel intensity) 294 (5), 249 (7), 165 (3), 116 (5), 105 (100), and 77 (29).

Anal. Calcd for $C_{18}H_{14}O_4$: 294.08920. Found: 294.08741.

Reaction of Cyclopropyl Aldehyde 5 with Wittig Reagents. Reaction with Triphenylphosphonium Methylide.—To a slurry of 4.32 g (12.0 mmol) of methyltriphenylphosphonium bromide in 95 ml of dry tetrahydrofuran (distilled from sodium benzophenone ketyl) was added 9.16 ml (12.0 mmol) of a 1.31 *M* hexane solution of *n*-butyllithium and the mixture was stirred for 20 min. A solution of 1.65 g (11.7 mmol) of aldehyde **5** in 5 ml of dry tetrahydrofuran was added in one portion at room temperature and the mixture was subsequently heated to 60° for 15 hr. The slurry was cooled and filtered to remove the precipitated triphenylphosphine oxide. The solvent was removed *in vacuo* and the crude material was chromatographed on 1 kg of silica gel G utilizing chloroform as eluting solvent. In this way 698 mg (44%) of the methylene compound **10** was obtained as a colorless oil: ir ($CHCl_3$) 1765, 1640, 985, and 909 cm^{-1}; nmr ($CDCl_3$) δ 5.27 (3 H, m), 4.33 (2 H, app t, J = 6.9 Hz), 2.23 (2 H, app t, J = 6.9 Hz), 2.02 (1 H, ddd, J = 8.9, 5.1, 4.5 Hz), 1.50 (1 H, dd, J = 8.9, 4.5 Hz), and 0.9 (1 H, dd, J = 6.4, 4.5 Hz); mass spectrum *m/e* (rel intensity) 138 (17), 137 (4), 123 (30), 110 (17), 93 (41), 91 (37), 79 (100), 77 (55), 66 (24), and 53 (27).

Anal. Calcd for $C_8H_{10}O_2$: 138.06807. Found: 138.06733.

Reaction with Triphenylphosphonium Crotylide.—As described above, 470 mg (1.20 mmol) of crotyltriphenylphosphonium bromide, 888 μl (1.16 mmol) of a 1.31 *M* hexane solution of *n*-

butyllithium, and 162 mg (1.15 mmol) of aldehyde **5** were converted into 50 mg (25%) of diene **13** after isolation by tlc utilizing chloroform as eluting solvent: ir ($CHCl_3$) 1773 cm^{-1}; nmr ($CDCl_3$) δ 4.6–6.5 (4 H, m), 4.22 (2 H, app t, J = 7.6 Hz), 2.27 (2 H, app t, J = 7.6 Hz), 1.9–2.3 (1 H, m), 1.79 and 1.73 (3 H, overlapping d, J = 6.0 Hz), 1.4 (1 H, m), and 0.95 (1 H, m); mass spectrum m/e (rel intensity) 178 (70), 163 (10), 150 (51), 133 (30), 119 (38), 105 (67), 93 (31), 91 (100), 81 (76), 80 (100), 79 (71), and 77 (53).

Anal. Calcd for $C_{11}H_{14}O_2$: 178.09937. Found: 178.09942.

Preparation of Dithiane Derivative of Aldehyde 5.—To a solution of 150 mg (1.07 mmol) of aldehyde **5** in 10 ml of chloroform at 0° was added 129 mg (1.2 mmol) of 1,3-propanedithiol and 150 μl of distilled boron trifluoride etherate. After stirring for 45 min, the reaction mixture was diluted with 50 ml of ether and washed with 2 × 50 ml of saturated aqueous sodium bicarbonate solution. After drying over anhydrous potassium carbonate, the solvent was removed *in vacuo*. Purification by tlc utilizing chloroform as eluting solvent yielded 170 mg (69%) of product as a colorless oil: ir ($CHCl_3$) 1755 cm^{-1}; nmr ($CDCl_3$) δ 4.47 (2 H, app t, J = 7.9 Hz), 3.47 (1 H, d, J = 10.1 Hz), 2.8 (4 H, m), 2.41 (1 H, dd, J = 6.7, 4.8 Hz), 2.0 (2 H, m), 1.55 (2 H, m); mass spectrum m/e (rel intensity) 230 (12), 132 (100), 123 (6), 106 (6), 99 (7), 97 (6), 73 (6), and 58 (6).

Anal. Calcd for $C_{10}H_{14}O_2S_2$: 232.05917. Found: 232.06102.

Preparation of 1-(2′-Hydroxyethyl)-2-vinylcyclopropanecarboxaldehyde. To a solution of olefin lactone **10** (26 mg, 0.19 mmol) in 3 ml of dry toluene cooled to −78° was added 140 μl (0.20 mmol) of a 1.42 M diisobutylaluminum hydride solution in toluene. The reaction was stirred for 5 min and then quenched by addition of 1 ml of absolute ethanol. The reaction mixture was poured into 5 ml of saturated aqueous ammonium chloride solution and 0.5 ml of glacial acetic acid was added. The product was extracted with ethyl acetate and the combined organic layers were washed with 20 ml of saturated aqueous sodium bicarbonate solution. After drying over anhydrous potassium carbonate and evaporation *in vacuo*, isolation of product was accomplished by tlc utilizing a 95:5 (v/v) chloroform–ether mixture to give 18 mg (70%) of product: ir (CCl_4) 3390, 2720, 1700, and 1635 cm^{-1}; nmr ($CDCl_3$) δ 8.84 (1 H, s), 4.9–5.9 (3 H, m), 3.70 (2 H, app t, J = 6.5 Hz), 2.64 (1 H, brs), 1.93 (1 H, ddd, J = 8.9, 7.0, 3.3 Hz), 1.51 (1 H, dd, J = 8.9, 5.0 Hz), and 1.13 (1 H, dd, J = 7.0, 5.0 Hz); mass spectrum m/e (rel intensity) 140 (8), 122 (14), 121 (12), 109 (74), 91 (54), 86 (58), 81 (60), 79 (100), 77 (68), 71 (98), 70 (44), 58 (88), and 53 (51).

Anal. Calcd for $C_8H_{12}O_2$: 140.08372. Found: 140.08314.

Preparation of 1-(2′-Hydroxyethyl)-2-(1″,3″-pentadienyl)-cyclopropanecarboxaldehyde.—As described above, 50 mg (0.28 mmol) of diene lacetone **13** upon treatment with 196 μl (0.28 mmol) of a 1.42 M toluene solution of diisobutylaluminum hydride in 3 ml of toluene yielded 36 mg (72%) of aldehyde product after tlc purification utilizing a 95:5 (v/v) mixture of chloroform–ether as the eluting solvent: ir ($CHCl_3$) 3571, 2717, 1700, and 1620 cm^{-1}; nmr ($CDCl_3$) δ 9.08, 8.89, and 8.81 (total 1 H, all s), 4.8–6.5 (4 H, m), 3.72 (2 H, app t, J = 6.3 Hz), 1.4–2.6 (6 H, m with superimposed singlet at 2.62 and doublets at 1.78 and 1.73), and 1.1 (1 H, m).

Metalation of α-Methylthio-γ-butyrolactone.—To a solution of 1.01 g (10 mmol) of diisopropylamine in 11 ml of dry tetrahydrofuran at −78° was added 8.86 ml (11.6 mmol) of n-butyllithium (1.3 M in hexane) over a 2-min period. After the solution was stirred for an additional 15 min, 1.32 g (10.0 mmol) of α-methylthio-γ-butyrolactone was added dropwise. Upon completion of the addition, stirring was continued for 15 min. Freshly distilled methyl iodide (1.42 g, 10.0 mmol) was added all at once. Reaction proceeded for another 15 min at −78° and slowly warmed to room temperature. Addition of 20 ml of water quenched the reaction and the products were extracted with ether. After drying over anhydrous potassium carbonate, the solvent was removed *in vacuo*. The crude material was purified by silica gel chromatography utilizing chloroform as eluting solvent to give 541 mg (37%) of α-methyl-α-methylthio-γ-butyrolactone: ir (CCl_4) 1760 cm^{-1}; nmr ($CDCl_3$) δ 4.28 (2 H, m), 2.2–2.7 (2 H, m), 2.14 (3 H, s), and 1.53 (3 H, s); mass spectrum m/e (rel intensity) 146 (35), 100 (100), 98 (14), 87 (20), 69 (18), and 55 (47).

Anal. Calcd for $C_6H_{10}O_2S$: 146.04015. Found: 146.04047.

Acknowledgment.—We wish to thank the National Science Foundation and the National Institutes of Health for their generous support of our programs. We also thank the National Science Foundation and the Wisconsin Alumni Research Foundation (administered by the Graduate School of the University of Wisconsin) for funds utilized for the purchase of the spectrometers used in the characterization of these compounds.

Registry No.—**1**, 40587-47-1; **2**, 40733-71-9; **4**, 40587-48-2; **5a**, 40587-49-3; **5b**, 40587-43-7; **6**, 40587-44-8; **7**, 40587-45-9; **8**, 40587-46-0; **9**, 40587-50-6; **10**, 40587-51-7; **12**, 40587-52-8; **13**, 40587-53-9; α-methylthio-γ-butyrolactone, 40587-54-0; α-bromo-γ-butyrolactone, 5061-21-2; dimethyl sulfide, 75-18-3; acrylonitrile, 107-13-1; benzalacetophenone, 94-41-7; diethyl maleate, 141-05-9; dimethyl fumarate, 624-49-7; methyl vinyl ketone, 78-94-4; acrolein, 107-02-8; benzil, 134-81-6; triphenylphosphonium crotylide, 40587-56-2; 1,3-propanedithiol, 109-80-8; dithiane derivative of **5**, 40587-57-3; 1-(2′-hydroxyethyl)-2-vinylcyclopropanecarboxaldehyde, 40587-58-4; 1-(2′-hydroxyethyl)-2-(1″,3″-pentadienyl)cyclopropanecarboxaldehyde, 40587-59-5; α-methyl-α-methylthio-γ-butyrolactone, 40587-60-8.