mol of phase-transfer catalyst. Solid Chloramine-T trihydrate (15.5 g, 0.0055 mol) was slowly added with stirring and cooling with a water bath. After addition was complete the water bath was removed; stirring was continued until the reaction was complete (usually 1–2 h) as ascertained by occasional monitoring by a thin-layer chromatography. The reaction mixture was washed with 200 mL of cold 5% aqueous sodium hydroxide followed by two washes with 200-mL portions of water. The dichloromethane layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude sulfilimine was recrystallized from methanol–water (9:1).

General Procedure for Preparation of Oxiranes. The *N*-(*p*-tolylsulfonyl)sulfilimine (3 mmol) was dissolved in 10 mL of dimethyl sulfoxide in a dry nitrogen atmosphere. After addition of 1 equiv of butyllithium in hexane the mixture was magnetically stirred for 10 min at room temperature, and the aldehyde or ketone (3.0 mmol) was added with a syringe. The reaction mixture, after stirring at ambient temperature for 18–20 h, was poured into 10% aqueous sodium chloride. The product was obtained by several extractions with hydrocarbon solvent, washing the combined extracts with water, drying over anhydrous sodium carbonate, and short-path distillation.

Reaction of Chloramine-T with 3-Methyl-1-(phenylthio)-2-butene (4, R = Ph). Sulfide **4** (R = Ph), bp 120–122 °C (6 mm), prepared in 93% yield by alkylation of sodium benzenethiolate with 1-bromo-3-methyl-2-butene in ethanol, was subjected to the general procedure given above for reaction of Chloramine-T with sulfides at both ambient temperature and 0 °C. In each case an oil was obtained in 63 and 53% yield, respectively, which was identified as *N*-(1,1-dimethyl-2-propenyl)-*N*-(phenylthio)-*p*-toluenesulfonamide (**6**, R = Ph): ^{1}H NMR ($CDCl_3$) δ 1.5 (6, s), 2.3 (3, s) 4.8–6.3 (3, vinyl multiplet), 7–8 (9, Ar).

Reaction of Chloramine-T with 3-Methyl-1-(methylthio)-2-butene (4, R = CH_3). Sulfide **4** (R = CH_3), bp 79–81 °C (77 mm), was treated with Chloramine-T according to the general procedure. The crude product was washed with ether to give the sulfilimine **5** (R = CH_3) (40%): mp 73.5–75 °C; ^{1}H NMR ($CDCl_3$) δ 1.68 and 1.72 (6, 2 s), 2.38 (3, s), 2.58 (3, s), 3.54 (2, d), 5.02 (1, t), 7–8 (4, AB quartet). These crystals were stored for several months in the refrigerator without noticeable deterioration.

Evaporation of the ether extract and chromatography of the residue gave, as an oil, the rearranged product *N*-(1,1-dimethyl-2-propenyl)-*N*-(methylthio)-*p*-toluenesulfonamide (**6**, R = CH_3) (19%); ^{1}H NMR ($CDCl_3$) δ 1.57 (6, s), 2.42 (6, s, ArMe and SMe), 4.9–6.4 (3, vinyl multiplet), 7–8 (4, AB quartet).

Acknowledgment. This work was supported by a grant from the National Science Foundation.

Registry No.—**1** (R = Ph; R′ = Me), 10330-22-0; **1** (R = Ph; R′ = Ph), 13150-76-0; **1** (R = *n*-C_6H_{13}; R′ = *n*-C_6H_{13}), 69745-50-2; **1** (R = Et, R′ = CH_2CH_2OH), 69745-51-3; **1** (R = $PhCH_2$, R′ = $PhCH_2$), 3249-66-9; **1** (R = *n*-$C_{12}H_{25}$, R′ = *n*-$C_{12}H_{25}$), 69745-52-4; **3a**, 69745-53-5; **3b**, 69745-54-6; **4** (R = Ph), 10276-04-7; **4** (R = Me), 5897-45-0; **5** (R = Me), 69745-55-7; **6** (R = Ph), 69745-56-8; **6** (R = Me), 69745-57-9; A, 6814-64-8; B, 5367-24-8; C, 30004-64-9; D, 69745-58-0; F, 29835-23-2; PhCHO, 100-52-7; cyclohexanone, 108-94-1; 4-*tert*-butylcyclohexanone, 98-53-3; PhCH=CHCOPh, 94-41-7; CH_3COCH_3, 67-64-1; phenyloxirane, 96-09-3; 1-oxaspiro[2.5]octane, 185-70-6; *cis*-6-*tert*-butyl-1-oxaspiro[2.5]octane, 7787-78-2; *trans*-6-*tert*-butyl-1-oxaspiro[2.5]octane, 18881-26-0; (*E*)-2-(benzylidenemethyl)-2-phenyloxirane, 69745-59-1; 2,3-diphenyloxirane, 17619-97-5; 2,2-dimethyl-3-phenyloxirane, 10152-58-6; 2-phenyl-1-oxaspiro[2.5]octane, 37545-92-9; sodium benzenethiolate, 930-69-8; 1-bromo-3-methyl-2-butene, 870-63-3; methyl phenyl sulfide, 100-68-5; diphenyl sulfide, 139-66-2; dihexyl sulfide, 6294-31-1; 2-(ethylthio)ethanol, 110-77-0; dibenzyl sulfide, 538-74-9; didodecyl sulfide, 43-9.

References and Notes

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Synthetic Application of Methyl(phenylthio)ketene. Synthesis of Vicinal-Substituted Cyclopentene Derivatives

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Methyl(phenylthio)ketene (**1**) reacts with olefins to yield α-*endo*-(phenylthio)cyclobutanones **3**, which are converted into α-methylenecyclobutanones **5**. On the other hand, the reaction of the ketene **1** with imines gives a mixture of *cis*- and *trans*-α-(phenylthio)azetidin-2-ones (**7** and **8**). α-Methyleneazetidin-2-one **10a** was obtained similarly from *cis*-α-(phenylthio)azetidin-2-one **7a**. The reaction of the cyclopentadiene adduct, 7-methyl-7-(phenylthio)bicyclo[3.2.0]-2-hepten-6-one (**3a**), with various nucleophiles was investigated. The synthetic evaluation and the stereochemistry of the products are discussed.

There has recently been considerable interest in synthetic applications of modified ketenes such as monohalo-,[2] dihalo-,[3] and dithioketenes[4] because ketenes can serve as one of the most powerful and regioselective reagents for vicinal alkylation of the C–C double bond. On the other hand, in connection with syntheses of natural products, many methods for introduction of α,β-unsaturated carbonyl units have been developed.[5] From these points of view, methyleneketene ($H_2C{=}C{=}C{=}O$) is expected to have great synthetic utility. However, with the exception of the flash vacuum pyrolysis of the cyclopentadiene adduct of 2,2-dimethyl-5-methylene-1,3-dioxane-4,6-dione,[6] methyleneketene has not been detected.

In our preliminary paper,[7] we reported a versatile synthetic reagent, methyl(phenylthio)ketene (**1**), which can be regarded as the synthetic equivalent of methyleneketene. We now wish to report the detailed results and further investigation of the reactions and applications of **1**.

Cycloaddition Reactions of 1 with Olefins 2 and with Imines 6. In the presence of excess cyclopentadiene (**2a**) at −15 °C, the ketene **1** generated in situ by dehydrochlorination of α-(phenylthio)propanoyl chloride with triethylamine af-

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Table I. Synthesis of α-(Phenylthio)cyclobutanones 3 from the Ketene 1 and Olefins 2

olefin 2	molar ratio olefin 1	product	yield,[a] %	mp (bp), °C
cyclopentadiene	5:1[b]	**3a**	82	52.5–54.0
indene	10:1[c]	**3b**	43	100
ethyl vinyl ether	13:1[b]	**3c**	26	(92 at 1 mm)
2,3-dihydropyran	5:1[c]	**3d**	65	85.0–85.5

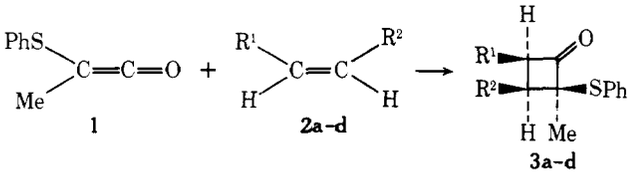
[a] Isolated yield. [b] *n*-Hexane reaction solvent. [c] Benzene reaction solvent.

Table II. Synthesis of *cis*- and *trans*-α-(Phenylthio)azetidin-2-ones 7 and 8 from the Ketene 1 and Imines 6

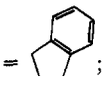
imine 6	product	yield,[a] %	product ratio 7/8	^{1}H NMR δ 3-Me[b] 7	8
PhN=CHPh	**7a**	58	100:0	1.63	
t-BuN=CHPh	**7b + 8b**	69[c]	40:60	1.52	1.04
EtN=CHPh	**7c + 8c**	42[d]	80:20	1.57	1.10

[a] Isolated yield. [b] $CDCl_3$ as a solvent. [c] As a mixture. [d] As a mixture; spectral yield 80%.

forded the α-(phenylthio)cyclobutanone **3a** in 82% yield. Many other cyclobutanones **3** from **1** and olefins **2** were also produced in a similar manner (Table I).



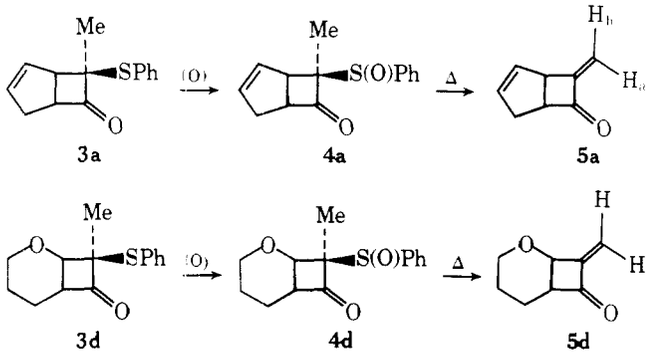
1 **2a–d** **3a–d**

a, R^1, R^2 =  ; b, R^1, R^2 = ; c, R^1 = H, R^2 = OEt;

d, R^1, R^2 = 

Regardless of the olefin substituents, all of the cyclobutanones formed had the phenylthio group in the endo configuration. These results suggest a concerted $[_2\pi_a + _2\pi_s]$ cycloaddition mechanism.[8]

Oxidation of **3a** with *m*-chloroperbenzoic acid (MCPBA) in $CHCl_3$ at −15 °C gave the corresponding sulfoxide **4a** in 94% yield. Thermolysis of **4a** at 150 °C in vacuo gave 7-methylenebicyclo[3.2.0]-2-hepten-6-one (**5a**) in 62% yield.[9]

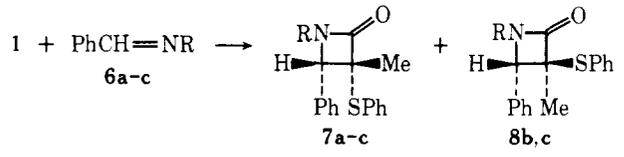


3a **4a** **5a**

3d **4d** **5d**

The infrared spectrum of **5a** exhibited C=O and C=CH_2 absorptions at 1747 and 1640 cm^{-1}, respectively. The ^{1}H NMR spectrum in $CDCl_3$ displayed methylene proton signals at δ 4.92 (s, 1 H, H_b) and 5.50 (s, 1 H, H_a). Similar treatment of the cyclobutanone **3d** also gave the corresponding product, 8-methylenebicyclo[4.2.0]-2-oxaoctan-7-one (**5d**), in 57% yield. The structural assignment of **5d** was similarly made by spectral data.[10]

In contrast to the reactions with olefins, reaction products of the ketene **1** with imines **6** were dependent on the substituents. While the reaction of **1** with benzylideneaniline (**6a**)

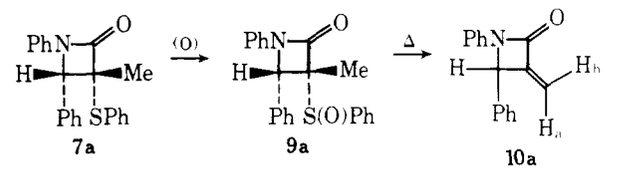


6a–c **7a–c** **8b,c**

a, R = Ph; b, R = *t*-Bu; c, R = Et

gave *cis*-α-(phenylthio)azetidin-2-one (**7a**) as a single isomer in 58% yield, use of *N*-*tert*-butyl- and *N*-ethylbenzylideneimines (**6b** and **6c**) led to the formation of a mixture of *cis*- and *trans*-α-(phenylthio)azetidin-2-ones **7b,c** and **8b,c** in fairly good yields. The results are summarized in Table II. The stereochemistry of the cycloadducts, **7** and **8**, was determined on the basis of the ^{1}H NMR spectral data as well as chemical reactivity. The 3-positioned methyl protons of the *trans*-azetidin-2-ones **8** were observed at ~0.5 ppm higher field than those of the corresponding cis isomers **7** due to the shielding effect of the 4-positioned phenyl group (Table II).

Oxidation of *cis*-α-(phenylthio)azetidin-2-one (**7a**) led to sulfoxide **9a** in 94% yield. α-Methyleneazetidin-2-one **10a** was



7a **9a** **10a**

similarly obtained in 77% yield by the thermolysis of **9a** in vacuo at 200 °C. The ^{1}H NMR spectrum of **10a** exhibited characteristic methylene proton signals at δ 5.09 (s, 1 H, H_a) and 5.76 (s, 1 H, H_b), respectively.

Thus, the formation of **10a** from **7a** suggests that the phenylthio group of **7a** is clearly situated at the cis position to the 4-positioned phenyl group.

The reaction of the ketene **1** with dicyclohexylcarbodiimide also gave the (*N*-cyclohexylimino)azetidin-2-one **11**, albeit in low yield.

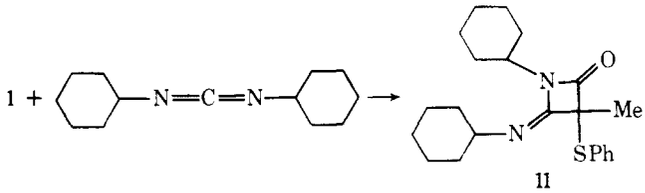


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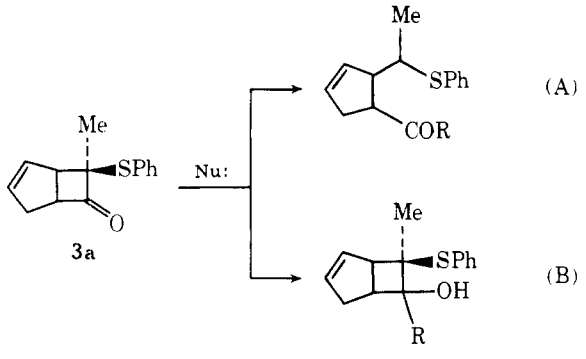
Table III. Reactions between the Cyclobutanone 3a and Nucleophiles

nucleophile	reaction type	product[a]	yield,[b] %	R
$CH_2^-S^+(O)Me_2$	type A	12	82	$CH^-S^+(O)Me_2$
KOH	type A	13	88	OH
MeMgI	type B	16	90	Me
n-BuLi	type B	17	93	*n*-Bu
n-BuMgBr	type B	18	84	H
n-PrMgBr	type B	18	62	H

[a] All products were stereochemically pure. [b] Isolated yield.

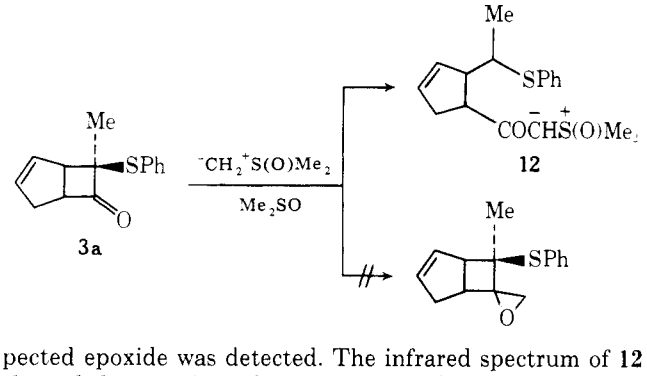
Reaction of the Cyclobutanone 3a with Various Nucleophiles. We have further investigated the reaction of **3a** with various nucleophiles for the synthesis of vicinal-functionalized cyclopentene systems which have the possibility of being converted into cyclopentane monoterpenes.[3c,d,f,11]

The results can be conveniently divided into two categories, that is, type A, ring cleavage of the cyclobutanone moiety of



3a, and type B, 1,2 addition of the nucleophile to the carbonyl group of **3a**, respectively (Table III).

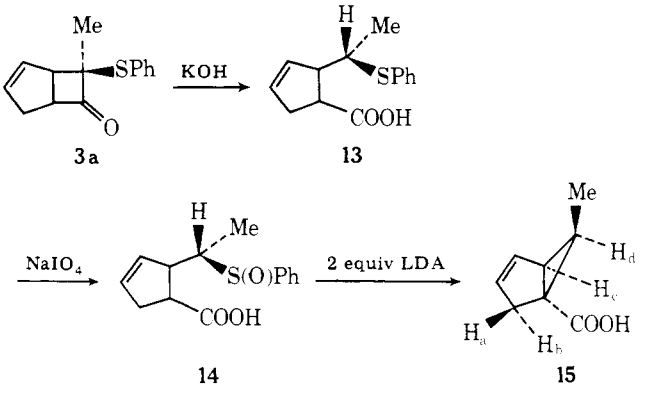
Treatment of **3a** with dimethyloxosulfonium methylide in dry dimethyl sulfoxide (Me_2SO) at room temperature produced stabilized ylide **12**[12] in 82% yield, but none of the ex-



pected epoxide was detected. The infrared spectrum of **12** showed characteristic absorption of C=O at 1560 cm^{-1}.

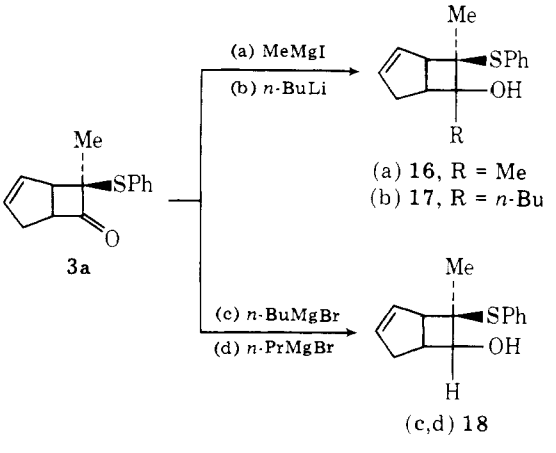
The reaction of **3a** with potassium hydroxide in *tert*-butyl alcohol[13] gave similarly the ring cleavage product 2-[1-(phenylthio)ethyl]-3-cyclopentenecarboxylic acid (**13**) in 88% yield. Oxidation of **13** with sodium metaperiodate ($NaIO_4$) in methanol produced the corresponding sulfoxide **14** in 91% yield. Interestingly, treatment of **14** with 2 equimolar amounts of lithium diisopropylamide (LDA) led to 6-*endo*-methylbicyclo[3.1.0]-3-hexenecarboxylic acid (**15**) as a sole product in 44% yield.

The ^1H NMR spectrum of **15** suggests that the bicyclic system has the cyclopropane ring,[2d,e] and the endo configuration of the methyl group was determined on the basis of the high-field signal of the methyl protons (0.83 ppm).[2d,e,14] The solvent effects on the protons such as methyl (H_a, H_b, H_c, and H_d) showed no contradiction to this configuration. These observations seem to suggest that the ring cleavage reaction



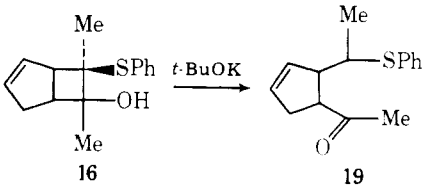
with potassium hydroxide proceeded with complete inversion of configuration at the C-7 carbon atom of **3a**.

In contrast, treatment of **3a** with methylmagnesium iodide in ether and with *n*-butyllithium in tetrahydrofuran (THF) yielded the 1,2-addition products, 6-alkylcyclobutanols **16** and



17, respectively. The reaction with Grignard reagents containing β-hydrogen atoms such as *n*-butyl- and *n*-propylmagnesium bromide gave the reduced product, cyclobutanol **18**, in good yields (see Table III).

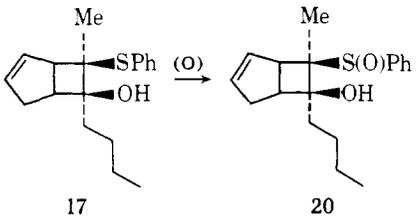
In general, these cyclobutanols could be expected to be converted into the ring cleavage products.[15] However, treatment of **16** with potassium *tert*-butoxide in DMF/THF led to the ketone **19** in only 25% yield. This result can be explained



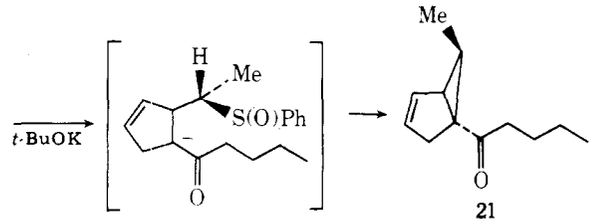
in terms of the differences in the stabilities of the carbanion formed by the ring cleavage between with the phenylthio group and with the dithio or dihalo group.

In a similar manner, the sulfoxide **20** from oxidation of **17** was investigated. Treatment of **20** with potassium *tert*-butoxide under similar conditions unexpectedly resulted in the

formation of 6-*endo*-methyl-1-pentanoylbicyclo[3.1.0]-3-hexene (**21**) in 43% yield. The stereochemistry of the ketone



17 20



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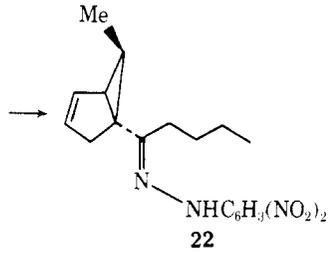

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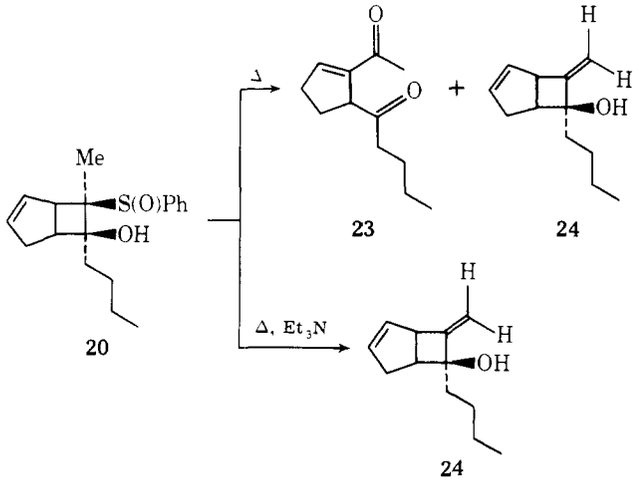
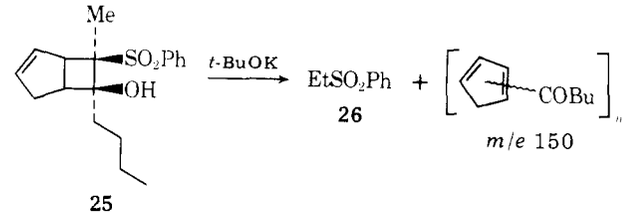
21 was likewise determined by its ^1H NMR spectrum. The ketone **21** was easily converted into the corresponding 2,4-dinitrophenylhydrazone derivative **22**.

On the other hand, thermolysis of **20** in a sealed tube gave the 1,4-diketone **23** and the allyl alcohol **24** in 21 and 2% yields,



respectively. In an attempt to improve the yields of the products, addition of an equimolar amount of triethylamine produced only **24** in 72% yield.

In contrast to **20**, treatment of the sulfone **25** with potassium *tert*-butoxide in Me_2SO produced ethyl phenyl sulfone (**26**)



25 26 *m/e* 150

in 71% yield as the only characterizable product, together with oily products which are considered to be polymerization products of the pentanoylcyclopentadiene moiety because they have the parent peak at *m/e* 150 in the mass spectrum.

In conclusion, methyl(phenylthio)ketene (**1**) gave the α-(phenylthio)cyclobutanones **3**, which can be easily converted into the α-methylenecyclobutanones **5**. The selective introduction of vicinal functional groups such as alkylcarbonyl, alkylcarboxyl, cyclopropane, and carbonylcarbonyl to the C–C double bond of olefins was accomplished by ring cleavage reactions of the cyclobutanones and the cyclobutanols having various oxidation states of sulfur substituents at α positions.

Experimental Section

All melting points of products were determined with a Yanagimoto micromelting point apparatus and are uncorrected. The ^1H NMR spectra were recorded with a JEOL-PS-100 or a JNM-PMX-60 spectrometer with tetramethylsilane as an internal standard. The infrared spectra were obtained with a Jasco IRA-1 spectrometer. The mass spectra were taken with a Hitachi RMU-6E spectrometer at an ionizing voltage of 70 eV.

α-(Phenylthio)propanoyl chloride[7] and imines **6** were prepared according to the established procedures. All reactions were carried out under nitrogen atmosphere.

α-(Phenylthio)cyclobutanones 3 from the Ketene 1 and Olefins 2. Cyclopentadiene Adduct 3a. To a stirred solution of 17.0 g (85 mmol) of α-(phenylthio)propanoyl chloride and 30 g (454 mmol) of cyclopentadiene in 100 mL of *n*-hexane was added a solution of 8.5 g (85 mmol) of triethylamine in 20 mL of *n*-hexane dropwise at −15 °C. The reaction mixture was stirred for 12 h at room temperature. Then the reaction mixture was poured into water, the organic layer was separated, and the aqueous layer was extracted with ether. The combined extracts were washed with water and dried (Na_2SO_4). Removal of the solvent and distillation gave 16.0 g (82%) of 7-methyl-7-(phenylthio)bicyclo[3.2.0]-2-hepten-6-one (**3a**) [bp 119–120 °C (1 mm)]. Recrystallization from *n*-hexane gave pure **3a**: mp 52.5–54 °C; IR (neat) 1760 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.24 (s, 3 H, CH_3), 2.40–2.64 (m, 2 H, CH_2), 3.28–3.44 (m, 1 H, CH), 3.95–4.15 (m, 1 H, CH), 5.60–5.96 (m, 2 H, CH=CH), 7.20–7.56 (m, 5 H, aromatic); mass spectrum, *m/e* 230 (M^+).

Anal. Calcd for $C_{14}H_{14}OS$: C, 73.02; H, 6.13. Found: C, 72.93; H, 6.11.

Indene Adduct 3b. Similar to the synthesis of **3a**, from 4.0 g (20 mmol) of the acid chloride and 23 g (200 mmol) of indene was obtained 2.4 g (43%) of 2,3-benzo-7-methyl-7-(phenylthio)bicyclo[3.2.0]heptan-6-one (**3b**) as white crystals. Recrystallization of **3b** from ethanol gave a pure sample: mp 100 °C; IR (Nujol) 1755 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.06 (s, 3 H, CH_3), 3.02–3.40 (m, 2 H, CH_2), 3.86 (d, 1 H, J = 8.2 Hz, CH), 4.12–4.36 (m, 1 H, CH), 7.12–7.60 (m, 9 H, aromatic); mass spectrum, *m/e* 280 (M^+).

Anal. Calcd for $C_{18}H_{16}OS$: C, 77.12; H, 5.75. Found: C, 76.85; H, 5.72.

Ethyl Vinyl Ether Adduct 3c. From 4.0 g (20 mmol) of the acid chloride and 19 g (260 mmol) of ethyl vinyl ether was obtained 1.25 g (26%) of 3-ethoxy-2-methyl-2-(phenylthio)cyclobutanone (**3c**) as a yellow liquid: bp 92 °C (1 mm); IR (neat) 1770 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.20 (t, 3 H, J = 6.75 Hz, CH_3), 1.43 (s, 3 H, CH_3), 3.02 (d, 1 H, J = 6.0 Hz, CH), 3.12 (d, 1 H, J = 6.5 Hz, CH), 3.50 (q, 2 H, J = 6.75 Hz, CH_2), 4.05 (dd, 1 H, J = 6.0 and 6.5 Hz, CH), 7.20–7.65 (m, 5 H, aromatic); mass spectrum, *m/e* 236 (M^+).

Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.08; H, 6.83. Found: C, 65.96; H, 6.90.

2,3-Dihydropyran Adduct 3d. From 12.0 g (60 mmol) of the acid chloride and 25 g (300 mmol) of 2,3-dihydropyran was obtained 9.6 g (65%) of 8-methyl-8-(phenylthio)bicyclo[4.2.0]-2-oxaoctan-7-one (**3d**) as white crystals. Recrystallization from ethanol gave pure **3d**: mp 85.0–85.5 °C; IR (Nujol) 1757 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.36 (s, 3 H, CH_3), 1.42–2.20 (m, 4 H, $2CH_2$), 3.10–3.40 (m, 1 H, CH), 3.70–3.92 (m, 2 H, CH_2), 4.13 (d, 1 H, J = 6.1 Hz, CH), 7.20–7.52 (m, 5 H, aromatic); mass spectrum, *m/e* 248 (M^+).

Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.73; H, 6.50. Found: C, 67.64; H, 6.54.

Synthesis of the Sulfoxides 4. 7-Methyl-7-(phenylsulfinyl)-bicyclo[3.2.0]-2-hepten-6-one (4a). To a stirred solution of 2.2 g (9.5 mmol) of the cyclobutanone **3a** in 30 mL of $CHCl_3$ was added a solution of 2.1 g (80% containing 9.7 mmol) of MCPBA dropwise at −15 °C. The mixture was stirred for 2 h and allowed to stand overnight. Then the mixture was poured into water. The $CHCl_3$ layer was separated and washed with aqueous $NaHSO_3$, aqueous $NaHCO_3$, and

water. The $CHCl_3$ layer was dried (Na_2SO_4) and concentrated to give 2.2 g (94%) of **4a** as colorless needles. Recrystallization of **4a** from *n*-hexane gave a pure sample: mp 94.5–96 °C; IR (Nujol) 1750 (C=O), 1045 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (s, 3 H, CH_3), 2.20–2.68 (m, 2 H, CH_2), 3.08–3.30 (m, 1 H, CH), 3.80–3.96 (m, 1 H, CH), 5.56–5.90 (m, 2 H, CH=CH), 7.50–7.60 (m, 5 H, aromatic); mass spectrum, *m/e* 246 (M^+), 120 (M^+ – PhSOH).

Anal. Calcd for $C_{14}H_{14}O_2S$: C, 68.28; H, 5.73. Found: C, 68.48; H, 5.71.

8-Methyl-8-(phenylsulfinyl)bicyclo[4.2.0]-2-oxaoctan-7-one (4d). Similar to the synthesis of **4a,** from 3.2 g (13 mmol) of the cyclobutanone **3d** was obtained 3.2 g (94%) of the sulfoxide **4d** as white crystals. A pure sample was recrystallized from ethanol: mp 118–120 °C; IR (Nujol) 1770 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.17 (s, 3 H, CH_3), 1.30–2.40 (m, 4 H, $2CH_2$), 3.20–4.10 (m, 3 H, CH_2 and CH), 4.50 (d, 1 H, J = 6.6 Hz, CH), 7.50–7.70 (m, 5 H, aromatic); mass spectrum, *m/e* 264 (M^+).

Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.62; H, 6.10. Found: C, 63.50; H, 6.23.

Synthesis of α-Methylenecyclobutanones 5. 7-Methylenebicyclo[3.2.0]-2-hepten-6-one (5a). Distillation of 1.55 g (6.3 mmol) of the sulfoxide **4a** at 15 mm afforded 0.47 g (62%) of a yellow irritating liquid **5a**: bp 68–71 °C (15 mm); IR (neat) 1747 (C=O), and 1640 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40–2.70 (m, 2 H, CH_2), 3.50–4.10 (m, 2 H, 2CH), 4.92 (s, 1 H, C=C**H**H), 5.50 (s, 1 H, C=CH**H**), 5.60–5.80 (m, 2 H, CH=CH); mass spectrum, *m/e* 120 (M^+).

Anal. Calcd for $C_8H_8OBr_2$:[16] C, 34.32; H, 2.88; Br, 57.09. Found: C, 34.50; H, 2.91; Br, 56.86.

8-Methylenebicyclo[4.2.0]-2-oxaoctan-7-one (5d). In a similar manner, from 2.0 g (7.6 mmol) of the sulfoxide **4d** was obtained 0.6 g (57%) of a yellow irritating liquid **5d**: bp 90 °C (15 mm); IR (neat) 1760 (C=O), 1655 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–2.50 (m, 4 H, $2CH_2$), 3.00–4.20 (m, 3 H, CH_2 and CH), 4.80 (d, 1 H, J = 7.0 Hz, CH), 5.40 (s, 1 H, C=C**H**H), 5.90 (s, 1 H, C=CH**H**); mass spectrum, *m/e* 138 (M^+).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.03;[17] H, 7.45.

***cis*- and *trans*-α-(Phenylthio)azetidin-2-ones 7 and 8 from the Ketene 1 and Imines 6. Benzylideneaniline Adduct 7a.** To a stirred mixture of 7.24 g (40 mmol) of benzylideneaniline and 2.0 g (20 mmol) of triethylamine in 25 mL of benzene was added a solution of 4.0 g (20 mmol) of the acid chloride in 10 mL of benzene dropwise at room temperature. The reaction mixture was stirred for 4 h at room temperature and then poured into water. The organic layer was separated, and the aqueous layer was extracted with ether. The combined extracts were washed with water and dried (Na_2SO_4). Removal of the solvent afforded 4.0 g (58%) of *cis*-3-methyl-1,4-diphenyl-3-(phenylthio)azetidin-2-one (**7a**) as a white powder. Pure **7a** was recrystallized from benzene: mp 193–196 °C; IR (Nujol) 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.63 (s, 3 H, CH_3), 4.91 (s, 1 H, CH), 6.84–7.40 (m, 15 H, aromatic); mass spectrum, *m/e* 345 (M^+).

Anal. Calcd for $C_{22}H_{19}NOS$: C, 76.50; H, 5.55; N, 4.06. Found: C, 76.76; H, 5.59; N, 4.04.

***N-tert*-Butylbenzylidenimine Adducts 7b and 8b.** Similarly, from 4.0 g (20 mmol) of the acid chloride and 10 g (62 mmol) of *N-tert*-butylbenzylidenimine was obtained 4.5 g (69%) of *cis*- and *trans*-1-*tert*-butyl-3-methyl-4-phenyl-3-(phenylthio)azetidin-2-one (**7b** and **8b**) as a mixture (4:6). Recrystallization from ethanol gave purified **7b** and **8b** as a mixture (7:3): mp 108–110 °C; IR (Nujol) 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.04 (s, 3.6 H, *t*-Bu and CH_3 of **8b**), 1.32 (s, 6.3 H, *t*-Bu of **7b**), 1.52 (s, 2.1 H, CH_3 of **7b**), 4.52 (s, 0.7 H, CH of **7b**), 4.58 (s, 0.3 H, CH of **8b**), 7.08–7.80 (m, 10 H, aromatic); mass spectrum, *m/e* 325 (M^+).

Anal. Calcd for $C_{20}H_{23}NSO$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.54; H, 7.12; N, 4.20.

Only the product **8b** was isolated in pure form: mp 118–120 °C; IR (Nujol) 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.04 (s, 12 H, $4CH_3$), 4.58 (s, 1 H, CH), 7.20–7.80 (m, 10 H, aromatic); mass spectrum, *m/e* 325 (M^+).

Anal. Calcd for $C_{20}H_{23}NSO$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.71; H, 7.15; N, 4.25.

***N*-Ethylbenzylidenimine Adducts 7c and 8c.** From 4.0 g (20 mmol) of the acid chloride and 5.3 g (40 mmol) of *N*-ethylbenzylidenimine was obtained 3.34 g (42%[18]) of a very viscous liquid, containing *cis*- and *trans*-1-ethyl-3-methyl-4-phenyl-3-(phenylthio)-azetidin-2-one (**7c** and **8c**) as a mixture (8:2): bp 170–172 °C (1 mm); IR (neat) 1750 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.65 (t, 0.6 H, J = 7.6 Hz, CH_3 of **8c**), 1.10 (s, 0.6 H, CH_3 of **8c**), 1.12 (t, 2.4 H, J = 7.6 Hz, CH_3 of **7c**), 1.57 (s, 2.4 H, CH_3 of **7c**), 2.50–4.00 (m, 2 H, CH_2), 4.62 (s, 1 H, CH), 7.20–8.10 (m, 10 H, aromatic); mass spectrum, *m/e* 297 (M^+).

Anal. Calcd for $C_{18}H_{19}NOS$: C, 72.70; H, 6.44; N, 4.71. Found: C, 72.36; H, 6.46; N, 4.63.

Only the product **8c** was isolated in pure form (recrystallized from *n*-hexane–ether): mp 98.0–98.5 °C; IR (Nujol) 1750 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.65 (t, 3 H, J = 7.6 Hz, CH_3), 1.10 (s, 3 H, CH_3), 2.50–3.90 (m, 2 H, CH_2), 4.62 (s, 1 H, CH), 7.20–8.10 (m, 10 H, aromatic); mass spectrum, *m/e* 297 (M^+).

Anal. Calcd for $C_{18}H_{19}NOS$: C, 72.70; H, 6.44; N, 4.71. Found: C, 72.59; H, 6.38; N, 4.54.

Synthesis of the Sulfoxide 9a. Similar to the synthesis of the sulfoxide **4a,** from 3.5 g (10 mmol) of **7a** was obtained 3.4 g (94%) of *cis*-3-methyl-1,4-diphenyl-3-(phenylsulfinyl)azetidin-2-one (**9a**) as a white powder. Pure **9a** was recrystallized from benzene: mp 202–203 °C dec; IR (Nujol) 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.40 (s, 3 H, CH_3), 5.08 (s, 1 H, CH), 7.00–7.60 (m, 15 H, aromatic); mass spectrum, *m/e* 361 (M^+).

Anal. Calcd for $C_{22}H_{19}NO_2S$: C, 73.11; H, 5.30; N, 3.88. Found: C, 72.82; H, 5.20; N, 3.50.

Synthesis of 3-Methylene-1,4-diphenylazetidin-2-one (10a). Similar to the synthesis of the α-methylenecyclobutanone **5a**, thermolysis of 1.5 g (4.1 mmol) of the sulfoxide **9a** at 200 °C (1 mm) gave 0.75 g (77%) of **10a** as white needles. Recrystallization of **10a** from methanol gave a pure sample: mp 151.0–151.5 °C; IR (Nujol) 1723 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 5.09 (s, 1 H, C=C**H**H), 5.33 (s, 1 H, CH), 5.76 (s, 1 H, C=CH**H**), 7.00–7.50 (m, 10 H, aromatic); mass spectrum, *m/e* 235 (M^+).

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.65; H, 5.41; N, 5.89.

Dicyclohexylcarbodiimide Adduct 11. Similar to the synthesis of the α-(phenylthio)azetidin-2-ones, from 4.0 g (20 mmol) of the acid chloride and 4.2 g (20 mmol) of dicyclohexylcarbodiimide was obtained 0.4 g (5%) of 1-cyclohexyl-4-(*N*-cyclohexylimino)-3-methyl-3-(phenylthio)azetidin-2-one (**11**). Pot distillation at 140–150 °C (1 mm) gave pure **11**: IR (neat) 1810 (C=O), 1690 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80–2.20 (m, 20 H, $10CH_2$), 1.63 (s, 3 H, CH_3), 2.90–3.50 (m, 1 H, CH), 3.50–4.10 (m, 1 H, CH), 7.20–7.80 (m, 5 H, aromatic); mass spectrum, *m/e* 370 (M^+).

Anal. Calcd for $C_{22}H_{30}N_2OS$: C, 71.32; H, 8.16; N, 7.56. Found: C, 70.95; H, 8.16; N, 7.37.

Reaction between the Cyclobutanone 3a and Nucleophiles. Stabilized Ylide 12. To a solution of oxosulfonium methylide[19] prepared from sodium hydride (0.85 g, 50% mineral oil dispersion, 18 mmol), trimethyloxosulfonium iodide (4.0 g, 18 mmol), and freshly distilled Me_2SO (30 mL) was added a solution of the cyclobutanone **3a** (4.0 g, 17.4 mmol) in 10 mL of Me_2SO dropwise at room temperature. The reaction mixture was stirred for 4 h at this temperature and then was heated to 50 °C for 1 h, poured into water, and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated to leave 4.60 g (82%) of dimethyloxosulfonium [2-[1-(phenylthio)ethyl]-3-cyclopenten-1-yl]carbonylmethylide (**12**) as white crystals. Recrystallization of **12** from ethanol gave a pure sample: mp 138–140 °C; IR (Nujol) 1560 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.18 (d, 3 H, J = 7.0 Hz, CH_3), 2.20–2.80 (m, 2 H, CH_2), 3.00–4.20 (m, 3 H, 3CH), 3.32 (s, 3 H, CH_3), 3.35 (s, 3 H, CH_3), 4.50 [s, 1 H, $^-CHS^+(O)$], 5.60–6.10 (m, 2 H, CH=CH), 7.10–7.60 (m, 5 H, aromatic); mass spectrum, *m/e* 322 (M^+), 244 (M^+ – Me_2SO).

Anal. Calcd for $C_{17}H_{22}O_2S_2$: C, 63.34; H, 6.88. Found: C, 63.19; H, 6.90.

2-[1-(Phenylthio)ethyl]-3-cyclopentenecarboxylic Acid (13). To a stirred solution of 3.0 g (13 mmol) of the cyclobutanone **3a** in 30 mL of *tert*-butyl alcohol was added 2.2 g (39 mmol) of powdered potassium hydroxide at room temperature. The reaction mixture was heated at 60 °C for 13 h. Then water was added and the aqueous layer was washed with *n*-hexane. The aqueous layer was acidified with concentrated hydrochloric acid and extracted with ether. The extract was washed with water and dried (Na_2SO_4). Removal of the solvent gave 2.85 g (88%) of **13** as white crystals. Recrystallization from benzene gave a pure sample: mp 75.0–76.0 °C; IR (Nujol) 3300–2500 (OH), 1670 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (d, 3 H, J = 6.2 Hz, CH_3), 2.50–2.90 (m, 2 H, CH_2), 3.20–4.10 (m, 3 H, 3CH), 5.80–6.20 (m, 2 H, CH=CH), 7.20–7.70 (m, 5 H, aromatic), 11.6 (s, 1 H, COOH); mass spectrum, *m/e* 248 (M^+).

Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.73; H, 6.50. Found: C, 67.55; H, 6.41.

2-[1-(Phenylsulfinyl)ethyl]-3-cyclopentenecarboxylic Acid (14). To a stirred solution of 8.2 g (33 mmol) of the acid **13** in 200 mL of methanol was added dropwise a solution of 7.3 g (34 mmol) of $NaIO_4$ in 100 mL of water at −15 °C. The reaction mixture was stirred for 15 h at room temperature and then filtered. The filtered cake of $NaIO_3$ was washed with $CHCl_3$. The filtrate was acidified with concentrated hydrochloric acid and extracted with $CHCl_3$. The extract

was washed with water and dried (Na_2SO_4). Removal of the solvent gave 7.95 g (91%) of **14** as white crystals. A pure sample was recrystallized from benzene: mp 127.0–128.0 °C; IR (Nujol) 3200–2600 (OH), 1730 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 and 0.99 (2d, 3 H, J = 6.6 Hz, CH_3), 2.50–3.00 (m, 2 H, CH_2), 3.00–4.02 (m, 3 H, 3CH), 5.50–6.20 (m, 2 H, CH=CH), 7.30–8.00 (m, 5 H, aromatic), 10.8 (s, 1 H, COOH); mass spectrum, m/e 138 (M^+ − PhSOH).

Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.62; H, 6.10. Found: C, 63.56; H, 6.11.

6-*endo*-Methylbicyclo[3.1.0]-3-hexenecarboxylic Acid (15). To a solution of lithium diisopropylamide (20 mmol) in 20 mL of THF was added a solution of 2.64 g (10 mmol) of the sulfoxide **14** in 10 mL of THF dropwise at −70 °C. The reaction mixture was stirred at room temperature for 12 h, refluxed for 4 h, and then poured into water. The mixture was acidified with concentrated hydrochloric acid and extracted with ether. The extract was washed with water and dried (Na_2SO_4). Removal of the solvent afforded 2.5 g of a viscous liquid. The liquid was chromatographed on silica gel (50:50 benzene–*n*-hexane as eluant) to afford 0.61 g (44%) of white crystals of **15.** Recrystallization from *n*-hexane gave a pure sample: mp 87.0–87.5 °C; IR (Nujol) 3200–2500 (OH), 1670 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (d, 3 H, J = 6.0 Hz, CH_3), 1.90–2.40 (m, 1 H, H_d), 2.18 (d, 1 H, J = 19.0 Hz, H_a), 2.60–2.90 (m, 1 H, H_c), 3.10 (d, 1 H, J = 19.0 Hz, H_b), 5.45–5.80 (m, 2 H, CH=CH), 11.9 (s, 1 H, COOH); ^1H NMR (C_6D_6) δ 0.62 (d, 3 H, J = 6.0 Hz, CH_3), 1.70–2.50 (m, 1 H, H_d), 2.08 (d, 1 H, J = 19.0 Hz, H_a), 2.50–2.83 (m, 1 H, H_c), 3.20 (d, 1 H, J = 19.0 Hz, H_b), 5.20–5.45 (m, 2 H, CH=CH), 12.8 (s, 1 H, COOH); mass spectrum, m/e 138 (M^+).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.45; H, 7.37.

6,7-Dimethyl-7-(phenylthio)bicyclo[3.2.0]-2-hepten-6-ol (16). To a stirred solution of methylmagnesium iodide (29 mmol) in 60 mL of ether was added a solution of 5.0 g (22 mmol) of the cyclobutanone **3a** in 60 mL of ether dropwise at room temperature. The reaction mixture was refluxed for 4 h and allowed to stand at room temperature for 12 h. The mixture was poured into water and acidified with concentrated hydrochloric acid. The ether layer was separated, and the aqueous layer was extracted with ether. The combined extracts were washed with water and dried (Na_2SO_4). Removal of the solvent and distillation gave 4.9 g (90%) of **16** as a pale yellow liquid: bp 134–139 °C (1 mm); IR (neat) 3600–3400 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 1.21 (s, 3 H, CH_3), 1.54 (s, 3 H, CH_3), 1.97 (s, 1 H, OH), 2.27–2.67 (m, 2 H, CH_2), 2.83–3.50 (m, 2 H, 2CH), 5.57–6.13 (m, 2 H, CH=CH), 7.20–7.80 (m, 5 H, aromatic); mass spectrum, m/e 246 (M^+).

Anal. Calcd for $C_{15}H_{18}OS$: C, 73.14; H, 7.37. Found: C, 73.10, H, 7.48.

6-Butyl-7-methyl-7-(phenylthio)bicyclo[3.2.0]-2-hepten-6-ol (17). To a stirred solution of 5.0 g (22 mmol) of the cyclobutanone **3a** in 50 mL of THF was added a solution of 28 mmol of *n*-butyllithium in 20 mL of *n*-hexane dropwise at −70 °C. The reaction mixture was stirred for 3 h at −70 °C and then poured into water and extracted with ether. The extract was washed with water and dried (Na_2SO_4). Removal of the solvent and distillation gave 5.8 g (93%) of **17** as a pale yellow liquid: bp 165 °C (1.5 mm); IR (neat) 3600–3400 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 0.57–2.13 (m, 10 H, *n*-Bu and OH), 1.23 (s, 3 H, CH_3), 2.23–2.57 (m, 2 H, CH_2), 2.87–3.50 (m, 2 H, 2CH), 5.47–6.10 (m, 2 H, CH=CH), 7.16–7.67 (m, 5 H, aromatic); mass spectrum, m/e 288 (M^+).

Anal. Calcd for $C_{18}H_{24}OS$: C, 74.97; H, 8.39. Found: C, 74.66; H, 8.55.

7-Methyl-7-(phenylthio)bicyclo[3.2.0]-2-hepten-6-ol (18). Similar to the synthesis of the cyclobutanol **16**, from 2.5 g (10.8 mmol) of the cyclobutanone **3a** and 14.2 mmol of *n*-butylmagnesium bromide was obtained 2.1 g (84%) of **18** as a yellow liquid: bp 129.5–131.5 °C (1 mm); IR (neat) 3600–3300 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 1.20 (s, 3 H, CH_3), 1.90 (d, 1 H, J = 8.0 Hz, OH), 2.30–2.75 (m, 2 H, CH_2), 3.10–3.50 (m, 2 H, 2CH), 4.46 (ddd, 1 H, J = 8.0, 6.2, and 4.2 Hz, CH), 5.60–6.10 (m, 2 H, CH=CH), 7.20–7.70 (m, 5 H, aromatic); mass spectrum, m/e 232 (M^+).

Anal. Calcd for $C_{14}H_{16}OS$: C, 72.39; H, 6.94. Found: C, 72.33; H, 6.99.

Similarly, from 4.0 g (17.4 mmol) of the cyclobutanone **3a** and 20 mmol of *n*-propylmagnesium bromide was obtained 2.5 g (62%) of **18.**

1-Acetyl-2-[1-(phenylthio)ethyl]-3-cyclopentene (19). To a stirred solution of 3.4 g (30 mmol) of potassium *tert*-butoxide in THF (30 mL)–DMF (30 mL) was added a solution of 3.6 g (14.6 mmol) of **16** in 10 mL of THF at −10 °C. The reaction mixture was stirred at room temperature for 5 h and then poured into water and extracted with ether. The extract was washed with water and dried (Na_2SO_4). After the solvent was removed, the residue was chromatographed on silica gel (30:70 benzene–*n*-hexane as eluant) to afford 1.2 g of a liquid. Distillation of the liquid gave 0.90 g (25%) of **19** as a pale yellow liquid: bp 130–133 °C (1 mm); IR (neat) 1710 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.25 (d, 3 H, J = 6.6 Hz, CH_3), 2.20 (s, 3 H, CH_3), 2.50–2.80 (m, 2 H, CH_2), 3.00–3.50 (m, 3 H, 3CH), 5.70–5.95 (m, 2 H, CH=CH), 7.20–7.75 (m, 5 H, aromatic); mass spectrum, m/e 246 (M^+).

Anal. Calcd for $C_{15}H_{18}OS$: C, 73.14; H, 7.37. Found: C, 72.92; H, 7.42.

6-Butyl-7-methyl-7-(phenylsulfinyl)bicyclo[3.2.0]-2-hepten-6-ol (20). Similar to the synthesis of the sulfoxide **4a,** from 2.3 g (8 mmol) of the cyclobutanol **17** and 1.8 g (80% containing 8.4 mmol) of MCPBA was obtained 2.15 g (88%) of the sulfoxide **20** as a white powder. Recrystallization from benzene–ether gave a pure sample: mp 136.5–137.0 °C; IR (Nujol) 3400–3200 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 0.80–1.80 (m, 10 H, $2CH_3$ and $2CH_2$), 2.00–4.10 (m, 6 H, $2CH_2$ and 2CH), 2.85 and 3.37 (2s, 1 H, OH), 5.00–5.60 (m, 1 H, CH=CH), 5.90–6.10 (m, 1 H, CH=CH), 7.40–7.90 (m, 5 H, aromatic); ^1H NMR (C_6D_6) δ 0.80–2.00 (m, 10 H, $2CH_3$ and $2CH_2$), 2.00–4.40 (m, 6 H, $2CH_2$ and 2CH), 3.12 and 4.32 (2s, 1 H, OH), 4.80–5.40 (m, 1 H, CH=CH), 5.70–5.90 (m, 1 H, CH=CH), 7.00–7.40 (m, 3 H, aromatic), 7.50–7.80 (m, 2 H, aromatic); mass spectrum, m/e 304 (M^+).

Anal. Calcd for $C_{18}H_{24}O_2S$: C, 71.02; H, 7.95. Found: C, 70.72; H, 8.00.

6-*endo*-Methyl-1-pentanoylbicyclo[3.1.0]-3-hexene (21). To a stirred solution of 1.18 g (10.5 mmol) of potassium *tert*-butoxide in THF (40 mL)–DMF (10 mL) was added a solution of 3.04 g (10 mmol) of the sulfoxide **20** in 20 mL of THF dropwise at −65 °C. The reaction mixture was stirred at room temperature for 12 h, heated to 50 °C for 5 h, and then poured into water and extracted with ether. The extract was washed with water and dried (Na_2SO_4). Removal of the solvent and distillation gave 0.78 g (43%) of **21** as a pale yellow liquid: bp 44.0–48.0 °C (0.5 mm); IR (neat) 1675 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.80–1.90 (m, 7 H, CH_3 and $2CH_2$), 0.87 (d, 3 H, J = 6.0 Hz, CH_3), 1.90–2.20 (m, 1 H, C-6 positioned CH), 2.20–2.50 (m, 3 H, $COCH_2$ and C-2 positioned CHH), 2.50–2.90 (m, 1 H, C-5 positioned CH), 3.10 (d, 1 H, J = 18.2 Hz, C-2 positioned CHH), 5.50–5.90 (m, 2 H, CH=CH); mass spectrum, m/e 178 (M^+).

6-*endo*-Methyl-1-[1-[*N*-(2,4-dinitrophenyl)hydrazono]pentyl]bicyclo[3.1.0]-3-hexene (22). To a solution of 0.70 g (3.5 mmol) of 2,4-dinitrophenylhydrazine in ethanol (17 mL)–water (5 mL)–sulfuric acid (4 mL) was added a solution of 0.60 g (3.4 mmol) of the ketone **21** in 30 mL of ethanol. The mixture was allowed to stand overnight. The precipitates were filtered and washed with water. Recrystallization from ethanol gave 1.2 g (99%) of orange crystals of **22:** mp 125.5–126.5 °C; IR (Nujol) 3300 (NH), 1620 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80–1.90 (m, 8 H, CH_3, $2CH_2$, and CH), 1.05 (d, 3 H, J = 6.0 Hz, CH_3), 2.20–2.60 (m, 5 H, $2CH_2$ and CH), 5.80–6.00 (m, 2 H, CH=CH), 8.15 (d, 1 H, J = 9.0 Hz, aromatic), 8.48 (dd, 1 H, J = 9.0 and 2.6 Hz, aromatic), 9.30 (d, 1 H, J = 2.6 Hz, aromatic), 11.4 (broad s, 1 H, NH); mass spectrum, m/e 358 (M^+).

Anal. Calcd for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 59.95; H, 6.10; N, 15.62.

1-Acetyl-2-pentanoyl-5-cyclopentene (23) and 6-Butyl-7-methylenebicyclo[3.2.0]-2-hepten-6-ol (24). A solution of 1.9 g (6.3 mmol) of the sulfoxide **20** in 20 mL of benzene was heated to 160 °C for 4 h in a sealed tube. After the benzene was removed, the residue was chromatographed on silica gel to give 0.84 g of a viscous liquid (50:50 benzene–ether as eluant). Distillation of the liquid gave 0.25 g (21%) of a yellow liquid **23** and 0.02 g (2%) of a yellow liquid **24.** 1,4-Diketone **23:** bp 81.0–84.0 °C (1 mm); IR (neat) 1710 (C=O), 1665 (C=O), 1610 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.70–2.30 (m, 9 H, CH_3 and $3CH_2$), 2.40 (s, 3 H, CH_3), 2.50–2.90 (m, 4 H, CH_2 and $COCH_2$), 3.90–4.20 (m, 1 H, CH), 6.90–7.10 (m, 1 H, CH=C); mass spectrum, m/e 194 (M^+), 85 (*n*-$BuCO^+$).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.16; H, 9.35.

Allyl alcohol **24:** bp 53.0–54.0 °C (1 mm); IR (neat) 3500–3400 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 0.70–1.80 (m, 9 H, CH_3 and $3CH_2$), 1.88 (s, 1 H, OH), 2.00–2.64 (m, 2 H, CH_2), 2.73–3.10 (m, 1 H, CH), 3.43–3.80 (m, 1 H, CH), 4.80 (d, 1 H, J = 2.0 Hz, C=CHH), 5.00 (d, 1 H, J = 2.0 Hz, C=CHH), 5.80–6.00 (m, 2 H, CH=CH); mass spectrum, m/e 178 (M^+), 121 (M^+ − *n*-Bu).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.60; H, 10.15.

A mixture of 2.5 g (8.2 mmol) of the sulfoxide **20** and 0.82 g (8.2 mmol) of triethylamine in 40 mL of benzene was heated to 140 °C for 4 h in a sealed tube. After the solvent was removed, the residue was chromatographed on silica gel to afford 1.70 g of a yellow liquid (ether as eluant). Distillation of the liquid gave 1.05 g (72%) of the allyl alcohol **24.**

6-Butyl-7-methyl-7-(phenylsulfonyl)bicyclo[3.2.0]-2-hepten-

6-ol (25). Similar to the synthesis of the sulfoxide **4a**, from 6.1 g (20 mmol) of the sulfoxide **20** and 4.7 g (80% containing 28 mmol) of MCPBA was obtained 6.0 g (95%) of the sulfone **25** as white crystals. Pure **25** was recrystallized from ethanol: mp 161.5–162.5 °C; IR (Nujol) 3500 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ 0.70–1.80 (m, 7 H, CH_3 and $2CH_2$), 1.20 (s, 3 H, CH_3), 1.90–3.00 (m, 5 H, $2CH_2$ and OH), 3.35 (m, 1 H, CH), 3.70–4.00 (m, 1 H, CH), 5.40–6.20 (m, 2 H, CH=CH), 7.50–8.20 (m, 5 H, aromatic); mass spectrum, *m/e* 320 (M^+).

Anal. Calcd for $C_{18}H_{24}O_3S$: C, 67.48; H, 7.55. Found: C, 67.19; H, 7.64.

Decomposition Reaction of the Sulfone 25. To a stirred solution of 1.12 g (10 mmol) of potassium *tert*-butoxide in 30 mL of Me_2SO was added a solution of 3.0 g (9.4 mmol) of the sulfone **25** in 20 mL of Me_2SO dropwise at room temperature. The reaction mixture was heated to 100 °C for 8 h and then poured into water and extracted with ether. The extract was washed with water and dried (Na_2SO_4). Removal of the solvent and distillation gave 1.2 g (71%) of ethyl phenyl sulfone (**26**): bp 101–103 °C (1 mm) [mp 41.5–42.5 °C (lit.[20] 42 °C)]; IR (neat) 1300 and 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 1.30 (t, 3 H, J = 7.3 Hz, CH_3), 3.20 (q, 2 H, J = 7.3 Hz, CH_2), 7.60–8.30 (m, 5 H, aromatic); mass spectrum, *m/e* 170 (M^+).

The aqueous layer was acidified with concentrated hydrochloric acid and extracted with $CHCl_3$. The extract was washed with water and dried (Na_2SO_4). Removal of the solvent and bulb-to-bulb distillation at 100–130 °C (3 mm) gave 0.2 g of a yellow liquid. The yellow liquid showed more than three peaks on GLC analysis; mass spectrum showed no peaks at more than *m/e* 150.

Registry No.—1, 66977-59-1; **2a,** 542-92-7; **2b,** 95-13-6; **2c,** 109-92-2; **2d,** 110-87-2; **3a,** 67010-75-7; **3b,** 66977-56-8; **3c,** 66977-57-9; **3d,** 66977-58-0; **4a,** 66977-60-4; **4d,** 69765-58-8; **5a,** 66977-61-5; **5d,** 66977-62-6; **6a,** 538-51-2; **6b,** 6852-58-0; **6c,** 6852-54-6; **7a,** 66977-63-7; **7b,** 66977-64-8; **7c,** 69765-59-9; **8b,** 66977-65-9; **8c,** 69765-60-2; **9a,** 66977-66-0; **10a,** 66977-67-1; **11,** 69765-61-3; **12,** 69765-62-4; **13,** 69765-63-5; **14,** 69765-64-6; **15,** 69765-65-7; **16,** 69765-66-8; **17,** 69765-67-9; **18,** 69765-68-0; **19,** 69765-69-1; **20,** 69765-70-4; **21,** 69765-71-5; **22,** 69765-72-6; **23,** 69765-73-7; **24,** 69765-74-8; **25,** 69765-75-9; **26,** 599-70-2; α-(phenylthio)propanoyl chloride, 29943-30-4; dicyclohexylcarbodiimide, 538-75-0; oxosulfonium methylide, 5367-24-8; methyl iodide, 74-88-4; *n*-butyllithium, 109-72-8.

References and Notes

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Synthesis and Properties of (*E*)-2-(Acylmethylene)tetrahydrofurans. 6-Hydroxy-1,3-hexanedione Equivalents

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Substituted 6-hydroxy-1,3-hexanediones **1** were prepared by sodium ethoxide catalyzed condensation of methyl ketones with 4-butyrolactone. Dehydration with triphenylphosphine and carbon tetrachloride or carbon tetrabromide gave the corresponding (*E*)-2-(acylmethylene)tetrahydrofurans **4**, which react with primary amines and hydrazine to give 3-propanol-substituted Schiff bases and 3,4-substituted pyrazoles by Michael additions. The (acylmethylene)tetrahydrofurans **4** are stable at high pH, but hydrolyze readily in the presence of acid to return the hydroxydiones **1**.

The 1,3-diketones as a class of compounds have been extensively investigated and have been frequently used in synthesis. The chemical reactivity of such molecules that makes them synthetically attractive also limits their utility under certain conditions. The condensation of an aldehyde or ketone with a 1,3-diketone (the Knoevanagel reaction) proceeds readily in the presence of base.[1] At high pH 1,3-diketones hydrolyze to ketone and carboxylic acid components.[2] The problems associated with the use of 1,3-diketone units increase with increasing functionality in the molecules.

Our group had need of the chemistry of 6-hydroxy-1,3-hexanediones (**1**) and came across synthetic equivalents of such molecules that were stable at high pH but readily gave the hydroxydiones **1** at low pH.

6-Hydroxy-1,3-hexanediones (**1**) have been prepared by the sodium amide catalyzed condensation of methyl ketones with

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