8 Hz), 7.32 (br d, 2, $J$ = 8 Hz), 6.96 (dd, 1, $J$ = 9, 15 Hz), 6.30 (d, 1, $J$ = 15 Hz), 5.58 (m, 1), 3.92 (m, 1), 2.46 (s, 3), 2.3–1.2 (m, 9); IR (neat) 3040, 2920, 2845, 1595, 1480, 1330, 1310, 1265, 1145, 1080, 810, 660 $cm^{-1}$. Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.52; H, 7.29; S, 11.60. Found: C, 69.70; H, 7.37; S, 11.35.

**Reaction of Methylenecyclohexane with 1.** Reaction with methylenecyclohexane (0.489 g, 2.0 equiv) for 4 days gave 0.72 g of crude product which NMR spectroscopy showed to be ~60% pure **7**. Chromatography of 0.350 g on 30 g of silica gel with 1:1 pentane–ether as eluant gave 0.102 g (37%) of an inseparable mixture consisting of 80% **7** and 20% of a 3:1 mixture of **5** and **6** as determined by NMR. The spectral data for **7** are as follows: NMR ($CDCl_3$) $\delta$ 7.78 (br d, 2, $J$ = 8 Hz), 7.32 (br d, 2, $J$ = 8 Hz), 6.95 (dt, 1, $J$ = 15, 5 Hz) 6.30 (br d, 1, $J$ = 15 Hz), 5.48 (m, 1), 2.82 (br d, 2, $J$ = 6 Hz), 2.45 (s, 3), 2.10–1.0 (m, 8); IR (neat) 3050, 2930, 2860, 1630, 1600, 1583, 1450, 1320, 1305, 1290, 1145, 1085, 915, 810, 730, 660 $cm^{-1}$; mol wt calcd for $C_{16}H_{20}O_2S$ 276.1184, found 276.1188.

**Reaction of Cyclohexene with 1.** Reaction with cyclohexene (0.164 g, 1.1 equiv) and $EtAlCl_2$ (2.55 mL of 1.57 M, 2.0 equiv) for 9 days gave 0.695 g of crude product. Chromatography of 0.500 g on 30 g of silica gel gave 0.116 g (31%) of an inseparable 2:1 mixture of ene adduct **8** and cyclobutene **9**, 0.058 g (19%) of **14**, and 0.015 g of cyclohexylbenzene. The spectral data are as follows: NMR ($CDCl_3$) (**8**) $\delta$ 7.74 or 7.79 (br d, 2, $J$ = 8 Hz), 7.32 (br d, 2, $J$ = 8 Hz), 6.95 (dd, 1, $J$ = 15, 7 Hz), 6.18 (dd, 1, $J$ = 15, 2 Hz), 5.85 (m, 1), 5.49 (br d, 1, $J$ = 9 Hz), 2.85 (m, 1), 2.46 (s, 3), 2.1–1.3 (m, 6); NMR ($CDCl_3$) (**9**) $\delta$ 7.74 or 7.79 (br d, 2, $J$ = 8 Hz), 7.32 (br d, 2, $J$ = 8 Hz), 6.72 (br s, 1), 3.15 (m, 2), 2.46 (s, 3), 2.1–1.3 (m, 6); IR (neat) 3040, 2920, 2860, 1600, 1460, 1300, 1160, 1080, 810, 675 $cm^{-1}$.

**Reaction of *trans*-2-Butene with 1.** Reaction with *trans*-2-butene (2 g, excess) for 11 days gave 2.28 g of a two-layer mixture. NMR spectroscopy showed that the bottom layer (~0.5 g) contained **10** and **11** and the top layer was mainly polymer. Chromatography of 0.200 g of the bottom layer on 35 g of silica gel with 1:1 pentane–ether as eluant gave 0.058 g (14%) of an inseparable 1:1 mixture of ene adduct **10** and cyclobutene **11**: NMR ($CDCl_3$) (**10**) $\delta$ 7.80 or 7.77 (br d, 2, $J$ = 8 Hz), 7.35 (br d, 2, $J$ = 8 Hz), 6.99 (dd, 1, $J$ = 16, 7 Hz), 6.31 (dd, 1, $J$ = 16, 2 Hz), 5.75 (ddd, 1, $J$ = 16, 7, 11 Hz), 5.10 (br d, 1, $J$ = 11 Hz), 5.06 (br d, 1, $J$ = 16 Hz), 3.11 (ddq, 1, $J$ = 7, 7, 7 Hz), 2.47 (s, 3), 1.20 (d, 3, $J$ = 7 Hz); NMR ($CDCl_3$) (**11**) $\delta$ 7.77 or 7.80 (br d, 2, $J$ = 8 Hz), 7.35 (br d, 2, $J$ = 8 Hz), 6.67 (br s, 1), 2.65 (br q, 1, $J$ = 7 Hz), 2.47 (s, 3), 2.42 (br q, 1, $J$ = 7 Hz), ~1.2 (2 d, 6, $J$ = 7 Hz); IR (neat) 3060, 2965, 2915, 2870, 1600, 1452, 1315, 1305, 1290, 1145, 1085, 812, 635 $cm^{-1}$.

**Reaction of 1-Hexene with 1.** Reaction with 1-hexene (0.40 g, 2.0 equiv) for 18 days gave 0.570 g of material which NMR spectroscopy showed to be ~25% **12**. Chromatography of 0.315 g on 30 g of silica gel with 1:1 pentane-ether as eluant gave 0.055 g (19%) of **12**: NMR ($CDCl_3$) $\delta$ 7.79 (br d, 2, $J$ = 8 Hz), 7.43 (br d, 2, $J$ = 8 Hz), 6.95 (dd, 1, $J$ = 16, 7 Hz), 6.30 (br d, 1, $J$ = 16 Hz), 5.4–5.7 (m, 2), 2.92 (dd, 1, $J$ = 6, 7 Hz), 2.46 (s, 3), 2.1–0.8 (m, 7); IR (neat) 3040, 2950, 2920, 2860, 1600, 1320, 1310, 1295, 1150, 1090, 820, 660 $cm^{-1}$; mol wt calcd for $C_{15}H_{20}O_2S$ 264.1184, found 264.1190.

**Chloroalumination of Sulfone 1.** A solution of sulfone **1** (0.360 g, 2.0 mmol) and $EtAlCl_2$ (2.55 mL of 1.57 M, 4.0 mmol, 2.0 equiv) in 10 mL of benzene was stirred for 5 days. Normal workup gave 0.413 g which NMR spectroscopy showed to be a 60:40 mixture of **14** and **1**. Chromatography of 0.200 g on 25 g of silica gel with 1:2 pentane–ether as eluant gave 0.121 g (58%) of **14** which crystallized on standing and 0.035 g (20%) of recovered **1**. The data for **14** are as follows: mp 47.5–48.5 °C [lit.[12] mp 48 °C]; NMR ($CDCl_3$) $\delta$ 7.95 (br d, 2, $J$ = 8 Hz), 7.42 (br d, 2, $J$ = 8 Hz), 6.86 (s, 2), 2.45 (s, 3); NMR (benzene-$d_6$) $\delta$ 7.82 (br d, 2, $J$ = 8 Hz), 6.85 (br d, 2, $J$ = 8 Hz), 6.27 (d, 1, $J$ = 7 Hz), 5.88 (d, 1, $J$ = 7 Hz), 1.95 (s, 3); IR ($CCl_4$) 3060, 2930, 2880, 1920, 1595, 1580, 1555, 1340, 1305, 1175, 1150, 1085, 855, 680, 610 $cm^{-1}$.

**Deuterium Trapping of 12.** Repetition of the above reaction for 1 day followed by addition of 3 mL of $D_2O$ and normal workup gave 0.421 g of yellow oil which NMR showed to be a 70:30 mixture of **14** and **1**. Chromatography of 0.200 g on 30 g of silica gel with 1:1 pentane–ether as eluant gave 0.074 g (37%) of pure **15** which was crystallized from pentane: mp 47.5–48.0 °C; NMR ($CDCl_3$) $\delta$ 7.95 (br d, 2, $J$ = 8 Hz), 7.42 (br d, 2, $J$ = 8 Hz), 6.86 (br s, 1), 2.45 (s, 3); NMR (benzene-$d_6$) $\delta$ 7.82 (br d, 2, $J$ = 8 Hz), 6.85 (br d, 2, $J$ = 8 Hz), 5.87 (br s, 1), 1.95 (s, 3); IR (neat), the spectrum is the same as that of **14** except for peaks at 2278, 1570 (shifted from 1580) and 965 (shifted from 1250) $cm^{-1}$; mass spectrum, $m/e$ 217 ($M^+$); mol wt calcd for $C_9H_8DClO_2S$ 217.0075, found 217.0079.

Quenching the reaction mixture with $D_2O$ after 5-min reaction time gave only traces of **15** and recovered **1**, indicating that addition of DCl does not occur during workup.

Attempted trapping of **13** with $I_2$, $CO_2$, or $CH_3I$ was unsuccessful.

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**Registry No.** **1**, 13894-21-8; **2**, 75233-10-2; **3**, 75233-11-3; **4**, 75233-12-4; **5**, 75233-13-5; **6**, 75233-14-6; **7**, 75233-15-7; **8**, 75233-16-8; **9**, 75233-17-9; **10**, 75233-18-0; **11**, 75233-19-1; **12**, 75233-20-4; **14**, 773-60-4; **15**, 775-90-6; *cis*-1,2-bis(*p*-tolylthio)ethylene, 4526-53-8; *cis*-1,2-dichloroethylene, 156-59-2; *p*-thiocresol, 106-45-6; (*p*-tolylthio)acetylene, 66823-38-9; 2,3-dimethyl-2-butene, 563-79-1; 2-methyl-2-butene, 513-35-9; ethylidenecyclopentane, 2146-37-4; 1-methylcyclohexene, 591-49-1; methylenecyclohexane, 1192-37-6; cyclohexene, 110-83-8; cyclohexylbenzene, 827-52-1; *trans*-2-butene, 624-64-6; 1-hexene, 592-41-6.

# Lewis Acid Catalyzed [2 + 2] Cycloaddition of Methyl 2,3-Butadienoate to Alkenes

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Methyl 2,3-butadienoate (1) undergoes $EtAlCl_2$-catalyzed stereospecific [2 + 2] cycloadditions with alkenes to give methyl cyclobutylideneacetates in good yield. The stereospecificity and ratios of *E* and *Z* isomers suggest a $[_\pi 2_s + _\pi 2_a]$ cycloaddition of the 1·$EtAlCl_2$ complex analogous to that of ketenes.

We have recently shown that acetylenic esters undergo Lewis acid catalyzed ene and stereospecific [2 + 2] cycloaddition reactions with alkenes,[2] while acrylic esters undergo ene reactions exclusively.[3] The Lewis acid catalyzed reactions of methyl 2,3-butadienoate (1) with al-

(1) Fellow of the Alfred P. Sloan Foundation, 1979–1981.

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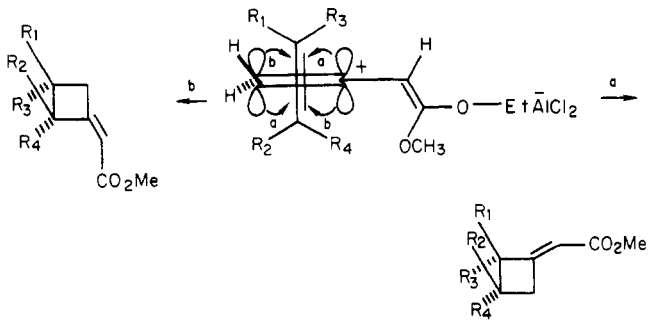
0022-3263/80/1945-5017$01.00/0 

Scheme I



kenes were explored to determine the reactivity of allenic esters.

Treatment of 1[4] with $EtAlCl_2$[2] and an alkene in $CH_2Cl_2$ for 1–5 days gives good yields of the corresponding methyl cyclobutylideneacetate (see Table I). The cycloaddition reactions with *cis*- and *trans*-2-butene are completely stereospecific. Where possible, mixtures of *E* and *Z* isomers are formed, whose structures were assigned on the basis of NMR spectroscopy (the carbomethoxy group deshields protons or methyl groups on the carbon cis to it) and GC chromatography (the *Z* isomer elutes first since the ester is more hindered).

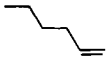
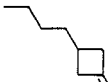
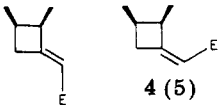
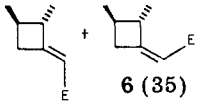
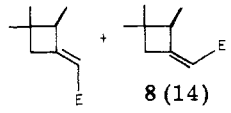
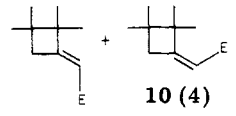
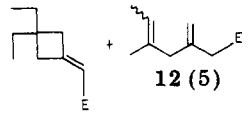
We believe that these reactions take place via a $[{}_\pi 2_s + {}_\pi 2_a]$ cycloaddition.[5] Cycloaddition may be taking place through the vinyl cation resonance form shown in Scheme I since the $1 \cdot EtAlCl_2$ complex is electronically similar to a ketene, whose addition to alkenes is believed to involve the vinyl cation resonance structure.[5] The stereospecific [2 + 2] cycloadditions of alkenes with vinyl cations formed by complexation of Lewis acids to the double bonds of allenes (as opposed to the ester of 1) have been observed.[6]

The ratios of cyclobutenes obtained from the four 2-butene derivatives are consistent with this explanation. For *cis*-2-butene, two orientations ($R_1 = R_2 = CH_3$, or $R_3 = R_4 = CH_3$) are possible. Steric interaction between $R_1$, $R_2$, and the 4$\alpha$ hydrogen of 1 should favor the later orientation from which path a leading to **3** should be greatly favored over b leading to **4** due to unfavorable interaction of $R_4$ (=$CH_3$) with the carbomethoxy group in the transition state of path b. Similar constraints should favor **9** over **10** in the reaction of 1 with 2,3-dimethyl-2-butene. The reaction of 1 with *trans*-2-butene can proceed through two equally favorable orientations. If $R_1 = R_4 = CH_3$ path a will lead to **5**. If $R_2 = R_3 = CH_3$ path b will lead to **6**. Formation of the *Z* isomer by path b is favorable if $R_4$ = H. The reaction of 2-methyl-2-butene is harder to analyze. Apparently path b ($R_4$ = H) can compete since the two sides of the double bond are more nearly symmetrical.

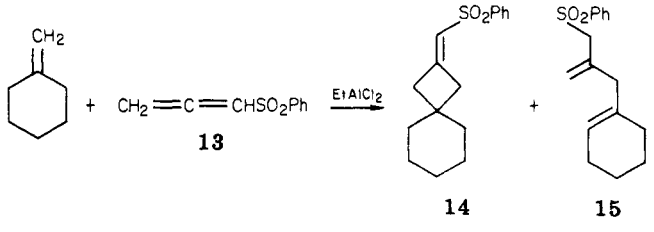
In the reaction of 2-ethyl-1-butene with 1 a small amount of ene adduct **12** is also formed. Previous studies with propiolate derivatives have shown that 1,1-disubstituted alkenes show the greatest propensity to undergo ene reactions rather than [2 + 2] cycloaddition.[2]

The Lewis acid catalyzed reactions of allenic sulfones with alkenes are analogous to those of 1, although they proceed in lower yield. $EtAlCl_2$-catalyzed reaction of phenyl propadienyl sulfone (**13**)[7] with methylenecyclohexane in benzene gives a 25% yield of an 8:1 mixture of **14** and **15**.[8b]

Table I. Adducts from $EtAlCl_2$-Catalyzed Reactions of Methyl 2,3-Butadienoate (1) with Alkenes

| alkene | adducts[b] (% yield[a]) |
|---|---|
|  |  **2** (35) |
|  |  **3** (65) **4** (5) |
|  |  **5** (45) **6** (35) |
|  |  **7** (44) **8** (14) |
|  |  **9** (52) **10** (4) |
|  |  **11** (40) **12** (5) |

[a] Yields were determined from GC analysis of mixtures which were greater than 90% pure. Pure products were isolated by preparative GC. [b] E = $CO_2Me$.



Methyl 2,3-butadienoate can react at either double bond. With alkenes it undergoes Lewis acid catalyzed [2 + 2] cycloadditions at the 3,4 double bond, while it undergoes an ene reaction to give **12** and undergoes thermal Diels–Alder reactions with dienes at the 2,3 double bond.[8,9]

## Experimental Section

NMR spectra were obtained on a Varian A-60, Perkin-Elmer

(3) Snider, B. B. *J. Org. Chem.* **1974**, *39*, 255. Snider, B. B.; Dunčia, J. V. *J. Am. Chem. Soc.*, **1980**, *101*, 5926.
(4) Eglinton, G.; Jones, E. R. H.; Mansfield, G. H.; Whiting, M. C.; *J. Chem. Soc.* **1954**, 3197.
(5) Woodward, R. B.; Hoffman, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781. Pasto has proposed alternate mechanisms for concerted cycloadditions of allenes: Pasto, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 37.
(6) Lukas, J. H.; Kouwenhoven, A. P.; Baardman, F.; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 709.
(7) Stirling, C. J. M. *J. Chem. Soc.* **1964**, 5856.
(8) (a) 2,3-Butadienenitrile undergoes a [2 + 2] cycloaddition with 1-(*N*-morpholino)cyclohexene at the 3,4 bond: Baldwin, J. E.; Fleming, R. H.; Simmons, D. M. *J. Org. Chem.* **1972**, *37*, 3963. (b) Propadienyl phenyl sulfone undergoes [2 + 2] cycloadditions with enamines derived from isobutyraldehyde at the 1,2 double bond. 2-Cyano-4-methyl-2,3-butadienenitrile reacts with the same enamines kinetically at the 2,3 double bond, and thermodynamically at the 3,4 double bond: Gommper, R.; Lach, D. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 567.
(9) Ethyl 2,3-butadienoate undergoes a Diels–Alder reaction with cyclopentadiene at the 2,3 double bond: Jones, E. R. H.; Mansfield, G. H.; Whiting, M. C. *J. Chem. Soc.* **1956**, 4073.

R-32, or JEOL FX 90Q spectrometer, IR spectra were obtained on a Perkin-Elmer 283 spectrometer, and mass spectra were obtained on an AEI MS-9 spectrometer. Gas chromatography was carried out on a 6 ft × 0.25 in. 10% XF-1150 on Chromosorb W column at 110 °C with a flow rate of 70 mL/min. Elemental analyses were carried out by Galbraith Laboratories. $EtAlCl_2$ was obtained from Texas Alkyls (25.5% in heptane, $d$ = 0.772, 1.57 M). $CH_2Cl_2$ was dried by distillation from calcium hydride. Phenyl propadienyl sulfone was synthesized by the procedure of Stirling.[7]

**Preparation of Methyl 2,3-Butadienoate (1).** Oxidation of 9.6 g (0.137 mol) of 3-butyn-1-ol by the procedure of Heilbron, Jones and Sondheimer[10] gave 6.052 g (53%) of 3-butynoic acid; NMR ($CDCl_3$) $\delta$ 13.05 (s, 1), 3.38 (d, 2, $J$ = 1.6 Hz), 2.25 (t, 1, $J$ = 1.6 Hz). Much lower yields were obtained when a magnetic stirrer (rather than overhead stirrer) was used.

Methyl 2,3-butadienoate was prepared from 3-butynoic acid by the procedure of Eglinton, Jones, Mansfield and Whiting for the preparation of the ethyl ester.[4] A solution of 3-butynoic acid (1.438 g, 0.017 mol) and 0.45 mL of $H_2SO_4$ in 12 mL of MeOH was stirred for 5 days at 25 °C. Water was added, and the mixture was extracted four times with ether, and the solution was then dried ($MgSO_4$). Concentration of the organic layer at 30 °C (90 torr) gave 0.733 g (44%) of methyl 3-butynoate; NMR ($CCl_4$) $\delta$ 3.79 (s, 3), 3.24 (d, 2, $J$ = 3 Hz), 2.12 (t, 1, $J$ = 3 Hz).

The crude methyl 3-butynoate (1.38 g, 0.014 mol) was added to 12.1 mL of 10% aqueous $K_2CO_3$ solution. The resulting mixture was shaken for 10 min and allowed to stand for 44 h. The reaction mixture was extracted three times with ether, the solution was dried ($MgSO_4$), and the solvent was evaporated at 25 °C (90 torr) to give 1.05 g (76%) of 1: NMR ($CCl_4$) $\delta$ 5.58 ($\nu_a$) and 5.19 ($\nu_b$) ($AB_2$, 3, $J$ = 6.8 Hz), 3.78 (s, 3); GC $t_R$ 12.3 min.

**Reaction with 1-Hexene with 1.** $EtAlCl_2$ (1.30 mL of 1.57 M, 2.04 mmol, 0.8 equiv) was added to 1 mL of $CH_2Cl_2$ in a flame-dried flask under $N_2$. Ester 1 (0.250 g, 2.55 mmol) in 0.5 mL of $CH_2Cl_2$ was added followed by 1-hexene (0.236 g, 2.8 mmol, 1.1 equiv) in 1.5 mL of $CH_2Cl_2$. The reaction mixture was stirred for 6 days at 25 °C, diluted with ether, and quenched by slow addition of saturated $NaH_2PO_4$ solution. Hydrochloric acid (10%) was added to dissolve the precipitated alumina. The two layers were separated and the aqueous layer was washed with three portions of ether. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo to give 0.441 g (62%) of 65% pure 2. Evaporative distillation (100 °C, 0.25 torr) gave 0.163 g (35%) of pure methyl (3-butylcyclobutylidene)acetate (2): $^1H$ NMR ($CCl_4$) $\delta$ 5.66 (tt, 1, $J$ = 2, 2 Hz), 3.76 (s, 3), 2.67–3.29 (m, 3), 2.13–2.63 (m, 2), 1.1–1.6 (m, 6) and 0.89 (t, 3, $J$ = 7 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 166.7, 165.0, 112.3, 50.7, 39.4, 38.1, 36.1, 31.3, 29.6, 22.6, 14.0; IR (neat) 2960, 2930, 2880, 2860, 1750, 1680, 1440, 1340, 1330, 1270, 1220, 1200, 1025, 860, 790 cm$^{-1}$; GC $t_R$ 17.8 min. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.53; H, 9.89. Found: C, 72.16; H, 9.77.

**Reaction of *cis*-2-Butene with 1.** Excess *cis*-2-butene was condensed, using a dry ice–acetone bath, and added to a solution of $EtAlCl_2$ (0.59 mL of 1.57 M, 0.91 mmol, 0.6 equiv) and ester 1 (0.15 g, 1.53 mmol) in 3.5 mL of $CH_2Cl_2$. After 24 h at 25 °C the reaction mixture was worked up in the normal manner to give 0.182 g (77%) of a 90% pure 14:1 mixture of 3 and 4 as determined by GC and NMR spectroscopy. Pure samples were obtained by preparative GC.

The spectral data for methyl (*cis*-2,3-dimethyl-(*E*)-cyclobutylidene)acetate 3 are as follows: NMR ($CCl_4$) $\delta$ 5.64 (dt, 1, $J$ = 2, 2 Hz), 3.69 (s, 3), 2.98–3.36 (m, 2) 2.41–2.81 (m, 2), 1.04 (2 d, 6, $J$ = 7 Hz); IR (neat) 2980, 2880, 1730, 1680, 1435, 1380, 1350, 1260, 1200, 1140, 1100, 1040, 1010, 885, 880 cm$^{-1}$; GC $t_R$ 11.9 min; mol wt calcd for $C_9H_{14}O_2$ 154.0994, found 154.0996.

The spectral data for methyl (*cis*-2,3-dimethyl-(*Z*)-cyclobutylidene)acetate (4) are as follows: NMR ($CCl_4$) $\delta$ 5.55 (br s, 1), 3.68 (s, 3), 2.80–3.68 (m, 2), 2.13–2.88 (m, 2), 1.20 (d, 3, $J$ = 7 Hz), 1.06 (d, 3, $J$ = 7 Hz); IR ($CDCl_3$) 2960, 2875, 1720, 1680, 1430, 1340, 1280, 1200, 1020, 830 cm$^{-1}$; GC $t_R$ 9.5 min.

The spectral data of 3 and 4 correspond well with those of the corresponding ethyl esters.[11] GC showed that 5 and 6 were not present in the crude product mixture.

**Reaction of *trans*-2-Butene with 1.** Excess *trans*-2-butene was condensed and added to a solution of $EtAlCl_2$ (0.81 mL of 1.57 M, 1.27 mmol, 0.6 equiv) and 1 (0.206 g, 2.10 mmol) in 3 mL of $CH_2Cl_2$. After 25 h at 25 °C the reaction mixture was worked up in the normal manner to give 0.290 g (90%) of a 90% pure 1.27:1 mixture of 5 and 6 as determined by GC and NMR spectroscopy. pure samples were obtained by preparative GC.

The spectral data for methyl (*trans*-2,3-dimethyl-(*E*)-cyclobutylidene)acetate (5) are as follows: NMR ($CCl_4$) $\delta$ 5.51 (dt, 1, $J$ = 2, 2 Hz), 3.64 (s, 3), 3.27 (ddd, 1, $J$ = 15, 7, 2 Hz), 2.31–2.89 (m, 2), 1.79–2.17 (m, 1), 1.19 (d, 3, $J$ = 6 Hz), 1.15 (d, 3, $J$ = 6 Hz); IR (neat) 2950, 2870, 1720, 1680, 1450, 1430, 1340, 1270, 1200, 1160, 1120, 1020, 790, 755, 500 cm$^{-1}$; GC $t_R$ 9.2 min.

The spectral data for methyl (*trans*-2,3-dimethyl-(*Z*)-cyclobutylidene)acetate (6) are as follows: NMR ($CCl_4$) $\delta$ 5.53 (dt, 1, $J$ = 1.9, 1.9 Hz), 3.62 (s, 3), 2.75–3.21 (m, 2), 1.87–2.41 (m, 2), 1.31 (d, 3, $J$ = 6.6 Hz), 1.17 (d, 3, $J$ = 6.5 Hz); IR (neat) 2950, 2860, 1720, 1660, 1430, 1340, 1270, 1210, 1200, 1100, 1020, 830 cm$^{-1}$; GC $t_R$ 6.6 min.

The spectral data for 5 and 6 correspond well with those of the corresponding ethyl esters.[11] GC showed that 3 and 4 were not present in the crude product mixture.

**Reaction of 2-Methyl-2-butene with 1.** 2-Methyl-2-butene (0.118 g, 1.68 mmol, 1.1 equiv) was added to a solution of 1 (0.150 g, 1.53 mmol) and $EtAlCl_2$ (0.58 mL of 1.57 M, 0.91 mmol, 0.6 equiv) in 3 mL of $CH_2Cl_2$. After 24 h at 25 °C the reaction mixture was worked up in the normal manner to give 0.166 g (65%) of a 90% pure 3.1:1 mixture of 7 and 8 as determined by NMR spectroscopy and GC. Pure samples were obtained by preparative GC.

The spectral data for methyl (2,2,3-trimethyl-(*E*-)cyclobutylidene)acetate (7) are as follows: NMR ($CCl_4$) $\delta$ 5.63 (dt, 1, $J$ = 1.8, 1.8 Hz), 3.68 (s, 3), 2.60 (m, 3), 1.19 (s, 3), 1.00 (d, 3, $J$ = 7 Hz), 0.98 (s, 3); IR (neat) 2950, 2860, 1740, 1680, 1470, 1430, 1370, 1340, 1270, 1210, 1190, 1160, 1095, 1060, 1020, 910, 880, 850 cm$^{-1}$; GC $t_R$ 15.8 min. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.57. Found: C, 71.10; H, 9.61.

This spectral data for methyl (2,2,3-trimethyl-(*Z*)-cyclobutylidene)acetate (8) are as follows: NMR ($CCl_4$) $\delta$ 5.64 (dt, 1, $J$ = 2, 2 Hz), 3.69 (s, 3), 2.95 (dddq, 1, $J$ = 2, 2, 2, 7 Hz), 2.58 (ddd, 1, $J$ = 13, 2, 2 Hz), 2.39 (ddd, 1, $J$ = 13, 2, 2 Hz), 1.20 (d, 3, $J$ = 7 Hz), 1.16 (s, 3), 1.06 (s, 3); IR (neat) 2960, 2870, 1760, 1680, 1650, 1430, 1390, 1260, 1210, 1170, 1110, 1050, 1020, 900, 870, 850 cm$^{-1}$; GC $t_R$ 13.5 min.

**Reaction of 2,3-Dimethyl-2-butene with 1.** 2,3-Dimethyl-2-butene (0.141 g, 1.68 mmol, 1.1 equiv) was added to a solution of 1 (0.150 g, 1.53 mmol) and $EtAlCl_2$ (0.58 mL, 0.91 mmol, 0.6 equiv) in 3.3 mL of $CH_2Cl_2$. After 24 h at 25 °C the reaction mixture was worked up in the normal manner to give 0.168 g (60%) of a 95% pure 12.5:1 mixture of 9 and 10 as determined by GC and NMR spectroscopy. Pure samples were obtained by preparative GC.

The spectral data for methyl (2,2,3,3-tetramethyl-(*E*)-cyclobutylidene)acetate (9) are as follows: NMR ($CCl_4$) $\delta$ 5.61 (t, 1, $J$ = 2.7 Hz), 3.68 (s, 3), 2.85 (d, 2, $J$ = 2.7 Hz), 1.13 (s, 6), 1.09 (s, 6); IR (neat) 2980, 2870, 1740, 1680, 1430, 1380, 1340, 1270, 1190, 1170, 1020, 910, 850, 730 cm$^{-1}$; GC $t_R$ 14.4 min. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.53; H, 9.89. Found: C, 72.34; H, 9.96.

The spectral data for methyl (2,2,3,3-tetramethyl-(*Z*)-cyclobutylidene)acetate (10) are as follows: NMR ($CCl_4$) $\delta$ 5.55 (t, 1, $J$ = 2.0 Hz), 3.65 (s, 3), 2.41 (d, 2, $J$ = 2.0 Hz), 1.21 (s, 6), 1.01 (s, 6); IR ($CCl_4$) 2970, 2860, 1730, 1680, 1340, 1240, 1170, 1130 cm$^{-1}$; GC $t_R$ 10.1 min.

**Reaction of 2-Ethyl-1-butene with 1.** 2-Ethyl-1-butene (0.268 g, 3.19 mmol, 1.1 equiv) was added to a solution of 1 (0.284 g, 2.9 mmol) and $EtAlCl_2$ (1.47 mL of 1.57 M, 2.31 mmol, 0.8 equiv) in 5.7 mL of $CH_2Cl_2$. After 48 h at 25 °C the reaction mixture was worked up in the normal manner to give 0.253 g (48%) of a 95% pure 7.7:1 mixture of 11 and 12 as determined by GC and NMR spectroscopy. Pure samples were obtained by preparative GC.

The spectral data for methyl (3,3-diethylcyclobutylidene)acetate (11) are as follows: NMR ($CCl_4$) $\delta$ 5.57 (tt, 1, $J$ = 2, 2 Hz), 3.60

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(s, 3), 2.73 (d, 2, $J$ = 2 Hz), 2.45 (d, 2, $J$ = 2 Hz), 1.51 (q, 4, $J$ = 7 Hz), 0.82 (t, 6, $J$ = 7.1 Hz); IR (neat) 2960, 2880, 2860, 1730, 1680, 1460, 1340, 1270, 1200, 1180, 1130, 1080, 1020, 910, 865, 800 $cm^{-1}$; GC $t_R$ 13.2 min. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.26; H, 9.74.

The spectral data for methyl 5-ethyl-3-methylene-5-heptenoate (**12**, $E$ + $Z$ isomers) are as follows: NMR ($CCl_4$) $\delta$ 5.32 and 5.18 (2 q, 1, $J$ = 6.5 Hz), 4.87 (br s, 2), 3.62 (s, 3), 2.90, 2.81, and 2.76 (3 br s, 4), 1.95 (m, 2), 1.59 and 1.56 (2 d, 3, $J$ = 6.5 Hz), 0.91 and 0.93 (2 t, 3, $J$ = 7 Hz); IR ($CCl_4$) 2960, 2880, 1740, 1460, 1430, 1330, 1230, 1210, 1150, 1000, 970, 900 $cm^{-1}$; GC $t_R$ 7.5 min; mol wt calcd for $C_{11}H_{18}O_2$ 182.1307, found 182.1304.

**Reaction of Methylenecyclohexane with Propadienyl Phenyl Sulfone (13).**[12] $EtAlCl_2$ (1.0 mL, 1.57 mmol, 0.9 equiv) was added to a solution of **13** (0.319 g, 1.77 mmol) in 10 mL of $CH_2Cl_2$ at 0 °C under $N_2$. Methylenecyclohexane (0.162 g, 2.0 mmol) was added. The solution was allowed to warm to 25 °C and was stirred for 14 days. Normal workup gave 0.414 g of crude product. Chromatography of 0.217 g on 10 g of silica gel with 1:2 hexane–ethyl acetate as eluant gave 64 mg (25%) of an 8:1 mixture of cyclobutane **14** and ene adduct **15**: NMR ($CCl_4$) (**14**) $\delta$ 7.95–7.7 (m, 2), 7.60–7.40 (m, 3), 6.03 (tt, 1, $J$ = 2,2 Hz), 2.89 (d, 2, $J$ = 2 Hz), 2.48 (d, 2, $J$ = 2 Hz), 1.48 (br, 8); NMR ($CCl_4$) (**15**) $\delta$ 7.95–7.7 (m, 2), 7.60–7.40 (m, 3), 5.42 (m, 1), 4.96 (br s, 1), 4.72 (br s, 1), 3.61 (br s, 2), 2.75 (br s, 2), 2.3–1.5 (m, 8); IR (neat) 3070, 2930, 2855, 1660, 1450, 1320, 1145, 1087, 830, 815, 760, 735, 710, 685 $cm^{-1}$; mass spectrum, $m/e$ 276 ($M^+$), 141, 135, 134, 125, 119, 115, 107, 106, 105, 97, 93, 83, 91, 81, 79, 78, 77; mol wt calcd for $C_{16}H_{20}SO_2$ 276.1184, found 276.1180.

(12) This experiment was performed by Robert Cordova.

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**Registry No.** **1**, 18913-35-4; **2**, 75232-99-4; **3**, 75233-00-0; **4**, 75281-69-5; **5**, 75281-70-8; **6**, 75281-71-9; **7**, 75233-01-1; **8**, 75233-02-2; **9**, 75233-03-3; **10**, 75233-04-4; **11**, 75233-05-5; (*E*)-**12**, 75233-06-6; (*Z*)-**12**, 75233-07-7; **13**, 2525-42-0; **14**, 75233-08-8; **15**, 75233-09-9; 3-butyn-1-ol, 927-74-2; 3-butynoic acid, 2345-51-9; methyl 3-butynoate, 32804-66-3; 1-hexene, 592-41-6; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-2-butene, 563-79-1; 2-ethyl-1-butene, 760-21-4; methylenecyclohexane, 1192-37-6; $EtAlCl_2$, 563-43-9.

# Cyclopentene Annulation via Intramolecular Addition of Diazo Ketones to 1,3-Dienes. Applications to the Synthesis of Cyclopentanoid Terpenes

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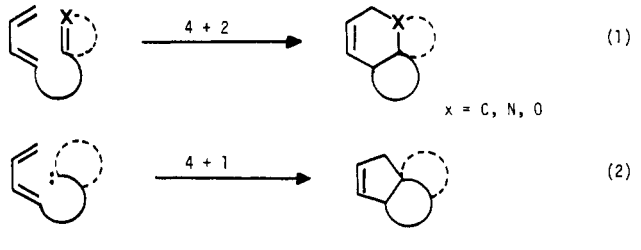
Initial model studies investigating the utility of a new intramolecular cyclopentene annulation procedure are described as pertaining to the preparation of bicyclo[3.3.0]octenones. Several 1-diazo-5,7-octadien-2-ones substituted at the 1-, 7-, or 8-position were decomposed in the presence of $Cu(acac)_2$ to yield stereospecifically the corresponding vinylcyclopropanes **13**, **16**, **21**, **24**, and **27**. The thermal as well as the rhodium-promoted modes of rearrangement to the appropriate cyclopentenes **14**, **17**, **22a,b**, and **28a,b** were studied. Where necessary, diastereomers were separated and structurally assigned by relying on $^{13}C$ NMR spectroscopy. $^{13}C$ NMR data are provided for all new compounds in the bicyclooctane series to serve as an aid in assignments of cyclopentanoid terpenes synthesized by this methodology. The intramolecular cyclopropanation–rearrangement sequence of dienic diazo ketones has been shown to provide facile access to bicyclo[3.3.0]octanes of the type **14**, **17**, **22a,b**, and **25a,b** which are of value as terpene synthons. Enhanced stereoselectivity was observed in the rhodium-promoted cyclopentene rearrangements in favor of the less concave diastereomers (**22a**, **25a**, and **28a**). Finally, the sesquiterpene hirsutene (**31**) was synthesized in 37% overall yield by this methodology. $^{13}C$ NMR data for several tricyclo[6.3.0.$0^{2,6}$]undecane compounds are also provided.

The methodology of simultaneous closure of two rings in an intramolecular fashion has been extensively utilized in the construction of carbocyclic systems. Complex natural products containing an annulated cyclohexene ring have been successfully synthesized by the application of an intramolecular Diels–Alder reaction.[1] Recently, this methodology has entered the alkaloid domain through the use of heteroatom analogues of dienes and dienophiles.[2] Other thermal processes have also been exploited in the context of natural product synthesis particularly where the creation of inaccessible quaternary centers[3] had excluded conventional methods of carbon–carbon bond formation. The ene reactions,[4] the Cope rearrangements, electrocyclic reactions, and their hetereoatom equivalents have all been used in an intramolecular sense.[5]

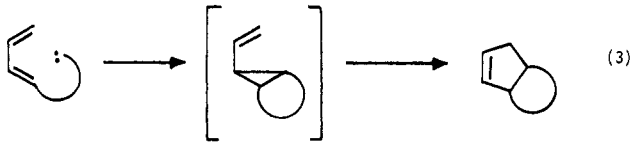
Scheme I




(1)

(2)

Scheme II



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