within the series, so that uncertainty exists only for those signals differing by less than one part per million.

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Synthesis and Thermal Rearrangements of Methylenecyclobutanes

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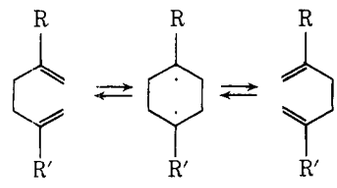
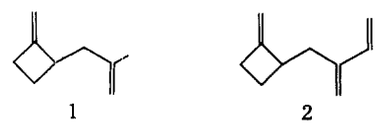
The Cope and Claisen rearrangements play a prominent role in contemporary synthetic organic chemistry; an understanding of the influence of substituents on the rate and mechanism of these reactions is of considerable importance.[1,2] Relatively few quantitative studies of this type, however, are available.[3] The influence of substituents at the 2 and 5 positions of 1,5-hexadiene is particularly important in the long-standing question regarding the possible intervention of 1,4-diradical intermediates in [3,3] sigmatropic rearrangements (eq 1).[4] We report here the synthesis and thermal re-



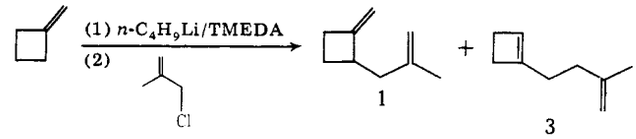
(1)

arrangements of methylenecyclobutanes **1** and **2**; a kinetic analysis of their thermal chemistry permits us to document the influence of a vinyl substituent in the Cope rearrangement.



1 2

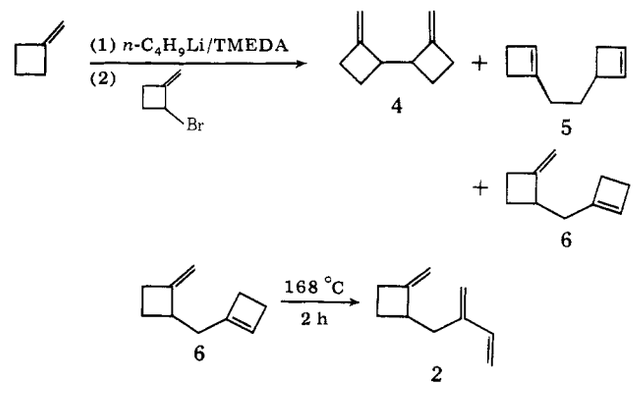
2-(2-Methyl-2-propenyl)methylenecyclobutane (**1**) was prepared by the reaction of 1-cyclobutenylmethyllithium with methallyl chloride.[5] The products (90%) consist of a mixture of isomers (**1**/**3**) in a ratio of 85:15. Pure **1** was isolated by



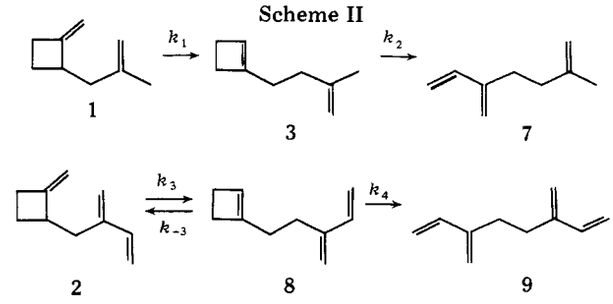
preparative VPC. Compound **2** was obtained by the procedure outlined in Scheme I. Condensation of 2-bromomethylenecyclobutane with 1-cyclobutenylmethyllithium results in the formation of three isomeric $C_{10}H_{14}$ hydrocarbons, **4**–**6**.[6] The unsymmetrical coupling product 2-(1-cyclobutenylmethyl)-methylenecyclobutane (**6**), when heated for 2 h at 168 °C, yields triene **2** and two additional isomeric olefins (vide infra).

Thermolysis of methylenecyclobutanes **1** and **2** initiates the sequence of rearrangements shown in Scheme II. Both Cope rearrangement products (**3** and **8**) react further via electrocyclic ring opening to produce polyenes **7** and **9**. During the course of our investigations it was noted that the rearrangement of **2** occurs under significantly milder conditions than that of **1**. This observation was quantified in the following manner. The rate of Cope rearrangement of **1** (k_1) was determined by monitoring its rate of disappearance over a range of temperatures (gas phase, sealed tubes) and extrapolating, k_1(170.6 °C) = 5.47×10^{-7} s^{-1}. The rate of electrocyclic ring opening (**3** → **7**) was also measured, k_2(170.6 °C) = 5.19×10^{-4} s^{-1}.[7] The rate of Cope rearrangement of **2**, k_3, was calculated as follows. Disappearance of **2** at 170.6 °C was found to be $k_{obsd} = 3.75 \times 10^{-5}$ s^{-1}. The ratio of k_4/k_{-3} was obtained from the rate of appearance of **9** and **2** during the initial stages of the reaction of **8**, $k_4/k_{-3} = 2.97$. A steady state approximation was then used to calculate k_3. The validity of this approximation was confirmed by computer simulation of concentration vs. time plots (assuming $k_2 = k_4$) using the MS1M4 program.[8] The best value for the rate of Cope rearrangement of **2** was found, k_3(170.6 °C) = 5.01×10^{-5} s^{-1}. Using this number to calculate the relative rate of Cope rearrangement, **2**/**1** = k_3/k_1 = 91 (170.6 °C).

Scheme I



Scheme II



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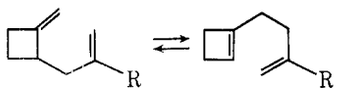
Methylenecyclobutanes 1 and 2 differ only with respect to the substituents at the 2 position of the 1,5-hexadiene chain (eq 2). The >90-fold rate enhancement resulting from sub-



(2)

1, R = CH_3
2, R = CH_2=CH

stitution of a vinyl for a methyl group ($\Delta\Delta G^{\ddagger}_{443.6}$ = 3.9 kcal/mol) implies that the Cope rearrangement of methylenecyclobutanes is quite sensitive to electron-delocalizing groups at the 2(5) position of the 1,5-hexadiene chain. The rate difference, however, is smaller than what one would expect on the basis of the relative radical stabilizing abilities of methyl and vinyl groups.

This finding is in qualitative agreement with the earlier results of Dewar and Wade,[9] who report a 69-fold rate increase at 189.8 °C when phenyl is substituted for hydrogen at the 2 position of 1,5-hexadiene. The similar response to phenyl and vinyl substituents in two disparate [3,3] sigmatropic rearrangements suggests the rate enhancement is a general phenomenon. These results are entirely consistent with, and have been interpreted in terms of,[9,10] a biradicaloid transition state that leads to a 1,4-diradical intermediate (eq 1). Electron-delocalizing groups are expected to stabilize transition states with developing unpaired electron density at the site of substitution. Implicit in this analysis, however, is the expectation that phenyl and vinyl groups will have little influence on the hypothetical pericyclic transition state.[11] This has indeed been proposed by Dewar and Wade[9] although it must be recognized that alternative explanations have been offered.[12]

Experimental Section

Infrared spectra were measured on a Perkin-Elmer 287 spectrophotometer. Only major infrared bands are given. Proton NMR spectra were recorded on either Varian A 56-60 or Bruker WH 90 spectrometers. Preparative VPC analyses were performed on a Varian Aerograph 920 gas chromatograph using a 15 ft, 30% SE-30 on 60/80 Chrom W (AW-DCMS) column at 100 °C. Analytical VPC were obtained on either a Hewlett Packard 700 laboratory chromatograph using a 10 ft, 10% Hi Eff on 60/80 Gas Chrom R column or a Hewlett Packard 5710A chromatograph equipped with a 15 ft, 8% SE-30 on 80/100 Gas Chrom Q column.

2-(2-Methyl-2-propenyl)methylenecyclobutane (1). Methylenecyclobutane[13] (9.8 mL, 100 mmol) was added over 5 min to a stirred solution of TMEDA (33 mmol), hexane (20 mL), and *n*-butyllithium (15 mL, 2.22 M, 33 mmol) at −78 °C under nitrogen. Stirring was continued at −78 °C for 15 min and then the reaction mixture was allowed to warm to room temperature. After stirring for 6 h the reaction mixture consisted of two yellow liquid phases. The mixture was cooled again to −78 °C, and 3-chloro-2-methylpropene (1.49 g, 16.5 mmol) in hexane (5 mL) was added over a 30-min period with stirring. The cold bath was removed, and the reaction mixture was stirred at room temperature for 3.5 h before it was quenched with saturated NH_4Cl (10 mL). The organic layer was washed (5% HCl, 3 × 10 mL), dried (Na_2SO_4), and then concentrated by distillation. Analysis and product isolation was performed by VPC. Two isomers were obtained in 93% yield; in order of elution, 2-(2-methyl-2-propenyl)methylenecyclobutane (1) [IR ($CDCl_3$) 3088, 2985, 2940, 2925, 1673, 1651, 1449, 1429, 1377, 872 cm^{-1}; NMR ($CDCl_3$) δ 1.7 (s, 3 H), 1.8–2.8 (m, 6 H), 3.0 (m, 1 H), 4.67 (br s, 4 H)] and 1-(3-methyl-3-butenyl)cyclobutene (3) [IR ($CDCl_3$) 3075, 3040, 2925, 2845, 1648, 1628, 1445, 1372, 874, 850 cm^{-1}; NMR ($CDCl_3$) δ 1.70 (s, 3 H), 2.12 (s, 4 H), 2.40 (s, 4 H), 4.65 (br s, 2 H), 5.65 (s, 1 H)]. The ratio of products 1/3 was 85:15.

Reaction of 1-Cyclobutenylmethyllithium with 2-Bromomethylenecyclobutane. In a similar manner 2-bromomethylenecyclobutane (0.95 g, 6.5 mmol)[14] was added to 1-cyclobutenylmethyllithium (one-half scale). After workup and distillation, the residue was vacuum transferred. Analysis and isolation were performed as before by preparative VPC. Three isomeric $C_{10}H_4$ hydrocarbons were formed in 85% overall yield; their relative yields, in order of increasing retention time, are 4 (22.5%), 6 (45.5%), and 5 (32%). 2-(2-Methylenecyclobutane)methylenecyclobutane (4): IR ($CDCl_3$) 3072, 2980, 2940, 2920, 2882, 1670, 1450, 1425, 1405, 874 cm^{-1}; NMR ($CDCl_3$) δ 1.4–2.5 (m, 8 H), 3.1 (m, 2 H), 4.7 (br s, 4 H). 2-(1-Cyclobutenylmethyl)methylenecyclobutane (6): IR ($CDCl_3$) 3075, 3050, 2925, 2850, 1675, 1630, 1430, 1300, 1075, 874, 855 cm^{-1}; NMR ($CDCl_3$) δ 1.3–2.0 (m, 2 H), 2.0–2.9 (m, 8 H), 3.0 (m, 1 H), 4.7 (br s, 2 H), 5.7 (s, 1 H). 1,2-Bis(1-cyclobutenyl)ethane (5): IR ($CDCl_3$) 3040, 2920, 2840, 1630, 1062, 853 cm^{-1}; NMR ($CDCl_3$) δ 2.13 (br s, 4 H), 2.35 (br s, 8 H), 5.65 (br s, 2 H).

2-(2-Methylidene-3-butenyl)methylenecyclobutane (2). 2-(1-Cyclobutenylmethyl)methylenecyclobutane (6) (11.7 mg, 0.087 mmol) was diluted with 0.7 mL of cyclohexane, degassed by several freeze–thaw cycles, and then sealed. After heating at 168 °C for 2 h, the tube was cooled, opened, and analyzed by VPC. Triene product 2 was found (81%) in addition to minor amounts of starting material (6, 3%), 5-(1-cyclobutenyl)-3-methylidene-1-pentene (8, 5%), and 3,6-dimethylidene-1,7-octadiene (9, 11%). Compound 2: IR (CS_2) 3085, 3070, 2970, 2930, 2910, 1672, 1595, 988, 900, 891, 871 cm^{-1}; NMR ($CDCl_3$) δ 1.5–2.7 (m, 6 H), 3.18 (m, 1 H), 4.75 (m, 2 H), 4.98–5.32 (m, 4 H), 6.39 (dd, *J* = 17.4 and 10.2 Hz, 1 H). Compound 8 showed the following: IR (CS_2) 3085, 3040, 2940, 2915, 1631, 1595, 988, 901, 891, 851 cm^{-1}; NMR ($CDCl_3$) δ 2.29–2.46 (m, 8 H), 5.01–5.33 (m, 4 H), 5.71 (s, 1 H), 6.39 (dd, *J* = 17.8 and 11.0 Hz, 1 H). Spectral properties of tetraene 9 are consistent with those reported.[15]

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Registry No.—1, 66290-31-1; 2, 66290-32-2; 3, 66290-33-3; 4, 66290-34-4; 5, 66290-35-5; 6, 66290-36-6; 8, 66290-37-7; 9, 3382-59-0; methylenecyclobutane, 1120-56-5; 3-chloro-2-methylpropene, 563-47-3; 2-bromomethylenecyclobutane, 32442-49-2; 1-cyclobutenylmethyllithium, 66290-38-8.

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Synthesis of Biphenyl 2,3-Oxide

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A recent study reported that the polynuclear aromatic hydrocarbons (PAH), including biphenyl, are ubiquitous pollutants which frequently reach concentrations of 0.1 ng/m^3.[1a]