droxide. A workup as above furnished 1.82 g (80%) of the crude alcohols **5** as a 3:2 mixture of *E*/*Z* diastereomers. The major component was assigned the *E* configuration on the basis of the chemical shift of the olefinic proton which is expected to appear at lowest field, being cis to the vicinal Br: ^{1}H NMR of *E* isomer δ 1.45 (6 H, s), 3.4 (1 H, brs), 3.7 (3 H, s), 6.6 (1 H, s); ^{1}H NMR of *Z* isomer δ 1.45 (l H, s), 3.4 (1 H, brs), 3.65 (3 H, s), 6.25 (1 H, s). The NMR spectrum showed contamination by ~10% aldehyde **6a**.

Chromatography of **5** (1.82 g) on silica gel with diethyl ether as the eluant furnished 1.75 g of a 4:1 mixture of 2-bromo-3-methyl-2-butenal and its methyl acetal 2-bromo-1,1-dimethoxy-3-methylbut-2-ene (**7**).

Compound **7** was identified from its reaction with aqueous HCl (which produced **6a** as the only product) as well as from its NMR spectrum: ^{1}H NMR δ 1.95 (6 H, m), 3.35 (3 H, s), 3.4 (3 H, s), 4.9 (1 H, s).

Registry No. **1a**, 23521-49-5; **1b**, 16339-88-1; **1c**, 77295-79-5; **2b**, 85371-39-7; **3**, 85371-47-7; **4a**, 85371-40-0; **4b**, 85371-41-1; (*E*)-**5**, 85371-42-2; (*Z*)-**5**, 85371-43-3; **6a**, 31058-93-2; **6b**, 65275-96-9; **6c**, 33603-90-6; **7**, 85371-44-4; Me$_2$CO, 67-64-1; PhCHO, 100-52-7; cyclopentanone, 120-92-3; 2,2,2-tribromo-1-chloro-1-methoxyethane, 85371-45-5; 2,2,2-tribromo-1-methoxyethanol, 85371-46-6.

Comment on the Purported Photoelectron Spectrum of 1,2-Dimethyl-3,4-dimethylenecyclobutene Dimer

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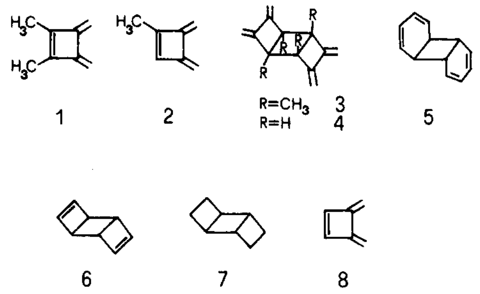
Chart I



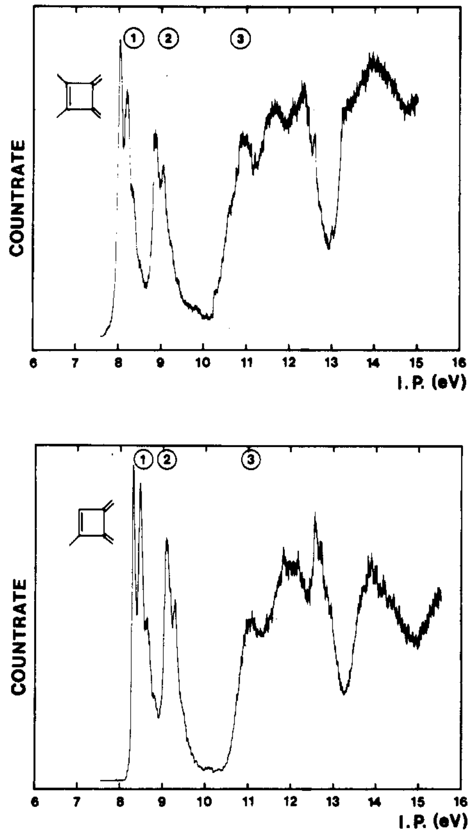


Figure 1. PE spectra of **1** (top) and **2** (bottom).

Table I. Vertical Ionization Potentials of 1 and 2

compd	band	$I_{V,J}$, eV	assignment
1 (C_{2v})	1	8.05	b$_1$ (π)
		8.20	
	2	8.87	a$_2$ (π)
		9.07	
	3	10.75 (sh)[a]	
		11.0	
2 (C_s)	1	8.34	a″ (π)
		8.90	
	2	9.12	a″ (π)
		9.32	
	3	11.1	

[a] sh = shoulder.

During our photoelectron (PE) spectroscopic investigations of 1,2-bridged cyclobutanes (e.g., **5**–**7**,[1-5] Chart I) we became interested in the PE spectrum of the tetraene **3** published by Borden et al.[6] We were puzzled by the circumstance that only two PE bands are observed below 11 eV. The two peaks close to 8 and 9 eV could possibly be assigned to butadiene π-type levels; however, additional ionizations are expected to occur below 11 eV, corresponding to ejection of electrons from the high-lying Walsh orbitals of the tricyclo[4.2.0.0^{2,5}]octane moiety of **3**. This is strongly suggested by the PE data for **6** and **7**.[1-3,5] We suspected that the spectrum published by Borden et al. was not the spectrum of **3** but of some other compound, most probably the triene **1**, i.e., the precursor in the photosynthesis of **3**.[6] We presently report the PE spectra of 1,2-dimethyl- and 1-methyl-3,4-dimethylenecyclobutene (**1** and **2**). Both spectra are shown in Figure 1. The first ionization potentials are given in Table I. The spectrum of **1** is identical within experimental error with that published by Borden et al., indicating that the spectrum recorded by these authors must be assigned to **1** and not to its dimer **3**. The latter compound is most likely unstable with respect to cycloreversion into two molecules of **1** under the conditions prevailing in the target chamber of the PE spectrometer. This assumption is consistent with the observed photochemical instability of this strained species[6] and is supported by the results of MINDO/3[7] calculations which predict a release of 35 kcal/mol when **3** is cleaved into two molecules of **1** (in contrast, the less crowded parent compound **4** is predicted to be thermo-

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[1] Gleiter, R.; Heilbronner, E.; Hekman, M.; Martin, H.-D. *Chem. Ber.* **1973**, *106*, 28.

[2] Spanget-Larsen, J.; Gleiter, R.; Paquette, L. A.; Carmody, M. J.; Degenhardt, C. R. *Theor. Chim. Acta* **1978**, *50*, 145.

[3] Gleiter, R. *Top. Curr. Chem.* **1979**, *86*, 197.

[4] Gubernator, K.; Gleiter, R. *J. Org. Chem.* **1981**, *46*, 1247.

[5] Gubernator, K. Thesis, University of Heidelberg, 1982.

[6] Borden, W. T.; Young, S. D.; Frost, D. C.; Westwood, N. P. C.; Jorgensen, W. L. *J. Org. Chem.* **1979**, *44*, 737.

[7] Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294. Bischof, P. *Ibid.* **1976**, *98*, 6844; *QCPE* **1979**, *12*, 383.

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dynamically stable with respect to fragmentation by 28 kcal/mol).[5]

The PE spectra of 1 and 2 are very similar to the previously published spectrum of 3,4-dimethylenecyclobutene (8).[8] Substituting one or two hydrogen atoms by methyl groups at the endo double bond of 8 yields the expected shift toward lower energies which can be explained by the hyperconjugative and inductive effect of a methyl group. The assignment given is based on the analogy of the spectra of 1, 2, and 8.

Experimental Section

The He(I) PE spectra were measured at room temperature on a PS-18 instrument (Perkin-Elmer Ltd., England) and calibrated with reference to the Ar line at 15.76 eV. A resolution of about 25 meV of the $^2P_{3/2}$ Ar line was obtained. 1-Methyl- (2) and 1,2-dimethyl-3,4-dimethylenecyclobutene (1) were prepared by pyrolysis (410 °C, flow system) of 1,5-heptadiyne and 2,6-octadiyne, respectively, according to published procedures.[9,10] Analytically pure samples were obtained by preparative gas chromatography with a 3-m 20% Carbowax column at 80 °C. The spectral data of 1 and 2 agree with those reported in the literature.[9,10]

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Registry No. 1, 25467-12-3; 2, 14309-11-6.

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[8] Heilbronner, E.; Gleiter, R.; Hopf, H.; Hornung, V.; de Meijere, A. *Helv. Chim. Acta* 1971, *54*, 783.

[9] Huntsman, W. D.; Wristers, H. J. *J. Am. Chem. Soc.* 1967, *89*, 342.

[10] Criegee, R.; Dekker, J.; Engel, W.; Ludwig, P.; Noll, K. *Chem. Ber.* 1963, *96*, 2362.

Regiospecific Alkylative Ring Expansion of 2,2-Disubstituted Cyclobutanones via α-Lithio Selenoxides

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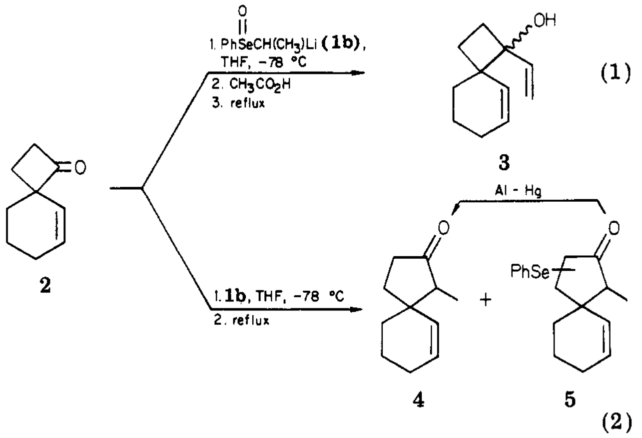
In connection with a synthetic program aimed at the total synthesis of cyclooctanoid natural products,[1] an efficient means for the preparation of 1,2-dialkenylcyclobutanols was needed. More specifically, a method was sought that avoided the formation of a labile 1,2-dialkenylcyclobutoxide intermediate. Such a method appeared to be the allylic alcohol synthesis of Reich and Shah,[2] involving the addition of an α-lithio selenoxide to a carbonyl compound, followed by neutralization and thermolysis to induce selenoxide elimination.

In practice, addition of 1-lithioethyl phenyl selenoxide (**1b**) to spiro[3.5]non-5-en-1-one (2) followed by neutralization with acetic acid and thermolysis in refluxing THF cleanly afforded the allylic alcohol 3 (eq 1) in 72% yield (8:1 mixture of diastereomers).[1] However, it was discovered somewhat serendipitously that if the reaction mixture was refluxed in THF without prior protonation, a regiospecific ring expansion occurred within minutes. Upon workup, the cyclopentanone 4 and its α-selenenylated derivatives 5 were isolated (eq 2). No trace of allylic alcohol 3 could be seen in the crude NMR spectrum. Conversion of the α-selenenylated ketones 5 into the cyclopentanone 4 could be accomplished most conveniently by treatment of the crude reaction mixture with aluminum amalgam. Simple Kugelrohr distillation of the crude product afforded pure 4 (1:1 mixture of diastereomers) in 71% yield from the cyclobutanone 2.



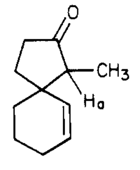
2

3 (1)

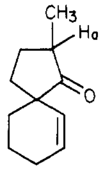
4

5 (2)

That the more highly substitued carbon atom had migrated exclusively was obvious by 270-MHz NMR analysis. Each diastereomer of 4 showed a one-proton downfield quartet (1.97 and 2.09 ppm, respectively) that collapsed to a singlet upon selective irradiation of the methyl group and thus was assigned to the methine proton (H$_a$). In contrast, the corresponding methine in the other possible regioisomer (**4a**) would have shown residual vicinal splittings after decoupling of the methyl group.

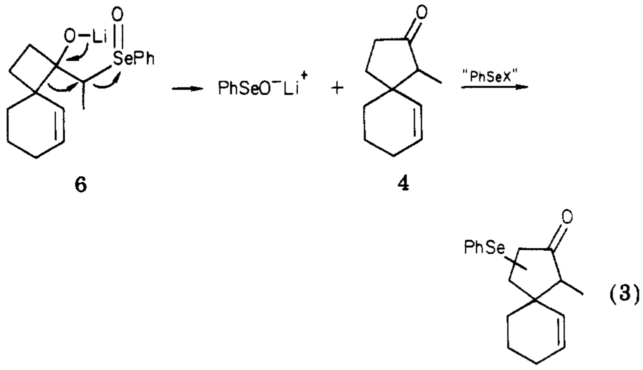


4



4a

The mechanism of this ring expansion is apparently a direct pinacol-like rearrangement of the initial adduct 6 (eq 3) in which the more highly substituted carbon migrates preferentially. No spirocyclic epoxide was ever isolated even in cases using lithiomethyl phenyl selenoxide as the nucleophile.[6e] The α-selenenylated ketones 5 presumably arise from reaction of the cyclopentanone 4 with electrophilic selenium species produced in the course of the reaction.[3]



6

4

5 (3)

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[1] Gadwood, R. C.; Lett, R. M. *J. Org. Chem.* 1982, *47*, 2268.

[2] Reich, H. J.; Shah, S. K. *J. Am. Chem. Soc.* 1975, *97*, 3250. Reich, H. S.; Shah, S. K.; Chow, F. *Ibid.* 1979, *101*, 6648.

[3] Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* 1975, *97*, 5434. Reich, H. J.; Wollowitz, S.; Trend, S. E.; Chow, F.; Wendelborn, D. F. *J. Org. Chem.* 1978, *43*, 1697.

0022-3263/83/1948-2098$01.50/0