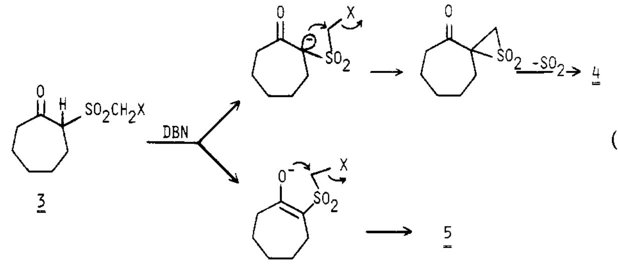
atom labeling are shown in Figure 1. The five-membered ring S–C1–O1–C7–C2 is rigorously planar, occupying the crystallographic mirror plane through $y = {}^1/_4$. The S–C2 distance is significantly shorter than S–C1, 1.727 (5) Å and 1.809 (5) Å, respectively, as a consequence of sp^2 hybridization at C2. The sulfone oxygen atoms O2 and O2′ are crystallographically equivalent, related through mirror symmetry. The six-membered ring C2–C3–C4–C5–C6–C7 is nonplanar, with C4 resting off the crystallographic mirror plane and disordered about the molecular plane. Other pertinent structural features are summarized in the figure caption.[7]

As summarized in eq 4, we suggest that reaction of **3a–c** with base generates an enolate ion which may undergo either intramolecular C-alkylation, giving an episulfone which loses sulfur dioxide affording enone **4** (Ramberg-Bäcklund reaction), or O-alkylation giving heterocycle **5**.



(4)

The preference for O-alkylation in **3b** (Cl leaving group) and C-alkylation in **3c** (I leaving group) is in accord with the hard–soft acid–base principle.[8a] The data in the table suggest that O-alkylation is also favored by polar solvents, conjugation, and conformational factors but is disfavored when the Br is on a secondary carbon (steric effects[8b]) and with smaller rings where the resultant heterocycle would be strained.

While other syntheses of α-alkylidene ketones from trimethylsilyl enol ethers have been reported[4] and a few examples of 1,3-oxathiole 3,3-dioxides are known,[9] our method should be particularly useful because of its simplicity.

Acknowledgment. We thank Professor Jon Zubieta for assistance in the determination of the X-ray structure, the National Science Foundation (Grant CHE 8303427), the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Société Nationale Elf Aquitaine, the John Simon Guggenheim Memorial Foundation (E.B.), and the National Institutes of Health (J.H.) for generous support.

Registry No. **1a**, 54730-18-6; **1b**, 59059-72-2; **1c**, 91586-90-2; **2**, 22081-48-7; **3a**, 91586-92-4; **3b**, 91586-93-5; **3c**, 91586-94-6; **4**, 3045-99-6; **5**, 91586-95-7; **6**, 91586-91-3; **7**, 91586-98-0; I (R′,R″ = $(CH_2)_4$, R = H), 3045-98-5; I (R′,R″ = $(CH_2)_3$, R = H), 1489-50-5; I (R′ = C_2H_5, R″ = CH_3, R = H), 25044-01-3; I (R′,R″ = $(CH_2)_5$, R = CH_3), 39896-78-1; I (R′,R″ = $(CH_2)_4$, R = CH_3), 7417-55-2; II (R′,R″ = $(CH_2)_4$, R = H), 91586-96-8; II (R′ = Ph, R″ = R = H), 21120-03-6; II (R′ = C_2H_5, R″ = CH_3, R = H), 91586-97-9; II (R′,R″ = $(CH_2)_4$, R = CH_3), 91586-99-1; 1-(trimethylsiloxy)-1-cyclohexene, 6651-36-1; 1-(trimethylsiloxy)-1-cyclopentene, 19980-43-9; 1-(trimethylsiloxy)-1-phenylethene, 13735-81-4; 3-(trimethylsiloxy)-2-pentene, 17510-47-3.

Supplementary Material Available: Tables of spectroscopic data and elemental analyses, atomic coordinates and temperature factors, bond lengths and angles, anisotropic temperature factors, hydrogen atom positions, and observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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[7] Crystal data: $C_7H_{10}O_3S$, $M = 174.2$; orthorhombic space group *Pcmn*; $a = 7.385$ (3) Å, $b = 7.964$ (3) Å, $c = 13.419$ (4) Å, $V = 789.2$ (6) Å^3, $d_{calcd} = 1.46$ g cm^{-3} for $Z = 4$; 643 independent reflections were collected by the θ–2θ scan technique. The structure was determined by direct methods and refined by full matrix least-squares of the positional and anisotropic thermal parameters of C, O, and S atoms and of the positional and isotropic thermal parameters of the H atoms. The final conventional discrepancy factor was 0.051, and the deviation in an observation of unit weight, 1.86.

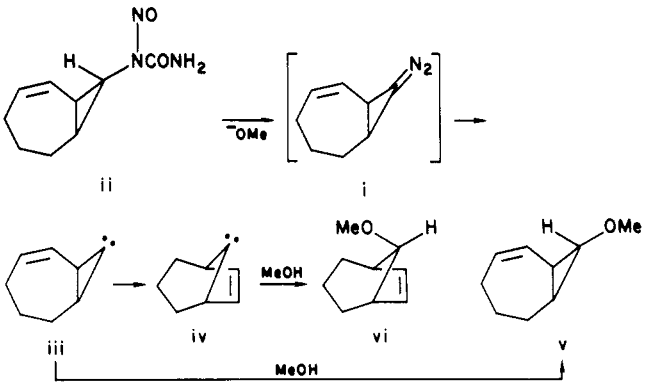
[8] (a) Ho, T.-L. "Hard and Soft Acids and Bases Principle in Organic Chemistry"; Academic Press: New York, 1977. (b) Since secondary carbons are considered *harder* than primary carbons it is necessary to invoke steric effects to explain our results.

[9] (a) Dickore, K. *Liebigs Ann. Chem.* **1964**, *671*, 135–146. 4-Phenyl-1,3-oxathiole 3,3-dioxide is formed in 46% yield on treatment of α-[(chloromethyl)sulfonyl]acetophenone with aqueous sodium hydroxide. (b) Nozaki, H.; Takaku, M.; Hayasi, Y.; Kondo, K.; *Tetrahedron* **1968**, *24*, 6563–6572. (c) Elliott, A. J. In "Comprehensive Heterocyclic Chemistry"; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: New York, 1984; Vol. 6, p 749.

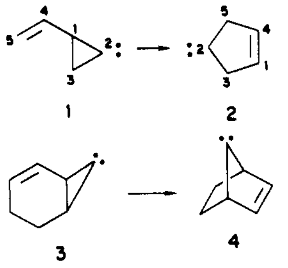
[10] Address inquiries on X-ray crystallography studies to Jon Zubieta at SUNY–Albany.

The Skattebol Rearrangement: Evidence for the Carbene to Carbene Mechanism

Summary: This paper addresses the question of whether a free vinylcyclopropylidene can rearrange to a cyclopentenylidene. A study of the decomposition of diazo intermediate i is reported. The concern is whether or not the diazo compound rearranges directly (i to iv) and/or whether iii rearranges to iv. By studying the product ratio (v/vi) as a function of [MeOH], it is concluded that iii does indeed rearrange to iv with a very low barrier of 1–4 kcal/mol.



Sir: The Skattebol rearrangement[1] is an example of a type II[2] carbene reorganization, in which the carbene center retains its identity throughout. As is seen from the two examples shown in eq 1, the reaction amounts to a sig-



(1)

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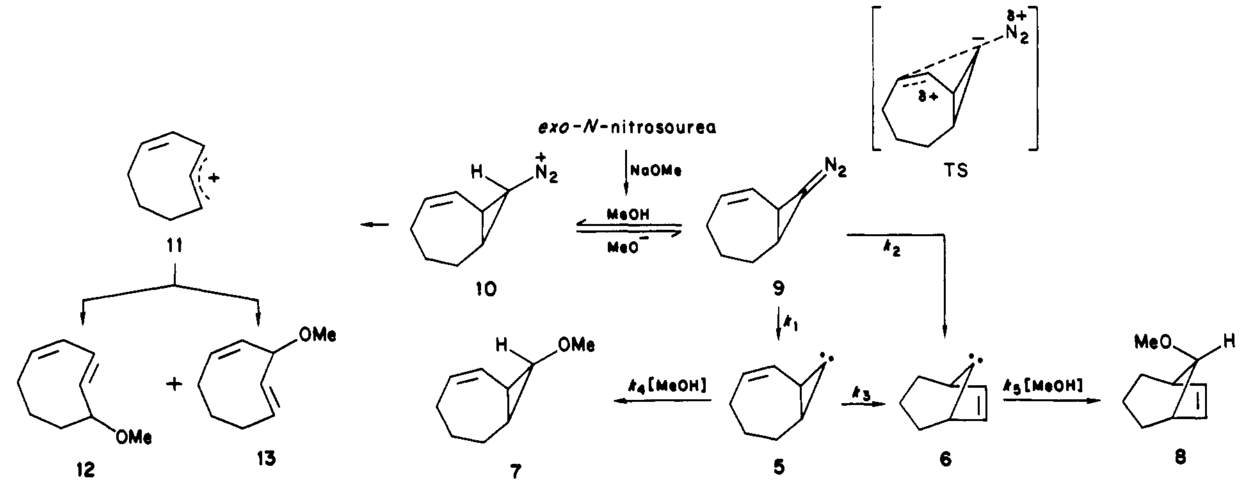
[1] Skattebol, L. *Tetrahedron* **1967**, *23*, 1107.

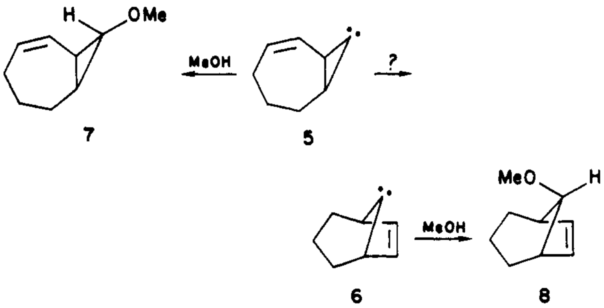
[2] Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353.

0022-3263/84/1949-3666$01.50/0

Scheme I



matropic shift of an electrophilic center. Several examples[1,3] of this process apparently proceed via carbenoids.[4] Recently, **1**[5] and **3**[6] were generated via diazo compound precursors, and both underwent the Skattebol rearrangement. In those cases, however, neither **1** nor **3** was trapped, although vinylallene, presumably derived from **1**, was produced. A third case,[7] shown in eq 2, gave products from both unrearranged (**5**) and rearranged (**6**) carbenes. This reaction thus provided a chance to test whether or not the rearrangement of **5** to **6** actually occurred.



(2)

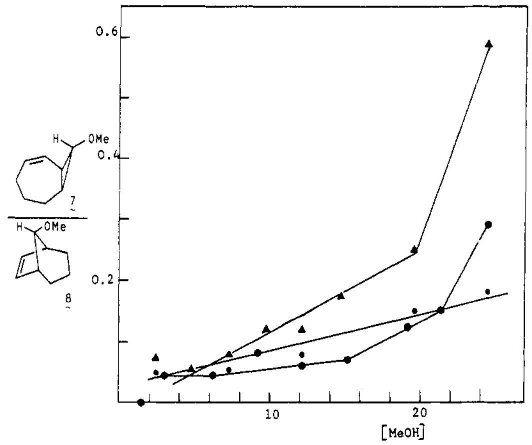


Figure 1. Product ratio (**7**/**8**) as a function of MeOH concentration in benzene/methanol mixtures at various base concentrations (room temperature). (●) NaOMe = 0.463 M; intercept = 0.018, slope = 5 × 10^{-3}, r = 0.88. (▲) NaOMe = 0.370 M; intercept = 0.015, slope = 1 × 10^{-2}, r = 0.94. (Not including 100% MeOH points for the above two). (●) NaOMe = 0.925 M; intercept = 0.011, slope = 6 × 10^{-3}, r = 0.98.

Scheme I details the mechanistic possibilities of concern here.[8] Diazo compound **9** is generated from the corresponding *exo*-nitrosourea via the action of base. Kirmse[7] showed that a weak base ($NaHCO_3$) shifted the reaction toward diazonium ion **10** and products **12** and **13** derived therefrom. At least under those conditions, no more than minor amounts of **7** and/or **8** can possibly arise from **10**. Under more strongly basic conditions (NaOMe), the products were mainly **7** and **8**. A simple kinetic analysis of the fate of **9** (steady-state assumption for **5** and **6**, and independent of any conformational equilibria in **5** or **9**) yields eq 3. Two limits are readily recognized: (1) k_3 = 0, whereby eq 3 reduces to eq 4; and (2) k_2 = 0, whereupon eq 5 results.

$$\frac{[8]}{[7]} = \left(\frac{k_3(k_1 + k_2)}{k_1 k_4}\right)\left(\frac{1}{[\mathrm{MeOH}]}\right) + \frac{k_2}{k_1} \tag{3}$$

$$\frac{[7]}{[8]} = \frac{k_1}{k_2} \text{ (if } k_3 = 0\text{)} \tag{4}$$

$$\frac{[7]}{[8]} = \frac{k_4}{k_3}[\mathrm{MeOH}] \text{ (if } k_2 = 0\text{)} \tag{5}$$

We first chose to study the reaction of **9** in MeOH/benzene solutions. Plots of the resulting data at three different NaOMe concentrations according to eq 3 or eq 5 (Figure 1) were all nonlinear, although reasonable linearity was obtained at [NaOMe] = 0.9 M (in the other cases, the proportion of **7** was greater than expected[10] in pure MeOH). Extrapolation to zero indicated a very small or zero contribution from k_2, but the nonlinearity made it impossible to precisely determine k_2. Nevertheless, the conclusion that $k_3 \neq 0$ (i.e., that the carbene–carbene rearrangement occurs) is inescapable.

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[3] (a) Baird, M. S.; Reese, C. B. *J. Chem. Soc., Chem. Commun.* **1972**, 523. (b) Baird, M. S.; Reese, C. B. *Tetrahedron Lett.* **1976**, 2895. (c) Holm, K. H.; Skattebol, L. *Ibid.* **1977**, 2347. (d) Brinker, U. H.; Fleischhauer, I. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 304. (e) Brinker, U. H.; Ritzer, J. *J. Am. Chem. Soc.* **1981**, *103*, 2116. (f) Arct, J.; Skattebol, L. *Tetrahedron Lett.* **1982**, *23*, 113.

[4] (a) Warner, P.; Change, S.-C. *Tetrahedron Lett.* **1978**, 3981. (b) Warner, P.; Chang, S.-C. *Tetrahedron Lett.* **1979**, 4141. (c) Warner, P. M.; Herold, R. D. *J. Org. Chem.* **1983**, *48*, 5411.

[5] Kirmse, W.; Van Chiem, P.; Henning, P. G. *J. Am. Chem. Soc.* **1983**, *105*, 1695.

[6] (a) Holm, K. H.; Skattebol, L. *J. Am. Chem. Soc.* **1977**, *99*, 5480. (b) Kirmse, W.; Jendralla, H. *Chem. Ber.* **1978**, *111*, 1873. (c) Kirmse, W.; Schnurr, O.; Jendralla, H. *Ibid.* **1979**, *112*, 2120.

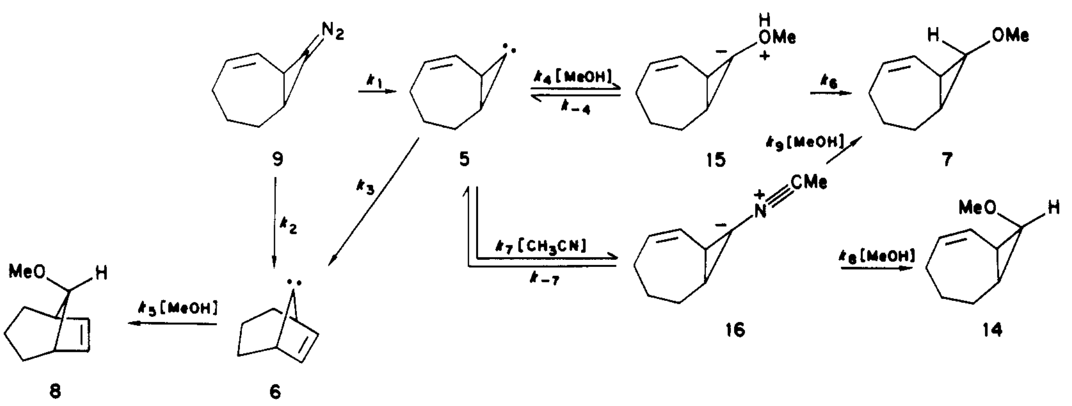
[7] Kirmse, W.; Richarz, U. *Chem. Ber.* **1978**, *111*, 1883.

[8] That a diazocyclopropane may directly rearrange to a product (with N_2 loss) has previously been considered by Jones.[9]

[9] Jones, W. M.; Walbrick, J. M. *J. Org. Chem.* **1969**, *34*, 2217.

[10] We do not yet understand this effect.

Scheme II



Because we suspected that the curvature was due to the change in solvent polarity[9] (benzene vs. methanol), we decided to use a cosolvent of nearly equal polarity to methanol (ϵ 32), namely, CH$_3$CN (ϵ 37). When **9** was generated in MeOH/CH$_3$CN (25 °C, [NaOMe] = 0.46 M), however, a new product, shown[11] to be *endo*-methoxide **14**, was formed (the overall yields, although not constant, were nearly so). This development required the analysis of a more complex kinetic situation, depicted in Scheme II. Based on the steady-state assumption for **5**, **6**, **15** and **16**, eq 6 and 7 were derived.

$$\frac{7}{14} = \left(\frac{k_9}{k_8}\right) + \left(\frac{k_4k_6k_{-7}}{k_7k_8(k_{-4}+k_6)}\right)\left(\frac{1}{[\mathrm{CH_3CN}]}\right) + \left(\frac{k_4k_6(k_8+k_9)}{k_7k_8(k_{-4}+k_6)}\right)\left(\frac{[\mathrm{MeOH}]}{[\mathrm{CH_3CN}]}\right) \qquad (6)$$

$$\frac{7+14}{8} = \left\{\frac{k_4k_6}{k_{-4}+k_6}[\mathrm{MeOH}] + \frac{k_7(k_8+k_9)[\mathrm{MeOH}][\mathrm{CH_3CN}]}{k_{-7}+(k_8+k_9)[\mathrm{MeOH}]}\right\} \Big/ \left\{\frac{k_2}{k_1}k_3 + \frac{k_4k_6}{k_{-4}+k_6}[\mathrm{MeOH}] + \frac{k_7(k_8+k_9)[\mathrm{MeOH}][\mathrm{CH_3CN}]}{k_{-7}+(k_8+k_9)[\mathrm{MeOH}]} + k_3\right\} \qquad (7)$$

Nonlinear least squares analysis of the eq 5 data points obtained for the **7**/**14** ratio gave a fit to eq 6 if (a) $k_9 = 0$ (rmsd = 0.061), whence $k_{-7}/k_8 = 3.5 \pm 0.8$, and $k_4/k_7 = 0.86 \pm 0.1$; or (b) $k_{-7} = 0$ (rmsd = 0.061), whence $k_9/k_8 = 0.16 \pm 0.04$, and $k_4/k_7 = 0.85 \pm 0.04$. Note that either analysis indicates that **5** reacts with MeOH only about 85% as fast as it reacts with CH$_3$CN.[12]

Similar analysis of the (**7** + **14**)/**8** ratio (seven data points) is severely hampered by the fact that the ratio changes only very slightly upon altering the [MeOH]/[CH$_3$CN] (since both solvents are reactive). One can try to fit eq 7 to either condition a or b above. Given that k_2/k_1 was already seen to be small in benzene/methanol, condition b provides a more reasonable fit for eq 7. A perhaps better approach is to take $k_2 = 0$,[16] and then see how the derived equations fit either condition a (eq 8) or b (eq 9). The results (eq 8, rmsd = 0.049, $k_7/k_3 = 0.014$

$$\frac{7+14}{8} = \left(\frac{k_7}{k_3}\right)\left(\frac{[\mathrm{MeOH}][\mathrm{CH_3CN}]}{3.5+[\mathrm{MeOH}]}\right) + 0.86[\mathrm{MeOH}] \qquad (8)$$

$$\frac{7+14}{8} = \frac{k_7}{k_3}[\mathrm{CH_3CN}] + 0.85[\mathrm{MeOH}] \qquad (9)$$

± 0.001; eq 9, rmsd = 0.013, $k_7/k_3 = 0.0127 \pm 0.0002$) clearly show a better fit for condition b.

The following conclusions may be drawn: (1) The carbene–carbene rearrangement (**5** to **6**) is operative in the two sets of solvents used. (To our knowledge, this is the first time the diazo rearrangement mechanism (e.g., **9** to **6**) has been ruled out as the sole mechanism.)[17] (2) The diazo rearrangement mechanism is minor to nonexistent in benzene/methanol, and possibly, but not conclusively so, in methanol/acetonitrile. (3) The best analysis of the data gives $k_3/k_4 = 94 \pm 4$. Since reaction with methanol probably occurs at a rate near the diffusion-controlled limit[15] of 2×10^{10} M^{-1} s^{-1}, $k_3 \approx 10^{10}$–10^{12} s^{-1}, which gives $\Delta G^{\ddagger} \cong$ 1–4 kcal/mol for the Skattebol rearrangement. This compares with an admittedly high theoretical estimate of 13.8 kcal/mol.[19]

Acknowledgment. We thank Professor James Espenson for help with the computer kinetic analyses.

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[11] Ethers **14** and **7** were independently synthesized by the reaction of ClCH$_2$OMe/LiI/BuLi with 1,3-cycloheptadiene; the synthetic mixture had the same GC and GC–MS properties (including coinjection) as the product mixture.

[12] The kinetic analysis requires specific interaction of **5** with CH$_3$CN, but is ylide **16** necessary? The possibility that CH$_3$CN merely acted as a base (to deprotonate **15**) was excluded by the use of several other bases, including diisopropylethylamine, none of which led to any **14**. 7-Norcaranylidene,[13] generated as was **5**, also gave endo methoxide only in the presence of CH$_3$CN. In this case, trapping[14] of the nitrile ylide with acrylonitrile was effected, although the adducts have not yet been fully characterized (the two carbene adducts were also obtained). An important point is that our data require that **5** reacts 1.2 times faster with CH$_3$CN than with MeOH; in contrast, fluorenylidene reacts some 400 times slower with CH$_3$CN than with MeOH.[15] It is possible that the greater electrophilic character of **5** leads to its greater reactivity with CH$_3$CN, and that reactivity with CH$_3$CN is more sensitive to carbene electrophilicity than is reactivity with MeOH.

[13] Kirmse, W.; Jendralla, H. *Chem. Ber.* **1978**, *111*, 1857.

[14] Kende, A. S.; Hebeisen, P.; Sanfilippo, P. J.; Toder, B. H. *J. Am. Chem. Soc.* **1982**, *104*, 4244.

[15] Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833.

[16] From deuterium isotope effect studies, we also know that $k_{-4} \ll k_6$ at room temperature.

[17] Additional evidence that **5** to **6** occurs was obtained in *t*-BuOH. Here the ratio of unrearranged to rearranged products decreased by a factor of 6 relative to MeOH. Others[18] have found a factor of 8 difference between the reactivity of MeOH and *t*-BuOH. If this factor is correct for carbene **5**, then ~95% of the rearrangement to **6** proceeds through **5**, and 5% is direct (k_2); 5% is probably the maximum contribution from k_2.

[18] Bethell, D.; Newall, A. R.; Wittaker, D. *J. Chem. Soc. B.* **1971**, 23.

[19] Schoeller, W. W.; Brinker, U. H. *J. Am. Chem. Soc.* **1978**, *100*, 6012.

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