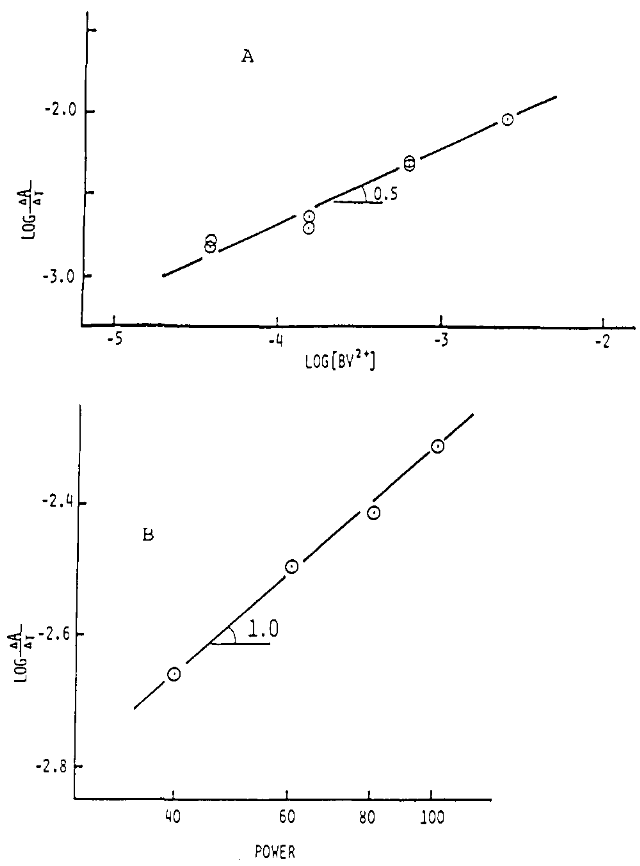

Figure 3. Logarithmic dependences of the rate of reduction on BV^{2+} concentration (A) and plasma power (B).

bromides of methyl-, *n*-propyl-, *n*-hexyl-, and *n*-laurylviologens both as solid or solvated samples even with 10 min of exposure to the plasma at 100 W.

The interesting feature here is that the spontaneous reduction occurs in the plasma-exposed DMF solution of BV^{2+} after the plasma is quenched. Thus, the absorbance of BV^{2+} in DMF (2.4 $\times$ 10^{-3} M), exposed to the plasma for 60 s at 100 W, increased ca. 8 times when the solution was held for 60 min at room temperature in vacuo. The reduction also took place when BV^{2+} was mixed with DMF that had been exposed to the plasma a few days prior to mixing. It was also found that plasma-exposed DMF is capable of initiating polymerization when vinyl monomers such as acrylamide, 2-hydroxyethyl methacrylate, or methacrylic acid are mixed instead of BV^{2+}. Gas chromatograms of plasma-exposed DMF showed no evidence of reaction product. These experimental facts imply that the reaction species generated by the act of the plasma are sufficiently long lived so as to induce "postreduction" and "postpolymerization" in DMF.

At present DMF and hexamethylphosphoramide are the only solvents in which the formation of the cation radical has been observed. No reduction of BV^{2+} occurs in Me$_2$SO, dioxane, acetonitrile, or water. Only frozen water exhibited the pale blue color of the cation radical at the surface when exposed to the plasma. The color, however, paled rapidly upon melting, presumably due to reoxidation via a back-electron transfer reaction.

The mechanism of the reduction under the effects of a low-pressure plasma has not been determined. However, the reduction is considered to occur by reaction with energetic electrons in the plasma directly at the gas-liquid interface, since the plasma penetrates only a few microns below most surfaces. It may also be possible that the reduction proceeds via solvated electrons which then transfer to BV^{2+} in DMF.

The results suggest not only a new method for quantitative studies of complicated elementary processes in plasma reactions but also provide a novel reducing intermediate for a variety of chemical reactions, including the production of hydrogen gas from water.

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Registry No. BV^{2+}·2Cl$^-$, 1102-19-8; BV^{+}·Cl$^-$, 77938-64-8; poly(xylylviologen dichloride), 81534-71-6; acrylamide, 79-06-1; 2-hydroxyethyl methacrylate, 868-77-9; methacrylic acid, 79-41-4; 4,4'-bipyridinebis-(chloromethyl)benzene copolymer, 81388-55-8.

Thermal Rearrangements of Encumbered Methylenecyclobutanes. 1. 6-Methylenebicyclo[3.2.0]heptane

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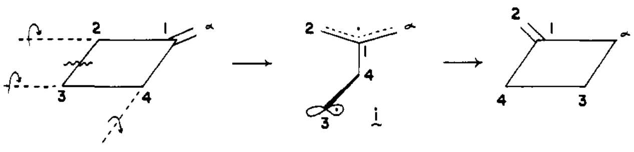
Upon being heated, methylenecyclobutanes undergo [1,3] sigmatropic rearrangements,[2-5] one-center epimerizations,[3-5] [2 + 2] cycloreversions,[6] and perhaps other reactions. This rich chemistry has been reviewed by Gajewski,[7] who earlier proposed[8] meshed conrotatory-bevel motions for the preferred manner of ring opening (eq 1). If these motions lead directly to [1,3] rearrangement as shown, C$_3$ will have migrated over the C$_2$–C$_1$–C$_\alpha$ allylic framework suprafacially (S) and with configurational inversion (I). Even though this SI combination constitutes one allowed[9,10] pathway, the measured activation parameters[2] and MINDO/2 calculations[13] for the degenerate rearrangement of the parent implicate a diradical intermediate or transition state such as i.



(1)

We report the thermal behavior of some encumbered bicyclic methylenecyclobutanes **1** which incorporate three useful structural features: the two allylic bonds (C$_1$–C$_5$, C$_1$–C$_7$) are distinct; [1,3] migration may only occur from cleavage of one of these (C$_1$–C$_7$), and in that event, the migrating C$_1$ can only move from C$_7$ to C$_\alpha$ with retention of configuration.

Compound **1a** is prepared[14] by Wittig methylenation of ketone

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[1] In part abstracted from Leber, P. A. Ph.D. Dissertation, University of New Mexico, Albuquerque, NM, 1981.

[2] Doering, W. von E.; Gilbert, J. C. *Tetrahedron Suppl. 7* **1966**, *22*, 397.

[3] Flowers, M. C.; Gibbons, A. R. *J. Chem. Soc. B* **1971**, 362.

[4] (a) Doering, W. von E., presented at the 21st National Organic Symposium, 1969. (b) Fossel, E. Ph.D. Dissertation, 1970, Harvard University, Cambridge, MA.

[5] (a) Baldwin, J. E.; Fleming, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 5249. (b) Baldwin, J. E.; Fleming, R. E. *Ibid.* **1973**, *95*, 5256. (c) Baldwin, J. E.; Fleming, R. E. *Ibid.* **1973**, *95*, 5261.

[6] Chesick, J. P. *J. Phys. Chem.* **1961**, *65*, 2170.

[7] Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; pp 90–94.

[8] Gajewski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 5254.

[9] Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim, 1970; pp 114 ff.

[10] The other is antarafacially with configurational retention (AR). The rare or unknown antarafacial mode might be particularly facile in this system;[11,12] however, see footnote 6 of ref 8.

[11] Berson, J. A. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, p 375.

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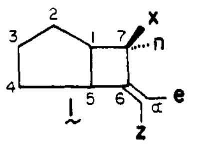
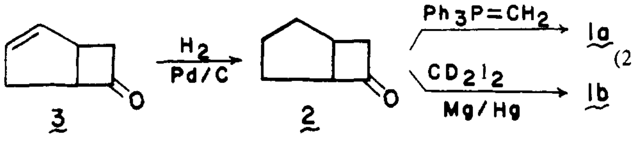


a, X = n = e = z = H
b, X = n = H; e = z = D
c, X = n = D; e = z = H

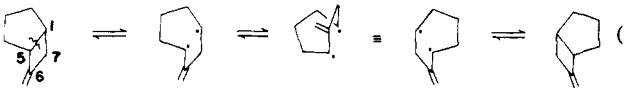
2, itself the product of catalytic hydrogenation of the known[15] dechlorinated adduct (**3**) of cyclopentadiene and dichloroketene[16] (eq 2). Optically active **1a** (**1a***) is obtained analogously, beginning with **3*** enantiomerically enriched after recovery from treatment with $^1/_2$ equiv of (+)-α-phenylethylamine.[17] Deuterated derivative **1b** is also prepared from **2**, but to avoid scrambling,[2] the Bertini[18] procedure is used. After purification by preparative gas chromatography (GC) **1a** (and **1a***) and **1b** have C/H analyses and spectral parameters[19] in accord with their assigned structures. Ozonolysis of **1a** (**1a***) affords **2** (**2***).



(2)

Pyrolyses were carried out at 320 ± 0.5 °C in the gas phase (pressure up to 275 ± 5 torr with N_2) in a well-seasoned Pyrex static reactor. Racemic **1a** is recovered unchanged (≥98% by analytical GC) after 24 h. However **1a*** racemizes and **1b** automerizes to **1c** under these conditions. The former reaction is followed by examining the molar ellipticity[20] of **2***, formed by microozonolysis of recovered **1a***, and comparing the values to that of **2*** prior to methylenation and pyrolysis.[21] The latter reaction is followed by measuring the growth of the vinyl signals of **1c** in the ^{1}H NMR spectrum. Table I presents the data.

Both reactions obey first-order approach-to-equilibrium kinetics. Racemization, with $(k_1 + k_{-1})_{\text{rac}} = (5.41 \pm 0.18)^{22} \times 10^{-5}\ \text{s}^{-1}$, is faster than automerization, with $(k_1 + k_{-1})_{\text{aut}} = (1.45 \pm 0.20)^{22} \times 10^{-5}\ \text{s}^{-1}$, by a factor of 3.7.[23] We attribute racemization to C_1–C_5 cleavage, followed by ring-flip, and C_1–C_5 rebonding with configurational inversion of both carbons (eq 3). Although such ring inversions have been observed before in more strained bicyclic systems,[27] this constitutes the first demonstration of a two-center epimerization of a methylenecyclobutane of which we are aware.[28] Our experiment does not identify the rotational senses of the inversion, but models show C_6–C_5/C_7–C_1 disrotation is sterically preferable to pure conrotation or a severely restrained conrotatory-bevel process.



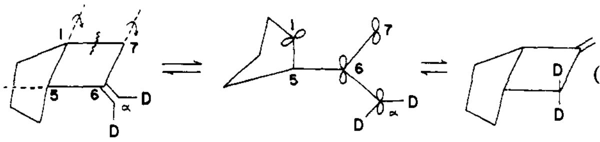
(3)

Table I. Experimental Data for Racemization (1a*) and Automerization (1b) at 320 °C in the Gas Phase

pyrolysis time, s	racemization, 1a* ($[\theta]_{310.5}$[a,b] of **2***)	automerization, 1b ⇌ 1c	
		v[c,d]	b[e,d]
0	1033 ± 10	3.06 ± 1.48	64.7 ± 0.6
3 600	823.0 ± 8.0	7.31 ± 0.85	71.4 ± 1.1
7 200	676.6 ± 9.0	12.7 ± 3.3	64.7 ± 2.9
14 400		16.1 ± 0.8	64.1 ± 2.1
20 700	332.9 ± 6.6		
32 400		27.4 ± 2.8	65.7 ± 2.4
[∞]	0[f]	38.6[g]	38.3[g]

[a] Molar ellipticity (deg $\text{cm}^2\ \text{dmol}^{-1}$) from the circular dichroism spectra of **2*** prepared from recovered 1a*; see text. [b] Uncertainties are estimated as 1–2% from the instrument specifications. [c] Integration (arbitrary units) of vinyl hydrogens at C_α of 1c + 1b. [d] Uncertainties are the average deviations of at least three separate integrations. [e] Integration (arbitrary units) of bridgehead hydrogen at C_5 used as an internal standard. [f] Assumed. [g] An independent measurement from a single pyrolysis at 360 °C for 5 days. Neglecting the 2 °C deuterium isotope effect and assuming K_{eq} for 1b ⇌ 1c = 1.00 make no difference in $(k_1 + k_{-1})_{\text{aut}}$.

We suggest automerization occurs via C_1–C_7 cleavage and migration of C_1 to C_α (eq 4). This reaction, which can occur by a restricted (in that C_1 must move with retention) conrotatory-bevel pathway, is slower by only a factor of ca. 5 than automerization of methylenecyclobutane itself[2] at the same temperature.



(4)

There is no doubt that fruitful bond cleavages in small rings must include rotational components in the vibrational mode leading to rupture.[29] We suggest that our results show that even if the meshed conrotatory-bevel motions are those favored for an unencumbered methylenecyclobutane ring-opening, they are not very different energetically from other rotational senses and combinations.

In due course we will report on the thermal reactions of several monomethyl and dimethyl derivatives of **1a**.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. R.W.H. thanks Professors Jerome A. Berson, William von E. Doering, and Joseph J. Gajewski for helpful discussions and records his special appreciation to the latter two, who each hosted half of his sabbatical year.

Registry No. 1a, 3642-22-6.

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(14) **1a** has been obtained previously (by a route unsuitable for our purposes), but no physical properties were reported: Lukas, J. H.; Kouwenhoven, A. P.; Baardman, F. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 709.

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(17) Huber, U. A.; Dreiding, A. S. *Helv. Chim. Acta* **1970**, *53*, 495.

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(19) **1a**: IR (neat, NaCl) 3070, 2950, 2855, 1670, 875 cm^{-1}; ^{1}H NMR (CDCl_3) δ 4.7 (2 H, m), 3.2 (1 H, br s), 2.7 (2 H, m), 2.0 (1 H, m), 1.6 (6 H, m); ^{13}C NMR (CDCl_3) δ 153.72 (s), 105.64 (t), 48.05 (d), 35.13 (t), 34.08 (d), 33.34 (t), 32.87 (t), 24.45 (t). **1b** shows the expected differences, and by ^{1}H NMR appears to be ≥98% deuterated.

(20) Computed from the circular dichroism spectra measured by a JASCO J-40C spectropolarimeter interfaced with a PDP-11 minicomputer. We thank the National Science Foundation for partial support (CHE 76-05684) toward the purchase of this instrument and Professor F. Allen and W. Rahe for their assistance.

(21) A control experiment established that racemization does not attend these chemical steps.

(22) The uncertainty quoted is 2σ of the slope of the least-squares line (95% confidence level).

(23) Remarkably close to a value of 4.1 calculated by assuming that the relative rate depends only on $\Delta\Delta H_f°$ of the two hypothetical diradicals (eq 3, 4) if each $\Delta H_f°$ is estimated by using the Benson[24] approach, corrected[25] values for several parameters, and the known[26] $\Delta H_f°$'s of ethylcyclopentane and cycloheptane. Details will be presented in the full paper.

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(28) Found absent in one system[4b] and not detectable by the analysis method in another.[5]

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