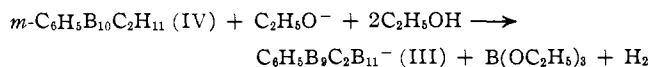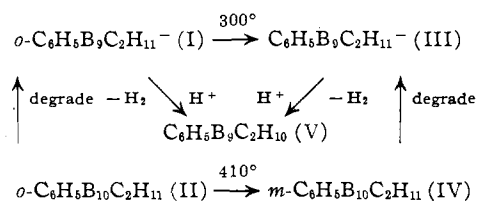were identical. The basic degradation reaction of IV to III was accomplished with ethanolic potassium hydroxide in an autoclave at 200° for 10 hr.

$$m\text{-}C_6H_5B_{10}C_2H_{11}\ (IV) + C_2H_5O^- + 2C_2H_5OH \longrightarrow$$
$$C_6H_5B_9C_2H_{11}^-\ (III) + B(OC_2H_5)_3 + H_2$$

A 60% yield of III was obtained as its cesium salt. *Anal.* Calcd. for $CsB_9C_8H_{16}$: B, 28.44; H, 4.71; C, 28.06. Found: B, 28.15; H, 4.78; C, 27.97. The infrared spectrum of cesium–III contained characteristic absorption bands at 3.98 (s), 7.93 (m), 8.96 (m), 10.22 (m), 11.86 (m), 13.40 (w), 13.62 (m), 13.88 (m), and 14.17 μ (s). The 19.3-Mc./sec. ^{11}B n.m.r. spectrum of III is complex, but has the over-all appearance of three doublets centered at 4.70, 22.5, and 35.3 p.p.m. from boron trifluoride diethyl etherate, with splittings of 130, 130, and 141 c.p.s., respectively. Treatment of III with polyphosphoric acid under an atmosphere of 500 mm. of nitrogen at 135° produced the recently reported[3] C-phenyldicarbaundecaborane-(11) (V) in 54% yield. The carborane product was identified by its characteristic infrared and ^{11}B n.m.r. spectra and melting point.

The cesium salt of I, when fused *in vacuo* at 300°, produced III in virtually quantitative yield after 3 hr. Purification was accomplished by recrystallization from water. The cesium–III produced by this route was identical with III obtained by degradation of IV as shown by infrared and ^{11}B n.m.r. spectra and X-ray powder diagrams. All interconversions are presented below.

$$o\text{-}C_6H_5B_9C_2H_{11}^-\ (I) \xrightarrow{300°} C_6H_5B_9C_2H_{11}^-\ (III)$$

degrade $-H_2$ ↑　↘ H^+　H^+ ↙ $-H_2$　↑ degrade
$$C_6H_5B_9C_2H_{10}\ (V)$$

$$o\text{-}C_6H_5B_{10}C_2H_{11}\ (II) \xrightarrow{410°} m\text{-}C_6H_5B_{10}C_2H_{11}\ (IV)$$

If the basic degradation reactions of II and IV proceed without motion of the two carbon atoms relative to each other, III might reasonably be described as an 11-particle icosahedral fragment with the two carbon atoms in the periphery of the pentagonal face, separated by a boron atom. Conversion of I and III to the carborane V strengthens the view[3] that the carbon atoms of V are separated and that the conversion of I to V proceeds with motion of the carbon atoms relative to each other.

The thermal rearrangement of I to III may involve an 11-particle cuboctahedral fragment as an intermediate or transition state analogous to the pathway suggested[4] for the rearrangement of *o*- to *m*-dicarbaclovododecaborane(12).

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(3) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 4222 (1964).

(4) (a) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963); (b) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962).

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Stepwise Mechanisms in the Oxy-Cope Rearrangement[1]

Sir:

A comparison of the behavior on pyrolysis of 2-*exo*-vinyl-2-*endo*-hydroxybicyclo[2.2.2]octene (**6a**)[2] and *syn*-7-vinyl-*anti*-7-hydroxynorbornene (**13**) with that of their respective epimers **5a** and **14** provides some insight into the mechanisms of the oxy-Cope rearrangements.[3] The products shown here from such experiments are derived from gas phase pyrolyses in evacuated vessels at 320°, although the distributions are rather insensitive to temperature and to large increases in surface–volume ratio. The indicated figures refer to percentages of volatile materials as determined by vapor chromatographic areas.
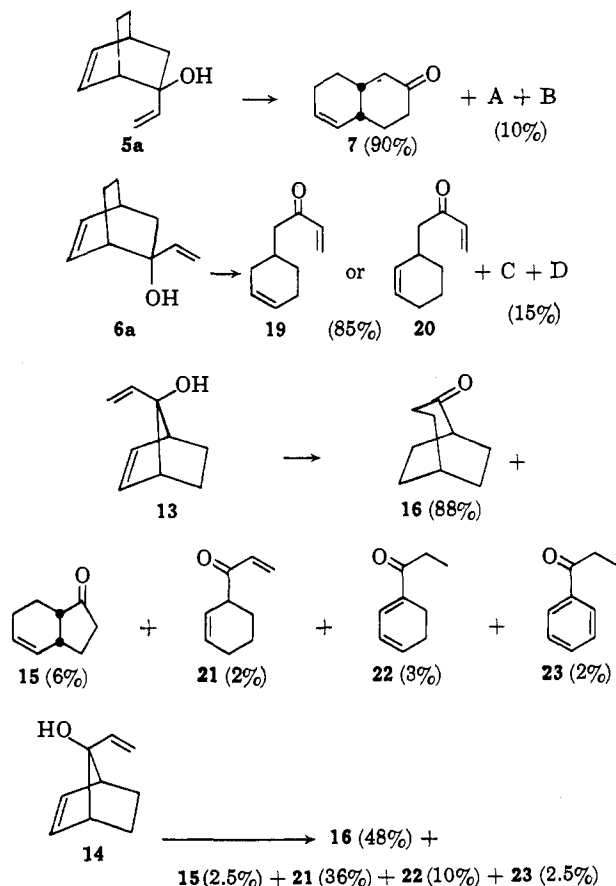
Grounds for the assignments of structure to products **7, 15,** and **16** have already been given.[3] Structure

(2) The formula numbers correspond to those of the accompanying paper.[3]

(3) J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.*, **86**, 5019 (1964).

19 or 20[4] is now assigned to the major product from 6a, and structures 21,[4] 22,[4] and 23 to the minor products from 13 and 14 by spectra and by hydrogenation or dehydrogenation to known compounds. Compound 22 may not be formed directly from 13 and 14, since, astonishingly, it is the major product of the pyrolysis of 21.

The four minor products A and B from 5a and C and D from 6a have not yet been identified.

The rearrangements of the vinylnorbornenols 13 and 14 are readily formulated as stepwise processes passing over the conformationally isomeric diradical intermediates 24 and 25. The rate-determining step presumably is C-1–C-7 bond cleavage in both cases, with no kinetic assistance being provided by incipient C-9–C-3 bond formation, even in the *syn*-vinyl isomer 13. Consistent with this picture is the observation that the rates of rearrangement of 13 and 14 are virtually the same; after incomplete conversion to products, starting material recovered from pyrolysis of a mixture of 68.6% of 13 and 31.4% of 14 consists of 69.5% of 13 and 30.5% of 14. Rotation about the C-4–C-7 bond interconverts the two systems. Since substantial amounts of cross-products are observed, the rotation must be competitive in rate with cyclization (by C-1–C-9 closure to give single-inversion product 16 and by C-3–C-9 closure to give double-inversion product 15 and hydrogen transfer (O to C-1 and/or C-4 to C-1 to give 21 or its enol).
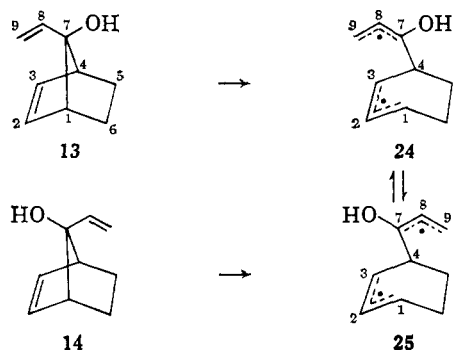
At first glance, the rearrangement of the *endo*-vinylbicyclo[2.2.2]octanol 5a, which occurs with highly efficient formation of double-inversion product 7, seems to behave so differently from 13 as to suggest the emergence of a concerted Cope process. Furthermore, models indicate that the ends of the hexadiene system of 5a can approach more closely than those of 13 and about as closely as those of other biallyls, for example, methacrolein dimer[5] and 8-hydroxy-*endo*-dicyclopentadiene,[6] which undergo smooth Cope rearrangements. At least the latter example surely is concerted, since its rate is much faster than that of the *exo* isomer,[7] in which such a process is sterically prohibited. The boat-like six-center transition state for the Cope rearrangement is derivable from a conformation that 5a can approximate with ease. Although unfavorable with respect to the chair-like four-center one by at least 6 kcal./mole,[8] the boat still must be a lower-energy state than that leading to cleavage

into two allyl radicals.[9] Experience[6–8,11] suggests that when the boat array or even an approximation to it is sterically accessible, the concerted process is preferred over the stepwise one. Nevertheless, we believe that the rearrangement of 5a is stepwise. Starting material from incomplete pyrolyses of mixtures of 5a and 6a at three temperatures is recovered with essentially no change in composition. Thus, the rate of rearrangement of 5a is virtually the same as that of 6a, where the concerted Cope process is sterically impossible.[12] Rearrangement of 5a is initiated by C-1–C-2 bond cleavage to give diradical 26, rotationally isomeric with that (27) derived from 6a. Cyclization at C-5–C-10 in 26 to give 7, and hydrogen transfer (O to C-5, or C-3 to C-1) in 27 to give 19 or 20, are rapid compared to 26 ⇌ 27 interconversion by rotation about the C-2–C-3 bond; this insulates the two systems and accounts for the high specificity.
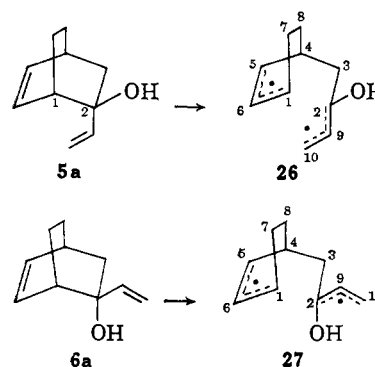
The preference for the stepwise path in the rearrangement of 5a is probably attributable, at least in part, to the perturbation introduced by the hydroxyl group. This would lower the activation energy for both the concerted six-center mechanism[13] and for the diradical cleavage to 26, but the latter transition state, involving more localized distribution of the electrons from the breaking bond, would be energetically more responsive to appropriately situated substituents. That is, the major effect of the hydroxyl would be to weaken the central bond of the biallyl system. In general, the two activation energies would converge, and it would not be unreasonable to expect that, as seems to be the case with 5a, their difference might actually change sign.

(9) W. von E. Doering and V. Toscano in unpublished work, cited by W. von E. Doering, Reaction Mechanisms Conference, Corvallis, Ore., June, 1964, estimate the activation energy for the biallyl rearrangement (presumably *via* the chair-transition state) as 36 kcal./mole and for the biallyl cleavage as at least 46 kcal./mole, a value substantially higher than the figure 31 kcal./mole reported in the literature[10] as the activation energy for over-all disappearance of biallyl. The minimum value for 46 kcal./mole is subject to the reservation of its authors that if the purely thermal cleavage is accompanied by radical-chain processes, further upward revision will be required.

(10) D. J. Ruzicka and W. A. Bryce, *Can. J. Chem.*, **38**, 827 (1960).

(11) G. S. Hammond and C. D. de Boer, *J. Am. Chem. Soc.*, **86**, 899 (1964); (b) D. J. Trecker and J. P. Henry, *ibid.*, **86**, 902 (1964).

(12) The formal alternative that both 5a → 7 and 6a → 19 or 20 are concerted requires fortuitous correspondence of both rates and activation energies. We consider this possibility remote.

(13) Conjugating substituents accelerate the concerted (presumably four-center) rearrangement: (a) E. G. Foster, A. C. Cope, and F. Daniels, *J. Am. Chem. Soc.*, **69**, 1893 (1947); (b) G. R. Aldridge and G. W. Murphy, *ibid.*, **73**, 11 (1951).

(4) Elemental analysis confirms the composition.

(5) R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2198 (1961).

(6) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(7) R. C. Cookson, N. S. Isaacs, and M. Szelke, *ibid.*, **20**, 717 (1964).

(8) W. von E. Doering and W. R. Roth, *ibid.*, **18**, 67 (1962).

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