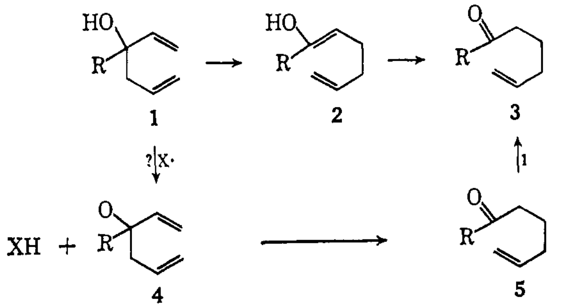
distance in the molecule. The unexpected conformation of the cyclohexadienone ring (shallow boat) may result from crystal packing forces transmitted at this contact point. No intermolecular hydrogen bonds exist in the crystal since the shortest intermolecular oxygen–oxygen distance [O(6)–O(6′)] is 3.71 Å.

Communications to the Editor

The Oxy-Cope Rearrangement. Evidence for an Intramolecular Mechanism and an Enolic Intermediate[1]

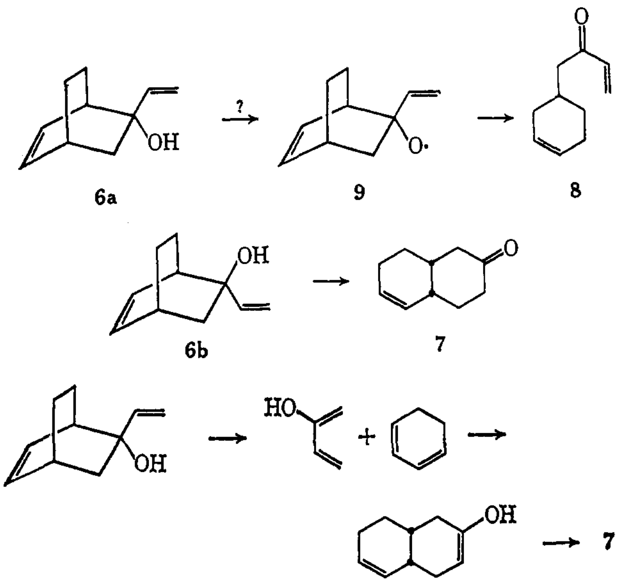
Sir:

The thermal rearrangements of 3-hydroxy-1,5-hexadienes (oxy-Cope rearrangements[2–4]) give unsaturated ketones as final products, hypothetically[2–4] by way of enolic intermediates **1** → **2** → **3**.



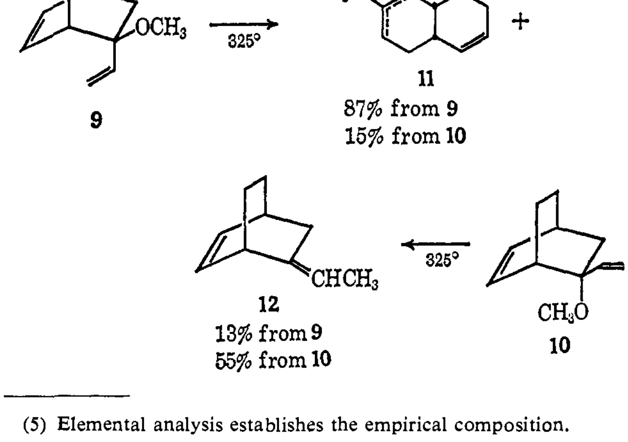
Alternatives to this scheme that have not been excluded rigorously include a mechanism in which hydrogen abstraction from the hydroxyl group, rearrangement (either concertedly or by β-eliminative fragmentation–recombination) of the resulting alkoxy radical (**4** → **5**), and abstraction from a second molecule of **1** would produce **3** and propagate a radical chain. This mechanism also would account for the hydrogen transfer products observed[2] when the two ends of the biallyl system are held remote from each other, as in 2-*exo*-vinyl-2-*endo*-hydroxybicyclo[2.2.2]oct-5-ene (**6a**). Although pyrolysis of the *endo* isomer **6b** gives largely the oxy-Cope rearrangement product **7**,[2] **6a** gives a substantial quantity of hydrogen-shifted monocyclic ketone **8**,[2] which might conceivably arise from β scission of a hypothetical 2-*exo*-vinyl-2-*endo*-alkoxy radical (**9**).

A second alternative mechanism for some of the observed[2] rearrangements is Diels–Alder retrogression–recombination. Although the hypothetical 2-hydroxy-1,3-butadiene intermediate might be expected to be unstable with respect to its tautomer, methyl vinyl ketone, the hydroxydiene is generated from pyrolysis in the vapor phase and therefore might very well survive long enough to be captured by cyclohexadiene before ketonization.



The present work in showing that 3-*methoxy*-1,5-hexadienes rearrange thermally to *enol ethers* provides strong presumptive evidence against the radical chain mechanism. Further experiments demonstrate the strict intramolecularity of the process and thereby eliminate the retro-Diels–Alder mechanism.

The epimeric ethers **9**[5] and **10**[5] are prepared from the corresponding alcohols[2] by successive treatment with potassium and methyl iodide. Identified in the mixture from gas-phase pyrolysis of either epimer are the



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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[2] J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.*, **86**, 5017, 5019 (1964).

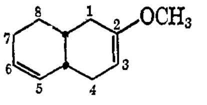
[3] (a) A. Viola and L. Levasseur, *ibid.*, **87**, 1150 (1965); (b) A. Viola, E. J. Iorio, K. K. Chen, G. M. Glover, U. Nayak, and P. J. Kocienski, *ibid.*, **89**, 3462 (1967).

[4] (a) E. Urion, *Ann. Chim.*, **1**, 5 (1934); (b) M. J. Wiemann and S.-L. T. Thuan, *Compt. Rend.*, **246**, 2903 (1958); (c) J. Chuche and J. Wiemann, *ibid.*, **262**, 567 (1966); (d) E. Brown, P. Leriverend, and J. M. Conia, *Tetrahedron Letters*, 6115 (1966); (e) for a comparable rearrangement of a 3-hydroxy-1-en-5-yne, see J. W. Wilson and S. A. Sherrod, Abstracts of Papers, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. S146; *Chem. Commun.*, 143 (1968).

[5] Elemental analysis establishes the empirical composition.

product from methoxy-Cope rearrangement (**11**),[5] that from a retro-ene reaction[6] (**12**),[5] and, especially in the case of the *exo*-vinyl ether **10**, one of those from a retro-Diels–Alder reaction (1,3-cyclohexadiene). Other so far unidentified volatile products also occur in the pyrolysis of **10**. The material balance in both pyrolyses is 90–100%.

The vinyl ether expected from methoxy-Cope rearrangement of **9** is 2-methoxy-$\Delta^{2,5}$-hexalin (**13**). It is a matter of little interest but some nuisance that in normal work-up from pyrolysis this material is accompanied by its double bond isomer **14**, with which it readily equilibrates upon treatment with a trace of *p*-toluenesulfonic in decalin or upon vapor chromatography. The equilibrium mixture can be approached from either side and contains 12% **13** and 88% **14**. Mild acidic hydrolysis of the equilibrium mixture or a 60:40 mixture gives only the known[2] *cis*-Δ^5-octalone-2 (**7**). The presence of an enol ether function is further confirmed by the infrared (6.0 μ) and nuclear magnetic resonance (nmr) (δ 4.4 ppm, broadened doublet, *J* = 3.5 Hz) spectra of the equilibrium mixture.



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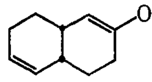

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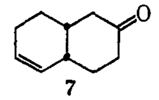


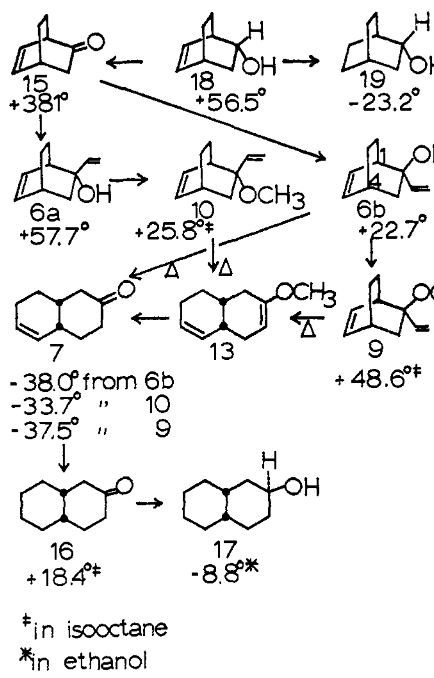
7

The structure of diene **12** is suggested by concordant spectral properties and by comparison with 2-ethylidenebicyclo[2.2.2]oct-5-ene (**12**), independently synthesized by the action of triphenylphosphonium ethylide on bicyclo[2.2.2]oct-5-en-2-one and hydrogenated to 2-ethylbicyclo[2.2.2]octane.[7]

Neither of the enol ethers **13** and **14** is formed when a mixture of 1,3-cyclohexadiene and 2-methoxybutadiene is heated at the temperature of the pyrolyses of **9** and **10**. It is difficult in this study to reproduce the concentration conditions that prevail when the addends are generated by Diels–Alder retrogression, and hence the control experiment is not completely decisive. Nevertheless, it strongly suggests that retrogression–recombination cannot be a major pathway for the formation of enol ether rearrangement product **13** from either **9** or **10**. The intermolecular mechanism for both the oxy-Cope and methoxy-Cope rearrangements is conclusively ruled out by the results of experiments with optically active materials (Scheme I).[8,9]

The configuration of the octalone rearrangement product **7** follows from its optical rotatory dispersion curve and that of the (+)-*cis*-2-decalone (**16**) to which it is hydrogenated. Both substances show negative Cotton effects, like that of the corresponding enantiomer of *cis*-9-methyl-3-decalone.[10] Conversion of **16** to *cis-trans*-2-decalol (**17**) gives material with about 71% of the maximum rotation reported.[11] If all of the steps of Scheme I are assumed to occur with

Scheme I



100% retention of configuration, [α]D(max) for 2-bicyclo[2.2.2]octanol (**19**) should be about 23.2/0.71 = 33°. This agrees with the value known approximately from other work.[12] More convincingly, the values of the rotation of rearranged octalone **7** are the same within experimental error from the pyrolyses of three different substrates (Scheme I). The configuration at C-4 in **10**, **6b**, and **9** thus is preserved completely in the pyrolysis of each, a result that is most readily accommodated if the C-3–C-4 bond remains intact throughout.

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(6) For analogous fragmentations, see R. C. Cookson and S. R. Wallis, *J. Chem. Soc., B*, 1245 (1966).

(7) J. A. Berson and E. J. Walsh, Jr., *J. Am. Chem. Soc.*, **90**, 4730 (1968).

(8) Unless otherwise indicated, the rotations shown refer to [α]D in chloroform. Correlations **18** → **19** and **18** → **15** are derived from data of K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962).

(9) Configurations are absolute as shown.

(10) C. Djerassi and D. Marshall, *ibid.*, **80**, 3986 (1958).

(11) (a) W. Hückel and C. Kuhn, *Ber.*, **70**, 2479 (1937); (b) W. Hückel, *Ann.*, **451**, 109 (1926).

(12) For a summary, see J. A. Berson, G. M. Clarke, D. Wege, and R. G. Bergman, *J. Am. Chem. Soc.*, **90**, 3238 (1968).

(13) National Institutes of Health Predoctoral Fellow, 1964–1966.

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Allylic and α-Oxygen Resonance Energy Effects on the "Strengths" of Carbon–Carbon Bonds. Activation Parameters in Stepwise Biallyl Rearrangements[1]

Sir:

Estimates of the amount by which the activation energy for bond cleavage can be lowered by α substituents are important for predictions of the rates of thermolysis reactions. Allylic resonance produces a large stabilizing effect on the transition state when the substituent is a double bond (**1**),[2] but very large effects also are noted in some cases when the substituent is a divalent oxygen function (**2**).[3,4] The electronic bases

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964), and references cited there.

(3) (a) R. K. Lustgarten and H. G. Richey, *Tetrahedron Letters*, 4655 (1966); (b) H. Prinzbach, M. Arguelles, and E. Druckrey, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1039 (1966); (c) H. Prinzbach and J. Rivier, *Tetrahedron Letters*, 3713 (1967).