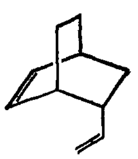
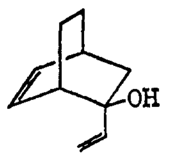
Competition experiments show that at 324° the ratios of rates of over-all disappearance for the vinyl compounds **4**:**5** is only 4.3, and the variation of this rate ratio over an 80° temperature range gives a $\Delta\Delta H^{\ddagger}$ of only 1.8 ± 1.5 kcal/mol, with the *exo* compound apparently having the lower $\Delta H^{\ddagger}$. These data and the product distributions argue against a concerted Cope rearrangement of the *endo*-vinyl compound **4** and are most simply interpreted in terms of a stepwise mechanism passing over diradical intermediates (**4** → **4a**). Similar conclusions have already been drawn for the alcohol **8** and its epimer.[14]

The first-order rate constants for pyrolyses of 2-*endo*-vinylbicyclo[2.2.2]oct-5-ene (**4**) and 2-*endo*-vinylbicyclo[2.2.2]oct-5-en-*exo*-2-ol (**8**)[14] determined at several temperatures in a stirred-flow reactor[15] give linear Arrhenius plots from which the indicated activation parameters are derived. The E_a value for the hydrocarbon **4** would be expected to be lower than that for biallyl (1,5-hexadiene) by an amount equal to the bond-weakening effect of two additional alkyl groups (~6 kcal/mol[6]) plus the difference in strain energy between **4** and the transition state leading to **4a** (roughly estimated from data in the literature[16] as perhaps 3–4 kcal/mol). These considerations make E_a for **4** compatible with a resonance energy of ~14 kcal/allyl group.



4



8

E_a (kcal/mol)	44.2 ± 1.2	41.8 ± 0.4
log A (sec)	12.8 ± 0.4	12.5 ± 0.2

Substitution of an α-hydroxy group lowers the BDE by 2.4 kcal/mol (compare E_a for **4** with that for **8**), an effect about the size that might have been expected from the very sparse and indirect data on the strengths of α-oxy-substituted carbon–carbon bonds (ΔBDE ~ 5 kcal/mol[6]). The result differs drastically from the α-oxygen effects of 16 kcal/mol and >15 kcal/mol observed in the thermolyses of 7-alkoxynorbornadienes[3a] and oxaquadricyclenes.[3b,c] This suggests either a large variation in the BDE values of α-oxygen-substituted bonds or a change in mechanism.[17]

---

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

[15] As described by (a) E. S. Lewis and W. C. Herndon, *ibid.*, **83**, 1955 (1961), and (b) W. C. Herndon, *J. Chem. Educ.*, **41**, 425 (1964), and modified in accord with suggestions of M. R. Willcott, III.

[16] (a) K. Alder and G. Stein, *Ber.*, **67**, 613 (1934); (b) G. Becker and W. A. Roth, *ibid.*, **67**, 627 (1934); (c) E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *J. Am. Chem. Soc.*, **87**, 2932 (1965); (d) P. von R. Schleyer, K. R. Blanchard, and C. D. Woody, *ibid.*, **85**, 1358 (1963).

[17] Here, as elsewhere, thei dentification of BDE values with kinetically determined E_a values rests on the assumption that the extent of chemically ineffective return of the diradical to starting material is constant throughout the series under examination.

[18] National Institutes of Health Predoctoral Fellow, 1964–1966.

Jerome A. Berson, Edward J. Walsh, Jr.[18]
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

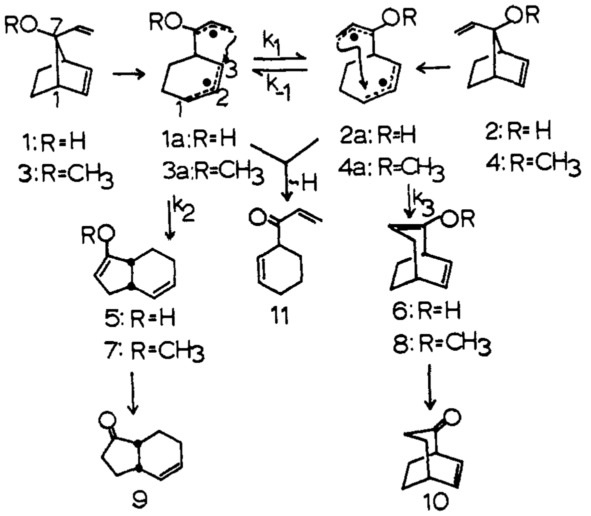
Received May 27, 1968

The Energy Barrier to Combination of Allylic Radicals. Relative Rates of Rotation and Ring Closure of a Rotameric Pair of Diradicals in the Oxy-Cope Rearrangement[1]

Sir:

Gas-phase pyrolytic rearrangements of the *syn*- and *anti*-7-vinyl-2-norbornen-*anti*- and *syn*-7-ols (**1** and **2**) are most simply formulated with a pair of conformationally isomeric diradical intermediates (**1a** and **2a**), which interconvert at a rate that is slow enough to provide partial insulation between the two systems.[2] Interconversion of the diradicals by bond rotation competes with cyclization and intramolecular hydrogen transfer. The complications introduced by hydrogen shift can be suppressed[3] by etherification of the hydroxyl groups, and an examination of the chemistry of the corresponding two diradicals from the methoxy dienes **3** and **4** permits an analysis in some detail of the act of cyclization. The results are pertinent to the question of the barrier for combination of allylic radicals and therefore bear significantly on the use of kinetically determined activation energies as bond dissociation energies.

Pyrolysis of the *syn*-vinyl compound **3**[5] in the gas phase at 250° converts it quantitatively to a mixture of 63% tetrahydroindene **7**[6] and 37% 2-methoxybicyclo[3.2.2]nona-2,6-diene (**8**).[6] Under the same conditions, the *anti*-vinyl compound **4** gives 5% **7** and 95%



---

[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] It now seems highly probable that hydrogen shifts from oxygen to C-1 in **1a** rather than from C-4 to C-1. The latter process should occur with about equal facility in the hydroxy and methoxy diradicals (**1a** and **3a**, **2a** and **4a**), but the O → C-1 rearrangement should be and is eliminated in the methoxy series (**3** and **4**), where pyrolysis gives no monocyclic enol ether corresponding to the ketone **11** that results from hydrogen shift in the 7-vinyl-7-norbornenols (**1** and **2**).[2] Similarly, no monocyclic hydrogen-shift products are observed in pyrolyses of the 2-methoxy-2-vinylbicyclo[2.2.2]oct-5-enes,[4] although in the corresponding alcohol series, the major product from the *exo*-vinyl isomer results from hydrogen shift.[2]

[4] J. A. Berson and E. J. Walsh, Jr., *ibid.*, **90**, 4729 (1968).

[5] Prepared from the alcohol **1**, which in turn is prepared from 7-norbornenone. The action of vinylmagnesium bromide on this ketone gives, in agreement with the previous report,[2] largely **1** (72% **1**, 28% **2**), but vinyllithium inverts the preference (38% **1**, 62% **2**). This inversion is also noted with bicyclo[2.2.2]oct-5-en-2-one.

[6] Elemental analysis confirms the composition.

8. Interconversion of the epimeric starting materials **3** and **4** does not occur.

Both products **7** and **8** show strong infrared absorption bands typical of enol ethers in the 6.0–6.1-μ range. The nuclear magnetic resonance (nmr) spectrum of each shows a methoxyl singlet in addition to a high-field (δ 3.9–4.3 ppm) vinylic absorption typical of a proton in the environment ROC=CH. Hydrolysis of the enol ethers leads to the respective ketones **9**[7] and **10**.

The composition of the product mixture is virtually unaffected by the duration of the pyrolysis, by the initial pressure, or by large increases in surface-to-volume ratio. It is also insensitive to a 30° temperature variation, which precludes an estimate of the difference in activation energies for the two processes but ensures that it is small.

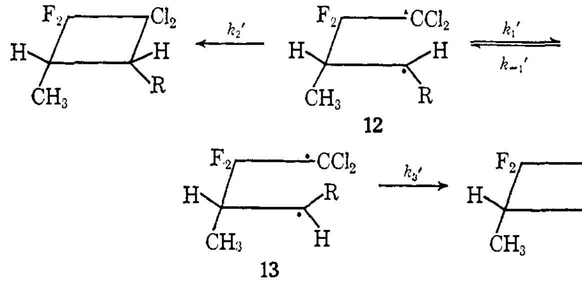
Competition experiments show that the *syn*- and *anti*-vinyl compounds differ but slightly in pyrolysis rate. The reactivity ratio **3**:**4** is only 2.0 ± 0.2 over a 25° temperature range. The appearance of single-inversion product **8** and the absence of any significant rate enhancement for the *syn*-vinyl compound **3** strongly suggest that the rearrangements proceed through diradical intermediates analogous to those proposed for the alcohol series **1** and **2**.[2]

Although depicted as the diradicals initially formed from **3** and **4** by homolysis of the C-1–C-7 bond, **3a** and **4a** in the kinetic scheme represent more generally the aggregates of conformationally related species that give **7** and **8**, respectively. The steady-state assumption for the concentrations of **3a** and **4a** permits the derivation[9] of the relationships of eq 1 and 2 between the rate constants of the scheme and the experimental product ratios from *anti* reactant **4**, $(\mathbf{8}/\mathbf{7})_{anti}$, and from *syn* reactant **3**, $(\mathbf{7}/\mathbf{8})_{syn}$.

$$\left(\frac{\mathbf{8}}{\mathbf{7}}\right)_{anti} = \frac{k_3(k_1 + k_2)}{k_{-1}k_2} \qquad (1)$$

$$\left(\frac{\mathbf{7}}{\mathbf{8}}\right)_{syn} = \frac{k_2(k_{-1} + k_3)}{k_1k_3} \qquad (2)$$

From eq 1 and 2 and the experimental data already given, the ratios of rates of ring closure and rotation in the two diradicals **3a** and **4a** can be calculated as $k_2/k_1 = 1.57$ and $k_3/k_{-1} = 11.6$. The corresponding ratios (k_2'/k_1' and k_3'/k_{-1}') for the 1,4-butadiyl radicals which are intermediates in the additions of 1,1-dichloro-2,2-difluoroethylene to 2,4-hexadienes (**12** and **13**, R = propenyl) are 0.082 and 0.38 at 100° (essentially temperature invariant).[9] Cyclization thus competes with internal rotation 19 and 31 times as effectively in diradicals **3a** and **4a** as in their mechanistic counterparts **12** and **13**. If the rotational barriers in **3a** and **4a** are comparable to those in **12** and **13**,[9,10] the apparently low rates of ring closure of **12** and **13** may result from the onset of cyclobutane ring strain in the transition state and from the birth of some fraction of these diradicals in conformations unfavorable to cyclization.



12

13

The assumptions of a sixfold rotational barrier of at most 3–5 kcal/mol[10] and a preexponential term[11] of $10^{11.5}$ lead to a rate of rotation (k_{-1}) between 0.3 and 1.2×10^{10} sec^{-1} at 250° for diradical **4a**. For cyclization (k_3), a small requirement for steric alignment would result in a preexponential term of about 10^{12} sec^{-1}, so that the computed k_3 ($11.6k_{-1}$) would be associated with a barrier to cyclization of not more than 2–4 kcal/mol.[12]

The total stabilization energy of an allyl and an α-methoxyallyl radical is about 30 kcal/mol. Nevertheless, although some of this must be sacrificed to pay for bond length changes, rehybridization, nonbonded repulsion, and other energy costs in reaching the transition state for combination, the present observations suggest that the loss is either very small or is closely balanced by the onset of bonding.[13] In either case, the net result is that the approach to the transition state from the direction of separated radicals is along a rather flat plateau of the energy surface. The height of this plateau, the activation energy for thermolysis of the biallylic bond, is then a good approximation of the bond dissociation energy.

---

(7) Supplementing the previous bases for assignments of structure to these ketones[2] is the observation that the substance **9** is readily distinguishable from an authentic sample of *cis*-bicyclo[4.3.0]non-3-en-7-one.[8]

(8) H. O. House and G. H. Rasmussen, *J. Org. Chem.*, **28**, 31 (1963). We thank Professor House for copies of the ir and nmr spectra of this ketone.

(9) See L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964), for a completely analogous treatment.

(10) E. B. Wilson, Jr., *Proc. Natl. Acad. Sci. U. S.*, 43, 816 (1957).

(11) Estimated according to H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968). We are indebted to these authors for advance information.

(12) The ratios of rates of ring closure to rotation (k_2/k_1 and k_3/k_{-1}) would be even greater if some crossover (direct **3a** → **8** and **4a** → **7**) occurred.

(13) Similarly, the relative rates of coupling and diffusion apart of solvent-caged radical pairs are remarkably insensitive to radical stability [P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967)]. The coupling of methyl and allyl radicals is estimated to have $E_a < 2$ kcal/mol [J. W. Simons, B. S. Rabinovitch, and F. H. Dorer, *J. Phys. Chem.*, 70, 1076 (1966)].

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

Jerome A. Berson, Edward J. Walsh, Jr.[14]
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received May 27, 1968

A Novel Allene Synthesis[1]

Sir:

We wish to report a novel synthesis of alkylallenes by the reaction of lithium dialkylcopper reagents[2] with ethynylcarbinol acetates. The following transformations (Table I) are typical for the reaction studied.

The lithium dimethylcopper reagent was prepared according to the published procedure,[2] and the lithium di-*n*-butylcopper reagent was prepared in a similar manner.[3]

---

(1) Publication No. 343 from the Syntex Institute of Steroid Chemistry. For Publication No. 342, see K. Hiller, B. Linzer, S. Pfeifer, L. Tökes, and J. Murphy, *Tetrahedron Letters*, in press.

(2) H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, 17, 1630 (1952).