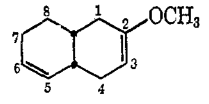
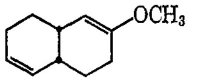
product from methoxy-Cope rearrangement (**11**),[5] that from a retro-ene reaction[6] (**12**),[5] and, especially in the case of the *exo*-vinyl ether **10**, one of those from a retro-Diels–Alder reaction (1,3-cyclohexadiene). Other so far unidentified volatile products also occur in the pyrolysis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

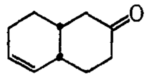
The vinyl ether expected from methoxy-Cope rearrangement of **9** is 2-methoxy-$\Delta^{2,5}$-hexalin (**13**). It is a matter of little interest but some nuisance that in normal work-up from pyrolysis this material is accompanied by its double bond isomer **14**, with which it readily equilibrates upon 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.



13



14



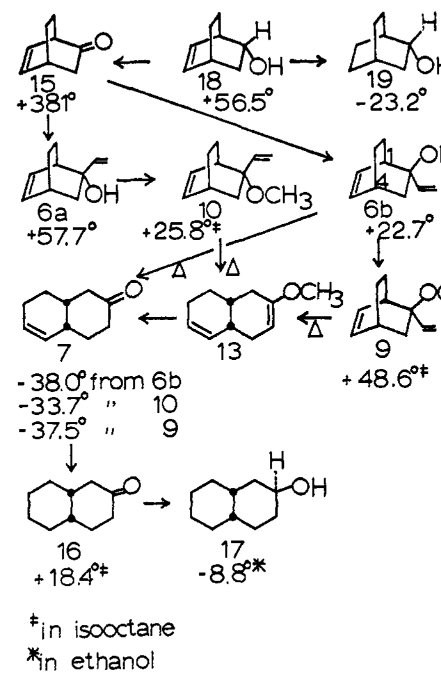
7

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 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.

Scheme I



---

[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.

Jerome A. Berson, Edward J. Walsh, Jr.[13]
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received May 27, 1968

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

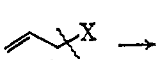
---

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

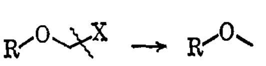
[2] K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964), and references cited there.

[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).

of the allylic and α-oxygen effects presumably are quite different, however, since the α-oxy radical is isoelectronic with a ketyl and, in contrast to the allyl radical, must have its first antibonding orbital singly occupied. The α-oxygen stabilizing effect therefore must represent the overbalance of this promotion energy by the strength of a carbonyl π bond. A further difference emerges in the damping of the conjugative effect that is expected in system **1** but not in **2**. Delocalization energies derived from simple molecular orbital calculations show that an adjacent double bond stabilizes an allyl radical (as in pentadienyl) less than it does an isolated alkyl radical (as in allyl), but an α-oxy group stabilizes allyl or isolated alkyl to about equal extents. The present paper evaluates the bond-weakening effect produced by a double bond and by an oxygen atom adjacent to the site of cleavage.

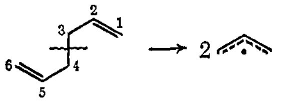


1



2

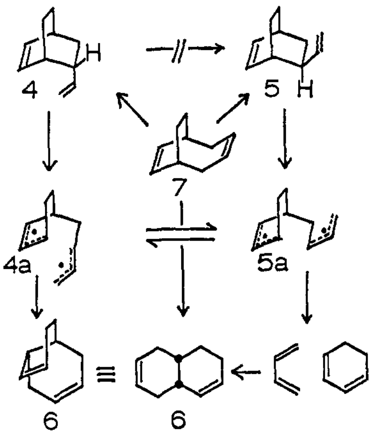
Estimates of the allylic resonance available to lower the bond dissociation energy (BDE) for thermolyses seem to cluster near the extremes of the range 12–25 kcal/mol.[2,5,6] Because it constitutes a point of reference on the energy surface of the Cope rearrangement, the BDE of the double allylic 3,4 bond in 1,5-hexadiene (**3**) is critically significant. From the assumptions that the bond-weakening effect in the absence of allylic resonance is the same as that of two alkyl groups (~2 × 3 kcal/mol), that the effects of the two double bonds are additive, and that the activation energy for the recombination of two allyl radicals is negligibly small,[6,7] one calculates from the C–C BDE in ethane (88 kcal/mol[6,8]) that BDE for **3** should be either 32 or 56 kcal/mol according to whether the allylic resonance energy is 25 or 13 kcal/mol.[8] Although one of the experimentally determined BDE values (56 kcal/mol[9a]) corresponds quite well to one end of this range, another (43–46 kcal/mol[9b,c]) falls between the extremes. The origin of the discrepancy is not obvious, but it is known that a major complication arises from a radical chain decomposition of **1**.[10] Since the radical centers freed upon cleavage of the 3,4 bond of a *cyclic* 1,5-hexadiene should be inefficient chain initiators, it seemed likely that a precise BDE value for a biallylic system would be derivable from the activation energy for the rearrangements of the epimers of 2-vinylbicyclo[2.2.2]-oct-5-ene (**4** and **5**).[11] These compounds are separated by preparative gas chromatography from the mixture (86% **4**, 14% **5**) obtained in high yield from a 90:10 mixture of *endo*- and *exo*-2-formylbicyclo[2.2.2]oct-5-enes[12] and triphenylphosphonium methylide.



3

Pyrolysis of the *endo*-vinyl compound **4** occurs smoothly at 325° in the gas phase to give *cis*-$\Delta^{1,6}$-hexalin (**6**)[11] in nearly quantitative yield. Also found are traces of products (1,3-cyclohexadiene and butadiene) resulting from formal Diels–Alder retrogression. The structure of **6** is established by spectral data, by catalytic hydrogenation to *cis*-decalin, and by partial hydrogenation with diimide to a mixture containing *cis*-decalin and both *cis*-Δ^1-octalin and *cis*-Δ^2-octalin.

Under the same pyrolysis conditions, the *exo*-vinyl compound **5** gives 50–60% **6** and 40–50% of retro-Diels–Alder products and materials derived from them. A mixture of 1,3-cyclohexadiene and 1,3-butadiene forms **6** in 15–20% yield under these conditions, an observation that permits a dissociation–recombination mechanism for the formation of some of the **6** derived from *exo*-vinyl compound **5**. The intramolecular part of the **5** → **6** reaction may involve cyclization of diradical **4a** formed by bond rotation in the initial diradical **5a**. An alternative (or supplementary) path may pass through bicyclo[4.2.2]deca-3,7-diene (**7**),[11,13] which is pyrolyzed to 75% **6**, 20% vinylbicyclo[2.2.2]-octenes (**4** and **5**, 1:3), and small amounts of fragmentation products. Since the rate of this pyrolysis is at least 200 times that of *exo*-vinyl compound **5**, diene **7** would not be an isolable intermediate in the pyrolysis of **5**. The conversion of *endo*-vinyl compound **4** to *cis*-hexalin (**6**), however, cannot pass over diene **7** to any appreciable extent, since the *exo*-vinyl compound **5** is a product from **7** but not from **4**.



---

(4) (a) R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Am. Chem. Soc.*, 88, 1353 (1966); (b) I. P. Fisher and E. Henderson, *Trans. Faraday Soc.*, 1342 (1967).

(5) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 50.

(6) S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965).

(7) For further justification, see J. A. Berson and E. J. Walsh, Jr., *J. Am. Chem. Soc.*, 90, 4719 (1968).

(8) (a) The argument is not materially changed by the use of the BDE for the 2,3 bond in *n*-butane as a standard (78–80 kcal/mol)[8b] or by the substitution of a somewhat lower value for the ethane BDE;[8b,c] (b) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, p 129; (c) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth & Co. (Publishers) Ltd., London, 1958.

(9) (a) R. J. Akers and J. J. Throssell, *Trans. Faraday Soc.*, 124 (1967); (b) J. B. Homer and F. P. Lossing, *Can. J. Chem.*, 44, 2211 (1966); (c) W. von E. Doering and V. Toscano, unpublished work (quoted by W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, 23, 3943 (1967)), give a value of ⩾ 46.5 kcal/mol.

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

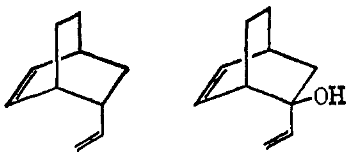
(11) (a) Elemental analysis establishes the empirical composition. (b) Hydrogenation of either 4 or 5 gives 2-ethylbicyclo[2.2.2]octane.

(12) B. A. Kazanskii and P. I. Zabeszhenskaya, *Dokl. Akad. Nauk SSSR*, 72, 57 (1950).

(13) A minor component of the 1,3-cyclohexadiene–1,3-butadiene reaction mixture, 7 is hydrogenated to bicyclo[4.2.2]decane, which is identified by comparison with an authentic sample kindly supplied by Dr. Maitland Jones, Jr. [M. Jones, Jr., and L. T. Scott, *J. Am. Chem. Soc.*, **89**, 150 (1967)].

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**

	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]

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

Received May 27, 1968

[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.

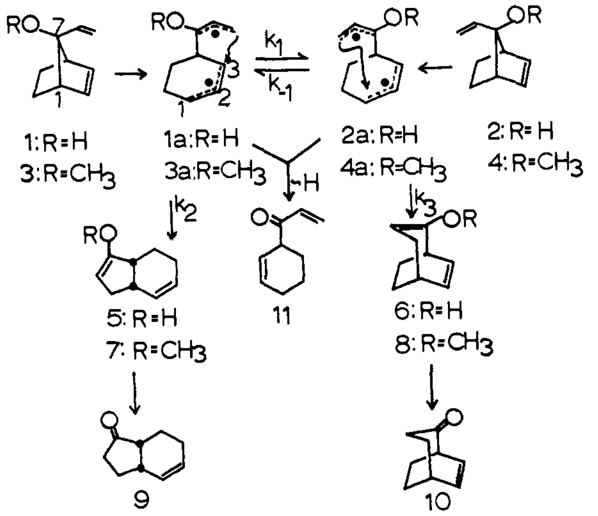
[18] National Institutes of Health Predoctoral Fellow, 1964–1966.

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.