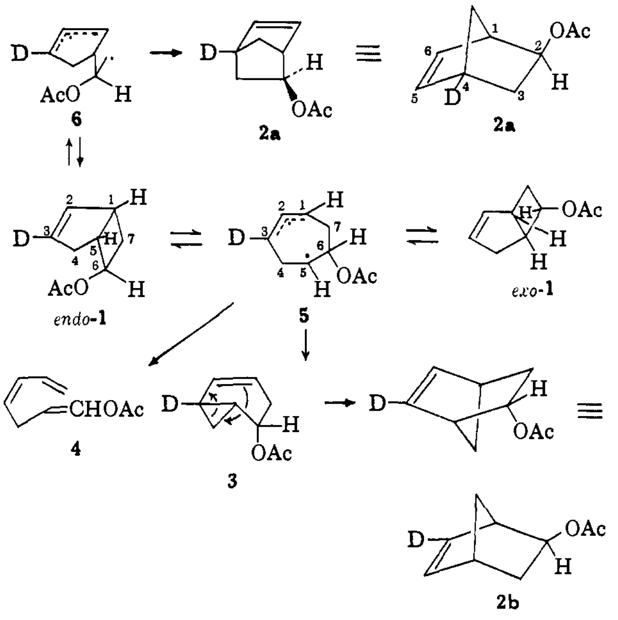
# On the Geometric Requirements for Thermolysis of Allylic Bonds. The 1,3-Sigmatropic Rearrangement of *syn,cis*-Bicyclo[3.2.0]hept-2-enyl 6-Acetate[1]

*Sir:*

A comparison of the rates of thermolysis of the C-1–C-7 and C-1–C-5 bonds of *endo*-bicyclo[3.2.0]-hept-2-enyl 6-acetate (*endo*-**1**) would permit an *intramolecular*[2] evaluation of the inhibition of normal allylic stabilization in the transition state for breaking a bond which lies in the π-nodal plane. We report here new information bearing on this point.

Cleavage of the bond (C-1–C-5) so situated in *endo*-**1** to give the diradical **5** should be followed by any or all of four consequences: (i) cleavage of **5** at C-6–C-7 to give triene **4**; (ii) conformational isomerization and recyclization at C-1 to give *exo*-**1**; (iii) recyclization at C-3 to give **3**, which (iv) might be imagined[3] to rearrange further to the bicycloheptene derivative **2b**. Cleavage of the other allylic bond (C-1–C-7) also could lead to a bicycloheptene (**2a**) by recyclization at C-3.



Pyrolysis of *endo*-**1** at 298° causes intramolecular rearrangement to *exo*-norbornenyl acetate.[3] Formation of *exo*-**1**, which is stable under these conditions, is at least 40-fold slower and may well be occurring by C-5–C-6 or C-6–C-7 rather than C-5–C-1 cleavage. No evidence for products **3** or **4** is found, the material balance being essentially quantitative in terms of the other identified materials previously reported.[3] Consequences i, ii, and iii expected from C-1–C-5 thermolysis thus are excluded. Consequence iv now is ruled out by the pyrolysis of *endo*-**1**-3-*d*.

Deuterioboration of the ethylene ketal[4] of bicyclo[3.2.0]hept-2-ene-6-one,[5] deketalization, and acetylation give a mixture of 2-acetoxy-3-deuterio- and 3-acetoxy-2-deuteriobicyclo[3.2.0]-6-heptanones (**7** and **8**). The stereochemistry of **7** and **8** is assigned as *cis*[6] and probably *exo*. Separation of the mixture by preparative vapor chromatography (vpc) gives pure **7** and **8**, the structures of which are assigned on the grounds that the ethylene ketals of the corresponding undeuterated analogs[4] (OH instead of OAc) give upon oxidation ketal ketones[4] which form monobenzylidene[4] and bisbenzylidene[4] derivatives, respectively.

Pure **7** is converted in seven steps to *endo*-**1**-3-*d* containing 0.95 atom of D/molecule, pyrolysis of which (0.66 *M* in decalin, 298°) is allowed to proceed to 6–9% conversion when norborn-5-enyl 2-*exo*-acetate predominates over its *endo* isomer by at least 26:1. Isolation by vpc gives **2a**, containing 0.95 atom of D (mass spectroscopy shows 95% $d_1$ and 5% $d_0$ species), with the deuterium exclusively at C-4. The gross location of deuterium on a bridgehead carbon (as in **2a**) rather than an olefinic one (as in **2b**) is evident from integration of the nmr spectrum, which shows a ratio of olefinic to α-acetoxy protons of 2.00 and of bridgehead to α-acetoxy protons of 1.10, in agreement with the predicted values for **2a** (0.95 D) of 2.00 and 1.05. Location at C-4 rather than at the mechanistically implausible alternative bridgehead C-1 is demonstrated by comparison of the 100-Mc nmr spectrum with that of the undeuterated isomer, which is analyzed by spin decoupling. The nmr integration and the sharpness of the downfield vinyl absorption in the spectrum of **2a**, as well as an independent check on the rate at which after-the-fact deuterium scrambling in **2a** by Diels–Alder retrogression–cyclopentadiene 1,5-hydrogen rearrangement[7]–recombination would have occurred,[8] permit the conclusion that the path leading to **2a** predominates over that leading to **2b** by at least 30:1. This may be used as a minimum value for the relative rates of C-1–C-7 and C-1–C-5 cleavage. A less conservative estimate of 40:1 is derived from the *exo*-**1**:**2a** ratio.[9]

*cis*-1,2-Dimethylcyclobutane thermolyzes at the C-1–C-2 bond faster than at the C-2–C-3 bond,[10] the difference in degree of substitution producing a $\Delta\Delta F^{\ddagger}$ at 298° of about 2.1 kcal/mole. If one can expect a roughly comparable bias toward C-1–C-5 rather than toward C-1–C-7 cleavage in *endo*-**1**, the present experiments show that this preference is overcome with at least 3.9 kcal/mole to spare. The total energy deficit associated with cleavage of the bond (C-1–C-5) in the π-nodal plane is thus at least 6 kcal/mole, about 30–50%

---

(1) The support of this work by grants from the National Science Foundation and the Air Force Office of Scientific Research is gratefully acknowledged.

(2) For *intermolecular* estimates, see (a) P. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **84**, 3411 (1962); (b) W. von E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, 7, 397 (1966); (c) M. R. Willcott and E. Goerland, *Tetrahedron Letters*, 6341 (1966).

(3) J. A. Berson and J. W. Patton, *J. Am. Chem. Soc.*, **84**, 3406 (1962).

(4) All new substances had elemental compositions in accord with theory within accepted limits of error (±0.3%) in parallel synthetic steps carried out in the undeuterated series. Structural identification in the deuterated series was achieved by comparisons of vapor chromatographic retention times with those in the undeuterated series.

(5) A. T. Blomquist and J. Kwiatek, *J. Am. Chem. Soc.*, 73, 2098 (1951).

(6) *Cf.* H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(7) See W. R. Roth, *Tetrahedron Letters*, 1009 (1964).

(8) Measured by observing the rate of racemization of optically active **2** at 298°.

(9) This conclusion is subject to an assumption common to all bond-breaking rate comparisons, namely that the "true" cleavage rate can be detected by the tests applied. If neither of the reversible first steps (*endo*-1 ⇌ 5 or *endo*-1 ⇌ 6) is rate determining for product formation, or if *endo*-1 ⇌ 6 is but *endo*-1 ⇌ 5 is not, the above estimate could be in error. In the absence of an operational criterion for the "no-reaction" reaction, *endo*-1 ⇌ 5, the estimate remains a working hypothesis.

(10) H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 3935, 4884 (1961).

of the allylic stabilization energy normally available[11] in uninhibited thermolyses.[12]

[11] (a) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964). (b) References cited in ref 2b. (c) We recognize that entropy effects may contribute to the observed *free energy* difference which therefore may not be directly comparable to the $\Delta\Delta H^{\ne}$ values.

[12] Although the result plausibly can be associated with a lower-lying transition state for diradical formation, the possibility exists that the *endo*-**1** → **2a** sigmatropic rearrangement is concerted. If so, the process is constrained to be suprafacial, and on orbital symmetry grounds the migrating carbon must suffer inversion of configuration.[13] This would be very unfavorable to the **2b**-forming path since the first step would require formation of a highly strained *trans*-fused **3**. The stereochemistry at C-7 in the *endo*-**1** → **2a** path is presently under investigation.

[13] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

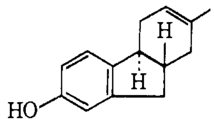
[14] National Institutes of Health Predoctoral Fellow, 1964–1966.

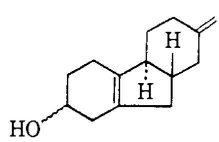
**Jerome A. Berson, Robert S. Wood**[14]
*Department of Chemistry, University of Wisconsin*
*Madison, Wisconsin 53706*
*Received November 5, 1966*

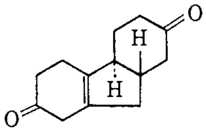
## Birch Reduction of Phenols[1]

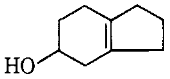
*Sir:*

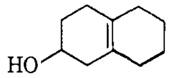
Birch reductions[2,3] of substances possessing free phenolic groups have been accomplished only in one special case, that of β-naphthol[4] and some of its derivatives.[5,6] On the basis of present concepts of the mechanism of the Birch reduction,[7] failure of such systems to undergo reduction must be ascribed to the high potential energy barrier to electron addition to the phenolate anion to form the required dianion radical intermediate.[8] In the course of studies of the stepwise reduction of 2-hydroxy-7-methoxyfluorene with lithium in ammonia[9] (1.5 *M*) it was noted that the mother liquors after removal of the major reaction product (I) contained several components, which on glpc[10] showed retention times shorter than that of I. Such mother liquors furnished after hydrolysis with 95% acetic acid the hydroxy ketone II (mp 152–153°;[11] $\lambda_{\max}^{\text{KBr}}$ 3.0 μ (OH), 5.9 μ (CO), no benzenoid absorption; nmr, no vinyl protons), the structure of which was established by Jones oxidation to the known diketone III, mp 95–97°.[9] This finding indicated that Birch reduction of phenolic systems was possible and that the reaction might be driven to completion by a further increase in the metal concentration. This was indeed found to be the case. Increasing the initial concentration of lithium from 1.5 to 4 *M* led to essentially complete reduction of the phenolic ring.[12] When similar conditions were applied in the reduction of 5-indanol and *ar*-2-tetralol (0.045 *M* in substrate and 3.4 *M* in Li) $\Delta^8$-hydrinden-5-ol (IV) and $\Delta^9$-octalin-2-ol (V) were obtained in 70 and 46% yield, respectively. With 4.3 *M* Li the latter yield was 76%. IV had bp 65–68° (3 mm);[11] $M^+$ 138; nmr (A-60), one proton (multiplet) centered at 240 cps (C*H*OH), no vinyl protons; positive nitromethane reaction; phenylurethan, mp 119–121°;[11] nmr, one-proton (quintet) at 311 cps ($J$ = 5.5 cps) (C*H*OR), no vinyl protons; and V had bp 72° (2 mm);[13] $M^+$ 152; phenylurethan, mp 134–135°,[11] nmr, one-proton (multiplet) centered at 307 cps (C*H*OR), no vinyl protons; positive nitromethane reaction. In contrast, 4-indanol was recovered unchanged under more drastic conditions (5.5 *M* Li) reminiscent of the unusually high concentrations of metal required for the reduction of compounds possessing the *ar*-1-methoxytetralin ring systems.[14,15]

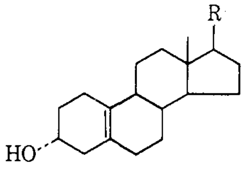

I


II


III


IV


V



VI, R = $<^{\text{OH}}_{\text{H}}$

VII, R = $<^{\text{O}-\text{CH}_2}_{\text{O}-\text{CH}_2}$

VIII, R = =O

The relative yields of IV and V obtained in parallel experiments suggested that the rate of reduction of 5-indanol was greater than that of *ar*-2-tetralol. Krapcho and Bothner-By[7] have shown by competition experiments that indan is reduced by Li–$NH_3$ 2.5 times faster than tetralin. Applying this method to the reduction of 5-indanol and *ar*-2-tetralol (0.022 *M* each,

---

[1] This investigation was supported by Public Health Service Research Grant CA 07445 and by Research Career Program Award 5-K6-AM-21846 from the National Institute of Arthritis and Metabolic Diseases.

[2] H. Smith, "Organic Reactions in Liquid Ammonia. Chemistry in Non-aqueous Solvents," Vol. 1, Part 2, John Wiley and Sons, Inc., New York, N. Y., 1963.

[3] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 50 ff.

[4] C. D. Gutsche and H. H. Peter, *Org. Syn.*, 37, 80 (1957).

[5] N. A. Nelson, R. S. P. Hsi, J. M. Schuck, and L. D. Khan, *J. Am. Chem. Soc.*, 82, 2573 (1960).

[6] The great ease of reduction in this case can be understood if one assumes the reaction to proceed *via* the α,β-unsaturated keto form. Several reactions of β-naphthol appear to involve this tautomeric form. *Cf.* Roberts and Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 908.

[7] A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959).

[8] *Cf.*, however, R. A. Benkeser, C. Arnold, Jr., F. Lambert, and O. H. Thomas, *ibid.*, 77, 6042 (1955), who reduced phenol with lithium in methyl- or ethylamine and produced cyclohexanone.

[9] J. Fried and N. A. Abraham, *Tetrahedron Letters*, 3505 (1965).

[10] Gas-liquid partition chromatography was performed on an F & M Model 400 instrument fitted with a 4-ft 3.8% SE 30 on Diatoport S column at a He flow rate of 100 cc/min.

[11] Analyses by J. Alcino, Metuchen, N. J.

[12] The complete composition of the reaction mixture will be described elsewhere. A typical reduction was conducted as follows. To a solution of 0.21 g-atom of Li in 50 ml of redistilled $NH_3$ at −40 to −50° is added 1.4 mmoles of 2-hydroxy-7-methoxyfluorene in 9 ml of dry THF without exclusion of air. Portions of ethanol (4 ml) are then added in 30-min intervals until the solution is decolorized (*ca.* 1.75 hr) and the reaction mixture is worked up in standard fashion.

[13] J. E. Starr and R. H. Eastman, *J. Org. Chem.*, 31, 1393 (1966).

[14] A. J. Birch, A. R. Murray, and H. Smith, *J. Chem. Soc.*, 1945 (1951).

[15] W. S. Johnson, B. Bannister, and R. Pappo, *J. Am. Chem. Soc.*, **78**, 6331 (1956).