The Stereochemistry of Sigmatropic Rearrangements. Tests of the Predictive Power of Orbital Symmetry Rules[1]

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The Woodward–Hoffmann rules make the unambiguous, interlocked, and "risky" predictions that suprafacial, thermal, concerted, sigmatropic rearrangements of carbon should proceed with inversion of configuration of the migrating group when 1,3 and with retention when 1,5. A number of 1,5 cases now are known from the chemistry of tropilidenes, but the stereochemistry has not yet been established. A study of an appropriate 1,3 case, the rearrangement of *endo*-bicyclo[3.2.0]hept-2-en-6-yl acetate to *exo*-norbornenyl acetate, has been completed. In accord with prediction, the configuration of the migrating group is cleanly inverted.

In a thermal unimolecular reaction, the atoms present in the reactant and in the transition state are the same. Only their relative positions change. Catalysts, solvent molecules, and outside reagents do not enter into consideration, and the problem of mechanism is reduced to its most elementary form: what is the geometry of the transition state?

Woodward and Hoffmann[2,3] have introduced one of the most useful theoretical approaches to the qualitative description of reactions of this class in the form of a set of rules based on orbital symmetry considerations. Before such rules can be elevated to the status of theory, they must be shown to perform not only a nomenclatural and correlative function but also a predictive one. Moreover, in tests of the theory, confirmations, in Popper's words, "should count only if they are the result of *risky predictions;* that is to say, if, unenlightened by the theory in question, we should have expected an event which was incompatible with the theory —an event which would have refuted the theory."[4] For reasons that will emerge, the subcategory of thermal unimolecular reactions called "sigmatropic rearrangements" are especially well suited for the construction of such tests.

In one kind of sigmatropic rearrangement, a σ-bonded atom or group (R) migrates from one end to the other of an allylic ($n = 1$) or polyenylic ($n = 2, 3$, etc.) chain

$$\underset{\text{C}}{\overset{\text{R}}{\diagdown}}\!\!-\!(C{=}C)_n \longrightarrow (C{=}C)_n\!\!-\!\underset{\text{C}}{\overset{\diagup \text{R}}{}}$$
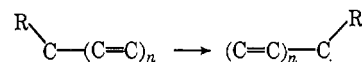
According to Woodward and Hoffmann,[2,3] if the migrating group R were to remain bonded to both ends of the unsaturated system throughout (concerted reaction), orbital symmetry constraints would be derived from the form of the highest occupied molecular orbital (MO) of the hydrocarbon radical corresponding to the polyenylic chains. Thus, for a 1,3-sigmatropic rearrangement, the model π-electron system would be allyl radical, the highest occupied MO of which (the nonbonding ψ_2 level) has the form shown. Similarly, a 1,5-sigmatropic rearrangement would, if concerted, be based upon the form of the nonbonding MO, ψ_3, of pentadienyl radical.

ψ_2, allyl radical ψ_3, pentadienyl radical
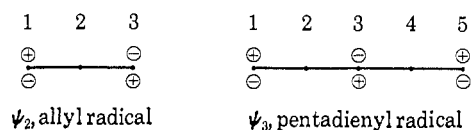
The nature of the orbital binding the migrating group R to the unsaturated system must also be specified. If it is a symmetric orbital (for example, s) or one lobe of an antisymmetric orbital (for example, p) (case I), a concerted 1,3-migration would require that R be bonded simultaneously to C-1 on one side of the plane of the unsaturated framework and to C-3 on the other, that is, *antarafacially*. In a concerted 1,5 migration, the transition state geometry would be *suprafacial* (on one side of the plane) if the R-binding orbital were of the above type (case I), and since the connecting atom of R would be bound to only *one face*, the configuration of R would be retained. On the other hand, if R used *both* lobes of an antisymmetric orbital (case

(1) This work was supported in part by grants from the Army Research Office-Durham, the Air Force Office of Scientific Research, the Petroleum Research Fund, the National Science Foundation, the National Institute of Arthritis and Metabolic Diseases, and the Wisconsin Alumni Research Fund. Further support was supplied by National Institutes of Health Postdoctoral Fellowships to M. R. Willcott, III (1964–1965), and D. R. Hartter (1966–1967), and by National Institutes of Health Predoctoral Fellowships to R. S. Wood (1964–1966), E. J. Walsh, Jr. (1964–1966), and G. L. Nelson (1967–).

(2) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.,* **87,** 2511 (1965), and references cited there.

(3) For surveys, see (a) R. B. Woodward in "Aromaticity," Special Publication No. 21, The Chemical Society, London; (b) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.,* **1,** 17 (1968).
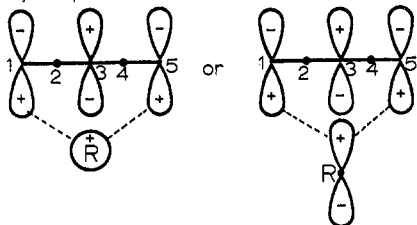
(4) K. R. Popper, "Conjectures and Refutations," Basic Books, New York, N. Y., 1963, p 36. I am indebted to Professor Kurt Mislow for this reference.

Case I: R uses symmetric orbital or one lobe of antisymmetric orbital.
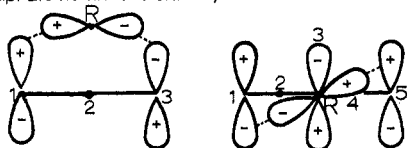
1,3: antarafacial: retention
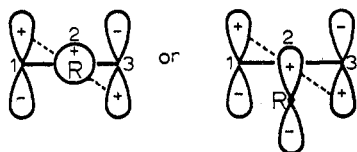
1,5: suprafacial: retention

Case II: R uses both lobes of antisymmetric orbital.

1,3: suprafacial: inversion.   1,5: antarafacial: inversion.

II), the geometry would be just reversed: 1,3 migration would be suprafacial and 1,5 antarafacial. Moreover, since the migrating group R would bond through *opposite faces* of its connecting atom, rearrangement would invert the configuration of R. Extension of this pattern to the higher polyenylic systems (1,7-, 1,9-, etc.) is obvious.

Experimental verification of all of these predictions would indeed provide strong support for the orbital symmetry rules, but we must be more modest in our goals because of the limitations imposed by ordinary steric factors. For example, it would be difficult to devise structures that would permit the 1,3-antarafacial bonding required in case I or even the 1,5-antarafacial bonding of case II. If the allyl or pentadienyl systems are to retain the approximate coplanarity required to permit the application of the orbital symmetry rules at all, the antarafacial transition states for the 1,3 and 1,5 rearrangements do not appear to be readily achievable. In practice, the study is therefore effectively restricted to the suprafacial class.

Within this class, it is clear that the information content potentially available from a study with a carbon migrating group (R) is much higher than with hydrogen. Because hydrogen cannot readily use bonding orbitals of principal quantum number greater than 1, it can furnish only the symmetric 1s orbital to the basis set of orbitals making up the transition state and therefore is not expected to participate in concerted 1,3-sigmatropic rearrangements. Moreover, although hydrogen could (and does) undergo 1,5-sigmatropic rearrangement, there is no way to examine the stereochemistry of this monovalent migrating atom. A carbon migrating group not only is capable of both 1,3- and 1,5-sigmatropic rearrangements, but also it provides the means of testing the interlocked predictions 1,3:

suprafacial: inversion and 1,5: suprafacial: retention. The tests involve first the construction of molecules that undergo the rearrangements and then the determination of the stereochemical fate of the migrating group. The subtle question of whether the rearrangements are concerted is thrust temporarily into the background but will reemerge. This program, although not yet completed, has progressed far enough to warrant a summarizing review of the results already obtained.

1,5-Sigmatropic Carbon Rearrangements. The Skeletal Reorganizations of Cycloheptatrienes and Norcaradienes (Tropilidenes)

Woods' observation[5] that pyrolysis of cycloheptatriene (1) gave toluene (2) provided the entry to the 1,5-carbon rearrangements. Woods proposed that the reaction passed through the bicyclic valency tautomer norcaradiene 3, which suffered bond cleavage to give the diradical 4. Hydrogen shift in 4 produced toluene.
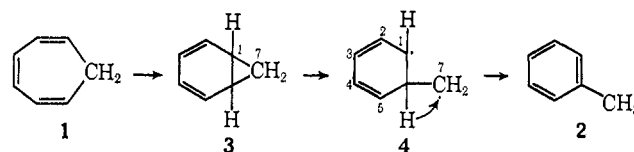
Implicit in this mechanism is the possibility that recyclization of diradical 4 might compete with the hydrogen shift. In 4, C-1 and C-5 are electronically equivalent, and since they also would be nearly so in an appropriately substituted derivative, such recyclization would lead in that case to a detectable skeletal rearrangement of the original cycloheptatriene. Whether the diradical 4 is a true intermediate or merely a convenient formalism for expressing the structural changes is not of major concern for the present. The essential feature is the proposed norcaradiene intermediate, which contains the structural requirements for a 1,5-sigmatropic rearrangement, necessarily suprafacial, and in which, as Woods' work shows, the bond between C-1 and the migrating group, C-7, can be broken by thermolysis.
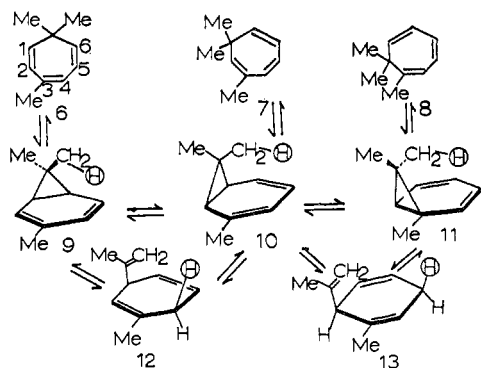
To facilitate the study of the skeletal rearrangement, it is desirable to work with 7,7-disubstituted tropilidenes to block the well-known[6] superficial hydrogen rearrangement that occurs readily when a 7-hydrogen is present (5a → 5b).
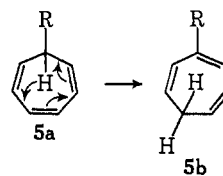
(5) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).
(6) (a) A. P. ter Borg, H. Kloosterziel, and N. van Meurs, *Proc. Chem. Soc.*, 359 (1962); *Rec. Trav. Chim.*, **82**, 717 (1963), and references therein cited; (b) G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **84**, 3104 (1962); (c) E. Weth and A. S. Dreiding, *Proc. Chem. Soc.*, 59 (1964).

The tropilidene skeletal rearrangement now is known to occur in several systems, perhaps the most complex of which is the original example, the x,7,7-trimethyl-cycloheptatriene group.[7] At temperatures above 300°, these substances (6, 7, and 8) interconvert by way of a skeletal rearrangement which is most simply formulated with norcaradiene intermediates 9, 10, and 11. Iso-

topic labeling studies exclude several other types of valency tautomers as intermediates and, in particular, demonstrate that the atoms C-1 through C-6 remain sequentially arranged throughout. The rearrangement formally consists of the circulation of C-7 and the associated *gem*-dimethyl group around the six-membered ring C-1 through C-6. Reattachment of C-7 can occur between any two adjacent ring carbons.

In detail, it is not entirely clear that this process is the sought-for sigmatropic carbon rearrangement. An alternative to the direct interconversion (*e.g.*, 9 → 10) involves a 1,5-sigmatropic hydrogen shift in which a hydrogen from the *gem*-dimethyl group is temporarily deposited on the ring (9 → 12) and then returns to the newly created isopropenyl group as recyclization produces a rearranged norcaradiene (12 → 10). Since the pyrolysis mixture is found to contain the isopropenyl 1,4-cyclohexadienes resulting from hydrogen shift (12 and 13), and since they do recyclize under the pyrolysis conditions to regenerate the cycloheptatrienes 6, 7, and 8,[7] the indirect alternative mechanism is quite plausible. At present, it is not known whether hydrogen shift is an obligatory mechanism for the rearrangements of 6, 7, and 8 or merely a process in competition with pure carbon rearrangement.

The situation can be simplified and the pure carbon rearrangement uncovered by the use of C-7 groups lacking transferable C–H bonds. Thus, the x-methyl-7,7-dicyanonorcaradienes (14, 15, 16) interconvert readily upon warming.[8] The 7,7-dicyanotropilidenes, as Ciganek[9] has shown, are true norcaradienes, but the trimethyl compounds 6, 7, and 8, are cycloheptatrienes. Since the key intermediates proposed for the rearrangements are norcaradienes, the trimethyl compounds
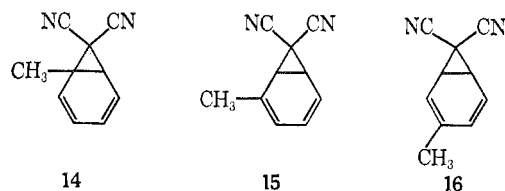
must perform a preliminary step (cycloheptatriene → norcaradiene) that is not required of the dicyano compounds. This extra process contributes its endothermicity (estimated[10] to be about 11 ± 4 kcal/mol) in the form of an increased activation energy for the rearrangements of the trimethyl compounds. Another profound difference between the systems derives from the dicyano substituents, which weaken the C-1–C-7 bond. The combined effect permits the 14 ⇌ 15 ⇌ 16 rearrangements to occur at 55°, whereas those of the trimethyl compounds are negligibly slow below 300°. In terms of activation energy, this facilitation amounts to about 18 kcal/mol.[8]

Further examples of pure carbon skeletal rearrangements are now available in the benzotropilidene series.[9,11]

If the tropilidene skeletal carbon rearrangements are concerted, that is, if the migrating atom (C-7) begins to bond to C-5 before becoming completely detached from C-1, the orbital symmetry considerations already discussed suggest that the *same face* of C-7 would be involved in bonding to the migration origin and terminus (17), so that its configuration would be retained.
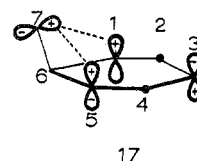
It is instructive to examine the stereochemical consequences of this type of transition state and those of the alternative contra-Woodward–Hoffmann type in which C-7 is bonded through *opposite faces* (inversion of configuration). In principle, a distinction between "same face" and "opposite face" bonding is available if an optically active tropilidene is used.[7c]

In the "opposite face" contra-Woodward–Hoffmann case (the "60°" mechanism), the stepwise motion of C-7 and its attached substituents around the six-membered ring has sixfold periodicity in a given circuit because a substituent (black circle) originally "inside" remains inside, and an "outside" one (white circle) remains outside. Thus, the location of a given kind of substituent inside or outside recurs every sixth of a revolution. This "60°" mechanism produces racemization, since passage by *back-side bonding* over the site of the lone substituent interconverts two enantiomeric norcaradienes. The orbital symmetry "forbidden" mechanism thus has the same eventual stereo-

(7) (a) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, 87, 2751, 2752 (1965); (b) *ibid.*, 88, 2494 (1966); (c) *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), 27, 139 (1966).

(8) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, III, *J. Am. Chem. Soc.*, 89, 4076 (1967).

(9) E. Ciganek, *ibid.*, 87, 652, 1149 (1965); 89, 1454, 1458 (1967).

(10) W. von E. Doering and M. R. Willcott, III, unpublished; M. R. Willcott, III, Ph.D. Dissertation, Yale University, 1963.

(11) E. Vogel in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 122.
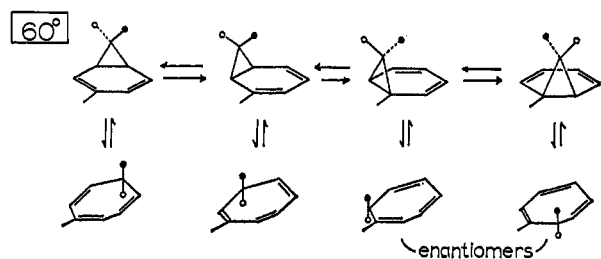
chemical result as a stepwise process in which C-7 becomes sufficiently detached from the migration origin to allow rotation about the C-6–C-7 bond before bonding to C-5 occurs.
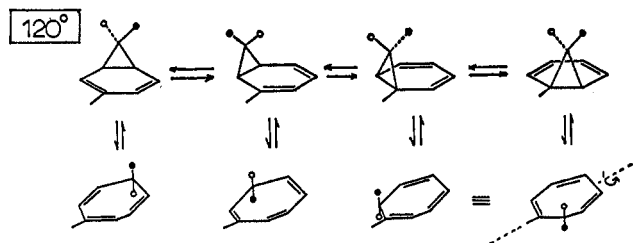
The orbital-symmetry "allowed" path, called the "120°" mechanism (threefold periodicity), uses the *same face* of C-7 to make the new bond at each step of its circuit around the ring. This imparts a stereochemical bias to the motion and causes an in–out–in–out alternation of the disposition of a given substituent. Passage over the site of the lone substituent now does *not* interconvert enantiomers, but merely reproduces a 1,7,7-trisubstituted compound of the same configuration as its precursor. Thus, in the "120°" mechanism an infinite number of circuits may be achieved with perfect preservation of optical purity.[12]

The synthesis of a suitable optically active tropilidene to provide a test of these alternatives is a project at which we continue to persevere despite a so far unbroken record of failure.

1,3-Sigmatropic Carbon Rearrangements. The Bicyclo[3.2.0]heptene → Norbornene Transformation

A few formal 1,3-sigmatropic carbon rearrangements were known at the outset of this study (for example, the thermal rearrangements of vinylcyclopropanes to cyclopentenes and of vinylcyclobutanes to cyclohexenes[13]), but these were not well suited for the examination of the stereochemical problems of interest here. The construction of an apposite system requires that the bond between the migrating group and the origin of migration be relatively weak so that thermolysis will occur selectively at that site, that the allyl system so

(12) (a) In the present context, it is immaterial whether the interconversion of the two enantiometric or superimposable 1,7,7-trisubstituted tropilidenes occurs by actual passage over the site of the lone substituent or by the more circuitous route in the other direction. Neither the "60°" nor the "120°" mechanism distinguishes clockwise from anticlockwise revolution. (b) Although 1,5 over-all, each of the present rearrangements might conceivably be achieved by two sequential 1,3 steps. This has been excluded for the trimethyltropilidene cases by the demonstration (M. R. Willcott, III, *J. Am. Chem. Soc.*, in press) that bornadiene is not an important intermediate.

(13) For a review, see H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966).

generated be of fixed geometry so that the migration will necessarily be suprafacial, and that the migrating carbon be structurally suited for easy incorporation of a group or label by which its stereochemical fate during rearrangement can be followed.

These requirements are met in *endo*-bicyclo[3.2.0]-hept-2-en-6-yl acetate (**18**). Pyrolysis of this substance at about 300° effects conversion to *exo*-norbornenyl acetate (**19**), the product expected from 1,3-sigmatropic rearrangement.[14] Although the reaction
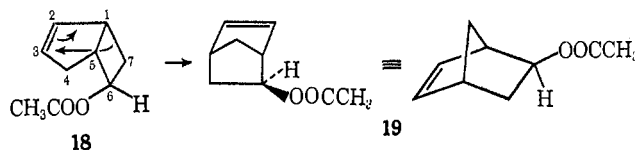
can be formulated as cleavage of the allylic C-1–C-7 bond and recyclization of C-7 at C-3 (in either a stepwise or a concerted manner), there are two alternative mechanisms that are not unreasonable and must be considered.

The first is an intermolecular dissociation–recombination process involving cleavage of the cyclobutane ring to give cyclopentadiene (**20**) and vinyl acetate (**21**), followed by Diels–Alder addition to give *exo*-norbornenyl acetate (**19**). Some temporary credence
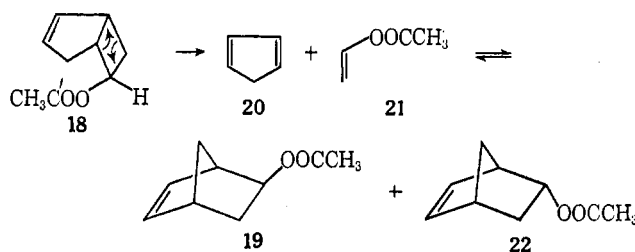
is lent to this possibility by the observation[14] that the fragmentation products **20** and **21** can be found in the pyrolysis mixture. This is not necessarily of mechanistic significance, however, because the norbornenyl acetates themselves dissociate slowly and reversibly to **20** and **21** under the pyrolysis conditions. (In fact, this Diels–Alder retrogression of the rearrangement product **19** is a considerable nuisance experimentally, as will become evident.) The intermolecular mechanism can be ruled out by observation of the pyrolysis products of **18** at only 5–10% conversion. Under these conditions **18** gives nearly exclusively *exo*-norbornenyl acetate (**19**) with little or no contamination by the *endo* isomer **22**. At longer reaction times, the *exo*:*endo* ratio (**19**:**22**) falls as Diels–Alder retrogression–recombination interconverts **19** with the addends (**20** and **21**) and with its *endo* isomer (**22**) (Figure 1). The kinetically controlled ratio *exo*:*endo* from the Diels–Alder combination of the addends is obtained by extrapolation of the product composition to zero time (Figure 1). This ratio is about 0.42, in contrast to the ratio obtained from short-

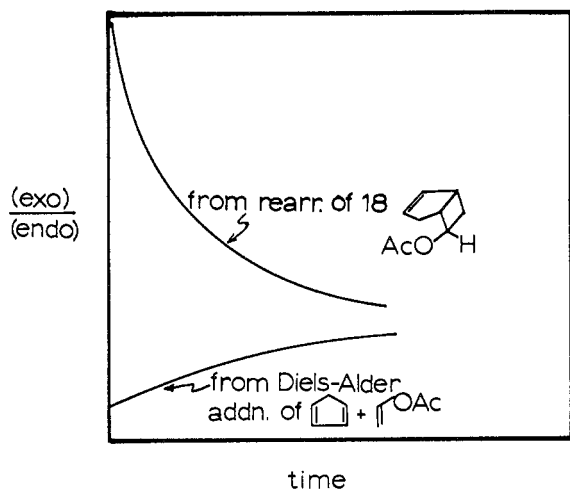(14) J. A. Berson and J. W. Patton, *J. Am. Chem. Soc.*, **84**, 3406 (1962).

Figure 1. Variation of the product composition (*exo*- and *endo*-norbornenyl acetates) as a function of time and source.

time pyrolyses of 18[14,15] which is at least 75. There must exist, therefore, an intramolecular, highly stereospecific pathway for the 18 to 19 rearrangement.

The second alternative mechanism meets these requirements and is more difficult to exclude. It consists of two successive sigmatropic rearrangements initiated by the cleavage of the C-1–C-5 bond of 18 and formation of the vinylcyclopropane derivative 23. Rearrangement of this substance to a cyclopentene (19) would be a reaction of a well-known[13] type. This
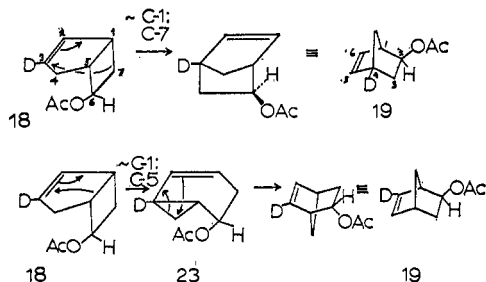

alternative is shown applied to 3-deuterio-18, from which it would give 6-deuterio-19, whereas the direct C-1–C-7 cleavage would give 4-deuterio-19. The location of the deuterium atom at one or the other of these sites would be readily distinguishable in the proton magnetic resonance spectrum (nmr).

With no little effort,[15b] a deuterium label can be affixed to C-3 of 18. The synthesis starts with the ethylene ketal 24 and involves the over-all strategy of *cis* addition of D–OH to the double bond and *trans* elimination of H–OH from the deuterated alcohol.

Since the rearrangement product 19 suffers Diels–Alder retrogression, and the resulting cyclopentadiene rapidly scrambles the deuterium by successive 1,5-hydrogen shifts,[16] prolonged exposure of specifically labeled 19, *e.g.*, 19-4-*d*, to the pyrolysis conditions would ensure position mixing of the label and miscarriage of

(15) (a) J. A. Berson and R. S. Wood, *J. Am. Chem. Soc.*, **89**, 1043 (1967);   (b) R. S. Wood, Ph.D. Dissertation, University of Wisconsin, 1966.
(16) W. R. Roth, *Tetrahedron Letters*, 1009 (1964).

the experiment. Pyrolyses thus must be carried out only to conversions just sufficient to provide a sample of
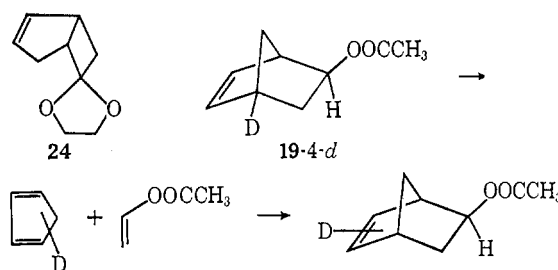
rearrangement product for nmr analysis.

Short pyrolysis of about 1 g of 18-3-*d* gives about 30 mg of rearrangement product which nmr shows to be exclusively 19-4-*d*, resulting from the one-step 1,3-sigmatropic rearrangement of C-7 from C-1 to C-3.[15] The two-step mechanism *via* vinylcyclopropane 23 thereby is ruled out.

The rearrangement of *endo*-bicyclo[3.2.0]heptenyl acetate (18) to *exo*-norbornenyl acetate (19) is therefore a true 1,3-sigmatropic process. The observed stereospecificity (*endo*-[3.2.0] → *exo*-norbornenyl) is consistent with the gross structural picture of the change, which involves no cleavage of bonds to C-6. Whatever the details of the mechanism, the pivoting action about the C-5–C-6 bond ensures that the "inside" *endo*-acetoxy group of 18 will turn "outside" to give an *exo*-acetoxy group in 19. There remains the crucial question of the stereochemistry of the migrating group, C-7.

The structures of 18 and 19 force the rearrangement to be suprafacial, since an antarafacial process would produce an unthinkably strained *trans*-bridged norbornene. The orbital symmetry-allowed concerted process thus would require that C-7 invert its configuration, whereas a stepwise reaction passing over some sort of intermediate in which the C-7–C-1 bond was broken but no bonding of C-7 to C-3 had developed would result either in randomization of the C-7 stereochemistry, or if reclosure at C-3 was sufficiently rapid,
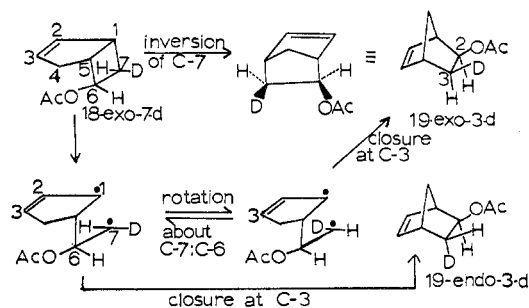
in retention of configuration. To observe the stereochemistry of C-7 of 18 (after rearrangement, this carbon atom becomes C-3 of 19), the starting material must be stereospecifically deuterated. This is done[17] by the synthetic sequence shown in Scheme I. The stereochemistry of 18-*exo*-7-*d* is established by the

(17) J. A. Berson and G. L. Nelson, *J. Am. Chem. Soc.*, **89**, 5503 (1967).
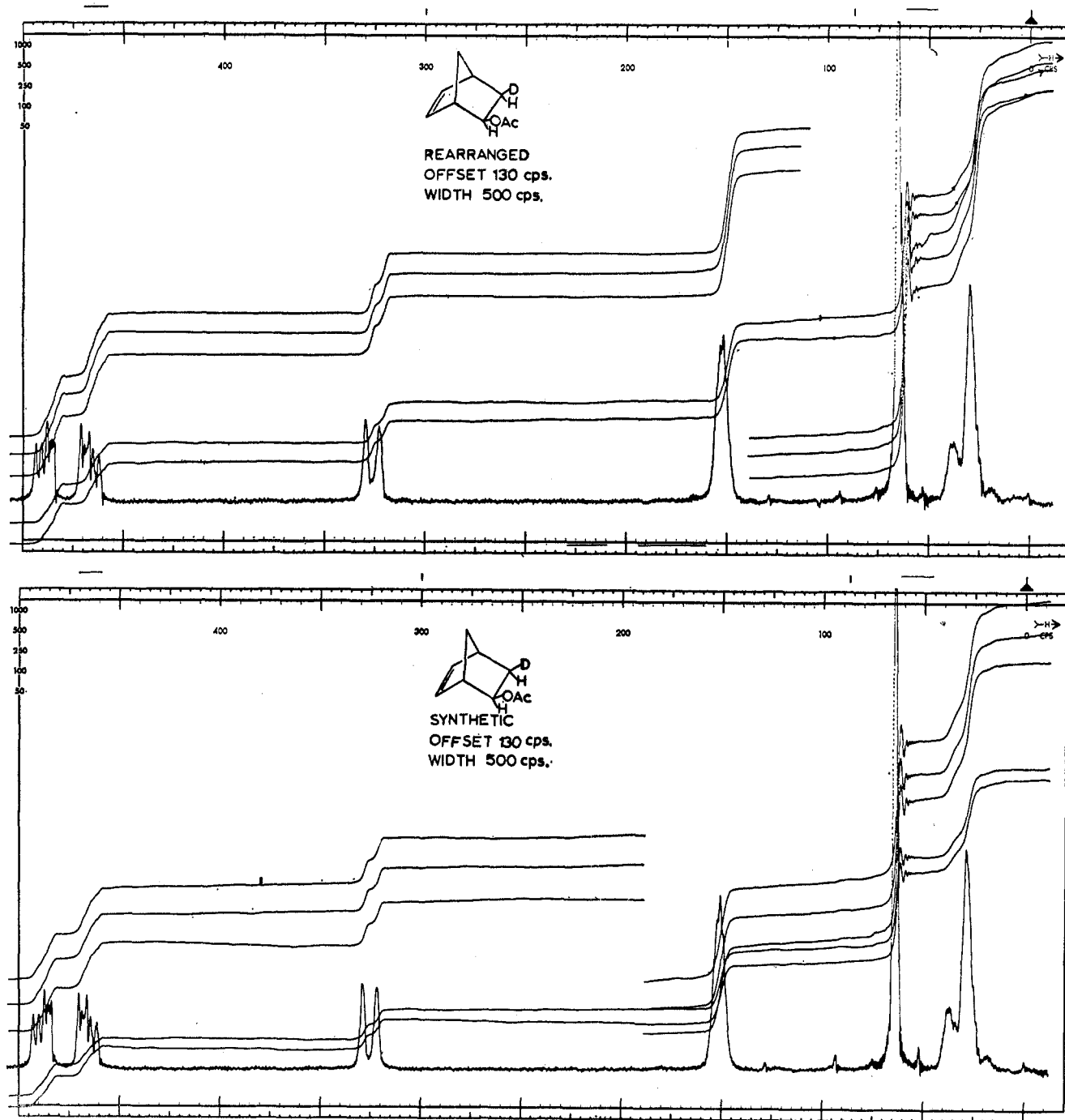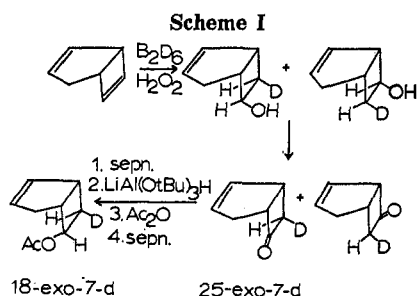
Figure 2. Nmr spectra of **19**-*exo*-3-*d* at 100 MHz.

method of synthesis and is confirmed by the 100-Mc nmr spectra of **18**-*exo*-7-*d* and the ketone **25**-*exo*-7-*d*, which are interpreted with the aid of double and triple

resonance techniques applied to **18**, **25**, and the corresponding 5-*d* and 5,7,7-*d*₃ analogs.

The distinction between the inversion and retention pathways for the pyrolytic rearrangement of **18**-*exo*-7-*d* rests on whether the deuterium and acetoxy groups of the *exo*-norbornenyl acetate product are respectively *cis* (**19**-*exo*-3-*d*) or *trans* (**19**-*endo*-3-*d*). The reversible dissociation of **19** to the Diels–Alder fragments, cyclopentadiene and vinyl acetate, need not be so serious an interference as in the pyrolysis of **18**-3-*d*, since as long as the vinyl acetate retains its stereochemistry (*e.g.*, deuterium and acetoxy *cis*), no perturbation of the experiment can result.
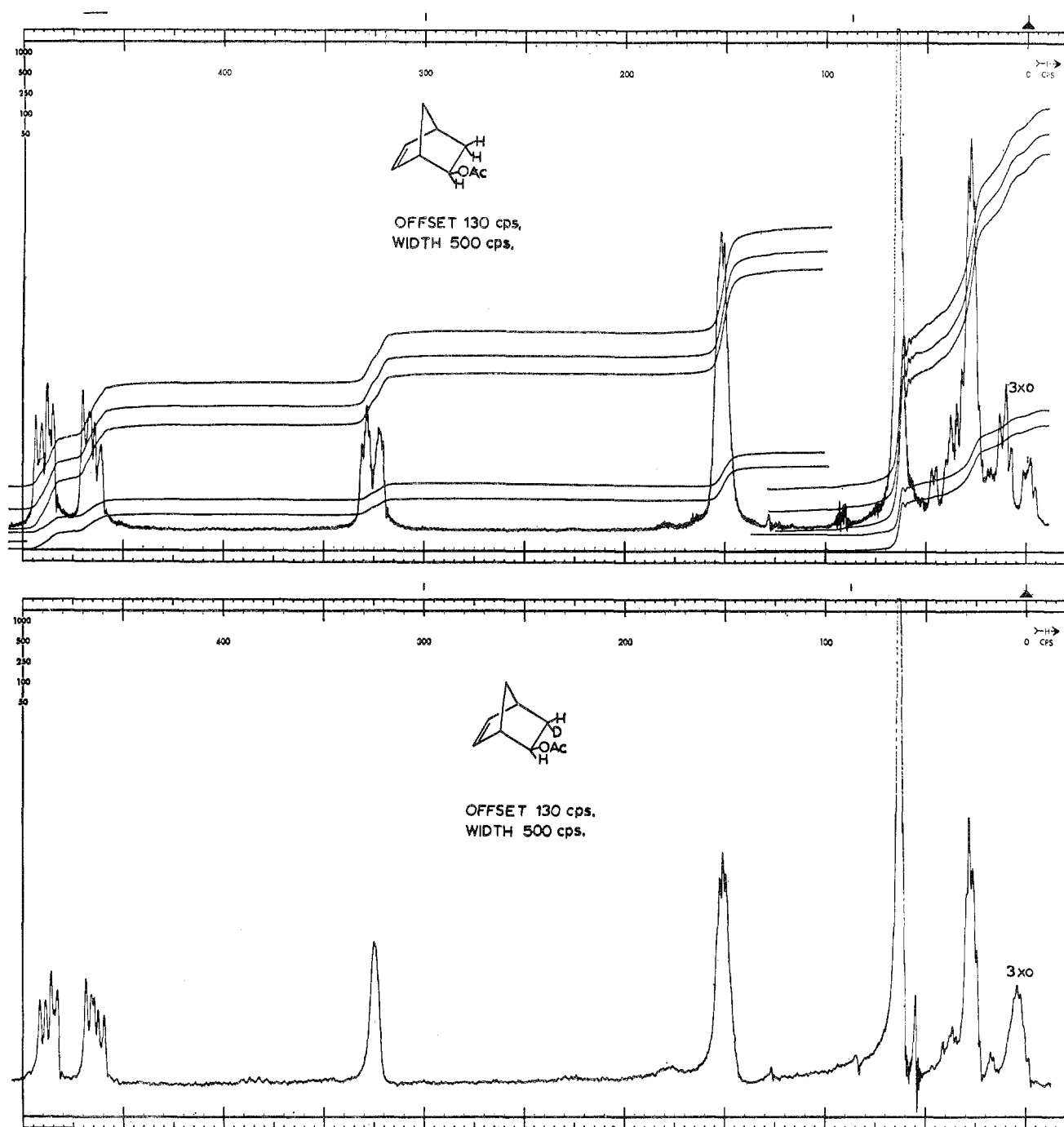
Scheme I

Figure 3. Nmr spectra of **19** and **19**-*endo*-3-*d* at 100 MHz.

Pyrolyses of **18**-*exo*-7-*d* at 306° in decalin solution to conversions of either 6 or 30% (two separate experiments) give reaction mixtures containing *exo*- and *endo*-norbornenyl acetates, as well as starting material, the latter being recovered as unchanged **18**-*exo*-7-*d* with no *endo* deuterium detectable (<2%). The *exo*-norbornenyl acetate is essentially pure **19**-*exo*-3-*d*, with the deuterium and acetoxy *cis* to each other. This becomes evident upon comparison (see Figure 2) of the 100-Mc nmr spectrum of the rearranged **19**-*exo*-3-*d* with that of a synthetic authentic sample prepared by

deuterioboration–oxidation–acetylation of norbornadiene.[18] The two spectra are virtually identical and are quite different from that of **19**-*endo*-3-*d*, which is available from an independent synthesis.

Particularly noteworthy is the complete absence in the spectra of both rearranged and synthetic **19**-*exo*-3-*d* of absorption in the furthest upfield region of the spectrum, where the 3-*exo* proton signals of both the undeuterated and 3-*endo*-deuterated compounds appear

(18) A method similar to that of S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2726 (1966).

18-exo-7-d   19-exo-3-d
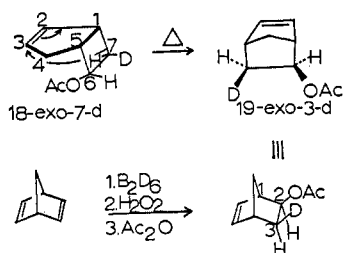
(Figure 3). Also, the signal due to the α-acetoxy proton (C-2) of **19**-*exo*-3-*d* appears as a slightly broadened doublet at about 450 cps with a spacing of 7 cps, ascribable to coupling with the *endo-cis* proton at C-3. This absorption is a broadened singlet in the 3-*endo*-deuterio compound. Time-averaged repeated-scan observation of the upfield 3-*exo*-proton region of the rearrangement product **19**-*exo*-3-*d* and comparison with the spectrum of **19**-*endo*-3-*d* show that not more than 5% of the latter material can be present.

The **18** → **19** rearrangement, necessarily suprafacial, thus occurs with highly specific *inversion* of configuratiion of the migrating group (C-7). The result is difficult to reconcile with a mechanism in which the C-1–C-7 bond of **18** simply stretches to break before appreciable C-7–C-3 bonding occurs, since this kind of process should cause retention or randomization. Instead, the favored approach to the transition state appears to require a much more complex kind of motion in which compression of the C-2–C-1–C-7 bond angle occurs simultaneously with torsional motions around the C-6–C-7 and C-5–C-6 bonds to produce the atomic arrangement **26**. Whether this half-migrated species
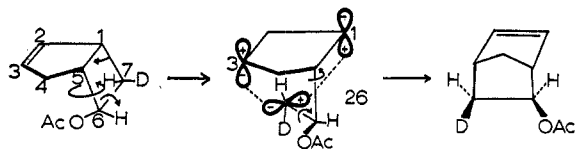
occupies a minimum in the potential energy curve or whether there is only a single transition state cannot be specified at present. What is clear is that bonds from C-7 to *both* C-3 and C-1 must exist throughout and that these connect *opposite faces* of C-7 to the origin and terminus of migration. The configurational inversion is reasonable only in terms of orbital symmetry control of the geometry of the transition state.

The stereochemical experiment also permits the conclusion (as a welcome and almost inseparable intellectual "fringe benefit") that the rearrangement is concerted. This would have been very difficult to establish by more conventional criteria. Usually, these involve determination of the kinetic quantities of activation from the temperature dependence of the rate constant. The reaction is assumed to be concerted if it has an activation energy substantially lower than that which would be associated with its stepwise diradical[19] counterpart. Although a thorough study of

the kinetics of the pyrolysis of *endo*-bicyclo[3.2.0]-hept-2-en-6-yl acetate is not yet complete, a rough estimate of the activation energy is available from the rate at one temperature and the assumption of a "normal" Arrhenius preexponential term. The derived value is about 45 kcal/mol. A guess at what the activation energy would be for a hypothetical diradical process could be obtained by subtracting that part of the allylic resonance energy normally thought to be available in thermolysis reactions (13–15 kcal/mol[20]) from the activation energy (62.6 kcal/mol[21a]) for pyrolysis of isopropylcyclobutane (presumably through the 1,4 diradical). This gives a value of 48–50 kcal/mol. Alternatively, the pyrolysis of isopropenylcyclobutane, which has[21b] $E_a = 51$ kcal/mol, could be assumed to be stepwise and thus could serve as a model. Since a number of small and not very accurate corrections for substituent effects, ring strain, intramolecular nonbonded repulsions, and other geometric factors would have to be made before these model values became suitable for interpretation, the small differences from the value for **18** (*ca.* 45 kcal/mol) cannot be considered to provide a firm basis for the concerted mechanism.

It is nevertheless a matter of the greatest interest to know the actual difference in energy between the transition states for the concerted and diradical processes, since this gives some estimate of the strength of the bonding forces in the formally pentavalent-carbon species **26**. From the time-averaged nmr analysis of the pyrolysis product **19** from **18**-*exo*-7-*d* described above, it would appear that perhaps as much as 3–5% of **19**-*endo*-3-*d* is present.[17] The origin of this material is not clear, since it may well result from contamination of the starting **18**-*exo*-7-*d* with an indetectably small amount of **18**-*endo*-7-*d* arising from not quite complete stereospecificity in the synthesis. If it is mechanistically significant, however, and if the diradical mechanism is considered to give randomization of stereochemistry, the diradical transition state could then be as little as $2.3RT \log 9$ or about 2.5 kcal/mol higher in free energy than the concerted one.

At the half-migrated stage (**26**), the migrating carbon and its two attached hydrogens lie in a plane perpendicular to the allyl plane. Therefore, whatever the net energy difference favoring the concerted over the diradical transition state, it consists of a balance between the favorable electronic interaction of the three-center bond involving the migrating carbon, the origin, and the terminus and the unfavorable repulsive interaction that develops as the hydrogen attached to the migrating group is thrust into the plane of the five-membered ring. Perhaps by attachment of bulkier groups to the *endo* C-7 position of the reactant, this steric interaction can be made so severe that the diradical mechanism assumes the dominant role.

It may well be that the rearrangement of **18** observed

(19) For want of a better term, we follow the path of least resistance and use "diradical" to refer to the intermediate with a fully broken bond.

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

(21) (a) M. Zupan and W. D. Walters, *J. Phys. Chem.*, **67**, 1845 (1963); (b) C. S. Ellis and H. M. Frey, *Trans. Faraday Soc.*, **59**, 2076 (1963).
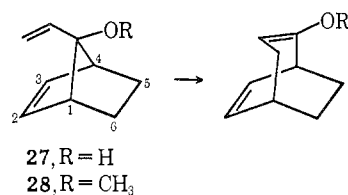
here represents an ideal combination of circumstances for the concerted 1,3-sigmatropic process and that in other systems, where the geometric relationship of the unsaturated system and the migrating group is not so favorably and rigidly determined, the reaction will not occur. Only further experiments can decide this. Certainly, suprafacial 1,3-sigmatropic rearrangements can occur in which inversion of the migrating group is prohibited. An example is provided by the rearrangement of the dienol 27 or its ether 28,[22] where inversion of the migrating carbon (C-1) would produce an impossibly strained *trans*-bridged rearrangement product. Reactions of this type presumably are nonconcerted.

Nevertheless, it is entirely likely that where such difficulties are absent, a large class of configuration-inverting concerted 1,3-sigmatropic rearrangements awaits discovery. These processes in principle should be just as general as the familiar configuration-retaining

27, R = H
28, R = CH₃

1,2-sigmatropic rearrangements of carbonium ion chemistry.

In any case, it seems clear that a prediction of the stereochemical outcome of the rearrangement of 18 based on orbital symmetry rules qualifies as "risky" in Popper's sense. The experiment thus serves as a confirmatory test of the theory.

(22) (a) J. A. Berson and M. Jones, Jr., *J. Am. Chem. Soc.*, 86, 5017, 5019 (1964); (b) J. A. Berson and E. J. Walsh, Jr., unpublished, E. J. Walsh, Jr., Ph.D. Dissertation, University of Wisconsin, 1968.