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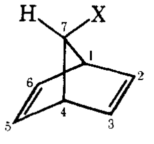
Anionic Rearrangement of 7-Norbornadienol: a 1,3-Sigmatropic Shift

Boris Franzus,*[1] Monte L. Scheinbaum, Deborah L. Waters, and Harold B. Bowlin

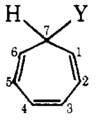
Contribution from the Department of Chemistry, East Tennessee State University, Johnson City, Tennessee 37601. *Received March 13, 1975*

Abstract: The major factors influencing rearrangement of 7-acetoxynorbornadiene to tropyl derivatives have been elucidated. 7-Acetoxynorbornadiene undergoes saponification to 7-norbornadienol which, in turn, via base catalysis, rearranges rapidly to the tropyl skeleton. Lack of deuterium incorporation in the product when the rearrangement was run in CH_3OD seemed to eliminate a "free" carbanion as a mechanistic possibility. Rearrangement of 7-deuterio-7-norbornadienol exclusively to 7-deuteriotropyl oxide clearly demonstrated that the bridge carbon, C-7, migrated intact with its deuterium and oxygen to the final tropyl skeleton. The rearrangement has been rationalized in terms of a 1,3-sigmatropic shift with inversion to a norcaradiene intermediate which in turn undergoes a symmetry-allowed disrotatory ring opening to product. The formation of tropyl products has been rationalized in terms of the proposed mechanism. The relationship of a very low enthalpy of activation (for rearrangement) and a rate acceleration due to oxide formation of 7-norbornadienol is discussed in terms of rearrangement via a 1,3-sigmatropic shift.

The isomerization of norbornadiene (**1a**, X = H) to cycloheptatriene (**2a**) takes place under relatively severe thermal conditions (452°);[2] however, 7-alkoxy (**1b**, X = OR) and 7-phenyl (**1c**, X = C_6H_5) substituted norbornadienes undergo a more facile (170 °) thermal rearrangement to the corresponding tropyl derivatives.[3] A similar reaction involving conversion of a norbornadiene system into a cycloheptatriene, occurring under milder conditions, was observed in the reduction of 7-acetoxynorbornadiene (**1d**, X = $OCOCH_3$) with lithium aluminum hydride in tetrahydrofuran.[4] The product obtained in this case using lithium aluminum deuteride was 1-deuteriocycloheptatriene (**2a**, Y = D).



1a, X = H
b, X = OR
c, X = C_6H_5
d, X = $OCOCH_3$
e, X = OH

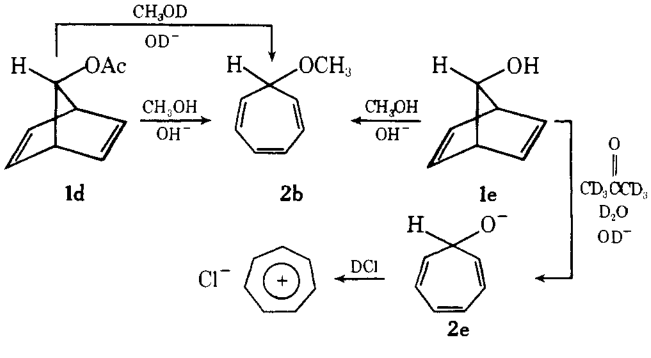


2a, Y = H
b, Y = OCH_3
c, Y = C_6H_5
d, Y = $OCOCH_3$
e, Y = OH
f, Y = OC_6H_5

Story[5] reported that attempted preparations of 7-norbornadienol (**1e**) by either acid- or base-catalyzed hydrolysis of the corresponding ester (**1d**) were unsuccessful, leading to complicated product mixtures. 7-Norbornadienol is known to be slowly converted to tropylium ion under strongly acidic conditions (fluorosulfonic acid, $k = 6.2 \times 10^{-4}\ s^{-1}$ at 47°) presumably via the intermediacy of the 7-norbornadienyl cation,[6] but failure to isolate (**1e**) under basic conditions does not support these conclusions.

In an earlier investigation of this rearrangement,[7] it was found that upon repeating Story's[5] work on the base-catalyzed reaction of 7-acetoxynorbornadiene (**1d**) in methanol, methyl tropyl ether[8] (**2b**) was isolated. Indeed, as shown in Scheme I, methyl tropyl ether (**2b**) is also formed by reaction of 7-norbornadienol (**1e**) with *catalytic* quantities of base in the presence of methanol. The course of these rearrangements is readily followed by NMR spectroscopy since

Scheme I



reactants and products absorb at different magnetic environments; **1d** and **1e** the acetate and the alcohol, respectively, exhibited proton multiplets (H_1, H_4) at $\delta \sim 3.6$ and 3.3, a single hydrogen multiplet (H_7) $\delta \sim 4.5$ and 3.8, and four vinyl hydrogens at $\delta \sim 6.7$ and 6.5. The product (**2b**) showed vinyl hydrogen absorption at $\delta \sim 6.6$ (H_3, H_4) which did overlap with reactant vinyl proton absorptions. However, vinyl protons H_2 and H_5 exhibited multiplets at $\delta \sim 6.0$ and H_1H_6 gave a clearly defined doublet of doublets at $\delta \sim 5.3$. In addition, the one allyl hydrogen, H_7, absorbed at $\delta \sim 3.6$ as a triplet of triplets. Rearrangement of 7-norbornadienol (**1e**) is very rapid. As a typical run exemplifying the rapidity of this rearrangement, a 3 M solution of 7-norbornadienol (30 mmol) in 0.08 M NaOH (0.8 mmol NaOH) in methanol completely rearranges to the tropyl skeleton within 5 min at ambient temperatures.

The possibility of a mechanistic pathway (for the rearrangement) involving a "free" carbanion formed by proton abstraction from carbon can be excluded by virtue of the fact that no deuterium incorporation is observed in compound **2b** by treatment of **1d** in CH_3OD-OD^- (see Scheme I). Futhermore, the presence of an alcohol such as methanol is *not* a necessary condition for reaction since 7-acetoxynorbornadiene (**1d**) readily rearranges to the tropyl skeleton in the presence of sodium deuterioxide, acetone-d_6 and deuterium oxide. The NMR of this product is consistent with either that of a tropyl derivative such as the unstable tropyl alcohol (**2e**) or ditropyl ether (**2f**). That the tropyl framework is indeed formed is further substantiated by noting that the NMR of **2e** (or **2f**) collapses to a singlet upon treatment with a large excess of mineral acid, completely consistent with the tropylium ion.[9]

The rearrangement requires base catalysis and is unlikely to involve carbonium ions since 0.02 M methanol solutions of either 7-acetoxynorbornadiene or 7-norbornadienol show no evidence of reaction after 6 months at ambient temperatures. We felt very strongly that the rearrangement involved the alkoxide of 7-norbornadienol (**1e**) since neither 7-*tert*-butoxynorbornadiene (**1b**, R = $C(CH_3)_3$)[5] nor 7-methoxynorbornadiene (**1b**, R = CH_3)[10] underwent *any* reaction with sodium hydroxide in methanol. The reaction appeared to be limited to the alcohol or the acetate. Although the acetate is not considered a good leaving group, it is vastly superior to OCH_3, O-t-C_4H_9, and OH; hence, any scheme accounting for the above facts must account for lack of reactivity of the ethers and the enhanced reactivity of the alcohol over the acetate. In summary, the following facts have to be rationalized: (i) a more rapid rearrangement of 7-norbornadienol (**1e**) over that of the acetate (**1d**), (ii) no deuterium incorporation, (iii) the necessity of base but not of alcohol, (iv) the unreactivity of 7-*tert*-butoxy- or 7-methoxynorbornadiene, and (v) the catalytic effect of hydroxide ion on the 7-norbornadienol rearrangement. A scheme (not a mechanism) consistent with the above data involves a relatively slow alkaline hydrolysis of 7-acetoxynorbornadiene (**1d**) to 7-norbornadienol (**1e**) followed by a more rapid rearrangement to the tropyl oxide (**2e**)′, which upon reaction with water regenerates the hydroxide ion (as catalyst) and tropyl alcohol (**2e**). Since it is assumed that k_1 is greater than k_2, the enhanced rate of rearrangement of alcohol over acetate is obvious; in addition, the O-H proton abstraction accounts for this lack of deuterium exchange on carbon. The above scheme does not rely on methanol for reaction but does require base for rearrangement. Since it is the oxide of 7-norbornadienol (**1e**)′ that undergoes rearrangement, it is apparent that there would be no pathway whereby the corresponding ethers (methoxy or *tert*-butoxy) could follow a similar course. Finally, it can be readily seen that reaction of 7-norbornadienol with base produces tropyl alcohol and regeneration of base, indicating that the hydroxide ion need be present only in catalytic quantities to effect rearrangement.

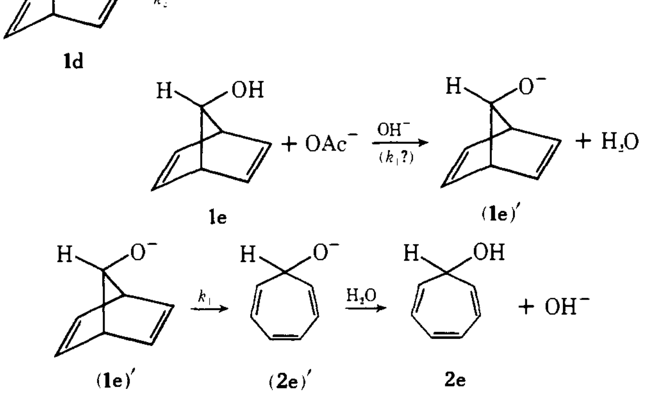


Table I. Kinetic Data for Hydrolysis[a] of 7-Acetoxynorbornadiene (1d) and Rearrangement of 7-Norbornadienol (1e)

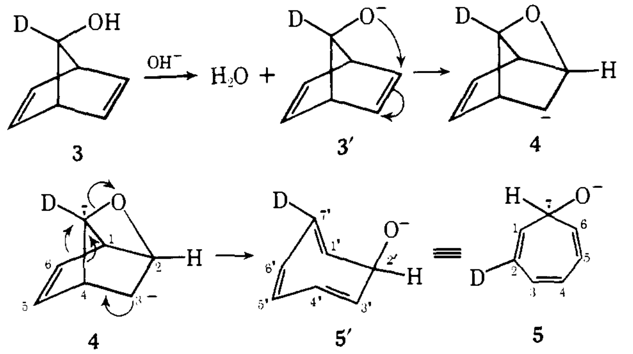
Compound[c] (M)	Base, M	$k_2 \times 10^3$, $M^{-1}\,s^{-1}$ titrimetric	$k_1 \times 10^4$, s^{-1} spectral	k_1 (cor) $\times 10^3$, $M^{-1}\,s^{-1}$ spectral
1d (0.07763)	0.07763	1.218		
1d (0.07970)	0.07970	1.210		
1e	0.00679		3.73	5.49
1e	0.00679		3.69	5.43
1e	0.00339		1.566	4.62
1e	0.00339		1.583	4.67

[a] Temperature for all the above kinetic runs, spectral and titrimetric, was 24.73 ± 0.05°. [b] Solvent used for all kinetic runs was 90/10 methanol–water. [c] All 7-norbornadienol (1e) concentrations were 5×10^{-4} M.

In order to confirm the above reaction scheme, titrimetric rates of 7-acetoxynorbornadiene to 7-norbornadienol and spectrophotometric rates of 7-norbornadienol to the tropyl skeleton were run (see Table I). As one would expect, titrimetric rates for 7-acetoxynorbornadiene to 7-norbornadienol were clearly second order ($k_2 = 1.214 \times 10^{-3}$ l. mol^{-1} s^{-1}). Spectrophotometric rates of 7-norbornadienol rearranging to tropyl alcohol were clearly "pseudo" first order. Thus at $OH^- = 0.00679$ M, $k_1 = 3.7 \times 10^{-4}$ s^{-1} or as a second-order rate, taking into account the base concentration, k_1(cor) = 5.45×10^{-2} l. mol^{-1} s^{-1}. At $OH^- = 0.00339$ M, $k_1 = 1.57 \times 10^{-4}$ s^{-1} or as a second-order rate k_1(cor) = 4.65×10^{-2} l. mol^{-1} s^{-1}. Thus the second step of the above scheme is some 40 times faster than the first step, confirming the predicted rearrangement scheme. Although the stepwise scheme appeared consistent with the experimental data, the mechanistic path for rearrangement of the alkoxide of 7-norbornadienol (**1e**)′ to the tropyl derivative had to be rationalized.

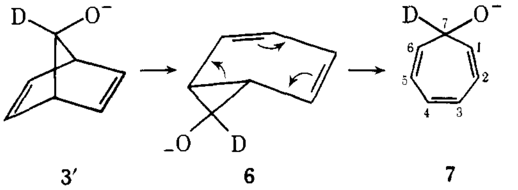
There seemed to us only two plausible mechanistic possibilities that should be considered if it is assumed that the rearrangement takes place via the alkoxide. In path A, oxetane (**4**) formation should be sterically facile. Although nucleophilic addition to the double bond should not be a favored reaction, there is some precedent[4] for such a conjecture. Rearrangement of the oxetane (**4**), as shown above, would give rise to 2-deuteriotropyl oxide (**5**). The pathway to **5**′ involves a synchronous "backside" oxetane ring opening at C-7 by the C-6-C-1 σ electrons, π-bond formation at C-1′-C-7′ via the C-4-C-7 σ electrons, and a C-3′-C-4′ π-bond formed by the lone pair of electrons at C-3.

Path A



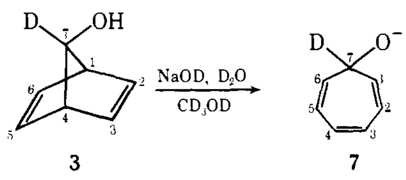
Alternatively (path B), tropyl alcohol formation can be rationalized by postulating that the alkoxide of norbornadienol (**3′**) undergoes a 1,3-sigmatropic shift with C-7 as the migrating carbon. Orbital symmetry considerations predict that such a concerted transformation to a norcaradienol (**6**) could occur with inversion about the C-7 atom.[11] The norcaradienol (**6**) would undergo disrotatory opening by a concerted, symmetry-allowed process to give the tropyl alcohol alkoxide. Thus, with the deuterium label in the 7 position of 7-norbornadienol, the appearance of deuterium at C-2 would be consistent with path A, whereas deuterium at C-7 would imply that rearrangement occurred via path B. The above results, of course, would imply no deuterium scrambling.

Path B



In order to determine whether path A or path B was operative, the synthesis of 7-deuterio-7-norbornadienol (**3**) was undertaken following the elegant synthetic pathways as outlined by Lustgarten, Brookhart, and Winstein,[6] modified but slightly in our laboratories.

The ^{1}H NMR of 7-deuterio-7-norbornadienol (**3**) in CD_3OD is shown in Figure 1a. It is apparent that absorption due to H-7 at δ 3.7 is missing from **3**. The tropyl oxide reaction product (**7**), formed in 2 min from reaction of **3** with NaOD in CD_3OD-D_2O, is shown in Figure 1b. The usual doublet of doublets at δ 5.42 (see inset Figure 1) has been reduced to a single doublet. This simpler splitting pattern arises from the fact that absorption due to H_7 is now absent; that is, no H_7 absorption at δ 3.6 appears. Clearly the product must arise from some mechanistic pathway akin to Scheme B since compound **7** with deuterium at C-7 is the only observable product from this rearrangement. In addition, the stability of the product is demonstrated by the fact that compound **7** showed *no* evidence of scrambling even after 1 week of standing at −10°. The integrity of the deuterium placement as evidenced by NMR spectroscopy is 95% or greater.



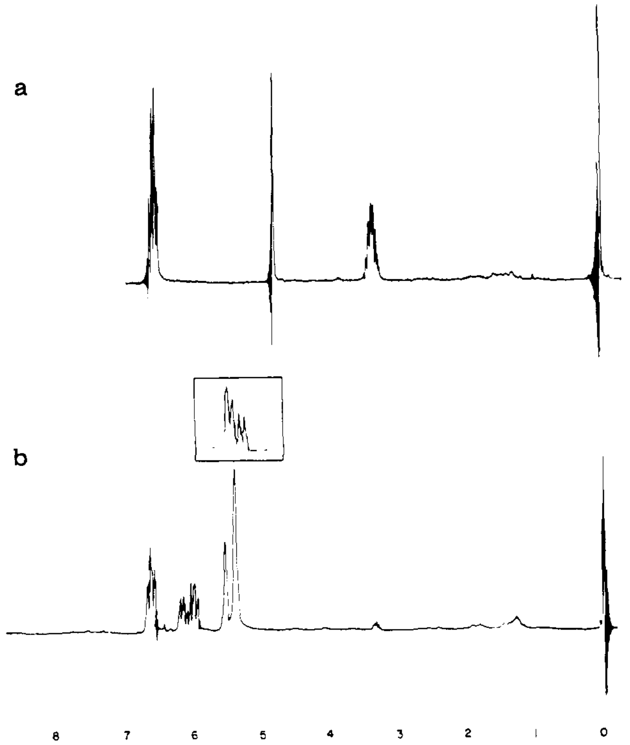
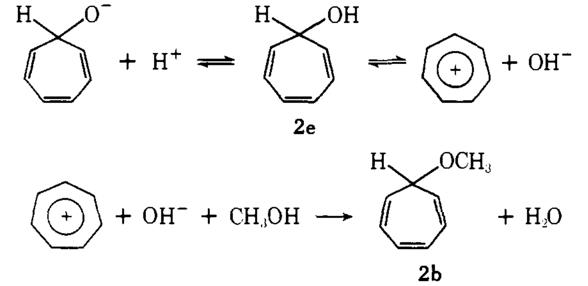


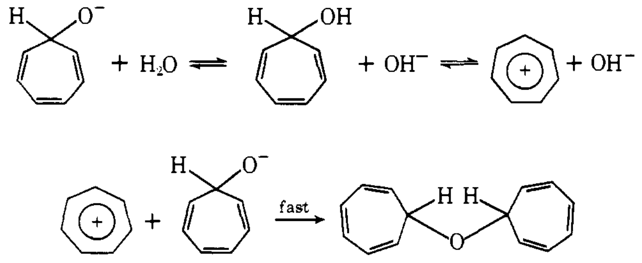
Figure 1. (a) The ^{1}H NMR of 7-deuterio-7-norbornadienol (**3**) (H_7 absorption should be δ ~3.7); (b) the ^{1}H NMR of 7-deuteriotropyl oxide (**7**) (H_7 absorption should be δ ~3.6); (inset) ^{1}H NMR of H_1, H_6, rearrangement of 7-norbornadienol (**1e**) to tropyl oxide (**2e**).

All the products from the rearrangement can now be rationalized. The formation of methyl tropyl ether (**2b**) can be readily explained. The usual preparation of methyl tropyl ether from 7-acetoxynorbornadiene (**1d**) or 7-norbornadienol (**1e**) involved reaction of **1d** or **1e** in methanol-sodium hydroxide, followed by *neutralization* of the alkaline solution with concentrated hydrochloric acid, dilution of the mixture with water, and extraction of the product from the mixture with methylene chloride. Formation of methyl tropyl ether via tropyl alcohol can be rationlized as shown in Scheme II. Doering[8] has shown that tropyl alcohol is in dynamic equilibrium with the tropylium ion (pK_a = 4.75), and that the amount of each species is pH dependent. The ethers on the other hand will cleave in strong acid but are relatively stable in mildly alkaline, neutral, and slightly acid solutions. Thus tropyl alcohol would be in equilibrium with the oxide and the tropylium ion; the latter should irreversibly capture the methanol to form the stable methyl tropyl ether. To further test this mechanism and show that in the alkaline methanolic media *no* methyl tropyl ether was formed but instead the alkoxide was the product of rearrangement, 7-norbornadienol (**1e**) was allowed to react with sodium hydroxide in methanol and the methanol removed under aspirator vacuum. Water was added to the reaction mixture and the product extracted with ether. Were any methyl tropyl ether formed during rearrangement, it would have been readily detected; however, in almost quantitative yields, ditropyl ether (**1f**) was the sole product. Again this

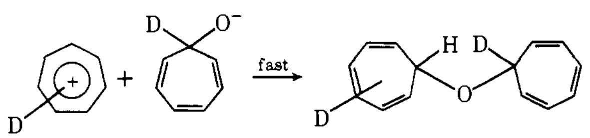
Scheme II



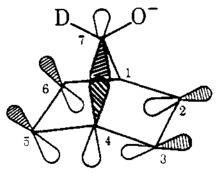
product can also be rationalized by the same mechanism evoked for explanation of methyl tropyl ether formation. Finally, should the above mechanism obtain, then one could anticipate that the ^{1}H NMR of ditropyl ether formed by rearrangement of 7-deuterio-7-norbornadienol (**3**) would indicate 50% deuterium scrambling. For total deuterium scrambling (both rings), one would obtain 85.72% vinyl H and 14.28% allyl H. Of course, if there were no scrambling, one would obtain 0% allyl H and 100% vinyl H. For 50% deuterium scrambling as depicted above (and implying *no reversal of product to reactants*), one should theoretically obtain 92.86% vinyl H and 7.14% allyl H. What was observed was 92% vinyl H and 8% allyl H in complete accord with the postulated mechanism.

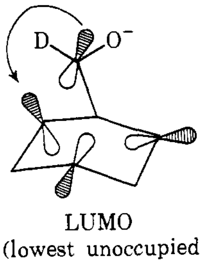


1f

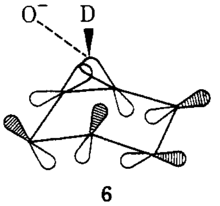


That the rearrangement proceeds via C-4–C-7 (or C-1–C-7) bond breaking appears inevitable since only that product labeled with deuterium at C-7 of the tropyl skeleton is formed. A mechanism involving a 1,3-sigmatropic shift is favored since the driving force for the 1,3-sigmatropic shift is provided by the generation of a pentadienyl system rather than an allyl system. Simple molecular orbital calculations[12] indicate an added stabilization of 0.66 β for the pentadienyl over the allyl system. In addition, a further driving force derives from the facile thermally allowed disrotatory ring opening of **6**[11,13] both by relief of bicyclic ring strain and obtention of conjugative stabilization energy from the conjugated triene product.





LUMO
(lowest unoccupied
molecular orbital)



6

Orbital symmetry allows only two processes for thermal allylic "type" migration: suprafacial with inversion at the migrating carbon (C-7) or antarafacial with retention at the migrating carbon (C-7). The latter case has been recognized by Baldwin,[14] and, in addition, forbidden 1,3-sigmatropic rearrangements have been clearly demonstrated by Berson.[15] Steric requirements dictate that a 1,3-suprafacial shift with inversion at the migrating carbon should be the preferred mode of rearrangement.[11,15-17] Molecular models of the norbornadienyl system in conjunction with Berson's data[15,17] seem to indicate this should be the preferred mode of rearrangement for the 7-norbornadienyl skeleton.

Table II. Activation Parameters for Rearrangement of 7-Norbornadienol (**1e**) to Tropyl Alcohol (**2e**)[a-c]

Temperature, °C	$k_1 \times 10^4$, s^{-1}	
15.13 ± 0.05	1.15	
15.13 ± 0.05	1.14	
24.73 ± 0.05	3.73	
24.73 ± 0.05	3.69	$\Delta H^{\ddagger} = -18.9 \pm 0.5$ kcal
34.63 ± 0.05	9.23	$\Delta S^{\ddagger} = -10.8 \pm 0.5$ eu
34.63 ± 0.05	9.23	

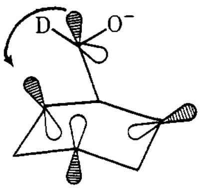
[a] Solvent was 90/10 methanol–water. [b] Concentration of 7-norbornadienol was about 5 × 10^{-4} M. [c] All base concentrations were 0.00679 M.

A diradical intermediate can be ruled out by the energetics of the system. We have followed Berson's calculations[17] and have estimated the endothermicity of the reaction roughly as 82 kcal/mol minus the sum of (a) the strain energy of the norbornadiene system,[18] about 26 kcal/mol, (b) the stabilizing effect of a pentadienyl system estimated at best to be about 22 kcal/mol (13 kcal/mol for allylic groups[19] + 0.66 (β) × 13 kcal/mol), and (c) 3 kcal/mol for an alkoxy (alcohol) group.[17] At best this calculation would predict that the heat of formation of the diradical would be about 31 kcal/mol above that of substrate. The observed activation energy of 19 kcal/mol (see Table II) does not permit the formation of a diradical as a reasonable entity.

Thus we are forced to conclude that the alkoxide of 7-norbornadienol (**3′**) is the species undergoing rearrangement. Further support for this deduction derives from the observation that the rearrangement rate of 7-norbornadienol in methanol-water did not vary significantly from that rate observed in pure methanol. This is similar to Cram's[20] observation, wherein water in methanol-potassium methoxide did not appreciably affect rates of base-catalyzed racemization of (—)-2-phenylbutyronitrile. Also consistent with the alkoxide postulate is our own observation that in the one run utilizing the *tert*-butyl alcohol-potassium *tert*-butoxide system, the rearrangement was so rapid we could only estimate a minimum second-order rate constant of 380 l. mol^{-1} s^{-1}. The velocity of the potassium *tert*-butoxide catalyzed rearrangement is about 10 000 times that of the methanol-sodium hydroxide rate; this parallels relative base strengths of sodium hydroxide in methanol as compared with potassium *tert*-butoxide in *tert*-butyl alcohol.[20] Thus if it is postulated that the observed enthalpy of activation is due to proton removal from the O-H of 7-norbornadienol, then it must also be concluded that the activation barrier to rearrangement must be still lower than the observed 19 kcal/mol. The 19-kcal/mol activation energy represents one of the lower activation parameters observed for a 1,3-sigmatropic shift. Yet this low-engery barrier is not without precedent in other symmetry-allowed processes since Bates[21a] has observed enthalpies of activation as low as 18 kcal/mol in 1,6-sigmatropic shifts of the pentadienyl carbanion system, and free energy ($\Delta G^{\ddagger}$) values as low as 9[21b] and 15 kcal/mol[21c] have been observed for cationic sigmatropic shifts.

It has been tacitly assumed that the rearrangement proceeds via the alkoxide of 7-norbornadienol to the norcaradiene type alkoxide (**6**); the possibility also exists that the rearrangement occurs directly to the cycloheptatriene system without first forming the norcaradiene intermediate. Although the driving force for such a rearrangement directly to product is not obvious at this time, it cannot be disregarded. However, we still favor the norcaradiene intermediate since the driving force to intermediate is symmetry allowed.

The transition state for formation of **6** can be envisioned as either resembling compound **8** with the negative charge still residing on oxygen or like **9** where the negative charge rests mainly in the pentadienyl system (nonbonding MO).



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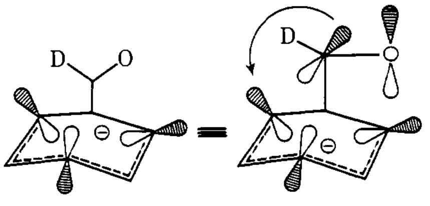
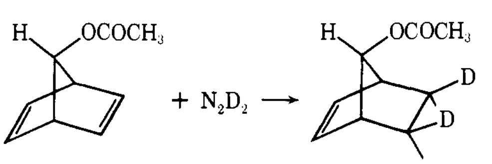


9 **9**

Either structure is still consistent with a 1,3-sigmatropic shift accompanied by inversion at C-7; indeed, it might be noted that structure **9** is somewhat similar to an intermediate proposed by Fukanaga in the thermal rearrangement of tropone ethylene ketals.[22] This same type of polar effect has been noted in the diimide reduction of 7-substituted norbornadienes (**1b,e**), wherein the *more* sterically hindered double bond was preferentially reduced.[23] In each case reduction occurred exo and on the same face as that occupied by the oxygen moiety. Since diimide reduction is a case of (4 + 2) cycloaddition,[24] one notes again a strong polar effect on a symmetry-allowed cycloaddition. It thus appears that one has reason to search for polar effects in symmetry-allowed reactions although the basis for such effects may not necessarily be abundantly clear.



Experimental Section

NMR spectra were obtained on a JEOLCO-C-60H NMR spectrometer; ultraviolet spectra and kinetics by ultraviolet were taken on a Cary 14 ultraviolet spectrometer. Deuterium analyses were run by the Joseph Nemeth Laboratories in Urbana, Ill. All other analyses were performed by the Galbraith Laboratories in Knoxville, Tenn.

Methyl Tropyl Ether (2b) from 7-Acetoxynorbornadiene (1d). To 6.0 g (0.04 mol) of 7-acetoxynorbornadiene dissolved in 10 ml of a 90/10 (v/v) methanol-water mixture was added 0.05 mol of sodium methylate (sodium hydroxide worked equally well) in 40 ml of methanol-water solution. The solution rapidly darkened to a deep yellow. Four minutes after addition of the base an aliquot of the solution was examined by ultraviolet spectroscopy and found to be greater than 90% converted to a tropyl derivative. The basic organic solution was slightly acidified with 2.6 ml of 12 N hydrochloric acid, diluted with 200 ml of water, and extracted with methylene chloride; the methylene chloride layer was washed first with 10% sodium bicarbonate, then with saturated sodium chloride solution. The methylene chloride layer was dried overnight with anhydrous sodium sulfate, the product concentrated by removing dichloromethane under reduced pressure with a rotary evaporator, and the product (1.47 g, 0.012 mol, 37%) distilled at 43° (4.25 mm). The NMR and infrared spectra and boiling point all agree with those of an authentic sample of methyl tropyl ether.[8] Methyl tropyl ether was obtained in 32% yield following the same procedure described above but using sodium hydroxide as base instead of sodium methylate.

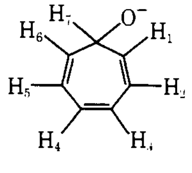
Reaction of 7-Acetoxynorbornadiene in Deuterated Solvents. To 6.0 g (0.04 mol) of 7-acetoxynorbornadiene (**1d**) dissolved in 10 ml of methanol-*d* (>97% deuterated as determined by NMR utilizing the natural ^{13}C abundance as a reference) in a 200-ml, three-neck reaction vessel under a dry nitrogen atmosphere was added 5 ml of a 40% sodium deuterioxide-deuterium oxide (>99% D) dissolved in 35 ml of methanol-*d*. The solution contained about 0.05 mol of sodium deuterioxide. The base solution was added to the diene in about 1 min, allowed to stand for a couple of minutes, and then neutralized with 12 N hydrochloric acid. The reaction mixture was diluted with water and extracted with methylene chloride. The methylene chloride layer was washed first with 10% sodium bicarbonate, then with saturated sodium chloride, and finally dried over anhydrous sodium sulfate. The organic layer was filtered; the product was concentrated in a rotary evaporator under reduced pressure, distilled at 25° at 2 mm, and collected in a receiver cooled with dry ice. The product (1.80 g, 0.015 mol, 37%) was again identical with an authentic sample of methyl tropyl ether. Deuterium analysis of the product indicated 0.25% excess D. In essence, there was no deuterium incorporation since 10 atom % excess D represents one deuterium per molecule.

Reaction of 7-Norbornadienol (1e) with Base. To 2.2194 g of 7-norbornadienol (80% GLC; 0.0164 mol) in a 10.00-ml volumetric flask was added 8 ml (0.8 mmol) of 0.1013 N sodium hydroxide in 95/5 methanol-water and enough methanol-water to give exactly 10.00 ml of solution. The reaction was exothermic and turned in color from colorless to a yellowish brown. A GLC sample (after 10 s) showed about 50% 7-norbornadienol 3.4 min from air and about 50% of another peak 3.7-4.0 min from air (5% Ucon polar, 1 m, 80°). A 3-min sample indicated only a single product about 3.7 min from air. The ultraviolet spectrum of a 5-μl (0.005 ml) sample diluted to 50.0 ml with methanol had λ_{max} 258 nm; $A = 0.652$. After 15 min there was no change in the GLC and essentially no change in the ultraviolet spectrum. The solution was carefully neutralized with 12 N hydrochloric acid: calculated for 0.8 mmol of base, 0.075 ml of 12 N hydrochloric acid; found, 0.075 ml of 12 N hydrochloric acid. Upon neutralization, the solution (reversibly) changed to a lemon yellow. The methanol was distilled at 25° and 100 mm. The mixture was distilled under reduced pressure, and the fraction boiling at 50-52° (10 mm) was collected. The yield was 1.35 g (0.011 mol; 67.5%). The following physical properites were noted: $d^{25}{}_4$ 0.971; $n^{20}{}_D$ 1.5107; catalytic hydrogenation (calcd for 1.013 mmol (123.8 mg)), 75.4 ml (found, 81.8 ml). Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.56, 78.37; H, 8.20, 8.16. The product was identical in index of refraction, density, boiling point, infrared, NMR, and uv with an authentic sample of methyl tropyl ether prepared by an alternate route.[8]

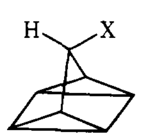
Reaction of 7-*tert*-Butoxynorbornadiene[5] with Base. A 20% solution (0.56 mmol) of 7-*tert*-butoxynorbornadiene and 0.04 ml of 10 M sodium deuterioxide in 0.5 ml of methanol-d_4 was placed in an NMR tube with tetramethylsilane as an internal standard. Absolutely no reaction was observed even after 1 week at 25°.

Reaction of 7-Methoxynorbornadiene with Base. 7-Methoxynorbornadiene[10] (0.3 mmol) and 0.04 ml of sodium deuterioxide (10 N) were diluted to 0.4 ml in an NMR tube with methanol-d_4 using tetramethylsilane as an internal standard. No reaction was observed by NMR spectroscopy either after 30 min or after 1 week of standing at 25°.

Reaction of 7-Acetoxynorbornadiene in D_2O. To an NMR tube were added 0.05 ml of 10 N sodium deuterioxide (0.5 mmol), 0.200 ml of acetone-d_6, 0.250 ml of deuterium oxide, and 0.025 g (0.167 mmol) of 7-acetoxynorbornadiene. The NMR was run immediately, and only the tropyl derivative was observed. The internal standard used was the monoprotonated acetone-d_6 impurity (five lines), and all chemical shifts reported are based on the assumption that δ for acetone is 2.17: H_1, H_6 (2 H) δ 5.45, quartet; H_2, H_5 (2 H) multiplet δ 6.05; H_3, H_4 (2 H) multiplet δ 6.62; H_7 (1 H) multiplet δ 3.60. Addition of excess deuterium chloride in deuterium oxide collapsed the spectra to a single peak at δ 10.15 fully consistent with the tropylium ion.[9]



Structural Formulas for Intermediates Formed in the Synthesis of 7-Deuterio-7-norbornadienol (3). Ring Closure of 7-Acetoxynorbornadiene to the Quadricyclic Acetate (10a) by Irradiation. 7-Acetoxynorbornadiene purchased from Frinton Laboratories was only



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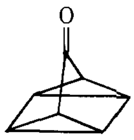

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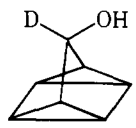
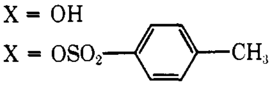


12

10a, X = OCOCH$_3$
b, X = OH
c, X = 

79% pure as determined by GLC (6 ft, 10% FFAP, 100–150°). Irradiation of the impure sample in *n*-pentane at 2537 Å (Rayonet reactor) inevitably led to an unwanted precipitate as an impurity. Simple vacuum distillation (58° at 4 mm) resulted in starting material of 94% purity. In a typical irradiation, reaction of 0.63 g (0.625 ml, 0.0042 mol) of **1d** in 125 ml of pentane (Burdick-Jackson Laboratories, inhibitor free) proceeded for 2.5–4.0 h. Chromatographic analysis (6 ft, 10% FFAP, 100–150°) indicated 100% conversion and almost *100%* yield to the quadricyclic acetate. This method is a modification of the procedure used by Lustgarten, Brookhart, and Winstein.[6] Concentration of the pentane solution and obtention of the solid quadricyclic acetate (**10a**) was as described by Lustgarten.[6]

7-Quadricyclanol (10b). Reduction of 7-quadricyclyl acetate (**10a**) by lithium aluminum hydride followed the procedure of Lustgarten;[6] no modification of this procedure was adopted.

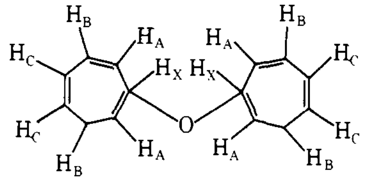
7-Quadricyclyl Tosylate (10c). The tosylates of quadricyclanol were made following Lustgarten's procedure;[6] no modification of this procedure was needed and yields of 60–80% were obtained.

Quadricyclanone (11). In this procedure the quadricyclic tosylate is oxidized by freshly distilled dimethyl sulfoxide (previously dried over freshly activated 4X molecular sieve) in the presence of sodium bicarbonate. Failure to dry and distill the dimethyl sulfoxide resulted in lower yields. Lustgarten's procedure was followed and 50% yields were obtained.

Reduction of Quadricyclanone (11) to the Quadricyclanol (12) with Sodium Borodeuteride. To a solution of 0.5 g (0.012 mol) of sodium borodeuteride (Merck Sharp and Dohme) in 12 ml of absolute ethanol at room temperature was added dropwise 1.0 g (0.009 mol) of the quadricyclanone (**11**) in 4 ml of absolute ethanol. The reaction was complete in 30 min; this was determined by analyzing for the carbonyl peak in the ultraviolet region at 280 nm ($n \rightarrow \pi^*$ transition). The ethanol solution was concentrated under aspirator vacuum in a rotary evaporator; the concentrated solution was carefully neutralized with cold dilute hydrochloric acid, diluted with 30 ml of water, and extracted four times with 20-ml portions of ether. The ether extracts were dried overnight over anhydrous sodium sulfate and filtered, and the ether was removed by aspirator vacuum in a rotary evaporator. An oil and a solid, left behind, were treated with dichloromethane, and the oil went into solution. The solution was filtered to separate the solid, and the dichloromethane solution was evaporated under aspirator vacuum in a rotary evaporator leaving 0.46 g (0.0042 mol; 45%) of 7-deuterioquadricyclanol (**12**), 96% isotopically pure by NMR. Sodium borodeuteride reduction with methanol as solvent resulted in a product with only 80% isotopic purity.

Synthesis of 7-Deuterio-7-norbornadienol (3). To the 0.46 g (0.0042 mol) of 7-deuterioquadricyclanol (**12**) was added 0.3 ml of carbon tetrachloride; the mixture was placed in an NMR tube, an NMR spectrum was taken to ascertain isotopic purity, and finally a few crystals of a Rh(I) catalyst, (μ-dichloro-tetraethylenerhodium(I))[6,25] were added to the NMR tube in order to open the quadricyclic ring to a norbornadiene ring.[6,25a] Based on NMR integration of the downfield to upfield spectra, deuterium at the 7 position was at *least* 96%. After the solution was allowed to stand overnight, the NMR spectra were again taken, showing complete ring opening to 7-deuterio-7-norbornadienol (**3**). The Rh(I) catalyst was filtered and the carbon tetrachloride removed under aspirator vacuum leaving 0.46 g of 7-deuterio-7-norbornadienol. Compound **3** was dissolved in methanol-d_4, the NMR spectrum taken (Me$_4$Si internal standard), and the amount of deuterium incorporation determined by comparing the area in the 7 position with the rest of the norbornadienyl skeleton. No proton absorption showed at the 7 position, assuring a minimum of 96% deuterium incorporation and probably closer to 99% incorporation. Fully consistent with these findings was the disappearance of the doublet of triplets in the vinyl hydrogen region (due to long-range coupling from the 7-H) to simply two triplets[26] and spectral simplification of the bridgehead region.

Formation of Ditropyl Ether (1f). To 3.25 g (0.0301 mol) of 7-norbornadienol was added 10 ml of 0.08 M sodium hydroxide (0.0008 mol) in methanol. The rearrangement, as monitored by NMR spectroscopy, indicated almost 100% rearrangement to the tropyl system in 5 min and complete rearrangement in 8 min. As monitored by NMR, no other peaks but product and solvent appeared. The reaction was allowed to proceed a total of 18 min after which the methanol was stripped at room temperature under aspirator vacuum on a rotary evaporator. Saturated salt solution (40 ml) was added to the reaction vessel and the aqueous layer extracted with three 25-ml portions of ether. The ether layer was dried over anhydrous sodium sulfate for 1 h at room temperature, filtered, and redried with anhydrous sodium sulfate stored and sealed under nitrogen at −10° for 2 days. The ether solution was filtered and the ether removed at room temperature under water aspirator vacuum in a rotary evaporator. The crude yield was 3.18 g (0.016 mol, 0.032 equiv; 100%). It has been reported by Doering[8] and ter Borg[27] that ditropyl ether is unstable in air and at room temperature, so a middle distillation fraction [0.735 g, bp 70–75° (0.05 mm), n^{23}D 1.5745 (lit.[8] n^{25}D 1.5735)] was taken; a portion of this fraction was sealed under nitrogen and stored at −10°, and another portion was sealed under nitrogen, kept at −78°, and driven to Galbraith Laboratories for elemental analysis and molecular weight. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12; mol wt, 198.25. Found; C, 84.75; H, 7.04; mol wt, 195. Infrared and NMR analyses and index of refraction were taken from this same middle fraction: ir (neat) 3010 (vinyl H), 2800 (C-H alkane), 1600 (C=C), 1110 (C-O), 700–750 cm^{-1} (CH=CH, cis). Although the NMR spectrum was that of an XAA′ BB′ CC′ system, some coupling constants were available via decoupling: NMR (CDCl$_3$) δ 3.63 (2 H, H$_X$ triplet of triplets, J_{AX} = 4.4 Hz, J_{BX} = 1.3 Hz), 5.30 (4 H, H$_A$ broad doublet of doublets, J_{AB} = 10.0 Hz, J_{AC} = 0.8 Hz), 6.05 (4 H, H$_B$, m) 6.57 (4 H, H$_C$, m).



Reaction of 7-Deuterio-7-norbornadienol (3) in Alkaline Methanol-d_4. To 0.0996 g (0.000913 mol) of 7-deuterio-7-norbornadienol in 0.4 ml of methanol-d_4 was added about 0.0015 mol of NaOD in D$_2$O (~0.015 ml of 10 M NaOD). By NMR spectroscopy the original dienol (**3**) was about 99% deuterated in the 7 position. The rearrangement product (by NMR) shows *no* allyl-hydrogen next to oxygen (H$_X$ $\delta \simeq 3.6$), and the NMR of the vinyl-hydrogen region (H$_A$, H$_B$, H$_C$) was essentially identical with that of an H$_X$-decoupled spectrum of ditropyl ether. Two minutes after addition of base, rearrangement was complete. NMR (CD$_3$OD; Me$_4$Si internal standard) δ 5.43 (2 H, H$_A$ broad doublet J = 10.0 Hz), δ 6.05 (2 H, H$_B$, m), δ 6.62 (2 H, H$_C$, m). No peak was at δ 3.6 indicating almost 100% positional integrity for the deuterium in the 7 position. The product of rearrangement was stable in base; it showed no change by NMR or any other evidence of scrambling after 1 week at −10° under nitrogen.

Formation of Ditropyl Ether from 7-Deuterio-7-norbornadienol (3). To 0.301 g (0.00276 mol) of 7-deuterio-7-norbornadienol (**3**) was added 0.4 ml of methanol-d_4, tetramethylsilane (as internal standard), followed by 0.01 ml of 10 M NaOD (0.001 mol). The NMR spectrum of the starting dienol (**3**) showed greater than 99% deuterium incorporation at the 7 position; that of the rearranged product showed greater than 99% deuterium at the allyl carbon indicating essentially 100% positional integrity of the deuterium atom. The above mixture was diluted with 10 ml of water and then extracted with 10-ml, 15-ml, and 10-ml portions of ether. The ether extracts were combined, dried over anhydrous sodium sulfate, filtered, and evaporated at room temperature under aspirator vacuum in a rotary evaporator. The weight of the crude product was 0.228 g (0.00114 mol, 0.00228 equiv, 82.5%); the NMR spectrum was fully consistent with that of ditropyl ether. For $C_{14}H_{12}D_2O$ totally scrambled: 85.72% vinyl H, 14.28% allyl H; for $C_{14}H_{12}D_2O$ nonscrambled: 100% vinyl H, 0.0% allyl H; for $C_{14}H_{12}D_2O$ with one ring nonscrambled and the other ring totally scrambled: vinyl H 92.86%, allyl H 7.14% (found: vinyl H 92%, allyl H 8%). Further evidence for the presence of partially scrambled product resided in the fact that the NMR of the H_A vinyl hydrogen region was essentially a broadened doublet similar in appearance to the NMR spectrum of compound **7** (7-deuterio-7-hydroxycycloheptatriene).

Reaction of 7-Norbornadienol with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol. To 0.1 g (0.0009 mol) of potassium *tert*-butoxide in a minimum amount of *tert*-butyl alcohol was slowly added 3.24 g (0.03 mol) of 7-norbornadienol. An NMR spectrum of the mixture indicated complete rearrangement to the tropyl skeleton. Water was added to the mixture, and the alcohol-water mixture was extracted with ether. The ether layer was dried over anhydrous sodium sulfate and filtered; the ether was removed at room temperature under water aspirator vacuum in a rotary evaporator. The NMR spectrum of the distillate fractions, obtained over a wide range of pressure and temperature, indicated more than one product. One *possible* product (by NMR) *might have* corresponded to *tert*-butyl tropyl ether. One product definitely obtained was ditropyl ether (0.68 g), bp 70–71° (0.05 mm).

Kinetics for Rearrangement of 7-Norbornadienol with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol. The reaction temperature for this rearrangement was raised to 25.3° in order to keep the *tert*-butyl alcohol from solidifying. The method for following the rates was the same as described with sodium hydroxide in methanol; however, the rapidity of this rearrangement only allowed for the obtention of a few points after 2 half-lives. The reaction was essentially complete in 2 min, the half-life being of the order of 10 s. Points at 0.335, 0.398, and 0.523 min were taken; the reaction was assumed to be pseudo first order, and with a concentration of potassium *tert*-butoxide of 3.3×10^{-4} M, the second-order rate constant was approximated at 382 $\text{l. mol}^{-1}\,\text{s}^{-1}$.

Kinetic Measurements. Rates of alkaline hydrolysis of 7-acetoxynorbornadiene were run conventionally via acid-base titrations at 24.73 ± 0.05°. Solutions of about 0.07 N in dienyl acetate and about 0.08 N in sodium hydroxide were quenched by cold dilute standard acid and back-titrated with standard base. The usual second-order expressions were used. $kt = 1/(b - a) \ln [1 - (a/b)\phi]/(1 - \phi)$ where a = initial acetate concentration, b = initial base concentration, and ϕ = fraction reacted.

Rates of Conversion of 7-Norbornadienol to Methyl Tropyl Ether. Rates of rearrangement of 7-norbornadienol to methyl tropyl ether were followed by ultraviolet spectroscopy (Cary 14) at 255 nm, since neither solvent nor 7-norbornadienol absorbed at 255 nm. Samples were made up at temperatures close to the kinetic runs, placed in uv cells, and set in thermostated holders; the temperatures and energetics are shown in Table II. The initial absorbance was obtained by extrapolation to zero time; absorbance at "infinite" time took 1–2 days. First-order plots were obtained as follows: ϕ = fraction reacted = $(A - A_0)/(A_\infty - A_0)$, where A = absorption at time t, A_0 = initial absorption, and A_∞ = absorption at infinity; $kt = \ln (1/1 - \phi)$. Rates were cleanly pseudo first order up to 2 or 3 half-lives; that is, the rate constant was directly proportional to the base concentration (which was always constant value) and to the concentration of the dienol (which of course varied with time).

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