

(16 mm) with >85% recovery. The ether fractions were distilled (at 0.05 mm) with >75% recovery.

The olefin was analyzed for deuterium content by both proton nmr and mass spectrometry at low electron energy. The composition of the ether mixture was determined by a combination of nmr and mass spectrometric techniques. Nmr analysis of 10–15% solutions in carbon tetrachloride allowed determination of the ratios of *cis* (3.14 ppm) and *trans* (3.36 ppm) protons β to the trideuteriomethoxy group. Mass spectrometric analysis at low electron energy allowed determination of the relative amounts of ma-

terial containing zero, one, or two hydrogens. These two types of data allowed extraction of the percentages of the four ethers.

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Elcb Reaction of 1-Methoxyacenaphthene. II. The Elimination Step

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Abstract: The stereochemistry of the alkoxide catalyzed elimination reaction of *cis*- and *trans*-2-deuterio-1-trideuteriomethoxyacenaphthenes has been investigated as a function of cation in *tert*-butyl alcohol and in methanol. The relative rates of *cis* and *trans* elimination vary by a factor of about 75 from exclusively *cis* elimination to predominantly *trans* elimination. Kinetic deuterium isotope effects (α,β and leaving group) have been determined for the preferential *cis* elimination in *tert*-butyl alcohol-potassium *tert*-butoxide. As with the exchange processes ion pairing has been proposed as an important factor in determining the elimination stereochemistry.

The study of the exchange reaction of deuterium labeled 1-methoxyacenaphthene revealed that exchange and elimination were in close competition suggesting that both the exchange and elimination processes could be investigated in the same substrate.¹ The interesting sensitivity of the stereochemistry of the exchange reaction to the nature of the medium seemed to provide a unique opportunity to study the stereochemistry of an elimination reaction near the E2–E1cb borderline. The close competition between exchange and elimination also provided an opportunity to measure α,β and leaving group kinetic deuterium isotope effects on an elimination reaction that seemed to be E1cb in nature.

The 1,2,2-trideuterio-1-trideuteriomethoxyacenaphthene (**4**) used in the exchange study was not an appropriate substrate for the elimination study since usually four differently labeled ethers were present in varying amounts during the reaction course. This made interpretation of the deuterium composition of the recovered acenaphthylene **5** very difficult.

Substrates

In order to study the elimination stereochemistry in the 1-methoxyacenaphthene system, preparation of specifically labeled substrates proved advantageous. Thus, *cis*-2-deuterio-1-trideuteriomethoxyacenaphthene (*cis*-**2**) and *trans*-2-deuterio-1-trideuteriomethoxyacenaphthene (*trans*-**2**) were prepared from the corresponding alcohols whose preparations are illustrated in Figure 1 and described in the Experimental Section. As shown in the accompanying paper,¹ exchange accompanies elimination and the isotopic composition of

substrate ether can change significantly during the course of the elimination reaction. The change in isotopic labeling can be minimized by appropriate choice of either *cis*-**2** or *trans*-**2** as substrate. Thus, for a medium where *cis* exchange² dominates, *trans* deuterated material (*trans*-**2**) was used (*vice versa* for *cis*).

As part of the study of the elimination isotope effects, 1-deuterio-1-trideuteriomethoxyacenaphthene (α -**2**), 1-trideuteriomethoxyacenaphthene (**1**), 1-methoxyacenaphthene (**3**), and 1,2,2-trideuterio-1-trideuteriomethoxyacenaphthene (**4**) were also prepared (Figure 2). The preparation of **3** and **4** is described earlier along with the details of the structural assignments.¹

Exchange and Elimination Procedures

To determine the stereochemistry of the elimination processes, the appropriate ether (**2**) was treated in alcohol-alkoxide media chosen to complement the exchange study of **4** described previously. As illustrated in Figure 3, if prior exchange of *cis*-**2** or *trans*-**2** is not extensive, the stereochemistry of the elimination process can be determined from the isotopic composition of isolated acenaphthylene **5**. To minimize errors due to exchange, the elimination reaction was run to varying extents (vpc analysis). The ether and olefin were separated by elution chromatography, and both recovered **2** and **5** were analyzed for exchange by nmr and mass spectrometry. Recovery was normally better than 85%.

Table I contains the conditions and analytical results obtained when *trans*-**2** was treated in lithium *tert*-butoxide, potassium *tert*-butoxide, and cesium *tert*-

(2) The terms *cis* and *trans* (rather than *syn* or *anti*) will be used throughout to designate the geometrical relationship of the proton (deuteron) to the methoxy group in both the exchange and elimination processes.

(1) D. H. Hunter, Y.-t. Lin, A. L. McIntyre, D. J. Shearing, and M. Zvagulis, *J. Amer. Chem. Soc.*, **95**, 8327 (1973).

Table I. Elimination Results for *trans*-2^a

Run	[Base], M	Temp, °C	Time, min	Olefin				Ether					
				Total % ^b	% <i>d</i> ₀ ^c	% <i>d</i> ₁ ^c	% <i>d</i> ₂ ^c	Total % ^b	% 1 ^b	% α-2 ^d	% <i>cis</i> -2 ^e	% <i>trans</i> -2 ^e	
Lithium <i>tert</i> -Butoxide													
1	0.14	152.4	462	21 ^f	2	18	1	79	6	9	0	64	
2	0.14	152.4	1,020	40 ^f	4	35	1	60	6	6	0	49	
3	0.14	152.4	1,535	50 ^f	6	43	1	50	5	7	0	38	
Potassium <i>tert</i> -Butoxide													
4	0.43	85.6	74	15	2.0	12.5	0.5	85	13	1	2	69	
5	0.43	85.6	182	32	6.0	25.0	1.0	68	15	5	1	47	
6	0.43	85.6	330	50	12.5	37.0	1.5	50	15	5	1	29	
7	0.37	65.0	38,880	>99.7	43.0	54.2	2.7	<0.3					
8	0.37	65.0	38,880	>99.7	43.6	54.2	2.2	<0.3					
9	0.37	65.0	585	4.7	0.6	4.0	0.1	95.3					
Cesium <i>tert</i> -Butoxide													
10	0.22	85.6	31	15	3.0	11.5	0.5	85	17	8	0	60	
11	0.22	85.6	104	40	13.0	26.0	1.0	60	26	7	3	24	
12	0.22	85.6	149	52	21.0	30.0	1.0	48	24	6	4	14	
				Starting material ^g									
								8 2 7 83					

^a The solvent is the conjugate acid of the base. ^b ±1. ^c ±0.3. ^d ±2. ^e ~±5, uncertainty due to *d*₀-ether in starting material. ^f Extensive loss of olefin due to side reactions. ^g Isotopic composition of *trans*-2 used in studies.

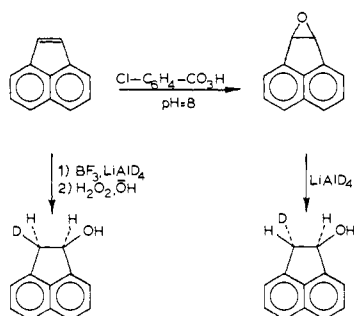


Figure 1. Preparative sequence for the alcohols leading to *cis*-2 and *trans*-2.

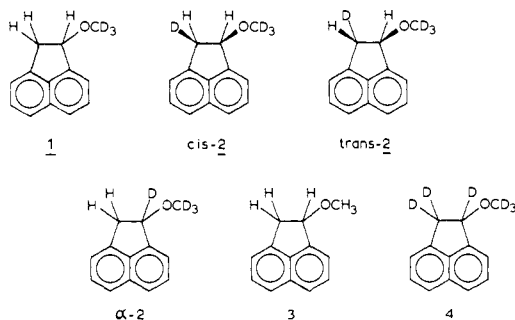


Figure 2. Ethers prepared for the elimination study.

butoxide each in *tert*-butyl alcohol. Table II contains data for *cis*-2 with potassium *tert*-butoxide complexed with 1 equiv of dicyclohexyl-18-crown-6 ether,³ cesium *tert*-butoxide, tetramethylammonium *tert*-butoxide in *tert*-butyl alcohol, and potassium methoxide in methanol. The isotopic composition of *cis*-2 and *trans*-2 are included in the tables for comparison.

It was demonstrated that **5** does not exchange significantly under the elimination reaction conditions in *tert*-butyl alcohol-potassium *tert*-butoxide. Exchange of **5** at the 1 and 2 positions occurred with a rate constant per deuteron of $10^{-4} M^{-1} \text{sec}^{-1}$ at 150.5° .⁴ This

(3) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

(4) D. H. Hunter, unpublished results.

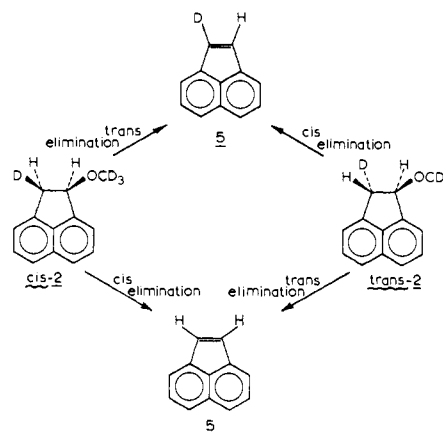


Figure 3. Possible stereochemical pathways for elimination.

roughly corresponds to a rate difference of 10^3 between exchange of **5** and elimination of **2**.

In the runs at higher temperature, lithium *tert*-butoxide and potassium methoxide at 152.4° , recoveries were low. Using dibenzyl as an internal standard it appeared that **5** was being lost rather than **2**. A sample of partially deuterated **5** was also submitted to the reaction conditions resulting in a significant loss of **5**. However, analysis of recovered **5** showed that its isotopic composition was unchanged and thus the side reaction(s) will not affect the validity of the elimination experiments.

Analysis of Exchange and Elimination Results

To make comparisons easier the elimination results contained in Tables I and II were converted into the relative rates of *cis* and *trans* elimination. The appropriate ratios of % *d*₀ and % *d*₁ in **5** were extrapolated to zero time to yield $k^{\text{cis}}/k^{\text{trans}}$ for elimination and these results are shown in Table III. The exchange results for **4**¹ are included for comparison.

To verify the validity of the extrapolation to obtain $k^{\text{cis}}/k^{\text{trans}}$ for elimination, both the exchange results for *cis*-2 and *trans*-2 and the elimination results were simulated using the scheme in Figure 4 as is described in the last section. Using reasonable relative values for k_1 ,

Table II. Elimination Results for *cis*-2^a

Run	[Base], M	Temp, °C	Time, min	Olefin				Ether			
				Total, % ^b	% <i>d</i> ₀ ^c	% <i>d</i> ₁ ^c	% <i>d</i> ₂ ^c	Total % ^b	% 1 ^c	% <i>cis</i> -2 ^c	% <i>trans</i> -2 ^c
Potassium <i>tert</i> -Butoxide											
13	0.37	65	734	6.1	4.9	1.2	0.0	93.9			
14	0.37	65	50,200	>99.7	87.6	11.8	0.6	<0.3			
15	0.37	65	50,200	>99.7	85.9	12.4	1.7	<0.3			
16	0.021 ^d	60	90	12.0	4.5	7.5	0.0		8.3	71.0	8.9
17	0.021 ^d	60	333	16.0	5.7	10.3	0.0	84	14.0	61.0	9.3
18	0.021 ^d	45	617	5.0	1.2	3.7	0.1	95	10.9	75.3	8.7
19	0.021 ^d	45	1,645	11.0	3.1	7.9	0.0	89	14.6	63.5	10.6
Cesium <i>tert</i> -Butoxide											
20	0.20	85.6	31	11	7.8	2.6	0.1	89	17.8	64.1	6.8
Tetramethylammonium <i>tert</i> -Butoxide											
21	0.10	45	90	10	2.4	7.5	0.1	90			
22	0.10	45	90	8	1.6	6.3	0.1	92	10.4	68.8	12.6
23	0.10	45	300	20	5.5	14.4	0.1	80	20.1	48.5	11.3
24	0.10	45	607	29	10.8	18.8	0.0	71	25.1	37.2	8.7
Potassium Methoxide											
25	0.48	152.4	45	7 ^e	3.3	3.7	0.0	93	19	53	21
26	0.48	152.4	150	15 ^e	8.4	6.6	0.0	85	38	27	20
27	0.48	152.4	350	32 ^e	22.0	9.9	0.0	68	50	9	9
Starting material ^f									4.0	84.0	12.0

^a The solvent is the conjugate acid of the base. ^b ±1. ^c ±0.5. ^d Equivalent of dicyclohexyl-18-crown-6 ether added. ^e Extensive loss of olefin due to side reactions. ^f Isotopic composition of *cis*-2 used in studies.

Table III. Extrapolated Relative Exchange and Elimination Rates^c

Runs	Base	Substrate	Temp, °C	k_{ex}/k_{elim}^a	k^{cis}/k^{trans}	
					Exchange ^a	Elimination
1-3	LiO- <i>t</i> -Bu	<i>trans</i> -2	152.4	0.6	31 ± 6	15 ± 1
4-6	KO- <i>t</i> -Bu	<i>trans</i> -2	85.6	2	1.6 ± 0.2	7.9 ± 0.3
10-12	CsO- <i>t</i> -Bu	<i>trans</i> -2	85.6	3	1.0 ± 0.1	6.5 ± 0.1
18, 19	KO- <i>t</i> -Bu ^b	<i>cis</i> -2	45	5	0.6 ± 0.1	0.25 ± 0.1
21-24	(CH ₃) ₄ NO- <i>t</i> -Bu	<i>cis</i> -2	45	5	0.3 ± 0.1	0.20 ± 0.1
25-27	KOCH ₃	<i>cis</i> -2	152.4	4	1.0 ± 0.1	0.70 ± 0.1

^a With **4** as substrate. ^b Added dicyclohexyl-18-crown-6 ether. ^c Extrapolated to zero time.

k_2 , k_3 , and k_4 , and varying each by about a factor of 4, it was apparent that for the percentages of reactions observed experimentally the extrapolation should be valid.

The possibility of **5** arising by an α elimination was tested using α -2 in *tert*-butyl alcohol-potassium *tert*-butoxide at 85.6° for 90 hr. Recovered **5** was isolated and analyzed for deuterium showing 97% d_1 , thereby ruling out significant contribution by α elimination.

Effect of Cation on Elimination Stereochemistry. As is clear from the results summarized in Table III, the relative rates of *cis* and *trans* elimination varied by about a factor of 75 when the base was changed from lithium to tetramethylammonium *tert*-butoxide in *tert*-butyl alcohol. The elimination results using *cis*-2 and *trans*-2 roughly parallel the exchange results obtained using **4**, with lithium *tert*-butoxide showing high *cis* selectivity and both tetramethylammonium and potassium *tert*-butoxide-crown ether showing preferential *trans* reaction. Potassium and cesium *tert*-butoxide show intermediate behavior but with a higher selectivity for *cis* elimination than for *cis* exchange. A most dramatic change occurs upon the addition of crown ether to potassium *tert*-butoxide where k^{cis}/k^{trans} changes by a factor of about 30 from mostly *cis* elimination to mostly *trans* elimination.

Any direct comparison of exchange and elimination rate ratios requires consideration of kinetic deuterium isotope effects on the elimination processes. As will be

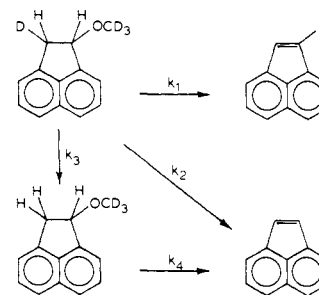


Figure 4. Kinetic model to simulate elimination and exchange results.

discussed in more detail later, kinetic isotope effects were measured for the reaction in *tert*-butyl alcohol with potassium *tert*-butoxide (Figure 4 and Table IV). The feature of importance here is the small magnitude of

Table IV. Initial Rate Constants for Elimination in 0.37 M KO-*t*-Bu-HO-*t*-Bu at 64.3°

Substrate	$k_{obad} \times 10^6 \text{ sec}^{-1}$	k^H/k^D^a
1	3.53 ± 0.07	
<i>cis</i> -2	2.52 ± 0.07	1.40 ± 0.07
<i>trans</i> -2	3.01 ± 0.11	1.17 ± 0.06
α -2	3.41 ± 0.14	1.04 ± 0.06
3	4.24 ± 0.12	1.20 ± 0.06
4	1.97 ± 0.02	1.79 ± 0.05

^a Ratio of individual rate constants relative to **1**.

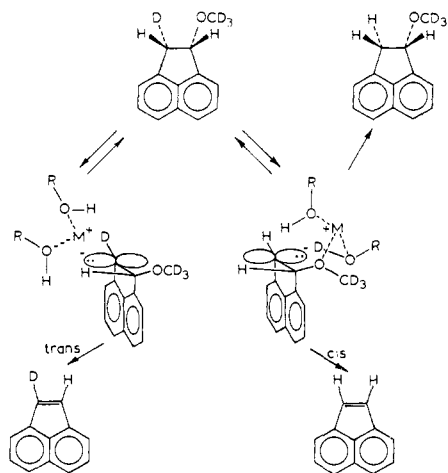


Figure 5. Mechanistic model for elimination and exchange of *cis*-2.

both the primary and secondary isotope effects. Thus, the corrections to the elimination ratios ($k^{\text{cis}}/k^{\text{trans}}$) will only be of the order of 20%.

As was detailed in the exchange study,¹ the effect of cation on the reaction rates shows that lithium, potassium, and cesium *tert*-butoxide exist primarily as ion pairs or agglomerates in *tert*-butyl alcohol. Since these cations also affect the relative rates of *cis* and *trans* elimination, the cations must also be present in the intermediates or transition states responsible for elimination. The negligible effect of added common ion or dilution on the exchange stereochemistry of the reaction of **4** with potassium *tert*-butoxide was taken as evidence for just one reactive base in solution.⁵ The nature of the reactive base in *tert*-butyl alcohol with tetramethylammonium or potassium-crown ether cations has not been clarified and could be either an ion-pair or dissociated base. But as with exchange tetramethylammonium shows the lowest *cis/trans* reactivity ratio and this can be interpreted as indicating a higher degree of dissociation. On the basis of the evidence presented earlier, it is likely that dissociated base is the active species with potassium methoxide in methanol.

Models for the Elimination Reaction. Since α elimination has been shown to be unimportant in this system, two types of β -elimination mechanisms seem most likely; E1cb or carbanion-like E2. The observation of concurrent and parallel carbanion formation strongly suggests an E1cb mechanism in which the carbanion partitions itself between exchange and elimination. Thus, the model postulated for the exchange process is readily adaptable to the elimination process as well (Figure 5).

Bonding of the cation in the base ion pair to substrate then serves two purposes in the *cis* intermediate. The barrier to *cis* proton removal and exchange is reduced and bonding to the methoxyl oxygen should produce a better leaving group. This could account for the higher *cis* selectivity in elimination than exchange when potassium and cesium cations are present.

An alternative but probably equivalent picture is possible for solvents of low dielectric constant where ion pairing is highly favored. The *cis* elimination pro-

cess results in both the negatively charged leaving group and the cation being generated in close proximity. In *trans* elimination they are separated by the olefin being produced (*i.e.*, product separated ion pairs).⁶ The difference in electrostatic energy between the two processes is then the determining factor.

Although the rationale has been developed around an E1cb model, such charge dipole interactions could equally well apply to a paenecarbanion E2 or to elimination reactions in general. Thus, ion pairing may be of general importance in elimination reactions.

The results with 1-methoxyacenaphthene seem to corroborate the suggestion of Sicher, *et al.*, that ion pairing should favor *syn* elimination. His suggestion was based on observations on the elimination reactions of the α - and β -deuterium labeled 1,1,4,4-tetramethylcyclohexyl-7 and 1,1,4,4-tetramethylcyclohexyl-8 tosylates,⁷ cyclohexyl bromide,⁸ and β -deuterium labeled bicyclo[2.2.2]oct-2-yl tosylate.⁹ It was found that with potassium *tert*-butoxide as base, larger percentages of *syn* elimination were observed with benzene and *tert*-butyl alcohol as solvent than with dimethylformamide or dimethyl sulfoxide. Bayne and Snyder¹⁰ have reported analogous results with *threo*-C₆H₅-CHD-CHDOTs and also placed importance on ion pairing.

Since the preliminary report on the results in our system,¹¹ it has been found that added crown ether¹² and changes in base concentration^{5a,b} may also reduce the percentage of *syn* elimination for 1,1,4,4-tetramethylcyclohexyl bromide and tosylate. However, the evidence is ambiguous since it rests on *cis/trans* olefin ratios rather than labeling experiments.¹³ The *trans*-2-phenylcyclopentyl tosylate system, originally studied by Depuy,¹⁴ has provided a more reliable example of the effect of added crown ether on the stereochemistry of an elimination reaction catalyzed by potassium *tert*-butoxide in *tert*-butyl alcohol.^{5c} Again, the extent of *syn* elimination was greatly reduced when crown ether was added.

It would appear that ion pairing may be of fairly widespread importance in interpreting elimination reactions.¹⁵ Further investigation of the few examples of *syn* elimination seems warranted and, in particular, the alicyclic examples.¹⁶

Isotope Effects on a *Cis* Elimination. To be able to relate the deuterium content of **5** produced from either *cis*-**2** or *trans*-**2** to the stereochemistry of elimination it is necessary to know the magnitude of the primary and

(6) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 154.

(7) M. Svoboda, J. Zavada, and J. Sicher, *Collect. Czech. Chem. Commun.*, **33**, 1415 (1968).

(8) J. Zavada, J. Krupicka and J. Sicher, *ibid.*, **33**, 1393 (1968).

(9) J. Zavada, M. Pankova, and J. Sicher, *Chem. Commun.*, 1145 (1968).

(10) W. F. Bayne and E. I. Snyder, *Tetrahedron Lett.*, 571 (1971).

(11) D. H. Hunter and D. J. Shearing, *J. Amer. Chem. Soc.*, **93**, 2348 (1971).

(12) M. Svoboda, J. Hapala, and J. Zavada, *Tetrahedron Lett.*, 265 (1972).

(13) While selectivity in the elimination process (*syn* \rightarrow *cis*, *anti* \rightarrow *trans*) has been nicely demonstrated in some media, it is not certain that this will be universal and generalization may be dangerous.

(14) (a) C. H. Depuy, G. F. Morris, J. S. Smith, and R. J. Smat, *J. Amer. Chem. Soc.*, **87**, 2421 (1965); (b) C. H. Depuy, R. D. Thurn, and G. F. Morris, *ibid.*, **84**, 1314 (1962).

(15) J. Zavada, M. Pankova, M. Svoboda, and M. Schlosser, *J. Chem. Soc., Chem. Commun.*, 168 (1973).

(16) For a recent and thorough review, see N. A. LeBel, *Advan. Alicycl. Chem.*, **3**, 195 (1971).

(5) (a) M. Svoboda and J. Zavada, *Collect. Czech. Chem. Commun.*, **37**, 3902 (1972); (b) J. Zavada and M. Svoboda, *Tetrahedron Lett.*, 23 (1972); (c) R. A. Bartsch and K. E. Wieggers, *ibid.*, 3819 (1972).

secondary kinetic deuterium isotope effects on the elimination processes. These were evaluated by comparing the rates of elimination of **1**, *cis*-**2**, *trans*-**2**, α -**2**, **3**, and **4** in 0.37 *M* potassium *tert*-butoxide in *tert*-butyl alcohol 64.3°. In this medium *cis* elimination is the major reaction pathway and thus *cis*-**2** should yield the primary isotope effect and the other deuterium labeled compounds will give various secondary isotope effects.

Since exchange at the β position occurred competitive with elimination, the rate constants were measured at small percentages of reaction ($\leq 3\%$) by following the rate of appearance of **5** spectrophotometrically. Under these conditions exchange should be minimized and the observed pseudo-first-order rate constants are listed in Table IV. These pseudo-first-order constants were converted to kinetic isotope effects by making the individual rates relative to **1**. These relative rates are then illustrated in Figure 6.

The most striking feature of the kinetic isotope effects on this *cis* elimination is their low magnitude; even the primary isotope effect is only 1.40. The observed $k^{\text{cis}}/k^{\text{trans}}$ ratio for elimination using *cis*-**2** should be reduced by a factor of 1.2 (1.40/1.17) if the *trans* elimination has a similar pattern of kinetic isotope effects (see later section).

A second feature of interest is the unique leaving group isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.20$) which can be attributed to an inductive effect. Analogously, trideuterioacetic acid is about 18% less acidic than acetic acid.¹⁷

The observed pattern of isotope effects is certainly consistent with an E1cb mechanism but a paenecarbanion E2 process cannot be ruled out. Although such a small primary isotope effect on an E2 reaction is unprecedented,¹⁸ values of $k_{\text{H}}/k_{\text{D}}$ in the range 1.62–1.92 have been observed for *syn* elimination of cyclopentylammonium salts.¹⁹

Stereochemistry of the Exchange Process. Two different carbanionic intermediates (*cis* and *trans*) have been proposed (Figure 5) to account for the exchange and elimination results. If these two intermediates do not interconvert, these exchanges will occur with retention. Inversion would provide a pathway for interconversion. Such an inversion component could be detected if *cis*-**2** were converted to *trans*-**3** (or vice-versa) by proton removal and reprotonation on the opposite face.

While the conclusions are only qualitative, it is interesting to note that when *trans*-**2** was used as substrate, the relative percentage of *cis*-**2** isolated was always lower than in starting material. Similar results were observed with *cis*-**2** as substrate except for methanol-methoxide where significant amounts of interconversion seem to be occurring. It would seem that inversion does not play a major role in *tert*-butyl alcohol and two intermediates are involved. Methanol acts more like one carbanionic intermediate (or two equilibrating intermediates) is being produced which reacts with similar ease at both faces of the carbanion. No attempt has been made to make a quantitative analysis of these exchange results but a consistent qualitative picture is apparent.

Relative Rate Constants for the Exchange and Elimination

(17) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 154 (1963).

(18) A. Fry, *Chem. Soc. Rev.*, **1**, 163 (1972).

(19) K. C. Brown and W. H. Saunders, *J. Amer. Chem. Soc.*, **92**, 4292 (1970).

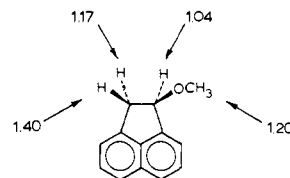


Figure 6. Summary of calculated $k_{\text{H}}/k_{\text{D}}$ isotope effects for eliminations in potassium *tert*-butoxide–*tert*-butyl alcohol at 64.3° from data in Table IV. Values shown are the $k_{\text{H}}/k_{\text{D}}$ rate ratio when the indicated hydrogen(s) is replaced by deuterium(s).

ination Process. The exchange and elimination results for *cis*-**2** and *trans*-**2** in *tert*-butyl alcohol–potassium *tert*-butoxide at 65° were analyzed according to the kinetic scheme in Figure 4 assuming each step is of the same pseudo order in base. The data obtained for *trans*-**2** allowed a straightforward determination of each of the rate constants. An approximate value for $k_1/k_2 = 6.2$ was given by the short elimination time value for % **5-d**₁/ % **5-d**₀ (run 9, Table I). The ratio, $k_1/(k_2 + k_3) = 1.25$, was given by the infinite time value for % **5-d**₁/ % **5-d**₀ (see runs 7 and 8 of Table I). The ratio, $k_4/(k_1 + k_2) = 1.17$, is the observed initial elimination rate constant ratio for *trans*-**2** and **1** (see Table IV). Relative rate constants were determined by setting $k_4 = 1.0$ and yielded $k_1 = 0.74$, $k_2 = 0.12$, and $k_3 = 0.47$. The results for *cis*-**2** were similarly analyzed with $k_1/k_2 = 0.24$ (run 13 of Table II), $k_1/(k_2 + k_3) = 0.14$, and $k_4/(k_1 + k_2) = 1.40$. Setting $k_4 = 1.0$ yields $k_1 = 0.14$, $k_2 = 0.58$, and $k_3 = 0.41$.

This analysis has two main uses. These rate constants were used as parameters to simulate the reaction profile and to show that the extrapolations are justified. The simulation involved computing expected ether and olefin compositions at various times using a simplified version of a more complex kinetic scheme described earlier.²⁰

These parameters also provided an estimate of the kinetic deuterium isotope effect for *trans* elimination. A comparison of k_1 for *cis*-**2** (0.14) and k_2 for *trans*-**2** (0.12) yields a composite of the primary and secondary isotope effect for the β position of 1.2 for *trans* elimination. A similar composite isotope effect of 1.3 (0.74/0.58) is obtained for *cis* elimination and verifies that neither isotope effect is large and they are similar in magnitude.

Experimental Section

The nmr spectra (CCl_4 with internal TMS) were run on a Varian HA-100. Mass spectra were obtained with a Varian M-66 mass spectrometer. The vpc analyses were run using a Varian Aerograph A90-P3 gas chromatograph with thermal conductivity detector and a recorder with a Disc integrator. Melting points and boiling points are uncorrected.

Substrates. *trans*-**1-Trideuteriomethoxy-2-deuterioacenaphthene**.

(a) **1,2-Epoxyacenaphthene.** The epoxidation of acenaphthylene with *m*-chloroperbenzoic acid was run as two-phase reaction consisting of sublimed acenaphthylene (19 g, 0.125 mol) in 200 ml of methylene chloride and a buffer solution (pH 8) of 170 g (1.25 mol) of potassium dihydrogen phosphate and 46 g (1.15 mol) of sodium hydroxide in 1.5 l. of water. To an efficiently stirred mixture was added slowly 48.3 g (0.25 mol) of *m*-chloroperbenzoic acid in 800 ml of methylene chloride. The temperature was maintained at 25° for 3.5 hr and then 15 g of sodium sulfite was added to destroy the excess peracid. The methylene chloride layer was then washed three times with water, dried, and solvent evaporated. Nmr indi-

(20) D. H. Hunter and R. W. Mair, *Can. J. Chem.*, **47**, 2361 (1969).

cated about 10% 1-acenaphthene and this greatly complicates purification of the 1,2-epoxyacenaphthene. With purified acenaphthylene recrystallization from petroleum ether is sufficient to obtain pure epoxide.

The crude product from commercial acenaphthylene was chromatographed on cellulose powder using ligroin to yield 17 g (80%) of yellow solid. This material was recrystallized from ligroin to yield 60% of material of mp 81.5–82.5° (lit.²¹ mp 83–84°). The nmr (CCl₄) showed a singlet (2 H) at δ 4.56 and a multiplet (6 H) at 7.0–7.7. The infrared spectrum had bands characteristic of epoxides at 775 and 805 cm⁻¹. The mass spectrum had a molecular ion at *m/e* 168.

(b) *trans*-2-Deuterio-1-acenaphthenol. 1,2-Epoxyacenaphthene (9.0 g, 53 mmol, containing ca. 10% 1-acenaphthenone) in 100 ml of THF was added dropwise to a stirred mixture of 1.13 g (27 mmol) of lithium aluminum deuteride in 100 ml of THF all in an argon atmosphere. After stirring for 16 hr at reflux, the reaction mixture was worked up using 100 ml of saturated sodium sulfate. Solvent was removed and the residue taken up in ether and water after extraction four times with 50 ml of ether. The combined ether layers were washed with water and saturated sodium chloride solution. After the solution was dried and the solvent removed, there resulted 7.1 g (78%) of crude alcohol, mp 134–138°.

Nmr showed ~10% deuterium incorporated α to the hydroxyl group and ~90% deuterium incorporation in one of the positions β to the hydroxyl group. It was also determined by nmr that the ratio of β protons *cis* and *trans* to the hydroxyl was approximately 85:15, respectively. Mass spectrometry showed ~6% *d*₂ material and a significant amount of nondeuterated product which could not be measured accurately due to an (*M* - 1) peak which occurred even at low electron energy.

(c) *trans*-1-Trideuteriomethoxy-2-deuterioacenaphthene. Following the previously described procedure,¹ 5.5 g (32 mmol) of *trans*-2-deuterio-1-acenaphthenol, 17.6 g of barium oxide, 5.0 g (34.5 mmol) of methyl iodide-*d*₃, 40 ml of dimethylformamide, and 1 ml of water were reacted. After work-up and purification by column chromatography followed by vacuum distillation, there resulted 3.4 g (56% based on alcohol) of *trans*-2. Nmr analysis (carbon tetrachloride) for relative amounts of protons *cis* and *trans* to the methoxyl group indicated 85% *cis*-H to 15% *trans*-H of the total (1.09 H) β to the methoxyl group and approximately 11% deuterium α to the methoxyl group. Isotopic analysis by mass spectrometry at low electron energy indicated 8% *d*₃, 86% *d*₄, and 6% *d*₅ material. This corresponds approximately to an isotopic mixture of 8% 1, 3% α -2, 3% *cis*-2, 6% *cis*- and *trans*-1-trideuterio-methoxy-1,2-dideuterioacenaphthene, and 80% *trans*-2.

cis-1-Trideuteriomethoxy-2-deuterioacenaphthene. (a) *cis*-2-Deuterio-1-acenaphthenol. Under an argon atmosphere, to 1.14 g (8 mmol) of boron trifluoride etherate (freshly distilled from calcium hydride) and acenaphthylene (13.7 g, 24 mmol) in 60 ml of ether was slowly added 0.25 g (6 mmol) of lithium aluminum deuteride. The reaction was stirred at ambient temperature for 12 hr and then worked up by adding saturated sodium sulfate and extracting with ether.

After solvent removal the residue was dissolved in 10 ml of 90% ethanol containing 0.27 g (5 mmol) of sodium hydroxide. Upon addition of 2.3 ml of 30% hydrogen peroxide, the temperature rose to 70° and was maintained for 10 min. After cooling and extraction using ether-water, the solvent was dried and evaporated to yield 3.6 g of crude material. After chromatography on alumina using 1% methanol-methylene chloride and recrystallization from benzene, material (1.4 g, 34%) of mp 143–143.5° was obtained.

Nmr (pyridine) indicated >90% β -*cis* deuterium. Isotopic analysis by mass spectrometry at low electron energy indicated >90% monodeuterated alcohol.

(b) *cis*-Trideuteriomethoxy-2-deuterioacenaphthene. Following the procedures reported earlier¹ and above, 6.5 g of *cis*-2-deuterio-1-acenaphthenol yielded 3.3 g (62%) of ether which contained 0.25% acenaphthylene. Nmr (carbon tetrachloride) indicated 87% hydrogen *trans* to the methoxy and 13% *cis* for a total of 1.05 atoms of H/molecule. Isotopic analysis by mass spectrometry at low electron energy indicated 5% *d*₃ and 96% *d*₄ material. This corresponds to an isotopic mixture of 4% 1, 12% *trans*-2, and 84% *cis*-2.

1-Deuterio-1-trideuteriomethoxyacenaphthene. (a) 1-Deuterio-1-acenaphthenol. A mixture of 16.0 g (95 mmol) of acenaphthen-1-one,¹ 1.0 g (24 mmol) of lithium aluminum deuteride, and 125 ml

of tetrahydrofuran was allowed to react and then worked up. The crude yellow product was recrystallized from benzene, the filtrate was chromatographed, and the resulting alcohol was recrystallized. The total yield of pale yellow alcohol was 11.5 g (71% based on ketone), mp 140.5–141.5°. The filtrate yielded a further 1.6 g of crude alcohol. Nmr analysis in pyridine solvent showed an AB quartet for the β hydrogens at δ 3.4 and 3.7 ppm and showed no absorption for the α hydrogen indicating complete α deuteration.

(b) 1-Deuterio-1-trideuteriomethoxyacenaphthene. Using the procedure mentioned above, 6.5 g of 1-deuterio-1-acenaphthenol yielded 5.4 g (80%) of ether containing less than 0.25% of acenaphthylene. Nmr (carbon tetrachloride) indicated 51% *cis*-H and 49% *trans*-H of the total hydrogens β to the methoxy group. There was complete deuterium incorporation α to the methoxyl group as no absorption was observed at δ 5.11 ppm. Isotopic analysis by mass spectrometry at low electron energy indicated 4% *d*₃ and 96% *d*₄ material. That is, the ether was an isotopic mixture of 4% 1 and 96% α -2.

Bases and Solvents. The *tert*-butyl alcohol was fractionally distilled from calcium hydride onto freshly baked molecular sieves (4A) and contained less than 0.002 *M* water. The methanol was distilled from magnesium turnings onto molecular sieves (\leq 0.002 *M* H₂O).

The lithium, potassium, and cesium *tert*-butoxide solutions were prepared by stirring the freshly cleaned metal at room temperature with *tert*-butyl alcohol under an argon atmosphere. These solutions were then titrated for water (0.002 *M* using a Photovolt Aquatest) and for total base (pH meter). Potassium methoxide methanol was prepared similarly keeping the methanol cool during the reaction. The tetramethylammonium *tert*-butoxide in *tert*-butyl alcohol was prepared as reported in the accompanying paper.¹

The solutions containing dicyclohexyl-18-crown-6 ether³ were prepared by adding the specified amount of crown ether to the base solution.

Exchange and Elimination Procedure. The procedures employed were essentially those reported in the accompanying article.¹ After the reaction was run for the reported time, the mixture was analyzed by vpc and the ether and olefin were separated and then analyzed for deuterium content.

Complications were encountered in the reactions at 152.4° since a substantial loss of material had occurred during the reactions. The reactions were repeated using dibenzyl as internal standard. For example, a mixture of 0.104 g (0.56 mmol) of *trans*-2 and 0.050 g (0.28 mmol) of dibenzyl was heated at 152.4° with 10 ml of 0.14 *M* LiO-*t*-Bu-HO-*t*-Bu solution (1.4 mmol) for the same length of time as run 1. After work-up the mixture was analyzed by vpc and the percentage loss determined. A mixture of 0.050 g (0.33 mmol) of acenaphthylene and 0.050 g (0.28 mmol) of dibenzyl was heated at 152.4° with 10 ml of 0.14 *M* LiO-*t*-Bu-HO-*t*-Bu solution (1.4 mmol) for the same length of time. After work-up the mixture was analyzed by vpc and the percentage loss of acenaphthylene was measured and seemed to account for the loss of material in run 1.

A mixture of 0.015 g (0.10 mmol) of deuterated acenaphthylene and 0.050 g (0.28 mmol) of dibenzyl was heated at 152.4° with 10 ml of 0.14 *M* LiO-*t*-Bu-HO-*t*-Bu solution (1.4 mmol) for the same length of time. After work-up the mixture was analyzed by vpc and the percentage loss of deuterated acenaphthylene was similar to that for the undeuterated acenaphthylene. Isotopic analysis by mass spectrometry at low electron energy of the starting deuterated acenaphthylene and the recovered deuterated acenaphthylene indicated 72% acenaphthylene-*d*₁ material in both cases. Therefore, negligible deuterium isotope effects occur in the loss of acenaphthylene in this reaction.

Kinetics of the Elimination of 1-Methoxyacenaphthene at 64.3° in 0.37 *M* KO-*t*-Bu-HO-*t*-Bu. A water-jacketed cylindrical quartz uv cell having a 10-mm path length and a sample volume of approximately 0.7 ml was installed within the sample compartment of a Jasco Model ORD/UV-5 spectrophotometer. The cell was attached to a water bath where the temperature was maintained constant within \pm 0.1° by means of a proportional temperature controller. The cell was flushed with argon and capped with a Teflon plug. To the cell was added 0.5368 g of 0.37 *M* KO-*t*-Bu-HO-*t*-Bu solution by means of a syringe and the temperature allowed to equilibrate. To this solution was added 0.0560 g (0.304 mmol) of 1-methoxyacenaphthene by means of a syringe and the cell tightly capped under an atmosphere of argon. The absorbance at 412 nm was followed over a period of 2 hr at 64.3°. A least-squares plot of absorbance vs. time gave the slope and the error in the slope from which the absolute rate constant for the elimination reaction could be calculated. At 412 nm, 5, the elimination product,

(21) T. H. Kinstle and P. H. Ihrig, *J. Org. Chem.*, **35**, 257 (1970).

absorbed with an extinction coefficient which was measured to be 138 whereas the substrate, 1-methoxyacenaphthene, and the base solution, 0.37 M KO-*t*-Bu-HO-*t*-Bu, did not absorb appreciably. **5** gave a linear Beer's law plot of absorbance *vs.* concentration at 412 nm over the concentration range used in the experiment. The density of the 1-methoxyacenaphthene solution in 0.37 M KO-*t*-Bu-HO-*t*-Bu was 0.773 g/ml at 65°. This was calculated from the

specific gravity of the solution at 25° and the density of water at 25° and corrected for the change in density of *tert*-butyl alcohol on heating to 65°.

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Nature of the Carbonium Ion. XI. The 2-Homobrendyl Cation^{1a}

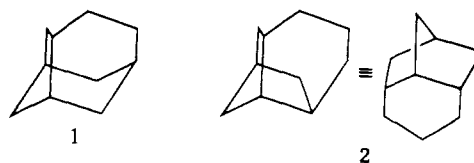
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Contribution from the Metcalf Research Laboratories, Brown University,
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Abstract: The syntheses of 3-(5-norbornen-endo-2-yl)propyl *p*-nitrobenzenesulfonate (**11a**) and its saturated analog **13a** are described. Product studies for the acetolysis, trifluoroacetolysis, and trifluoroethanolysis of **11a** were conducted. The acetolysis derived products were the corresponding acetate **11c**, or the products of acid-catalyzed acetic acid addition to **11c** (**34a** and **34b**), depending on the buffer present in the medium. Only the structurally identical acetate **13b** was obtained from **13a**. Rate measurements of the acetolyses of **11a** and **13a** revealed no π -orbital participation in ionization of the unsaturated compound. Also described are the syntheses of 2-*endo*- (**32b**) and 2-*exo*-tricyclo[3.3.1.1^{3,9}]decyl ("2-homobrendyl") *p*-bromobenzenesulfonates (**33b**). Solvolysis product studies were conducted in the manner utilized for **11a**. Acetolysis products from **32b** and **33b** were nearly identical in proportion and consisted of only two compounds, *exo*-2-homobrendyl acetate (**33c**) and 4-*exo*-tricyclo[4.4.0.0^{3,7}]decyl ("4-homobrexyl") acetate (**35b**). Despite the similarity of products a substantial *exo*:*endo* rate ratio (**33b**:**32b** = 953) was detected by kinetic measurements of the acetolyses. Trifluoroacetolyses of **32b** and **33b** afforded considerably more complex product mixtures which underwent a slow transformation toward 2-adamantyl trifluoroacetate due to secondary ionizations of the initial products with prolonged reaction times. A consolidated interpretation of the cationic pathways from the 2-homobrendyl cations is given.

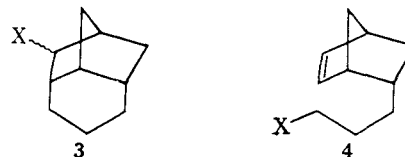
The discovery by Schleyer and Donaldson of a simple and effective route to the adamantyl ring system *via* multiple carbonium ion rearrangements of polycyclic materials³ has allowed the syntheses and studies of large numbers of derivatives of this complex rigid skeleton. Of particular interest and importance were the observations of biological activities for a number of these compounds.⁴

It has been apparent to us that polycyclic structural isomers of adamantyl derivatives should also be of chemical and biological interest. For this reason we have explored means of synthesizing these isomers and have detailed their rearrangements under ionizing conditions. Of primary concern to us have been skeletons whose ions were implicated³ as precursors to the adamantyl ions derived from Lewis acid catalyzed "adamantization" of perhydrodicyclopentadiene. In earlier work we therefore studied derivatives of protoadamantane (**1**)⁵ since ions of this isomer are viewed as the immediate precursors of adamantyl ions. Having



shown that the adamantyl skeleton (and several other isomers) can indeed be obtained from solvolysis-generated σ - and π -route 2-protoadamantyl cations, we have next turned our attention to a ring skeleton, homobrendane (**2**),⁶ unrepresented in the rearrangement products from the protoadamantyl cations, and presumably precedent to these in the routes from perhydrodicyclopentadienyl to adamantyl cations.

The choice of the 2-homobrendyl derivatives (**3**) as targets for synthesis and study was dictated by the pos-



sibility that their ionizations would be related to those of the easily accessible 3-(5-norbornen-endo-2-yl)propyl derivatives (**4**) in a fashion similar to the σ route, π route relationship which we had observed in the aforementioned protoadamantyl studies. It was hoped

(6) We have adopted the trivial name "homobrendane" for tricyclo[3.3.1.1^{3,9}]decane, "homobrexane" for tricyclo[4.4.0.0^{3,7}]decane, and "crístane" for tricyclo[5.3.0.0^{3,9}]decane to facilitate reference.

(1) (a) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstracts, ORGN-155. (b) Taken in part from the Ph.D. Thesis of J. G. Henkel, Brown University, 1972.

(2) Alfred P. Sloan Fellow, 1973-1975.

(3) For a review, see R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); V. V. Sevost'yanova, M. M. Krayushlein, and A. G. Yurchenko, *Usp. Khim.*, **39**, 1721 (1970); R. C. Bingham and P. v. R. Schleyer, *Fortschr. Chem. Forsch.*, **18**, 1 (1971).

(4) See, for example, E. W. Davies, *et al.*, *Science*, **144**, 862 (1964); H. Wendel, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **23**, 387 (1964); Grunert, *et al.*, *Virology*, **26**, 262 (1965).

(5) Paper X of this series: L. A. Spurlock and K. P. Clark, *J. Amer. Chem. Soc.*, **94**, 5349 (1972); also **92**, 3829 (1970).