E1cb Reaction of 1-Methoxyacenaphthene. I. The Nature of the Carbanion-Forming Step

D. H. Hunter,* Y-t. Lin, A. L. McIntyre, D. J. Shearing, and M. Zvagulis

Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario. *Received June 18, 1973*

Abstract: The stereochemistry of the alkoxide catalyzed H–D exchange component of the E1cb reaction of 1-trideuteriomethoxy-1,2,2-trideuterioacenaphthene (**1**) has been investigated as a function of cation in *tert*-butyl alcohol and methanol. Isotopic exchange occurred almost exclusively at the position β to the methoxy with a β/α rate ratio of about 50 and a ratio of about five powers of ten faster than exchange in the aromatic ring. The relative rates of cis and trans exchange at the β position changed by a factor of about 90 when the cation was varied; lithium, potassium, cesium, tetramethylammonium, and potassium complexed with crown ether. Bonding between base, substrate, and cation has been proposed to account for the observed trends in β exchange.

Interest in elimination reactions has not abated in recent years and two features that are receiving attention are E1cb reactions and stereochemistry. Sicher and coworkers[1] observation of significant amounts of syn elimination with onium salts in medium ring systems marked a renewal of interest in stereochemistry of elimination. Subsequently, a number of studies have been directed at probing the scope of the syn elimination process. Consequently, syn elimination has been found in both cyclic and open-chain systems[2] and with tosylate[3] and halides[4] as leaving groups. Many of the factors that determine the extent of syn elimination are yet to be elucidated, but it would appear that ion pairing of the base is important.[3c,5]

Examples of possible E1cb reactions have become far more abundant since Banthorpe[6] placed them in the category of "Less Usual Mechanisms" in 1963. Sufficiently so that in 1972, Bordwell[7] suggested that perhaps it is the concerted processes that should be in the *less usual* category. Nonetheless, opportunities to study the stereochemistry of E1cb reactions (Figure 1) are rare and require a delicate balance of rate processes. If the carbanionic intermediate partitions too preferentially to starting material ($k_{-1} > k_{-2}$), then it is likely that the stereochemical integrity of starting material will be lost. If on the other hand the intermediate yields mostly elimination products ($k_{-2} > k_{-1}$), it becomes difficult to obtain even permissive evidence for prior carbanion formation.

1-Methoxyacenaphthene seems to be a fortunate example where partitioning of the intermediate between exchange and elimination is in close competition.[8] Thus, it has become possible to study the stereochemistry of both the exchange process and the elimination process in the same substrate. The stereochemistry of an E1cb reaction is of interest since, as summarized and discussed by McLennan,[9] stereochemistry has been cited as evidence for E1cb mechanisms. Also, orbital symmetry has been invoked to rationalize expected syn elimination in E1cb reactions.[10]

Analysis of the apparent E1cb reactions of 1-methoxyacenaphthene is divided into two parts. This paper describes isotopic exchange experiments designed to characterize the carbanions formed in this system. The second deals[11] with experiments directed at characterizing the elimination process and its stereochemical demands.

Substrate

To simplify a study of the exchange reactions of 1-methoxyacenaphthene, the hexadeuterio derivative **1** was prepared and then exchanged in protic solvent. The rate of appearance of broadened singlets due to cis and trans protons (*cis*-**2**, *trans*-**2**) is simpler to monitor by nmr than changes in complex patterns especially at small percentages of isotopic exchange.

Synthesis. The procedures used to prepare the substrate, 1-trideuteriomethoxy-1,2,2-trideuterioacenaphthene (**1**), are detailed in the Experimental Section and are summarized in Figure 2. The 1,1,2,2-tetradeuterioacenaphthene was prepared essentially by the method of Trost[12] with modifications that are noted in the Experimental Section. Analogously the protio counterpart, 1-methoxyacenaphthene, was prepared by both procedures and the 1-trideuteriomethoxyacenaphthene used for nmr assignments was prepared from methanol-d_4 and 1-bromoacenaphthene.

Proton Assignments. The three protons at the 1 and

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[1] (a) J. Zavada, M. Svoboda, and J. Sicher, *Collect. Czech. Chem. Commun.*, 33, 4027 (1968); (b) J. Sicher, *Angew. Chem., Int. Ed. Engl.*, **11**, 200 (1972).

[2] (a) M. Pankova, J. Zavada, and J. Sicher, *Chem. Commun.*, 1142 (1968); (b) D. S. Bailey and W. H. Saunders, *ibid.*, 1598 (1968); (c) M. P. Cooke and J. L. Coke, *J. Amer. Chem. Soc.*, **90**, 5556 (1968); (d) J. L. Coke and M. C. Mourning, *ibid.*, 90, 5561 (1968); (e) D. S. Bailey and W. H. Saunders, *ibid.*, 92, 6904 (1970); (f) J. Zavada, M. Pankova, and J. Sicher, *Collect. Czech. Chem. Commun.*, 37, 2414 (1972);, (g) M. Pankova, A. Vitek, S. Vasickova, R. Rericha, and J. Zavada, *ibid.*, 37, 3456 (1972).

[3] (a) M. Svoboda, J. Zavada, and J. Sicher, *ibid.*, 33, 1415 (1968); (b) J. Zavada, M. Pankova, and J. Sicher, *Chem. Commun.*, 1145 (1968); (c) W. F. Bayne and E. I. Snyder, *Tetrahedron Lett.*, 571 (1971).

[4] J. Zavada, J. Krupicka, and J. Sicher, *Collect. Czech. Chem. Commun.*, 33, 1393 (1968).

[5] (a) D. H. Hunter and D. J. Shearing, *J. Amer. Chem. Soc.*, **93**, 2348 (1971); (b) R. A. Bartsch and K. E. Wiegers, *Tetrahedron Lett.*, 3819 (1972); (c) J. K. Borchardt and W. H. Saunders, *ibid.*, 3439 (1972); (d) J. Zavada and J. Svoboda, *ibid.*, 23 (1972); (e) M. Svoboda, J. Hapala, and J. Zavada, *ibid.*, 265 (1972); (f) M. Svoboda and J. Zavada, *Collect. Czech. Chem. Commun.*, 37, 3902 (1972); (g) J. Zavada, M. Pankova, M. Svoboda, and M. Schlosser, *J. Chem. Soc., Chem. Commun.*, 168 (1973).

[6] D. V. Banthrope, "Elimination Reactions," Elsevier, London, 1963, Chapter 4.

[7] F. G. Bordwell, *Accounts Chem. Res.*, **5**, 374 (1972).

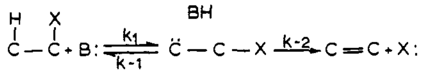
[8] D. H. Hunter and Y-t. Lin, *J. Amer. Chem. Soc.*, **90**, 5921 (1968).

[9] D. J. McLennan, *Quart. Rev., Chem. Soc.*, 21, 490 (1967).

[10] N. T. Anh, *Chem. Commun.*, 1089 (1968).

[11] D. H. Hunter and D. J. Shearing, *J. Amer. Chem. Soc.*, **95**, 8333 (1973).

[12] B. M. Trost, *ibid.*, **89**, 1847 (1967).



$$\overset{H}{\overset{|}{C}}-\overset{X}{\overset{|}{C}}+B:\ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}\ \overset{BH}{\ddot{C}-C-X}\xrightarrow{k_{-2}}C{=}C+X:$$

Figure 1. Generalized scheme for E1cb reactions.

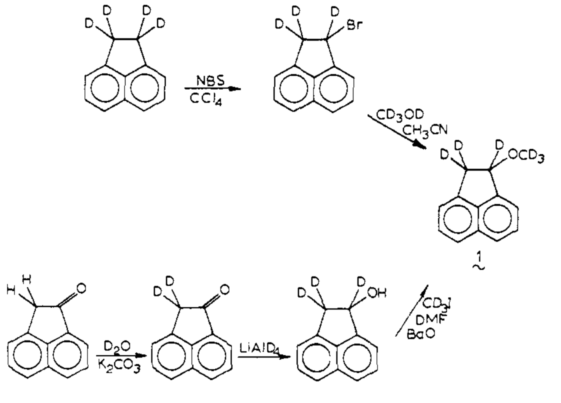


Figure 2. Preparative routes to **1**.

2 positions in 1-methoxyacenaphthene were assigned on the basis of four consistent pieces of evidence. The first assignment was on the basis of coupling constants obtained by an ABX analysis of the proton spectrum of 1-trideuteriomethoxyacenaphthene ($\delta_{\text{cis}-2}$ 3.14 ppm, $\delta_{\text{trans}-2}$ 3.36 ppm, δ_1 5.11 ppm, and $J_{\text{cis}-2,\text{trans}-2} = -17.7$ Hz, $J_{1,\text{cis}-2} = 2.6$ Hz, $J_{1,\text{trans}-2} = 7.1$ Hz) obtained with decoupling of the appropriate ring protons. The trideuteriomethoxy group proved essential throughout this study due to the unfortunate overlapping of the OCH_3 signal and the signal of the 2-protons. These parameters fit nicely into a series of about 20 1-substituted acenaphthenes studied by Sternhell.[13] The second assignment is based upon the observed relative chemical shifts of the 2-protons which are in agreement with the series of 1-substituted acenaphthenes.[13] The cis proton occurs consistently at higher field. The third procedure involved the stereoselective synthesis of *cis*-1-trideuteriomethoxy-2-deuterioacenaphthene.[11] The ether was obtained from *cis*-2-deuterio-1-acenaphthenol which in turn was obtained upon deuterioboration of acenaphthylene. Analogously the fourth assignment consisted of synthesis of *trans*-1-trideuteriomethoxy-2-deuterioacenaphthene.[11] The *trans*-2-deuterio-1-acenaphthenol was prepared by lithium aluminum deuteride reduction of 1,2-epoxyacenaphthene.[14]

Exchange Results

In an attempt to assess the stereoselectivity of exchange under basic conditions of the deuterons (protons) β to the methoxy group (OCD_3), the substrate **1** was treated with selected base-solvent pairs. With the chemical shifts of the bridge protons assigned, recovered substrate could be analyzed for the ratio of cis and trans β protons by nmr integration and for α protons which were always near zero. Mass spectra then allowed more complete analysis of recovered ethers into **1**, *cis*-**2**, *trans*-**2**, and **3**. Formation of acenaphthylene **4** (elimination product) occurred concurrently with exchange. The percentage of acenaphthylene was estimated by vpc analysis. Its deuterium content was also analyzable by mass spectrometry. Figure 3 summarizes the species involved and the likely interconversions that are occurring.

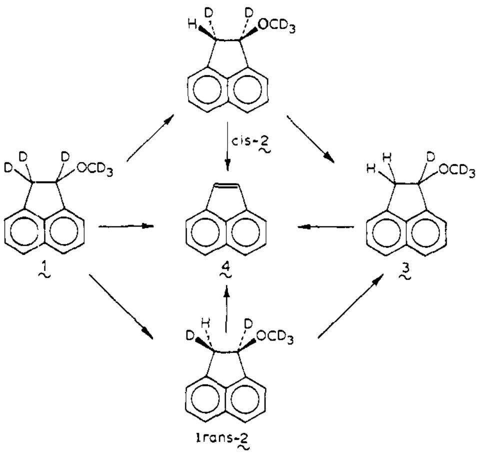


Figure 3. Scheme for exchange and elimination reactions of **1**.

Two solvents were chosen for study, *tert*-butyl alcohol and methanol, and the corresponding alkoxides were used as bases. Since ion pairing is common in *tert*-butyl alcohol, the counterion was varied: lithium, potassium, cesium, tetramethylammonium, and potassium complexed with dicyclohexyl-18-crown-6 ether.[15] The effect of added nitrobenzene and oxygen was also noted. The potassium salt was studied in the more polar solvent, methanol, and the effect of dicyclohexyl-18-crown-6 ether upon the exchange rate and stereochemistry was also determined.

Table I contains the results of this study organized according to the metal alkoxide and in most cases the recovered ethers have been further analyzed into the percentages of **1**, *cis*-**2**, *trans*-**2**, and **3** present in the reaction mixture. To facilitate comparison, the results for each run have been further organized by listing the relative rates of exchange and elimination ($k^{\text{ex}}/k^{\text{elim}}$) which is defined as

$$k^{\text{ex}}/k^{\text{elim}} = (\%\ \textit{cis-}\mathbf{2} + \%\ \textit{trans-}\mathbf{2})/\%\ \text{acenaphthylene}$$

The relative rates of cis and trans exchange in the recovered ether are also summarized under the heading $k^{\text{cis}}/k^{\text{trans}}$ which is defined as $k^{\text{cis}}/k^{\text{trans}}$ = [log (1 − fraction cis exchange)]/[log (1 − fraction trans exchange)] or operationally

$$k^{\text{cis}}/k^{\text{trans}} = \left[\log\left(1 - \frac{\%\ \textit{cis-}\mathbf{2} + \%\ \mathbf{3}}{\%\ \text{total ether}}\right)\right] \bigg/ \left[\log\left(1 - \frac{\%\ \textit{trans-}\mathbf{2} + \%\ \mathbf{3}}{\%\ \text{total ether}}\right)\right]$$

To determine these ratios with greater precision, in several cases the individual values were extrapolated to zero percentage reaction and these extrapolated values are shown in Table II. Of the two ratios, the $k^{\text{cis}}/k^{\text{trans}}$ exchange ratio did not change significantly with percentage of reaction and thus the extrapolated values are not very much different from the observed values. On the other hand, it is to be expected that,

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[13] (a) S. Sternhell, private communication; (b) L. M. Jackman and S. Sternhell, "Applications of NMR Spectroscopy in Organic Chemistry," Vol. 5, Pergamon Press, Elmsford, N. Y., 1969, p 233.

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

[15] (a) Dicyclohexyl-18-crown-6 ether was kindly provided by H. K. Frensdorff, E. I. duPont de Nemours and Co., Wilmington, Del. (b) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967).

Table I. Exchange Results for Ether-**1**[a]

Run	[Base], *M*	Temp, °C	Time, min	% acenaphthylene[b]	Ether						Exchange
					Total %	% **1**[c]	% *trans*-**2**[c]	% *cis*-**2**[c]	% **3**[d]	k^{ex}/k^{elim}	k^{cis}/k^{trans}
Potassium *tert*-Butoxide											
1	0.43	85.6	90	10	90	71	6	13	0	1.9 ± 0.3	2.1 ± 0.4
2	0.43	85.6	188	23	77	44	10	19	4	1.3 ± 0.2	1.8 ± 0.2
3	0.43	85.6	500	57	43	11	4	18	10	0.4 ± 0.2	2.6 ± 0.2
4	0.43[e]	85.6	135	17	83		*f*			1.5 ± 0.2	2.1 ± 0.2
5	0.022	85.6	1830	8	92	67	6	16	3	2.7 ± 0.6	2.3 ± 0.2
6	0.021[g]	60.0	107	8	92	65	15	6	6	2.6 ± 0.6	0.56 ± 0.07
7	0.021[g]	45.0	1818	4	96	73	13	8	2	5.2 ± 1.4	0.62 ± 0.10
8	0.37	65.0	700	4	96	64	8	19	5	7 ± 2	1.9 ± 0.3
9	0.37	65.0	1600	10	90	57	7	20	6	2.7 ± 0.6	2.2 ± 0.3
10	0.40	85.0	120	19	81		*k*			2.2	
11	0.40	85.0	120	15	85		*l*			2.8	
12	0.53	85.0	120	20			*m*			2.6	
13	0.11	45.0	600	44	56		*n*			1.0	
Cesium *tert*-Butoxide											
14	0.20	85.6	37	11	89	54	15	14	6	2.6 ± 0.5	0.92 ± 0.1
15	0.20	85.6	124	30	70	22	16	16	15	1.1 ± 0.2	1.0 ± 0.1
16	0.20	85.6	291	54	46	6	11	8	20	0.4 ± 0.1	0.95 ± 0.1
Lithium *tert*-Butoxide											
17	0.14	160	1010	34[h]	66	50	0.3	16	0	0.5 ± 0.1	45 ± 23
18	0.14	160	1900	51[h]	49	30	1	18	0	0.4 ± 0.1	22 ± 6
19	0.14	160	4023	76[h]	24	7	0	15	2	0.2 ± 0.2	22 ± 4
Tetramethylammonium *tert*-Butoxide											
20	0.11	44.8	100	6	94	67	21	6	0	4.5 ± 0.8	0.26 ± 0.04
21	0.11	44.8	500	9	91	55	25	9	2	3.8 ± 0.6	0.37 ± 0.05
22	0.11	44.8	4842	8	92	54	26	10	2	4.5 ± 0.7	0.40 ± 0.05
23	0.11	44.8	319	24	76	21	36	8	11	1.8 ± 0.2	0.34 ± 0.03
Potassium Methoxide											
24	0.40	150.3	200	8[h]	92		*i*			3.3 ± 0.7	1.0 ± 0.1
25	0.40	150.3	810	30[h]	70		*j*			2.4 ± 0.1	1.0 ± 0.1
26	0.12	152.4	396	7	93	41	19	19	14	5.4 ± 0.8	1.0 ± 0.1
27	0.12[g]	152.4	1196	18	82	13	18	19	32	2.0 ± 0.3	1.0 ± 0.1

[a] The solvent is the alcohol corresponding to the base. [b] Absolute error is estimated to be ±1. [c] ±1. [d] ±2. [e] 0.06 *M* in potassium acetate. [f] 0.52 β hydrogen in the ratio of cis/trans = 1.9 in recovered ether. [g] Added equivalent of dicyclohexyl-18-crown-6 ether. [h] Extensive loss of product due to side reactions. [i] 0.53 β hydrogen in the ratio cis/trans = 1.0 in recovered ether. [j] 1.42 β hydrogens in the ratio cis/trans = 1.0 in recovered ether. [k] 0.42 atom of D/molecule in recovered ether; argon atmosphere. [l] 0.44 atom of D/molecule in recovered ether; oxygen atmosphere. [m] 0.52 atom of D/molecule in recovered ether; oxygen atmosphere and 0.58 *M* in nitrobenzene. [n] 0.56 atom of D/molecule in recovered ether; evacuated tube containing 0.36 *M* nitrobenzene and 0.106 *M* dicyclohexyl-18-crown-6 ether.

Table II. Relative Exchange and Elimination Rates[a] for Ether-**1**

Runs	Base	Temp, °C	k^{ex}/k^{elim}	Exchange k^{cis}/k^{trans}
17–19	LiO-*t*-Bu	160	0.6	31 ± 6
1–3	KO-*t*-Bu	86	2	1.6 ± 0.2
8, 9	KO-*t*-Bu	65	9	1.6 ± 0.3
14–16	CsO-*t*-Bu	86	3	1.0 ± 0.1
20–23	$(CH_3)_4$NO-*t*-Bu	45	5	0.30 ± 0.05
6	KO-*t*-Bu[b]	60	3	0.56 ± 0.1
7	KO-*t*-Bu[b]	45	5	0.62 ± 0.1
24–26	$KOCH_3$	150	4	1.0 ± 0.1
27	$KOCH_3$[b]	152	2	1.0 ± 0.1

[a] Extrapolated to zero time when more than one run involved. [b] With added dicyclohexyl-18-crown-6 ether.

as a result of the definition, the ratio k^{ex}/k^{elim} would be sensitive to extent of reaction and thus the extrapolated values are not highly significant. These are used merely as an indication of the competition between the exchange and elimination processes.

α *vs.* β Exchange. A feature common to all bases used was the nearly complete lack of deuterium exchange α to the methoxy group even when β exchange was extensive. In an attempt to assess the extent of α exchange, the recovered ether from run 27 (potassium methoxide in methanol) was analyzed by nmr showing 1.5% proton incorporation at the α position. This corresponds roughly to a factor of 50 slower than either cis or trans β exchange which are occurring at the same rate in this medium. A sample of 1,1,2,2-tetradeuterioacenaphthene was subjected to exchange under the same conditions as run 27 and on a per deuteron basis it also exchanged a factor of 50 slower than each of the β deuterons in **1**. Thus, the methoxy group acts to enhance the exchange rate of β deuterons but has little effect on the α deuteron's kinetic acidity.

A number of studies have shown similar substituent effects with oxygen and particularly with fluorine; an alkoxy or fluorine acts to stabilize a β carbanion but when joined directly (α) to a planar or near-planar carbanionic center results in destabilization or mild stabilization. A general concensus seems to have been reached in the literature[16] that these phenomena are the result of two opposing effects: inductive stabilization and destabilizing electron–electron repulsion.

It has been postulated that this effect is indicative of a planar or near-planar rather than a pyramidal car-

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(16) (a) A. Streitwieser and D. Holtz, *J. Amer. Chem. Soc.*, **89**, 692 (1967); (b) A. Streitwieser, A. P. Marchand, and A. H. Pudjaatmaka, *ibid.*, **89**, 693 (1967); (c) A. Streitwieser and F. Mares, *ibid.*, **90**, 2444 (1968); (d) K. J. Klabunde and D. J. Burton, *ibid.*, **94**, 5985 (1972); (e) J. Hine and P. D. Dalsin, *ibid.*, **94**, 6998 (1972).

banion.[16c] Thus, the important role delocalization plays in stabilizing the anion and the recent crystallographic studies on benzyllithium,[17a] fluorenyllithium,[17b] and triphenylmethyllithium[17c] all support the suggestion of a nearly planar carbanionic intermediate in exchange of **1**.

Bridge *vs.* Ring Exchange. The intermediacy of a planar delocalized carbanion raises the possibility of reprotonation occurring competitively in the aromatic ring as well as on the ethano bridge. To investigate this possibility, the relative rates of ring and bridge exchange of acenaphthene in potassium *tert*-butoxide–*tert*-butyl alcohol-*O-d* were measured as a model for **1**.[18] It was found that deuterons were incorporated at the ethano bridge positions at a factor of about 10^5 faster than in the aromatic ring. Thus, it is probable that the anion formed as an intermediate during exchange of **1** at the β position also reacts exclusively at the β position.

Effect of Cation on the Reaction Rates. As seen in Tables I and II, the change of cation in *tert*-butyl alcohol from lithium to potassium–crown ether resulted in a change in rate of elimination of about four powers of ten (115° temperature difierence). Thus, lithium, potassium, and cesium *tert*-butoxide must exist primarily as ion pairs or aggregates in *tert*-butyl alcohol. Ion pairing is also suggested by conductivity experiments;[19] sodium *tert*-butoxide changes the conductivity of *tert*-butyl alcohol only slightly whereas benzyltrimethylammonium salts appear significantly dissociated. Kinetics of some hydrogen–deuterium exchange reactions[20] are also consistent with aggregation; kinetic order in added potassium *tert*-butoxide is found to be greater than one ($\sim$1.5).

The effect of ion pairing on kinetic basicity is also illustrated by the effect of added crown ether on the reaction catalyzed by potassium *tert*-butoxide (runs 6 and 7 of Table I). The rate of elimination was increased by a factor of about 300 as was the rate of exchange when an equivalent of crown ether was added. The catalytic effect of crown ether due to ion pairing in *tert*-butyl alcohol has been reported for other systems.[21]

In contrast to *tert*-butyl alcohol, added crown ether had no significant effect on the rates of the reactions run in methanol implying that potassium methoxide is predominantly dissociated in methanol. The reaction in methanol (and in lithium *tert*-butoxide–*tert*-butyl alcohol) was complicated by side reactions. At these temperatures (150–160°), the acenaphthylene reacts competitively to form products of yet unknown composition. However, controls show 1-methoxyacenaphthene is not among them. The instability of the tetramethylammonium *tert*-butoxide solutions (see Experimental Section) made rate constant measurements impossible but comparisons within any run should be valid (*e.g.*, cis/trans exchange; or exchange/elimination).

Electron transfer[22] was investigated as an independent probe for carbanion formation and these results are reported in runs 10–13. The effect of oxygen and nitrobenzene on the exchange reaction in *tert*-butyl alcohol with potassium *tert*-butoxide was investigated. No effect on either the rate of exchange or elimination processes was noted. While the presence of crown ether accelerated both processes as expected, again there was no evidence of electron transfer from the carbanionic intermediates to the nitrobenzene. These results are in contrast to triphenylmethane[22b] where efficient trapping by nitrobenzene occurred. Thus, although **1** and triphenylmethane have similar kinetic acidities, their rates of electron transfer seem to be quite different.

Effect of Cation on the Exchange Stereochemistry. As the results summarized in Table II indicate, the stereochemistry of the hydrogen–deuteron exchange reaction is also markedly affected by the nature of the cation. The stereochemical selectivity changes from exclusive cis exchange with lithium to preferential trans with either tetramethylammonium or potassium–crown ether. The rate of cis exchange has changed by a factor of at least 90 relative to trans exchange.

Since the large reactivity differences upon changing the cation necessitated a change of temperature, the effect of temperature change on the exchange stereochemistry was also investigated. With both potassium *tert*-butoxide at 86 and 65° and potassium *tert*-butoxide–crown ether at 60 and 45°, no discernible change in the relative rates of cis and trans exchange was noted. Thus, the change in stereoselectivity of the exchange process seem primarily related to the cation present in solution.

Both potassium *tert*-butoxide and cesium *tert*-butoxide show stereoselectivity intermediate between lithium and tetramethylammonium *tert*-butoxides. The possibility that this intermediate selectivity represented a competition between two or more active basic species,[5f] one reacting with highly selective cis exchange (*e.g.*, associated base) and one with preferential trans exchange (*e.g.*, dissociated base), was investigated in two ways using potassium *tert*-butoxide. In one experiment the base concentration was changed by a factor of 20 (runs 1–3 and 5) and in the other (run 4) potassium acetate (0.06 *M*) was added resulting in no observable change in the cis/trans exchange rate ratio. Since either dilution or added common ion would be expected to alter the proportions of two species having different extents of association, it would appear that the intermediate stereoselectivities are characteristic of one reactive base in solution. This observation is in contrast to a recent report invoking changes in relative amounts of associated and dissociated potassium *tert*-butoxide in *tert*-butyl alcohol to rationalize small changes in elimination stereochemistry.[5b]

Potassium methoxide in methanol showed no preference for cis exchange over trans exchange and added crown ether produced no change in the exchange rates. Thus, it would appear that dissociated methoxide ion is the active base in methanol and is showing little selectivity between the diastereotopic deuterons at the β position.

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[17] (a) S. P. Patterman, I. L. Karle, and G. D. Stucky, *J. Amer. Chem. Soc.*, **92**, 1150 (1970); (b) J. J. Brooks, W. Rhine, and G. D. Stucky, *ibid.*, **94**, 7339 (1972); (c) J. J. Brooks and G. D. Stucky, *ibid.*, **94**, 7333 (1972).

[18] (a) D. H. Hunter, A. I. Johnson, J. B. Stothers, A. Nickon, J. L. Lambert, and D. F. Covey, *ibid.*, **94**, 8582 (1972); (b) D. H. Hunter and J. B. Stothers, *Can. J. Chem.*, **51**, 2884 (1973).

[19] W. H. Saunders, D. G. Bushman, and A. F. Cockerill, *J. Amer. Chem. Soc.*, **90**, 1775 (1968).

[20] O. Kower and C. Boelhouwer, *Recl. Trav. Chem. Pays-Bas*, **88**, 696 (1969).

[21] J. N. Roitman and D. J. Cram, *J. Amer. Chem. Soc.*, **93**, 2231 (1971).

[22] (a) R. D. Guthrie, A. T. Young, and G. W. Pendygraft, *ibid.*, **93**, 4947 (1971); (b) R. D. Guthrie, *ibid.*, **92**, 7219 (1970); (c) R. D. Guthrie, *ibid.*, **91**, 6201 (1969).

Model for the Exchange Reactions. The sensitivity of the rates of the exchange and elimination reactions to the cation in solution require that the *tert*-butoxide salts of lithium, potassium, and cesium exist in solution as ion pairs or agglomerates. The sensitivity of the cis/trans exchange rates to cation requires that these cations also be present in the intermediates responsible for hydrogen–deuterium exchange. Thus, the salts of lithium, potassium, and cesium would appear to exist and also react as ion pairs or agglomerates.

It is tempting to postulate a specific role for the cations since the preference for cis exchange parallels the expected solvation energies[23] of these cations in *tert*-butyl alcohol. In the postulated intermediate for cis exchange (Figure 4), the cation is bonded to the ether oxygen of substrate, while in the intermediate for trans exchange, this bonding interaction is absent. Bonding between substrate and the cation present in the base ion pair would serve to lower the activation energy for cis deuteron removal and for reprotonation on the cis side. As this bonding interaction becomes stronger (Li$^+$ > K$^+$ > Cs$^+$), the preference for cis reaction increases.

The observation of preferential trans exchange with crown ether–potassium *tert*-butoxide seems consistent with this type of interpretation as does the results using tetramethylammonium cation. For both these cations bonding to substrate should be greatly reduced although the active base may still be ion pairs. Ion pairing is suggested since potassium–crown ether and tetramethylammonium ions do show somewhat different exchange preferences. The low cis/trans exchange ratio with tetramethylammonium cation is also consistent with this base being the most dissociated in *tert*-butyl alcohol of those studied.

The stereochemistry of the exclusive cis isotopic exchange reaction with lithium *tert*-butoxide can be deduced from the relative rates at which *cis*-**2** and **3** are produced from **1** (Figure 3). Exchange of the cis deuteron with retention would yield *cis*-**2** as the only product; **3** would arise only through removal of trans deuterons or by involvement of an inversion component. Exchange of the cis deuteron with inversion would require selective removal from the backside of **1** and selective protonation of the front side to form *cis*-**2**. However, this would lead to further exchange of *cis*-**2** and the rapid production of **3**. As can be seen in runs 17–19, **3** is being produced at a rate much slower than *cis*-**2**. This is consistent only with a retention mechanism. The results with the other cations are not as readily interpretable in terms of retention and inversion components.

The stereoselectivity of these exchange reactions has been interpreted as primarily due to asymmetry induced by the substrate on its environment rather than reflecting the preferential stability of the carbanions themselves. Even with potassium methoxide in methanol, where it seems methoxide itself is the active base, it is not clear that the relative rates of exchange ($k^{cis}/k^{trans} = 1$) reflect "pure" carbanion stabilities.

Exchange of diastereotopic protons α to a sulfoxide grouping provides other examples of this phenomenon. While it is possible to interpret relative rates of exchange in terms of preferred carbanion stability[24] again, there are now several examples of marked changes in the relative reactivity of diastereotopic protons.[25] Thus, it would appear that assignment of carbanion stabilities should be made with caution.

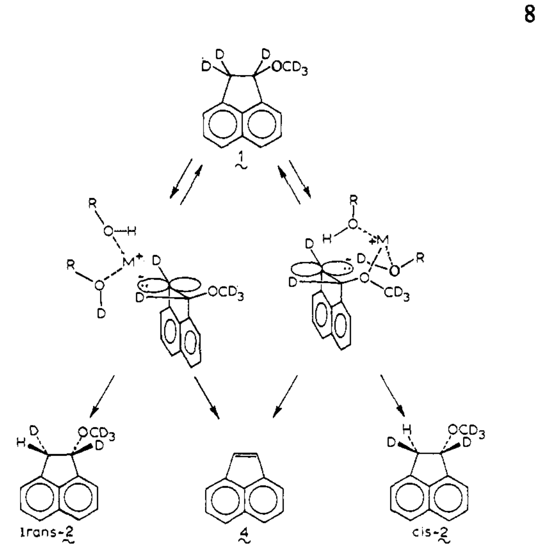

Figure 4. Model for exchange stereochemistry of **1**.

Exchange Stereochemistry and No-Bond Resonance. No-bond resonance has received attention as a possible stabilizing influence particularly with fluorine substitution.[26] While presumably less effective than with fluorine, this type of hyperconjugation is still possible for oxygen. Stereochemistry of exchange provides a probe for this interaction, since a coplanar deuteron should be preferentially acidified relative to other orientations. Thus, if no-bond resonance were of dominant energetic importance, exchange of the deuteron cis to the methoxy should be favored. In general, this is not observed in **1**, and thus while no-bond resonance may be contributing, it is apparently not of major significance.

Experimental Section

The nmr spectra (CCl$_4$ and internal TMS) were run on a Varian HA100 or a Varian A60A using a C-1024 time average computer. Mass spectra were obtained using a Varian M-66 mass spectrometer. Melting points and boiling points are uncorrected. The vpc analyses were run using a Varian Aerograph A90·P3 gas chromatograph with thermal conductivity detector and a recorder with a Disc integrator.

Substrates. 1-Methoxyacenaphthene. (a) A mixture of acenaphthene (7.7 g, 50 mmol) and *N*-bromosuccinimide (98 g, 55 mmol) was refluxed for 15 min in 100 ml of carbon tetrachloride. After cooling and filtration, the solvent was evaporated leaving crude 1-bromoacenaphthene. This oily material, which showed mainly one component by tlc, was used immediately without further purification.

To the crude 1-bromoacenaphthene and 6.0 g (60 mmol) of sodium bicarbonate was added 5 ml of acetonitrile. This mixture was rapidly stirred and 1.7 g (55 mmol) of methanol was added. After stirring for 30 hr, the reaction mixture was treated with pentane and washed four times with water. After the mixture was dried and solvent removed, the residual oil was chromatographed on 0.5 kg of silica gel using 10% ether in pentane. The later fractions containing the 1-methoxyacenaphthene were combined and

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[23] S. Goldman and R. G. Bates, *J. Amer. Chem. Soc.*, **94**, 1476 (1972).

[24] S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972).

[25] For example, R. R. Fraser, F. J. Schuber, and Y. Y. Wigfield, *J. Amer. Chem. Soc.*, **94**, 8795 (1972).

[26] (a) D. Holtz, *Chem. Rev.*, **71**, 139 (1971); (b) J. A. Jafri and P. G. Jesaitis, *Tetrahedron*, **28**, 3363 (1972); (c) K. J. Klabunde and D. J. Burton, *J. Amer. Chem. Soc.*, **94**, 820 (1972).

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distilled. The fraction boiling at 72° at 0.01 mm was collected (7.7 g; 84%) and analyzed by vpc to contain less than 0.1% acenaphthylene.

(b) A mixture of acenaphthen-1-ol[27] (5.0 g, 29 mmol), barium oxide (17.6 g, 115 mmol), methyl iodide (4.9 g, 34 mmol), water (0.4 ml), and 30 ml of *N,N*-dimethylformamide (freshly distilled from CaO) was shaken for 18 hr in a degassed, argon filled, light shielded flask.[28] The reaction mixture was dissolved in 300 ml of methylene chloride and 300 ml of water. The water layer was extracted with methylene chloride and the organic layers were combined. These were washed with water until neutral to litmus paper indicating removal of all dimethylformamide. After the solution was dried over anhydrous sodium sulfate, the solvent was removed on a steam bath. The resulting oil was triturated with pentane to remove the unreacted alcohol. After filtration the filtrate was concentrated on a steam bath and chromatographed on silica gel using 10% ether in pentane. The appropriate fractions were combined and distilled collecting the material of bp 72° (0.01 mm), 3.3 g (62% yield).

1-Trideuteriomethoxyacenaphthene. Following procedure (a) for 1-methoxyacenaphthene described above 15.4 g of acenaphthene was brominated and the crude 1-bromoacenaphthene was treated with 12 g (120 mmol) sodium bicarbonate and 3.8 g (110 mmol) of methanol-d_4 in 10 ml of acetonitrile. A yield of 6.4 g (34%) of material containing less than 0.05% acenaphthylene was obtained.

In the nmr the aromatic protons appeared as a multiplet (6 H at δ 7.3) and the remaining three protons were analyzed as an ABX (δ_{cis} 3.14 ppm, δ_{trans} 3.36 ppm, δ_{x} 5.11 ppm, $J_{\text{cis,trans}} = -17.7$ Hz, $J_{\text{cis,x}} = 2.6$ Hz, $J_{\text{trans,x}} = 7.1$ Hz).

Mass spectrometry using low electron energy indicated <2% of d_2 material and >98% of d_3 material.

1-Trideuteriomethoxy-1,2,2-trideuterioacenaphthene. Procedure (a). Acenaphthen-1-one. A sample of 1-naphthaleneacetyl chloride prepared from 56 g (0.3 mol) of 1-naphthalene–acetic acid and 60 g (0.5 mol) of thionyl chloride was reacted at room temperature for 3 hr with 66 g (0.5 mol) of aluminum chloride in 500 ml of methylene chloride. Work-up using 1 l. of dilute hydrochloric acid, and washes of water, sodium bicarbonate, and water twice more, drying, and solvent evaporation yielded a crude dark product. Vacuum sublimation yielded 29.8 g (59%) of light yellow product of mp 119.5–120.5°.

2,2-Dideuterioacenaphthen-1-one. A mixture of 17.0 g (0.10 mol) of acenaphthen-1-one, 50.0 ml (2.7 mol) of deuterium oxide, and 5.0 g of potassium carbonate was degassed and flushed with nitrogen in a 250-ml round-bottomed flask fitted with a reflux condenser. After refluxing and stirring for 2 hr, the mixture was cooled and filtered and the ketone air dried and vacuum sublimed. The sublimed ketone (15.5 g, mp 117–118°) was refluxed 2 hr under nitrogen with a further 50.0 ml of deuterium oxide and 5.0 g of potassium carbonate. After work-up and sublimation there resulted 14.5 g (85% yield), mp 119–120°, of 2,2-dideuterioacenaphthen-1-one. Nmr analysis in deuteriochloroform gave only a small peak at δ 3.20 ppm which corresponded to 95% d_2 material.

1,2,2-Trideuterio-1-acenaphthenol. In a 500-ml, three-necked, round-bottomed flask was placed 14.5 g (85 mmol) of 2,2-dideuterioacenaphthen-1-one with 1.2 g (29 mmol) of lithium aluminum deuteride in a side arm. The system was degassed and flushed with argon and then 250 ml of tetrahydrofuran, which had been freshly distilled from lithium aluminum hydride, was added. The system was degassed again flushing with argon. The solid lithium aluminum deuteride was added portionwise while cooling the mixture with an ice bath. An orange color formed and after stirring overnight at room temperature, the mixture was refluxed for 3 hr prior to work-up. To the cold mixture was added slowly 1 *M* hydrochloric acid (125 ml) and the tetrahydrofuran was removed by film evaporation. The residue was dissolved in 500 ml of methylene chloride and then washed with saturated sodium bicarbonate solution and dried, and the solvent was removed. A crude yellow solid weighing 14.0 g crystallized out during the evaporation. This solid was recrystallized from benzene. The filtrate was chromatographed on 300 g of alumina using methylene chloride. The total yield of alcohol was 10.1 g (68% yield based on ketone), mp 146–147° (lit.[27] 144.5–145.5°). Nmr analysis in pyridine solvent showed no absorption for the β hydrogen at δ 3.4 and 3.7 ppm and no absorption for the α hydrogen at δ 5.9 ppm. Stereochemical assignments are based upon coupling constants obtained from an ABX analysis of the spectrum of 1-acenaphthenol (δ_{cis} 3.42 ppm, δ_{trans} 3.71 ppm, δ_{X} 5.92 ppm, $J_{\text{cis,trans}} = 17.2$ Hz, $J_{\text{cis,x}} = 2.8$ Hz, $J_{\text{trans,x}} = 7.1$ Hz).[13]

1-Trideuteriomethoxy-1,2,2-trideuterioacenaphthene. Following the procedure for 1-methoxyacenaphthene, 5.9 g (35 mmol) of the previously prepared 1,2,2-trideuterioacenaphthen-1-ol yielded 8.8 g (82%) of product containing less than 0.1% of acenaphthylene. Nmr analysis in carbon tetrachloride indicated the absence of α hydrogens at δ 5.1 ppm and less than 1% β hydrogen and methoxyl hydrogens at δ 3.2 ppm. Isotopic analysis by mass spectrometry at low electron energy indicated 1% d_4, 8% d_5, and 91% d_6 material. Thus, the ether was an isotopic mixture of 1% 1-trideuteriomethoxy-1-deuterioacenaphthene, 8% *cis*-**2** and *trans*-**2**, and 91% **1**.

Procedure (b). $\alpha,\alpha,\alpha',\alpha'$-Tetradeuterio-1,8-di(bromomethyl)-naphthalene. To a cold stirred solution of 20.1 g (0.1 mol) of $\alpha,\alpha,\alpha',\alpha'$-tetradeuterio-1,8-di(hydroxymethyl)naphthalene[12] and 50 g (1.6 mol) of tetrabutylammonium bromide in 500 ml of methylene chloride was added rapidly 83 g (0.3 mol) of phosphorus tribromide. Following a 1-hr reflux, the methylene chloride was washed twice with water, once with sodium bicarbonate, and once with water, dried, and evaporated. The residue was chromatographed on silica gel with 10% ether in pentane to yield 28.6 g (90%) of material, mp 124–127° (lit.[12] mp 129–131°).

Addition of tetraalkylammonium bromide eliminates the otherwise significant amounts of the cyclic ether 1*H*,3*H*-naphtho[1,8-*c,d*]pyran that is produced.

1-Trideuteriomethoxy-1,2,2-trideuterioacenaphthene. The previously prepared 1,8-di(bromomethyl)naphthalene-d_4 was converted to 1,1,2,2-tetradeuterioacenaphthene which was then reacted according to the procedure (a) described earlier for 1-methoxyacenaphthene. A sample of 1.2 g (26%) of material containing less than 0.1% acenaphthylene was obtained. Nmr analysis in carbon tetrachloride indicated the absence of β hydrogen and methoxyl hydrogen at δ 3.2 ppm and α hydrogen at δ 5.1 ppm. Isotopic analysis by mass spectrometry at low electron energy indicated 6% d_5 and 94% d_6 material. Thus the ether was 94% **1**.

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 (<0.002 *M* H_2O).

The lithium *tert*-butoxide, potassium *tert*-butoxide, and cesium *tert*-butoxide solutions were prepared by stirring the cleaned metal at room temperature with degassed *tert*-butyl alcohol under an argon atmosphere. These solutions were titrated for water (<0.002 *M*) and for total base which is reported in the Results. Potassium methoxide in methanol was prepared similarly except the methanol was cooled during reaction. The solutions containing dicyclohexyl-18-crown-6 ether[15] were prepared by adding a weighed amount of the crown ether to the base solution. The solution of crown ether with potassium *tert*-butoxide–*tert*-butyl alcohol was not indefinitely stable and seemed to have decomposed within 2 months. Neither did the crown ether solution survive when heated to 180°.

The solution of tetramethylammonium *tert*-butoxide in *tert*-butyl alcohol was prepared by dissolving freeze dried tetramethylammonium hydroxide in *tert*-butyl alcohol and then freeze drying. This procedure was repeated three times to remove the bulk of the water. Molecular sieves were added to the final solution which was typically 0.25 *M* in H_2O. After about 2 days the solution was down to 0.05 *M* in H_2O and 0.11 *M* in base. This base solution must be used immediately since it decomposes within days to a weaker base (presumably trimethylamine and *tert*-butyl methyl ether).

Exchange and Elimination Procedure. The routine was effectively the same for all base solutions and substrates. Usually about 200 mg of substrate and 10 ml of base solution were twice degassed and sealed under vacuum in a Carius tube. After immersing in a constant-temperature bath for the indicated time, the tube was cooled and opened and the contents dissolved in pentane and water. The pentane layer was washed four times with water, dried, and evaporated through a Vigreux column.

The mixture was analyzed by vpc (8 ft × 0.25 in. column of 10% SE-30 on 45–60 Chromosorb W; injector 192°; column 155°; detector 240°; He 100 ml/min). The area % of acenaphthylene and 1-methoxyacenaphthene was converted to mole % using a calibration curve.

The mixture of olefin and ether was then separated on silica gel (60–120 mesh) eluting with 10% ether in pentane. The fractions containing acenaphthylene were combined and sublimed (~70°

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[27] J. Cason, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 3.

[28] R. Kuhn and H. Taischmann, *Chem. Ber.*, **94**, 2258 (1961).

(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° wt % 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 material containing zero, one, or two hydrogens. These two types of data allowed extraction of the percentages of the four ethers.

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E1cb Reaction of 1-Methoxyacenaphthene. II. The Elimination Step

D. H. Hunter* and D. J. Shearing

Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario. *Received June 18, 1973*

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 exchange[2] 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*-

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

[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.