Dehydrogenation Mechanisms. On the Mechanism of Dehydrogenation of Acenaphthene by Quinones

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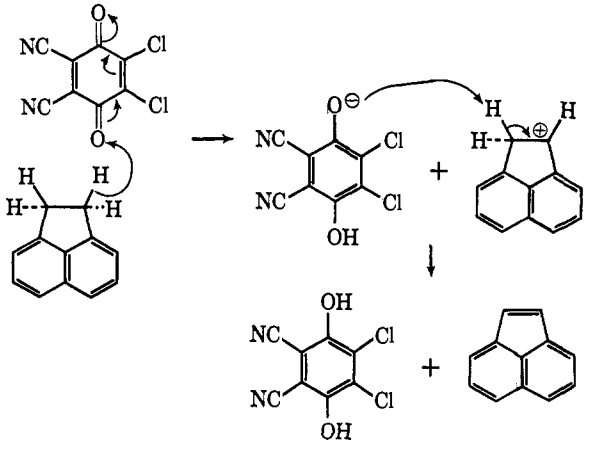
Abstract: The mechanism of the dehydrogenation of acenaphthene by quinones has been investigated. Dehydrogenation of *cis*-1,2-dideuterioacenaphthene utilizing 2,3-dichloro-5,6-dicyanobenzoquinone proceeded with 77.7% *cis* elimination and employing tetrachloro-*o*-benzoquinone with 62.9% *cis* elimination. These data require modification of the existing mechanism of dehydrogenation. The large isotope effect, the lack of 1,2 shifts, and the stereochemistry of elimination support the intermediacy of classical carbonium ions. Initial ion-pair formation and partial collapse of the ion pair to product before dissociation accounts for the observed net *cis* elimination. The amount of net *cis* elimination decreases as solvent polarity increases, an observation in support of the ion-pair hypothesis.

The mechanisms of a large number of 1,2-elimination reactions have been investigated in great detail. However, the simplest and perhaps most important vicinal elimination reaction, dehydrogenation, has received almost no attention. The scarcity of experimental data on the mechanism of this process suggested the need for further studies.

Linstead, Jackman, and co-workers established a polar rather than homolytic nature for dehydrogenation by quinone.[1] Consequently, they proposed a two-step mechanism illustrated in Scheme I for the dehydrogenation of acenaphthene by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). Hydride abstraction by quinone produces the carbonium ion from which a proton is abstracted to yield olefin. However, on the basis of

Scheme I. Linstead Mechanism of Dehydrogenation by Quinones



the available data, a concerted process involving a polar transition state in which the first C–H bond is broken to much larger extent than the second C–H bond cannot be eliminated. Furthermore, the crude schematic above does not delineate the nature of the carbonium ion intermediate or whether more than one intermediate is involved in the reaction. We undertook this study to provide firm support for a stepwise rather than a lopsided concerted reaction and to define the nature of the intermediate(s).

(1) For leading references to this series of papers see L. M. Jackman, in "Advances in Organic Chemistry, Methods and Results," Vol. II, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.

To examine the validity of this hypothesis and to investigate the details of this reaction, we chose to study the stereochemical course of dehydrogenation. Our interest in the chemistry of acenaphthenes and the conversion of acenaphthenes to acenaphthylenes led us to choose this system for study. In addition, there are several other advantages to this selection. First, the requisite labeled compounds were easily available. Second, in any free classical carbonium ion, no steric preference for either *cis* or *trans* elimination should exist.

For this study, samples of 1,1,2,2-tetradeuterioacenaphthene (I), 1,1-dideuterioacenaphthene (II), and *cis*-1,2-dideuterioacenaphthene (III) were required. Chart I summarizes the preparation of these compounds. The deuterium content was determined by mass spectrometry at low ionizing voltages, and the

Chart I. Preparation of Deuterated Acenaphthenes

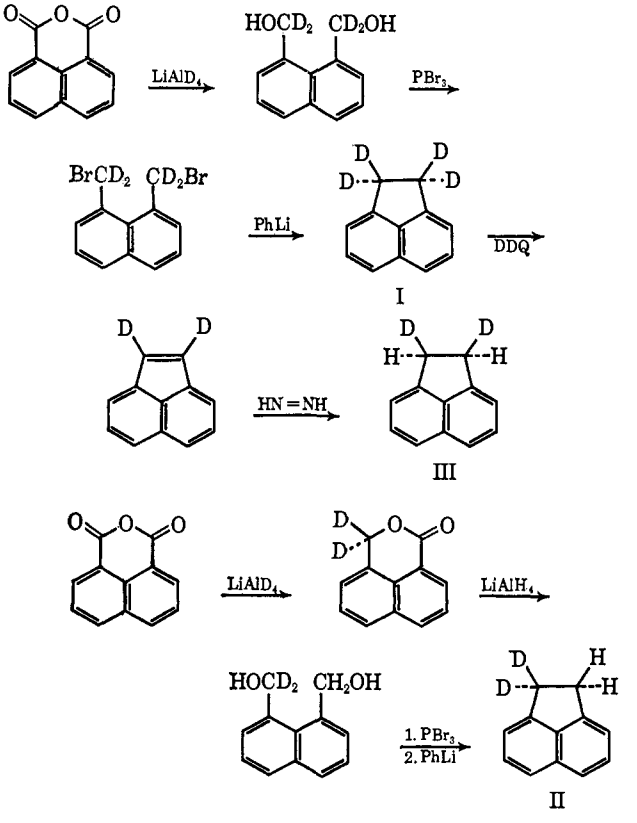


Table I. Deuterium Distribution[a] in Acenaphthylene Product

Reactants	Solvent	d_0	d_1	d_2	$(d_2 + d_0)/d_1$
III + DDQ[b]	Benzene	12.2	22.3	65.5	3.48
III + DDQ[b]	Phenetole	14.0	26.3	59.7	2.80
III + DDQ[b]	Dimethylformamide	9.1	31.0	59.9	2.23
III + TOQ[c]	Benzene	7.4	37.1	55.5	1.69
DDQ[b] + I + acenaphthene	Benzene	81.0	...	19.0	...
TOQ[c] + I + acenaphthene	Benzene	83.5	...	16.5	...

[a] Determined by mass spectrometry at 20 and 30 ev. All results are average of two runs. [b] 2,3-Dichloro-5,6-dicyanobenzoquinone. [c] Tetrachloro-*o*-benzoquinone.

position of deuterium is based upon the mode of synthesis and supported by the spectral data. The *cis* stereochemistry of III follows from the known *cis* nature of the diimide reduction.[2]

In a concerted process, *cis* elimination would occur exclusively, whereas a stepwise pathway would produce either *trans* elimination (vide infra) or both *cis* and *trans* elimination. To differentiate between these possibilities, we studied the dehydrogenation of *cis*-1,2-dideuterioacenaphthene (III). Treatment of III with DDQ and tetrachloro-*o*-benzoquinone (TOQ) in benzene at 80° produced acenaphthene with the deuterium distribution listed in Table I. The ratio of $d_2 + d_0$ to d_1 species corresponds to the ratio of *cis* to *trans* elimination. The large amount of both *cis* and *trans* elimination occurring in both cases suggest a nonconcerted nature for the reaction. Furthermore, models clearly show that the *o*-quinone should exhibit a greater preference for *cis* elimination over a *p*-quinone in any concerted-type pathway. The larger *cis:trans* ratio of DDQ than TOQ clearly indicates the reverse is true and supports the stepwise pathway, originally suggested by Linstead.

The isotope effect for dehydrogenation was obtained by dehydrogenating a mixture of 1,1,2,2-tetradeuterioacenaphthene and acenaphthene to about 10% completion. The deuterium distribution listed in Table I corresponds to a k_H/k_D for the DDQ reaction of 3.49[3] and a value of 4.14[3] for the TOQ reaction. These values represent maxima for the isotope effects for C–H bond cleavage, although they are a fair measure of it. Superimposed upon the primary isotope effect are the secondary isotope effects[4] associated with replacement of α- and β-hydrogens by deuterium in the carbonium ion. Nevertheless, the magnitude of these isotope effects are inconsistent with both C–H bonds being broken in the transition state.[4] They indicate a considerable amount of single C–H bond breakage in the transition state, which is consistent with the hydride abstraction as the rate-determining step. The larger value for TOQ compared to DDQ is consistent with the lower oxidation–reduction potential of TOQ.[1] Because of its lower reactivity in hydride abstraction, the transition state will involve greater C–H bond breakage.[5]

With the verification of the stepwise carbonium ion nature of the reaction, it is necessary to demonstrate lack of deuterium scrambling to ensure that the deuterium distribution of the acenaphthylene products is a reflection of the stereochemistry of dehydrogenation. In particular, the possibility of hydride transfers either intermolecularly or intramolecularly in any carbonium ion intermediates must be excluded. Dehydrogenation of a mixture of acenaphthene and its deuterated partner I would lead to undeuterated and dideuterated acenaphthylene only if no intermolecular scrambling occurred. When a mixture containing 55.0% acenaphthene and 45.0% 1,1,2,2-tetradeuterioacenaphthene was dehydrogenated employing 2,3-dichloro-5,6-dicyanobenzoquinone in benzene at 80°, the isolated acenaphthylene contained 55.0% d_0 and 45.0% d_2 species, clearly in support of no intermolecular scrambling.

The possibility of intramolecular 1,2-hydride shifts in any possible carbonium ion intermediates were examined employing 1,1-dideuterioacenaphthene (II). Dehydrogenation of II would produce ions IV and V (or their nonclassical counterparts) which might be in equilibrium with ions VI and VII, respectively. Proton or deuteron abstraction would then produce a mixture of 1,2-dideuterioacenaphthylene (VIII), acenaphthylene (IX), and 1-deuterioacenaphthylene (X). If hydride (or deuteride) shift was appreciably slower than proton (or deuteron) abstraction only X would be produced. Treatment of II containing 72% d_2, 6% d_3, and 22% d_4 species with DDQ in benzene at 80° yielded acenaphthylene that contained 27.0% d_2 and 73.0% d_1 species in excellent agreement with the expected distribution calculated on the basis of the distribution in the starting material (calculated distribution in product, 28.0% d_2 and 72.0% d_1).

The nature of this carbonium ion(s) was next investigated. We considered the possibility of the bridge carbonium ion XI as the intermediate which would arise as depicted below. (The same conclusions are reached if a proton is initially abstracted.) Such bridging in the transition state predicts an over-all *trans* elimination process, a prediction not fulfilled. Furthermore, the possibility that no net *trans* elimination occurred because of rapid equilibration of the bridged ions XIa, b, c, and d has been eliminated by the dehydrogenation of 1,1-dideuterioacenaphthene. Equilibration of these ions produces net 1,2-hydrogen (or deuterium) shifts which are found not to occur (*vide supra*). Thus, the evidence strongly supports classical carbonium ions as the intermediates. Dewar and Fahey[6] found that the same classical carbonium ion is involved in the addition of hydrogen halides to acenaphthylene.

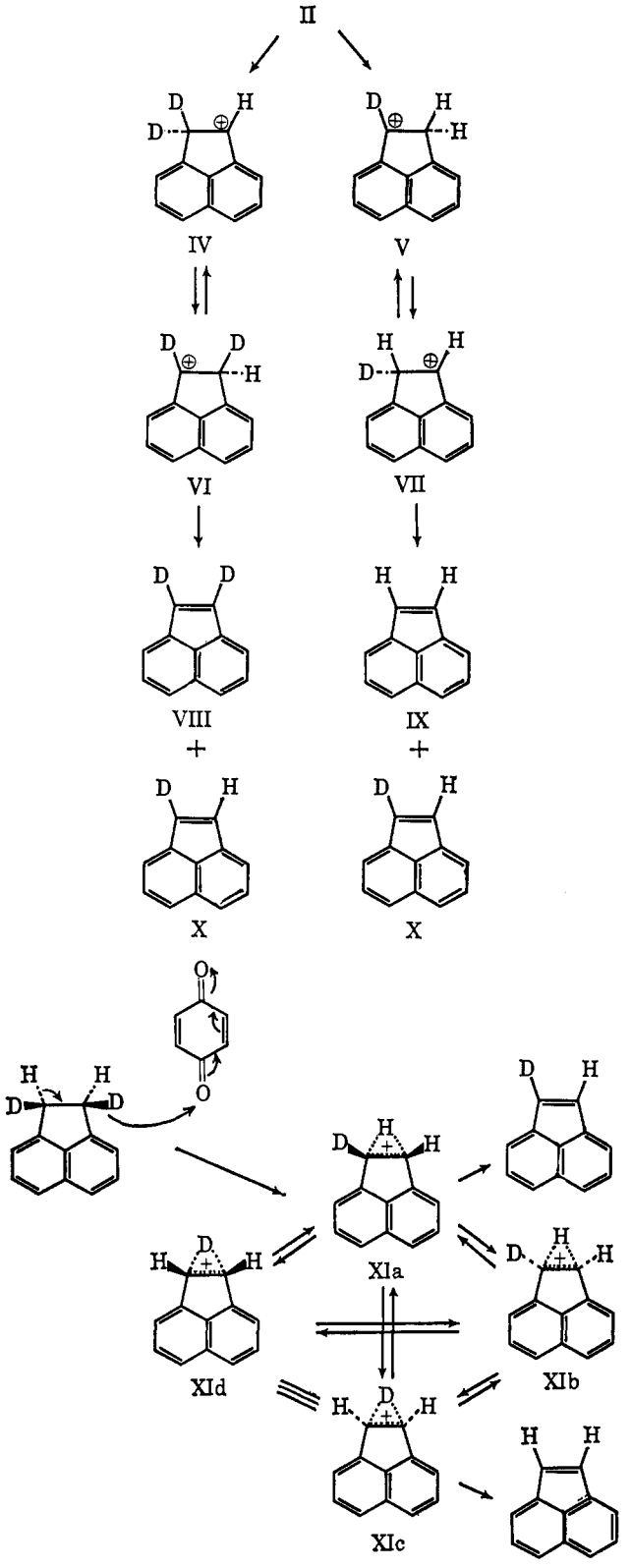
(2) S. Hünig, H. R. Müller, and W. Thies, *Angew. Chem. Intern. Ed. Engl.*, 4, 271 (1965).

(3) This value is obtained after correction for the isotopic composition of the starting material.

(4) (a) K. B. Wiberg, *Chem. Rev.*, 55, 713 (1955); (b) L. S. Bartell, *J. Am. Chem. Soc.*, 83, 3567 (1961).

(5) G. S. Hammond, *ibid.*, 77, 334 (1955).

(6) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, 85, 2245 (1963).



Nevertheless, the data summarized in Tables I and II clearly demonstrate that the reaction proceeds with net *cis* elimination, a fact that requires involvement of more than a free classical carbonium ion as suggested by Linstead. If their proposed scheme were correct, the amount of *cis* and *trans* elimination would be the same. In the case of *cis*-1,2-dideuterioacenaphthene, the ratio of *cis* to *trans* elimination would solely be determined by the isotope effect for proton abstraction in the intermediate ions VI and VII. A reasonable k_H/k_D range for proton abstraction in a carbonium ion of 1.0–1.8 can be obtained from similar processes in carbonium ions generated under solvolyses conditions.[7] Employing these numbers, the amount of $d_2 + d_0$ species (*i.e.*, the amount of *cis* elimination) expected is 50–58%.[8] Experimentally, in every case, this value is substantially larger. Table II summarizes the amount of *cis* elimination in excess of the calculated amount on the basis of random proton abstraction.

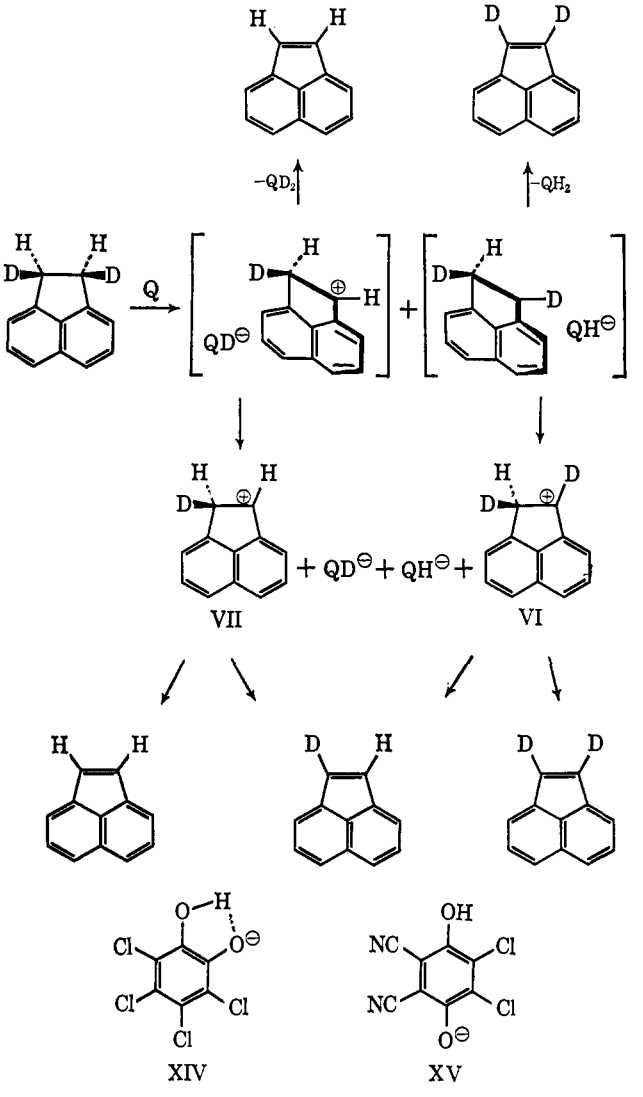
Table II. Stereochemistry of Elimination

Quinone	Solvent	% *cis*	Net *cis*[a]
DDQ	Benzene	77.7	19.7–27.7
DDQ	Phenetole	73.7	15.7–23.7
DDQ	Dimethylformamide	69.0	11.0–19.0
TOQ	Benzene	62.9	4.9–12.9

[a] The first number corresponds to k_H/k_D for proton loss in the carbonium ion of 1.8 and the second to 1.0.

The large amount of both *trans* and *cis* elimination supports the intervention of the free ions VI and VII;

Scheme II. Dehydrogenation of Acenaphthene



(7) (a) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, 75, 2925 (1953); (b) C. E. Booyer and E. S. Lewis, *ibid.*, 76, 794 (1954).

(8) In these calculated ranges, the first value given is for assuming a k_H/k_D of 1.0 for proton abstraction by anion and the second value given is for assuming a k_H/k_D of 1.8 for this step.

however, the stereoselectivity demands the intervention of another intermediate between starting materials and these ions. The simplest suggestion involves the formation of ion pairs and is outlined in Scheme II. The initial product of hydride abstraction, ion pairs XII and XIII, may collapse to product (to give *cis* elimination) or separate into ions VI and VII. The lower basicity of the hydroquinone anion XIV compared to XV would favor separation of ions over abstraction of a proton in the initial ion pair and lead to less net *cis* elimination. This reasoning is in excellent agreement with the experimental facts.

Further support for the ion-pair hypothesis arises from the effect of solvent on the course of the reaction. As the polarity of the solvent increases, the separation of the ion pairs is favored and the ratio of $d_2 + d_0$ to d_1 species should decrease. The data in Table I show that this ratio changes from 3.48 in benzene to 2.80 in phenetole and 2.23 in dimethylformamide, clearly in support of the involvement of ion pairs.

The mechanism of dehydrogenation of acenaphthene by quinone remarkably resembles the addition of hydrogen halide to acenaphthylene. Dewar and Fahey[6] found this latter reaction occurs with net *cis* addition which is also a function of solvent polarity. To account for these observations, they propose an ion-pair mechanism very similar to that proposed here for the reverse process, elimination. In their case, the ion pair either collapses by charge neutralization or separates, whereas, in the present case, the ion pair either collapses by proton abstraction or separates. Therefore, the difference in net *cis* addition in the former case to the net *cis* elimination in the latter should be a reflection of the difference in activation energy for charge neutralization and proton abstraction. Since different solvents and temperatures were employed, no quantitative comparison can be made; however, qualitatively (after suitable adjustments for solvent and temperature) it appears both processes have very similar activation energies. Furthermore, these observations suggest that E1 eliminations in acenaphthenes also should proceed with marked stereoselectivity which will be a function of both solvent and basicity of the leaving group.

Experimental Section[9]

Preparation of 1,8-Dihydroxymethylnaphthylene-d_4. A suspension of 15.0 g (0.0758 mole) of 1,8-naphthalic anhydride in 300 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride) was prepared under nitrogen. It was cooled in an ice bath and, subsequently, 3.30 g (0.0787 mole) of lithium aluminum deuteride[10] was stirred for 15 hr during which time it was allowed to warm to room temperature. It was then refluxed 1 hr. Upon cooling, ethyl acetate was added to destroy excess lithium aluminum deuteride, and the mixture was diluted with 300 ml of 10% aqueous hydrochloric acid. The resulting solid was filtered and recrystallized from benzene to yield 13.0 g (92.4% yield) of colorless needles, mp 154–155° (lit.[11] for undeuterated diol, mp 153.5–155.5°). The infrared spectrum[12] showed the C–D stretching bands between 2100 and 2225 cm^{-1}.

Preparation of Acenaphththene-d_4. The above diol was converted into 1,8-bis(bromomethyl)naphthylene-d_4 by the method of Bergmann and Szmuszkovicz.[11] From 13.0 g (0.0701 mole) of diol-d_4 was obtained 18.5 g (83.0% yield) of dibromide-d_4, mp 129–131° (lit.[11] for undeuterated compound, mp 129–131°). The dibromide (18.5 g, 0.0581 mole) was dissolved in 50 ml of 2:1 benzene–ether solvent mixture under nitrogen and cooled to −5°. To this solution was added 31.0 ml of 1.9 *M* phenyllithium solution (0.0590 mole) in 2:1 benzene–ether. Upon completion of the addition, the mixture was stirred at −5° for 30 min, at 25° for 30 min, and at reflux for 1 hr. Then 2 ml of D_2O was added and the mixture taken up in 300 ml of ether. The ether layer was washed with dilute aqueous hydrochloric acid, then aqueous sodium bicarbonate, and finally water. After drying and evaporation of solvent, the residue was sublimed to yield 7.9 g (86.0% yield) of colorless product, mp 93–95° (lit.[11] for undeuterated compound, mp 92–93°). The infrared spectrum[13] showed C–D stretching vibrations between 2100 and 2225 cm^{-1}. The nmr spectrum showed the aromatic region to be essentially identical with that of the undeuterated compound but showed no detectable absorption at 3.20 ppm indicating the complete deuteration of the ethano bridge. Mass spectral analysis showed the compound to be 97% d_4 and 3% d_3.

Preparation of *cis*-1,2-Dideuterioacenaphthene. A solution of 316 mg (2.00 mmoles) of acenaphthene-d_4 and 567 mg (2.50 mmoles) of 2,3-dichloro-5,6-dicyanobenzoquinone in 25 ml of dry benzene was refluxed 15 hr under nitrogen. The mixture was cooled and the white solid removed by filtration. This solid was washed several times with benzene. The combined benzene fractions were washed with 10% aqueous sodium hydroxide and then water. After drying and evaporation of solvent, the residue was sublimed *in vacuo* to yield 272 mg (88.4% yield) of yellow flakes, mp 90–92° (lit.[14] for undeuterated compound, mp 91–92°). Vpc analysis indicated the presence of 5% 1,1,2,2-tetradeuterioacenaphthene. The infrared spectrum[13] of a collected sample[15] showed C–D stretching bands between 2100 and 2325 cm^{-1}. The nmr spectrum showed an aromatic region identical with acenaphthylene, but no detectable absorption at 7.00 ppm indicating the complete deuteration of the unsaturated bridge. Mass spectral analysis of a sample collected from vpc showed only the presence of dideuterated species.

The dipotassium salt of azodicarboxylic acid was prepared by adding 1.0 g (8.61 mmoles) of azodicarbonamide portionwise to a solution of 2.5 g of potassium hydroxide in 2.5 g of water cooled in an ice bath. The yellow needles of the potassium azodicarboxylate were collected by filtration and washed first with ethanol followed by acetone. A solution of 210 mg (1.36 mmoles) of 1,2-dideuterioacenaphthylene in 5.0 ml of ethanol was prepared under nitrogen. After addition of the dipotassium salt, a solution of 2.5 g of acetic acid in 5.0 ml of ethanol was dropped in over a period of several hours. The mixture was stirred overnight during which time a white suspension in a colorless solution formed. This mixture was poured into water and extracted with ether. The ether layers were washed with dilute aqueous hydrochloric acid and then saturated aqueous sodium bicarbonate. After drying, evaporation followed by sublimation of the residue produced 208 mg (99% yield) of colorless needles, mp 93–95°. The infrared spectrum showed C–D stretching vibrations at 2100–2225 cm^{-1}. The nmr spectrum showed an aromatic region pattern essentially identical with that of acenaphthene and a broad singlet at 3.20 ppm in the ratio of 3.0:1.0. Mass spectral analysis indicated the compound contained 95.0% d_2 and 5.0% d_0 species.

Preparation of 1,1-Dideuterioacenaphthene. A suspension of 990 mg (5.00 mmoles) of 1,8-naphthalic anhydride in 35 ml of dry THF under nitrogen was cooled to 0°. Portionwise, 105 mg (2.50 mmoles) of lithium aluminum deuteride was added. After stirring 1 hr at 0° and 5 hr at room temperature, addition of a few drops of ethyl acetate destroyed any excess deuteride. The mixture was

(9) Melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Models 11 and 15 spectrophotometers. Nmr spectra were determined on a Varian Associates Model A-60 spectrometer fitted with a variable-temperature probe. Chemical shifts are given in ppm relative to TMS as an internal standard. Mass spectra were taken on a CEC 103 C mass spectrometer fitted with an electron multiplier at an ionizing current of 40 ma and ionizing voltages of 20, 30, and 70 v. Unless otherwise indicated, extractions were performed with chloroform, and magnesium sulfate was employed as a drying agent. Vpc analyses were performed on an Aerograph Model 90P instrument.

(10) Available from Alfa Inorganics, Inc., Beverley, Mass.

(11) E. D. Bergmann and J. Szmuszkovicz, *J. Am. Chem. Soc.*, 75 2760 (1953).

(12) Determined as a pellet in KBr.

(13) Determined as a solution in carbon tetrachloride.

(14) A. G. Anderson, Jr., and R. B. Anderson, *J. Am. Chem. Soc.*, 77, 6610 (1955).

(15) A 20% diethylene glycol succinate on Chromosorb P vpc column was employed.

poured into aqueous hydrochloric acid solution and extracted with ether. After drying and evaporation, 560 mg of crude product remained whose infrared spectrum indicated the presence of some diol in addition to the desired lactone (carbonyl band at 1720 cm^{-1}). This crude material was dissolved in 35.0 ml of dry THF under nitrogen and treated with 500 mg of lithium aluminum hydride in the manner described above. There was obtained 450 mg (47.5% yield from anhydride) of 1,8-bis(hydroxymethyl)naphthylene-d_2 (contaminated with d_4 species) after recrystallization from benzene, mp 155–157°. This diol was converted to 1,8-bis(bromomethyl)-naphthylene-d_2, mp 130–131°, as described above in 72% yield. Subsequent treatment of 530 mg (1.67 mmoles) of this dibromide with phenyllithium as described above produced 150 mg (58% yield) of 1,1-dideuterioacenaphthene after sublimation, mp 93–95°. Mass spectral analysis indicated this compound had 72% d_2, 6% d_3, and 22% d_4 species.

Dehydrogenation of Mixtures of Acenaphthene and 1,1,2,2-Tetradeuterioacenaphthene. A. With 2,3-Dichloro-5,6-dicyanobenzoquinone. A solution of 39.5 mg (0.231 mmole) of 1,1,2,2-tetradeuterioacenaphthene, 43.6 mg (0.283 mmole) of acenaphthene, and 300 mg (1.32 mmoles) of 2,3-dichloro-5,6-dicyanobenzoquinone in 5.0 ml of dry benzene was refluxed 15.0 hr under nitrogen. After cooling, filtration removed the suspended solid. This solid was washed well with ether and the ether layer combined with the benzene layer. These combined layers were washed with aqueous 10% sodium hydroxide and then water. After drying and removal of solvent by evaporation, the residue revealed the presence of only acenaphthylene. Mass spectral analysis revealed the presence of 55.0% d_0 and 45.0% d_2 species, identical with the predicted amounts based upon the composition of the starting material (55.0% acenaphthene and 45.0% acenaphthene-d_4). The presence of only d_0 and d_2 species indicates the lack of any intermolecular scrambling in the intermediate carbonium ions.

B. With 2,3-Dichloro-5,6-dicyanobenzoquinone. The identical mixture of acenaphthenes (39.5 mg, 0.231 mmole of d_4 and 43.6 mg, 0.283 mmole of d_0) as above was dehydrogenated with 22.7 mg (0.100 mmole) of 2,3-dichloro-5,6-dicyanobenzoquinone in 5.0 ml of refluxing benzene. After work-up as above, vpc analysis showed the presence of 90.0% acenaphthenes and 10.0% acenaphthylene. A collected sample of acenaphthylene showed it to contain 81.0% d_0 and 19.0% d_2 species. Allowing for the ratio of d_0 to d_4 species in the starting material (*i.e.*, 55:45), this deuterium distribution indicates a k_H/k_D ratio of 3.49.

C. With Tetrachloro-*o*-benzoquinone. The identical mixture of acenaphthenes (39.5 mg, 0.231 mmole, of d_4 and 43.6 mg, 0.283 mmole, of d_0) was treated with 56.0 mg (0.226 mmole) of tetrachloro-*o*-benzoquinone as described above for 2,3-dichloro-5,6-dicyanobenzoquinone. After the same work-up, vpc analysis indicated the presence of 88% acenaphthene and 12% acenaphthylene, The deuterium content of the latter determined by mass spectrometry was 83.5% d_0 and 16.5% d_2. Allowing for the initial ratio of acenaphthene-d_4 to acenaphthene-d_0, this distribution indicates a k_H/k_D ratio of 4.14.

Dehydrogenation of 1,1-Dideuterioacenaphthene. A solution of 31.5 mg (0.202 mmole) of 1,1-dideuterioacenaphthene and 60.0 mg (0.264 mmole) of 2,3-dichloro-5,6-dicyanobenzoquinone in 5.0 ml of benzene was treated as described above. After work-up, vpc analysis indicated the presence of 20% acenaphthene and 80% acenaphthylene. A collected sample of the latter had 27.0% d_2 and 73.0% d_1 species as determined by mass spectrometry. This distribution is identical with that expected for simple 1,2 elimination (predicted 28.0% d_2 and 72.0% d_1), a fact which demonstrates the lack of any 1,2 intramolecular hydrogen shifts in the carbonium ions.

Dehydrogenation of *cis*-1,2-Dideuterioacenaphthene. A solution of 25.0 mg (0.160 mmole) of *cis*-1,2-dideuterioacenaphthene was treated with 0.247 mmole of the stated quinone in 5.0 ml of solvent at 80° for 15 hr. After this time, it was cooled and any suspended solid removed by filtration. The solutions were diluted with ether and washed with 10% aqueous sodium hydroxide followed by water. After drying and evaporation of solvent, a sample of acenaphthylene was collected by preparative vpc for mass spectral analysis. A summary of the reaction conditions appears in Table III and of the deuterium distributions in Table I. The latter are the results of at least two runs.

Table III. Reaction Conditions for Dehydrogenation

Expt	Quinone	Solvent
1	2,3-Dichloro-5,6-dicyanobenzoquinone	Benzene
2	2,3-Dichloro-5,6-dicyanobenzoquinone	Phenetole
3	2,3-Dichloro-5,6-dicyanobenzoquinone	Dimethylformamide
4	Tetrachloro-*o*-benzoquinone	Benzene

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