saturated 1,2-diketones.[46] The photoinduced hydrogen migration from the alkyl chain to the ketonic oxygen in *n*-alkyl *p*-benzophenonecarboxylates[47] closely resembles the electron impact induced hydrogen migration from the alkyl chain to the anhydride group of 4-*n*-alkyl esters of trimellitic anhydride.[26] Hydrogen migration in the former occurs from a wide range of sites, and deuterium labeling shows that the process is no more selective in the latter.[48] Localized activation could be a means of introducing a measure of selectivity into both.

Experimental Section

Materials. The syntheses of the acids and alcohols studied are reported elsewhere.[49] The 6-phenylhexanol-*6-d* and 5-phenylpentanol-*4-d*$_2$ were intermediates in the preparation of 6-phenylhexanoic acid-*6-d* and -*5-d*$_2$, reported earlier.[22] In both cases, the isotopic compositions found for the alcohols are essentially the same as those of the acids prepared from them and of the derived methyl esters.[20]

Mass Spectrometry. Mass spectra were measured on a Consolidated Model 21-103 instrument with the source and inlet at 250°. Isotopic analyses were derived from low-voltage measurements,[50] made with the repellers at an average potential of 3 V, the exact values being selected to give maximum sensitivity. Isotopic compositions of the $[M - H_2O]\cdot^+$ ions were estimated from 70-eV spectra. For 6-phenylhexanol-*5-d*$_2$ and -*4-d*$_2$, these compositions were also estimated from measurements at ionizing voltages over a range of 2.5 eV slightly above the appearance potential. The values so found were constant over this range and indistinguishable from the 70-eV values.

Acknowledgment. We are pleased to acknowledge stimulating discussions with M. M. Green, of the University of Michigan, who has independently arrived at a model characterized by chain coiling, which he also views as a means of internal solvation in the isolated molecule. We are indebted also to F. P. Lossing, of the National Research Council, for provocative comments in response to a preliminary version of this report.

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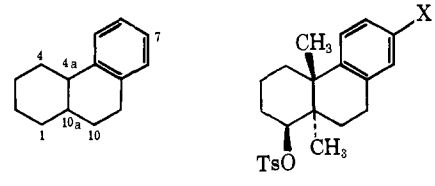
Solvolytic Rearrangements Accompanied by Multiple Alkyl Shifts

H. W. Whitlock, Jr.,* and L. E. Overman[1]

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received January 19, 1970*

Abstract: Synthesis and solvolytic rearrangement of the toluenesulfonate ester of 4aβ,10aα-dimethyl-1α,2,3,4,4a,-9,10,10a-octahydro-1-phenanthrol (**1a**) and its 7-methoxy analog (**1b**) are described. Buffered solvolysis of **1a** afforded the unrearranged olefin **14a**, the singly backbone rearranged olefins **13a** and *trans*-**15a**, the doubly backbone rearranged olefin *trans*-**7a**, and the aryl migrated olefin **17a**. Similar products were obtained from solvolysis of **1b**. Ethanolysis rates for **1a** and **1b** were measured at three temperatures, and the presence of the 7-methoxy substituent resulted in only a small rate acceleration (k_{1b}/k_{1a} = 1.6 at 47°). The results are interpreted in terms of ionization followed by a set of sequential 1,2 shifts, proceeding *via* discrete carbonium ion intermediates. Examination of the acid-catalyzed isomerization of the solvolytic olefins revealed that a skeletal isomerization that occurs readily when the intermediate carbonium ions are produced solvolytically does not occur when they are produced by olefin protonation. The relationship of this study to the biochemical analogs of these rearrangements is discussed.

Backbone rearrangements,[2,3] a series of methyl and hydrogen 1,2 shifts, are an integral part of currently accepted biosynthetic pathways to multicyclic triterpenes.[4,5] The apparent facility with which these presumed carbonium ion rearrangements occur has led to considerable speculation as to the timing of the various migration steps, whether they are at one mechanistic extreme concerted, stepwise but "nonstop," or at the other extreme proceed *via* solvent captured species as intermediates. We wish to report our studies on a model of these transformations, the solvolysis of toluenesulfonates **1a** and **1b**.[6] We conclude below that solvolytic rearrangement of the carbon skeletons of



1a, b

these molecules proceeds in a stepwise "unconcerted" manner, and that the fate of carbonium ions in this

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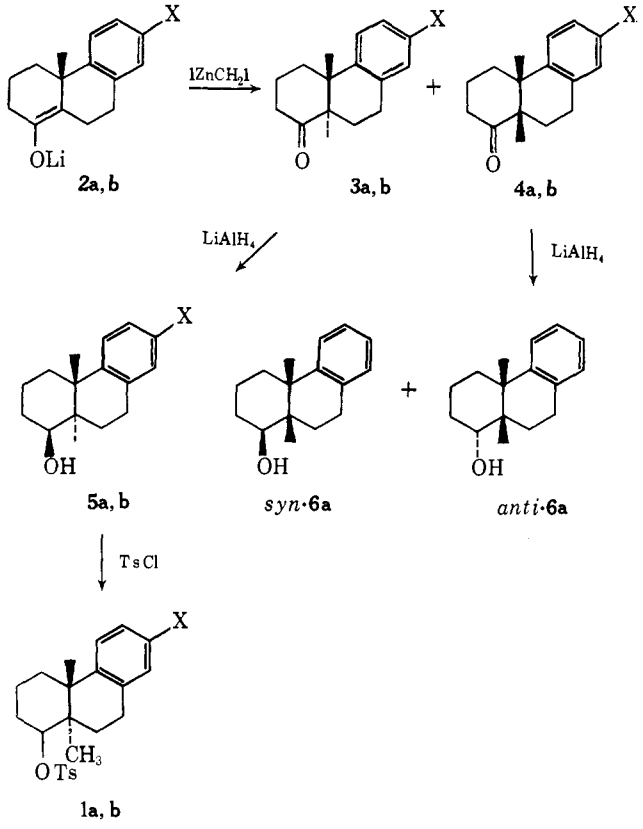
(6) Nomenclature: suffix a indicates no substitution; suffix b indicates 7-methoxy substitution on numbered structures.

series is dependent on whether they are produced solvolytically or by way of olefin protonation.

Results and Discussion

Synthesis of Toluenesulfonates. Scheme I outlines the synthesis of toluenesulfonates **1a** and **1b**. Angular

Scheme I. Synthesis of Toluenesulfonates **1a** (X = H) and **1b** (X = OCH_3)



methylation of the lithium enolate **2a** (or **b**) to afford a mixture of ketones **3a** (or **b**) and **4a** (or **b**) has been described[7] (Scheme I). The stereochemical assignments rest on the following observations. (1) One expects the major product arising from attack of a reagent at the 10a position of the enolate ion **2** to possess a cis ring fusion.[8] The major product (3:1 (X = H) and 7:3 (X = OCH_3)) in both cases is assigned a cis ring fusion. (2) Lithium aluminum hydride reduction of **3a** (or **b**) affords a single alcohol **5a** (or **b**). Its nmr spectrum (δ 3.68, C*H*OH, $\nu_{1/2}$ = 4 Hz) indicates that the hydroxyl group is axial[9] while the marked downfield shift of the benzylic methyl group, δ 1.38, is consistent with its 1,3 diaxial relationship with the hydroxyl group.[10] Reduction of **4a**, on the other hand, affords a mixture of two alcohols, *syn*- and *anti*-**6a**, the nmr spectra (δ 3.7, 3.8, C*H*OH, $\nu_{1/2}$ = 18 Hz for each isomer) of which indicate each to be equatorial.[9] (3) The doubly backbone rearranged solvolysis product *trans*-**7a**, derived from **1a**, was synthesized by a stereochemically rational route (Scheme II). Since isotope incorporation experiments

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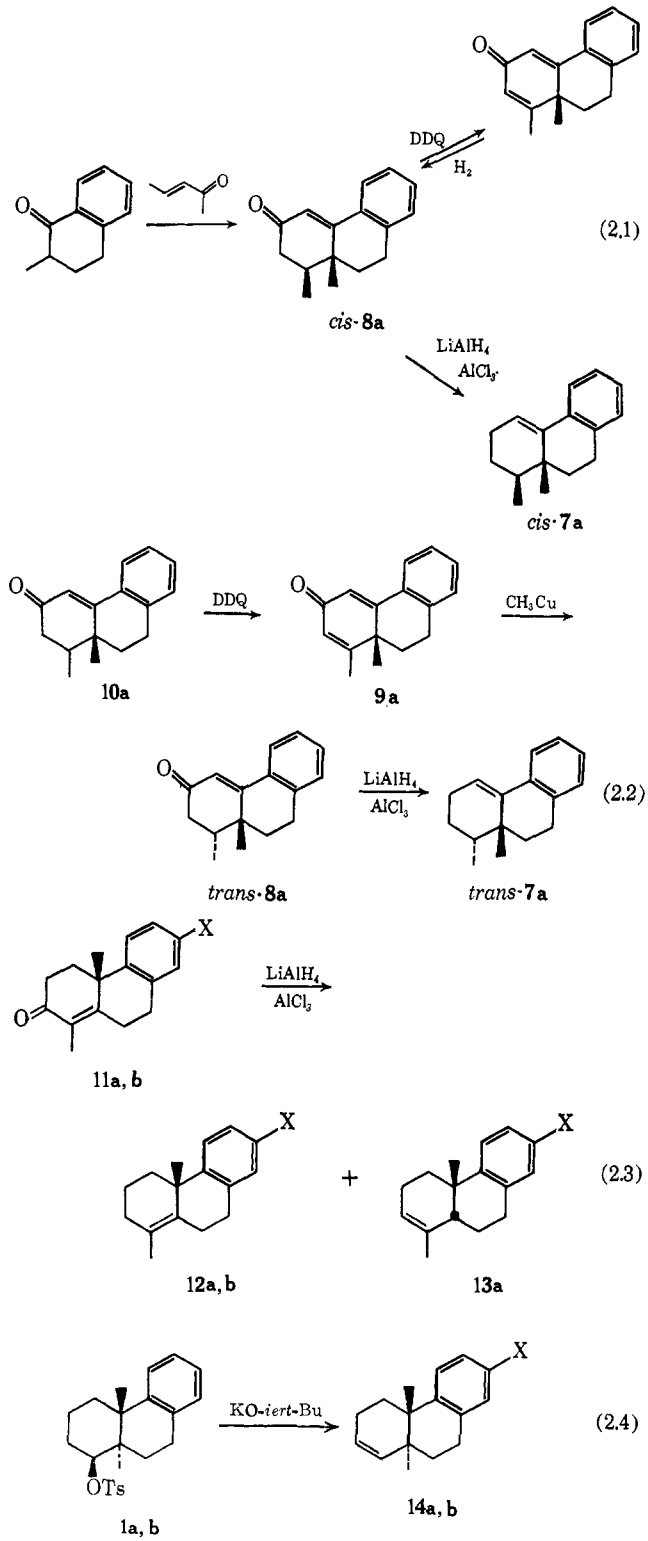
Scheme II. Synthesis of Solvolysis Products Arising from **1a** (X = H) and **1b** (X = OCH_3)



show that *trans*-**7a** arises from **1a** without the intermediacy of any olefins, the two must bear the same stereochemical relationship between the methyl groups, therefore fixing the ring fusion of **1a** as trans.

Synthesis of Solvolysis Products. Considerable effort was expended in the independent synthesis of various solvolysis products (Scheme II). Both cis and trans stereoisomers of **7a** were synthesized (Scheme II: 2.1, 2.2). Robinson annelation of 2-methyl-1-tetralone with *trans*-methyl propenyl ketone afforded *cis*-**8a**

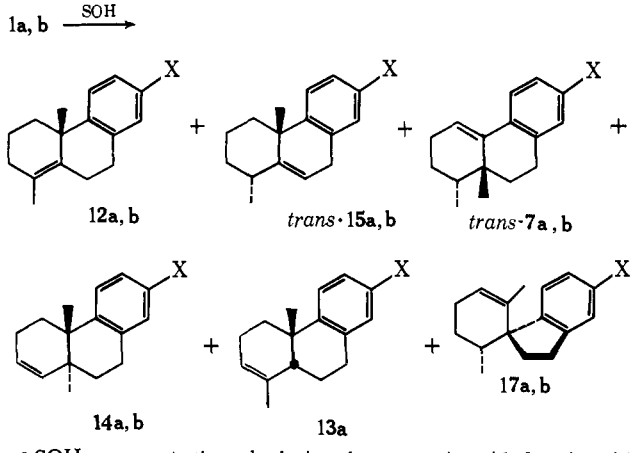
as the only detectable annelation product. Deoxygenation of *cis*-**8a** with lithium aluminum hydride–aluminum chloride afforded *cis*-**7a**. Attempted inversion of the configuration of the secondary methyl group of *cis*-**8a** by sequential quinone dehydrogenation and catalytic hydrogenation merely regenerated *cis*-**8a**. The desired trans isomer was, however, obtained by stereospecific axial addition of methyl copper to dieneone **9a** (prepared by quinone dehydrogenation of **10a**[11]) to afford exclusively *trans*-**8a** (Scheme II: 2.2). Lithium aluminum hydride–aluminum chloride deoxygenation of *trans*-**8a** afforded *trans*-**7a**. Stereospecificity of the above type in the Robinson annelation procedure is precedented,[12-15] as is the preferential axial addition[16,17] of methylcopper to dienone **9a**. Further evidence that the secondary methyl is indeed axial in *trans*-**7a** comes from nmr spectra which show a larger vicinal coupling constant for the secondary methyl in *trans*-**7a** (J_{vic} = 7.5 Hz) than in *cis*-**7a** (J_{vic} = 6.5 Hz). The greater J_{vic} of axial than equatorial secondary methyl groups has been previously observed.[15,17,18]

Lithium aluminum hydride–aluminum chloride deoxygenation of enone **11a**[19] (or **b**) afforded as the major product the tetrasubstituted olefin **12a** (or **b**) (Scheme II, eq 2.3). A minor product, trisubstituted olefin **13a**, was assigned a cis ring fusion from the presumed preferred attack of hydride from the side of the angular methyl.[8,20]

Potassium *tert*-butoxide treatment of toluenesulfonate **1a** (or **b**) afforded the trans-disubstituted olefin **14a** (or **b**) (Scheme II, eq 2.4).

Solvolysis. Preparative acetolysis of **1a** in refluxing buffered acetic acid afforded a quantitative yield of olefins (Scheme III, Table I). Nmr and infrared spectra

Scheme III. Product Mixture from Solvolysis of Toluenesulfonates **1a** and **1b**[a]



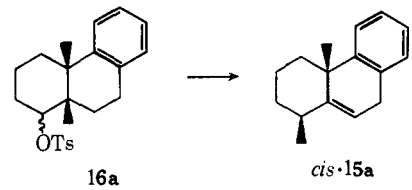
[a] SOH represents the solvolysis solvent, acetic acid, formic acid, or ethanol.

Table I. Yield of Products from Buffered Solvolysis of Toluenesulfonates **1a** and **1b**[a]

Solvent	Ethanol		Acetic acid		Formic acid (15 min)	Formic acid (60 min)
Toluenesulfonate	**1a**	**1b**	**1a**	**1b**	**1a**	**1a**
Products	Amount, %					
17a, b	1.4	19.9	3.2	17.8	1.5	
14a, b	5.6	6.6	2.6	2.4		
13a	2.6		2.9		18	40
12a, b	39.5	40.2	51.7	43.8	37	20
trans-**15a, b**	43.0	20.0	25.7	16.9	7	4
trans-**7a, b**	7.9	9.8	13.9	13.8	36	31

[a] Solvolyses were run in sealed ampoules for 10 half-lives at 90° (50° for formic acid). Assignments are by peak enhancements on addition of authentic samples. The percentages are the average of three determinations and are estimated to be reliable to ±2%.

of the acetolysis product mixture indicated the absence of acetates. Preparative glpc separated the mixture into four fractions. (1) The two major olefins, **12a** and *trans*-**15a**, were collected together. Fractional crystallization afforded a pure sample of **12a** that was identified by comparison with an authentic sample prepared as above. The structure of air-sensitive *trans*-**15a** was inferred from the spectral properties of the **12a**–*trans*-**15a** mixture. Several attempts at its synthesis failed. The nmr of this mixture combined with decoupling experiments (see Experimental Section) established the presence of an $ArCH_2CH{=}CCHCH_3$ part structure for *trans*-**15a**. Comparison of the vicinal coupling constant of the secondary methyl[21] (J_{vic} = 6.5 Hz) with that of the corresponding olefin *cis*-**15a** (J_{vic} = 7.5 Hz), isolated from the solvolysis of the cis-fused toluenesulfonate[22] **16a**, suggests that the former methyl is equatorial.[16-18] Consistent with this assignment is the observed long-range coupling (J = 1 Hz) of the olefinic and the axial methine hydrogen in *trans*-**15a** and the absence of this coupling in the nmr spectrum of *cis*-**15a**.[23] (2) The doubly backbone rearranged product *trans*-**7a**, a homogeneous oil, comprised the second fraction. Its structure was established by comparison with a sample of *trans*-**7a** synthesized as described. (3) Spiro olefin **17a**, a homogeneous oil, which arises from phenyl migration, comprised the third fraction. The structure follows from the nmr spectrum which shows a secondary methyl group[21] at noticeably high field, 0.68, and the structural sequence $CH^a_3C{=}CH^bCH^c_2$, δ^a = 1.46, δ^b = 5.95, δ^c = 2.06, J_{ab} = 1 Hz, J_{ac} = 1.9 Hz, and J_{bc} = 2.5 Hz. Models show that the shielding of the secondary methyl by the aromatic ring is greatest if there is a cis relationship between the two. Also consistent with this



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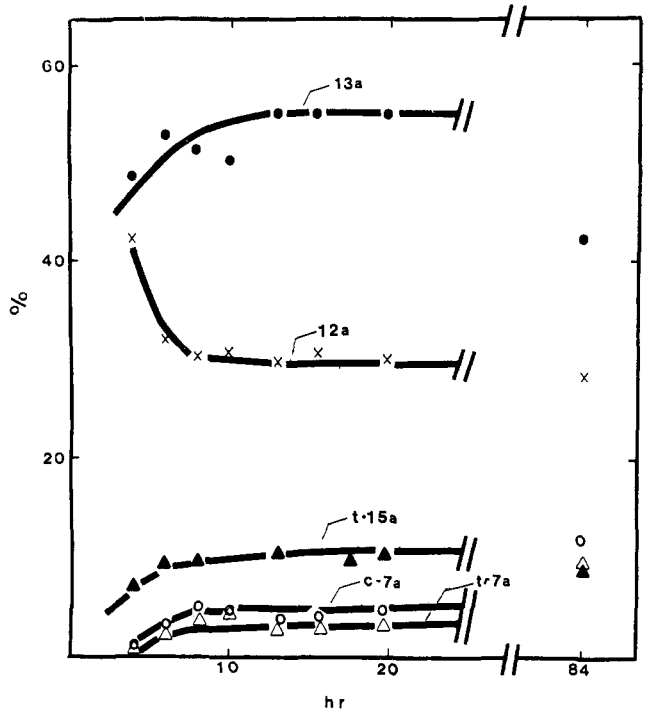
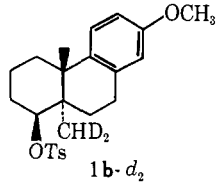


Figure 1. Plot of per cent composition *vs.* time for equilibration of **12a** with 5 m*M* toluenesulfonic acid in acetic acid at 120°. Assignments are by peak enhancement on addition of authentic samples. The material balances (from glpc internal standard) were excellent (94–103%) up to 24 hr, but decreased thereafter.

structure is the prominent P − C_3H_6 peak in the mass spectrum which could be derived from a retro-Diels–Alder fragmentation cracking pattern.[24] (4) The fourth fraction was an inseparable mixture of **13a** and **14a**. The nmr spectrum of the mixture was a composite of those of the individually synthesized components and the two components of the mixture co-chromatographed with authentic **13a** and **14a**.

Preparative acetolysis of **1b** afforded a closely similar product mixture (Table I) that was separated by preparative glpc into three major fractions: (1) fraction 1, a mixture of **12b** and *trans*-**15b**, afforded pure **12b** on recrystallization. As with *trans*-**15a**, *trans*-**15b** was too air sensitive to isolate in a pure form. Its nmr spectrum (inferred from that of the **12b**–*trans*-**15b** mixture) was very similar to that of *trans*-**15a**. In addition the signal at δ 1.09, assigned to the secondary methyl, was reduced in intensity by two-thirds in trans-**15b**-d_2 derived from **1b**-d_2.[7] (2) The doubly backbone rearranged olefin *trans*-**7b**, a low-melting solid, comprised the second fraction. Its spectral properties were those



1b-d_2

expected for the 7-methoxy derivative of *trans*-**7a**. An alternate genesis of *trans*-**7b**, by a single 1,3-methyl shift, is incidently ruled out by the observation that *trans*-**7b**-d_2, from **1b**-d_2, possesses a CHD_2CH part structure. (3) Spiro olefin **17b**, the third fraction collected, was identified by the similarity of its spectral properties with those of **17a**. In addition the nmr signal at δ 0.68, assigned to the secondary methyl, was reduced in intensity by $^2/_3$ in **17b**-d_2, derived from **1b**-d_2.

The following incidental observations were made. Ethanolysis follows good first-order kinetics (Table II).

Table II. Ethanolysis Rates of Toluenesulfonates **1a** and **1b**

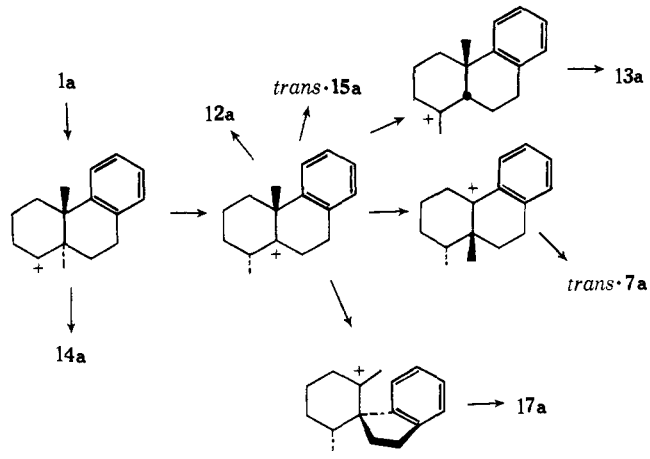
Toluene sulfonate	Temp,[a] °C	10^5k, sec^{-1} [b]	$\Delta H^{\ddagger}_{57°}$, kcal/mol	$\Delta S^{\ddagger}_{57°}$, eu
1a	47.29	2.49 ± 0.21		
1a	57.11	9.43 ± 0.90	27.8 ± 1.8	6.7 ± 5.4
1a	67.17	33.9 ± 1.7		
1b	47.30	4.02 ± 0.13		
1b	57.10	14.1 ± 0.54	26.3 ± 0.8	3.3 ± 7.4
1b	67.18	47.5 ± 2.7		

[a] ±0.02°. [b] Average of two or three determinations.

There is only a small accelerating affect on introduction of the *p*-methoxy substituent (k_{1b}/k_{1a} = 1.6 at 47°). All products are stable under ethanolysis and acetolysis (but not formolysis) conditions; acetolysis in buffered acetic acid-d_1 produced deuterium-free olefins.

A set of sequential 1,2 shifts proceeding *via* discreet carbonium ions best fits our data (Scheme IV). The

Scheme IV. Scheme for Formation of Solvolysis Products *via* Stepwise Rearrangements



small rate acceleration by *p*-methoxy substitution undoubtedly reflects only a long-range inductive effect[25–27] and requires no special explanation. It is interesting to note that the only large effect of introduction of a *p*-methoxy group is to increase the extent of aryl participation with formation of the spiro olefin **17a**, **b** (3% from **1a**, 18% from **1b**). The *p*-methoxy group is singularly ineffective at influencing the second methyl migration with formation of *trans*-**7a**, **b** (14% from acetolysis of both **1a** and **1b**). Similar effects have been seen elsewhere.[28] On the other hand increasing solvent polarity is quite effective in this respect (10, 14, and 36% of *trans*-**7a** from ethanolysis, acetolysis,

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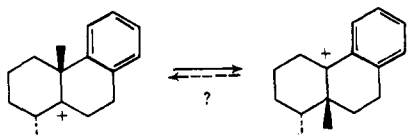
and formolysis, respectively, of **1a**). It seems likely that this is a kinetic (an increase in the rate of rearrangement relative to irreversible deprotonation, as in Scheme IV) rather than a thermodynamic (changing the composition of a set of rapidly interconverting carbonium ions) phenomenon.[22]

Olefin Isomerization. Examination of acid-catalyzed isomerization of the solvolytic olefins produced the surprising observation that the skeletal isomerization



that occurs readily when the carbonium ions are produced solvolytically does not do so when they are produced by olefin protonation. Olefin **12a** on heating in acetic acid containing toluenesulfonic acid was converted into a steady-state mixture of **12a**, *trans*-**15a**, and **13a**, the latter predominating[29,30] (Figure 1). Only small amounts of material corresponding in retention time and nmr spectrum to *trans*-**7a** could be isolated. It was contaminated with an equal amount of its cis isomer, *cis*-**7a**. The very slow formation of *trans*-**7a** is not due simply to its instability, as under these conditions *trans*-**7a** goes over only slightly (9% after 18 hr) to the **12a**, *trans*-**15a**, **13a** set.

Heating the above olefins in toluenesulfonic acid in acetic acid-d_1 produced the results expected on the basis of carbonium ion mediated isomerizations. *trans*-**7a** rapidly exchanged its vinyl hydrogen for deuterium and the **12a**, *trans*-**15a**, **13a** set was heavily deuterated in the C1, C2, C10, C10a region, but interconversion between *trans*-**7a**, and the **12a**, *trans*-**15a**, **13a** set did not occur. It appears, therefore, that carbonium ions in this series behave differently depending on their mode of formation. One might ascribe these discrepancies to either a counterion[31] or a "pure" conformational[32,33] effect. We speculate without going into details that the chair to boat conversion necessarily accompanying a 1,2 shift in a chair[34,35] cyclohexyl carbonium ion is responsible for the differences noted, *i.e.*, a conformational effect. If correct one must seriously consider the consequences of enzymatic control of conformation on the rate and point of termination of biochemical analogs of the above rearrangements.

Experimental Section[36]

4aβ,10aα-Dimethyl-1α,2,3,4,4a,9,10,10a-octahydro-1-phenanthrol (5a). Reduction of **3a**[7] with lithium aluminum hydride in ether afforded **5a** in 79% yield: mp 36–39° (hexane); nmr δ ($CDCl_3$) 3.68 (1 H, singl, $\nu_{1/2}$ = 4 Hz, C*H*OH), 1.38 (3 H, singl, 4a-CH_3), 0.74 (3 H, singl, 10a-CH_3). Only the one alcohol could be detected by nmr.

Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.28; H, 9.63.

Similarly prepared in 88% yield from methoxy ketone **3b**[7] was alcohol **5b**: mp 137.5–139° (hexane); nmr δ ($CDCl_3$) 3.55 (1 H, singl, $\nu_{1/2}$ = 5 Hz, C*H*OH), 1.35 (3 H, singl, C4a-CH_3), 0.76 (3 H, singl, C10a-CH_3). The latter methyl peak was replaced by a broad singlet (1 H) in the nmr spectrum of **5b**-d_2.

Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.37; H, 9.23.

***cis*-4a,10a-Dimethyl-1,2,3,4,4a,9,10,10a-octahydro-1-phenanthrols (*syn*-, *anti*-6a).** Reduction of *cis*-ketone **4a** with lithium aluminum hydride afforded in 97% yield a 4:1 mixture of two alcohols. Preparative tlc afforded the pure higher R_f material: mp 112–114° (hexane), in 72% yield; nmr δ ($CDCl_3$) 3.7 (1 H, mult, $\nu_{1/2}$ = 18 Hz, C*H*OH), 1.11 (3 H, singl, CH_3), 1.00 (3 H, singl, CH_3).

Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.22; H, 9.64.

The lower R_f isomer, mp 104–105° (hexane), was similarly isolated in 20% yield: nmr δ ($CDCl_3$) 3.8 (1 H, mult, $\nu_{1/2}$ = 18 Hz, C*H*OH); 1.33 (3 H, singl, CH_3), 0.97 (3 H, singl, CH_3).

Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.49; H, 9.58.

4aβ,10aα-Dimethyl-1α,2,3,4,4a,9,10,10a-octahydro-1-phenenthrol *p*-Toluenesulfonate (1a). To a stirred solution of 100 mg (0.438 mmol) of **5a** in 5 ml of dry tetrahydrofuran at 0° was added 0.63 ml of a 2.07 *M* hexane solution of *n*-butyllithium. The reaction mixture was stirred for 2 min and then added to a stirred solution of 341 mg (1.74 mmol) of *p*-toluenesulfonyl chloride and 5 ml of tetrahydrofuran at 0° under a nitrogen atmosphere. After stirring at room temperature for 2 hr, the reaction mixture was worked up with water to afford, on recrystallization (hexane–ether), 103 mg (64% yield) of **1a**. A crystalline sample of **1a** was unstable at 25°; hexane–ether solutions of it were, however, stable indefinitely at 25°. The sample used for kinetic studies was purified by repeated recrystallization: mp 66–68° dec; nmr δ ($CDCl_3$) 4.49 (1 H, singl, $\nu_{1/2}$ = 4 Hz, C*H*OS), 1.23 (3 H, singl, CH_3), 0.77 (3 H, singl, CH_3).

Similarly prepared from **5b** was toluenesulfonate **1b**: mp 74–75° dec (hexane–ether); nmr δ ($CDCl_3$) (1 H, singl, $\nu_{1/2}$ = 4.6 Hz, C*H*OS), 1.20 (3 H, singl, CH_3), 0.77 (3 H, singl, CH_3).

Acetolysis of Toluenesulfonate 1a. Isolation and Identification of Products. A solution of 350 mg (0.917 mmol) of toluenesulfonate **1a**, 120 mg (1.46 mmol) of fused sodium acetate, and 150 ml of anhydrous acetic acid (0.01 *M* in acetic anhydride) was stirred at reflux under a nitrogen atmosphere for 2.5 hr (~10 half-lives). The cooled solution was diluted with water and extracted twice with ether. The ether extracts were washed with water, saturated sodium bicarbonate solution, and water, dried ($MgSO_4$), and evaporated to afford 208 mg (107%) yield of a colorless oil which showed no acetate absorption in either its infrared (5.8 μ) or nmr (δ 2.1) spectrum. The infrared and nmr spectra of a sample collected by glpc were identical with those of the crude acetolysis mixture. Analysis of the solvolysis mixture by capillary glpc (150-ft Apiezon L) indicated the composition of the mixture to be that shown in Table I.

Preparative glpc (190°, 5 ft × 0.25 in. column of 20% Carbowax 20M on Chromosorb P) afforded the following four fractions in order of elution.

Fraction 1 was a colorless oil, homogeneous by glpc, assigned structure **17a**: nmr δ ($CDCl_3$) 7.1 (4 H, mult, Ar*H*), 5.55 (1 H, mult, $\nu_{1/2}$ ~ 10 Hz, C*H*=), 1.45 (3 H, double triplet, $J_{allylic}$ = 1.9 Hz, $J_{homoallylic}$ = 1.0 Hz, $CH_2CH{=}CCH_3$), 0.68 (3 H, doub, J = 7 Hz, CH_3CH); uv λ_{max}^{EtOH} 272 mμ (log ε 2.73), 265 (2.72); *m/e* 212 (P), 197 (P − CH_3), 170 (base, P − $CH_3CH{=}CH_2$).

Fraction 2 was a 3:1 mixture (nmr and glpc) of **13a** and **14a**. The nmr spectrum showed resonances due to the major component: δ 4.45 (1 H, mult, C*H*=), 1.76 (3 H, mult, C=CCH_3), 1.28 (3 H, singl, CH_3). They were identical with those of **13a** prepared as shown in Scheme II, eq 2.3. Authentic **13a** cochromatographed on glpc with the major component of fraction 2. The minor component cochromatographed with an authentic sample of **14a** and gave rise to absorptions at δ 5.53 (2 H, vinyl H), 1.12 (3 H, CH_3), and 0.82 (3 H, CH_3), corresponding to those of authentic **14a**.

Fraction 3 was a 1.6:1 mixture (nmr and glpc) of **12a** and *trans*-**15a**. Allowing the mixture to stand in the air led to decomposition by autoxidation of *trans*-**15a**. Recrystallization then afforded pure **12a**, mp 48.0–50.5°. Its identity was established by comparison (ir, nmr, uv, mass spectrum, mmp (48.5–50.0°)) with an authentic

(29) The same steady-state olefin mixture could be obtained by identical treatment of **13a** or the *trans*-**15a**-rich acetolysis mixture.

(30) Acid-catalyzed isomerization of 1,10-dimethyl-8,9-octalin has been reported to give a similar product mixture: J. A. Marshall and A. R. Hochstetler, *J. Amer. Chem. Soc.*, **91**, 648 (1969).

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(36) High-resolution mass spectra were determined on an MS-902 instrument. Nmr spectra were determined at 60 and 100 MHz.

sample. Resonances in the 100-MHz spectrum of the **12a**-*trans*-**15a** mixture assignable to *trans*-**15a** were: δ 5.5 (1 H, mult, C*H*=), 3.5 (2 H, mult, C=CHCH_2Ar), 1.39 (3 H, singl, CH_3), and 1.09 (3 H, doub, J = 6.5 Hz, CH_3CH).

Fraction 4 was an oil, homogeneous by glpc, established to be *trans*-**7a** by comparison (ir, nmr, uv, glc, mass spectrum) with an authentic sample.

Acetolysis of Toluenesulfonate 1b. Product Identification. Refluxing a solution of **3b** in dry buffered acetic acid for 2 hr and work-up as above afforded a high yield of olefinic products (for composition by analytical glpc see Table I) that was separated by preparative glpc as above into the three following fractions.

Fraction 1 was an oil, homogeneous by glpc, assigned structure **17b**: nmr δ ($CDCl_3$) 7.2–6.5 (3 H, mult, ArH), 5.55 (1 H, mult, C*H*=), 3.79 (3 H, singl, OCH_3), 2.8 (2 H, mult, CH_2Ar), 1.46 (3 H, double triplet, $J_{allylic}$ = 1.9 Hz, $J_{homoallylic}$ = 1.0 Hz, CH_3C=CHCH$_2$), 0.67 (3 H, doub, J = 7 Hz, CH_3CH). Decoupling (100 MHz) of the spectrum confirmed these coupling assignments: mass spectrum *m/e* 242 (P), 227 (P − CH_3), 200 (base, P − CH_3-CH=CH_2). The nmr spectrum of the corresponding fraction from acetolysis of **1b**-d_2[7] was the same as above except for replacement of the δ 0.67 doublet by a broad singlet of area 1 H.

Fraction 2 was a 2.5:1 mixture of **12b** and *trans*-**15b** that afforded a solid, mp 61–62.5°, on recrystallization. This was identified as **12b** by comparison with an authentic sample. The 3 H singlet at δ 1.67 due to the vinyl methyl of **12b** was replaced by a 1 H singlet in **12b**-d_2 from solvolysis of **1b**-d_2. The 100-MHz spectrum of the **12b**–*trans*-**15b** mixture showed resonances due to *trans*-**15b** at δ 5.5 (1 H, mult, C*H*=), 3.4 (2 H, mult, =CCH_2Ar), 1.37 (3 H, singl, CH_3), and 1.09 (3 H, doub, J = 6.5 Hz, CH_3CH (replaced by a broad 1 H singlet in mixture from acetolysis of **1b**-d_2)).

Fraction 3 was an oil, homogeneous by glpc that was evaporatively distilled (60°, 0.3 mm) to afford a semicrystalline material assigned structure *trans*-**7b** on the basis of its spectral properties and similarity between them and the spectra of *trans*-**7a**: nmr δ 7.45 (1 H, mult, ArH), 6.7 (2 H, mult, ArH), 6.08 (1 H, tripl, J = 3.5 Hz, C*H*=), 3.78 (3 H, singl, OCH_3), 2.85 (2 H, mult, CH_2Ar), 1.07 (3 H, singl, CH_3), 0.94 (3 H, doub, J = 6.5 Hz, CH_3CH (replaced by a broad 1 H singlet in the corresponding material from **1b**-d_2)); mass spectrum *m/e* 242 (P), 227 (base, P − CH_3), 200 (P − CH_3CH=CH_2).

1,4a-Dimethyl-2,3,4,4a,9,10-hexahydrophenanthrene (12a) and *cis*-1,4a-Dimethyl-3,4,4a,9,10,10a-hexahydrophenanthrene (13a). To a solution of 180 mg of lithium aluminum hydride and 1.32 g of aluminum chloride in 6 ml of ether under nitrogen was added a solution of 400 mg (1.77 mmol) of enone **11a**.[19] The reaction mixture was stirred at room temperature for 45 min and worked up to afford 340 mg (91% yield) of an oil (18% **13a** and 70% **12a** by glpc). Preparative glpc afforded **13a**, a colorless oil [δ ($CDCl_3$) 5.45 (1 H, mult, C_2-*H*), 1.75 (3 H, broadened singl, C_1-CH_3), 1.28 (3 H, singl, C_{4a}-CH_3); *m/e* 212 (P)], and olefin **12a** [mp 50–51° (hexane)]. The latter showed δ ($CDCl_3$) 1.67 (3 H, singl C_1-CH_3), 1.38 (3 H, singl, C_{4a}-CH_3); *m/e* 212 (P).

Anal. (**12a**) Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.27; H, 9.49.

Reduction of the methoxy analog[37] afforded on preparative glpc and recrystallization from hexane at −30° **12b** (40% yield): mp 62–64°; δ ($CDCl_3$) 3.77 (3 H, singl, OCH_3), 1.68 (3 H, singl, C_1-CH_3), 1.37 (3 H, singl, C_{4a}-CH_3); *m/e* 242 (P).

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.57; H, 9.03.

***cis*-1,10a-Dimethyl-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (*cis*-8a).** A solution of 2.00 g (12.5 mmol) of 2-methyl-1-tetralone[38] and 1.70 g of potassium *tert*-butoxide in 40 ml of dry *tert*-butyl alcohol was stirred at 25° for 15 min and cooled to 5°. To this was added 1.63 g (19.4 mmol) of *trans*-3-penten-2-one,[39] keeping the pot temperature below 20°. The reaction mixture was stirred at room temperature for 14 hr and worked up to afford after distillation and recrystallization 850 mg (17% yield) of *cis*-**8a**: mp 78.5–80.0° (hexane); bp 150–164° (0.08 mm); $\lambda_{max}^{CHCl_3}$ 6.07 μ; λ_{max}^{EtOH} 296 mμ (log ε 3.92); δ ($CDCl_3$) 6.54 (1 H, singl, *H*4), 1.05 (3 H, doub, J = 6 Hz, CH_3CH), 1.02 (3 H, singl, CH_3); *m/e* 226 (P).

Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.24; H, 7.87.

***cis*-1,10a-Dimethyl-1,2,3,9,10,10a-hexahydrophenanthrene (*cis*-7a).** Reduction of enone *cis*-**8a** with lithium aluminum hydride–aluminum chloride as was done above for **11a** afforded *cis*-**7a** in 66% yield: mp 32–32.5° (hexane); δ ($CDCl_3$) 6.08 (1 H, tripl, J = 4 Hz, *H*C=), 0.97 (3 H, doub, J = 6.1 Hz, CH_3CH), 0.87 (3 H, singl, CH_3); λ_{max}^{EtOH} 253 mμ (log ε 3.85), 285 (3.10); *m/e* 212.1587 (calcd for $C_{16}H_{20}$, 212.1565), 197 (base, P − CH_3), 170 (P − CH_3CH=CH_2).

1,10a-Dimethyl-9,10-dihydro-3(10a*H*)-phenanthrone. Hydrogen chloride was bubbled through a solution of 400 mg (1.77 mmol) of *cis*-**8a** and 440 mg (1.94 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, in 40 ml of dry dioxane at 10° for 5 sec. After stirring under a nitrogen atmosphere at room temperature for 4 hr, an additional 200 mg (0.882 mmol) of the quinone was added and the solution was refluxed for 1 hr and worked up to afford on preparative tlc, 265 mg (67%) of the title dienone. Sublimation (80° (0.03 mm)) afforded a sample: mp 58–60° (hexane); $\lambda_{max}^{CHCl_3}$ 6.00 μ; δ 6.62 (1 H, doub, J = 1.7 Hz, *H*4), 6.20 (1 H, mult, *H*2), 2.08 (3 H, doub, J = 1.4 Hz, CH_3C=), 1.25 (3 H, singl, CH_3).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.42; H, 7.28.

Hydrogenation of the title dienone at atmospheric pressure with 30% Pd on charcoal, platinum oxide, or ruthenium on alumina afforded exclusively enone *cis*-**8a** by nmr.

10a-Methyl-9,10-dihydro-3(10a*H*)-phenanthrone (9a). Dehydrogenation of 10a-methyl-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (**10a**)[11] with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone as described above for *cis*-**8a** afforded after sublimation in 85% yield **9a**: mp 82–83° (hexane); $\lambda_{max}^{CHCl_3}$ 6.03 μ; δ ($CDCl_3$) 6.89 (1 H, doub, $J_{1,2}$ = 10 Hz, *H*1), 6.65 (1 H, doub, $J_{2,4}$ = 1.6 Hz, *H*4), 6.30 (1 H, double doublet, J = 10 and 1.6 Hz, *H*2), 1.23 (3 H, singl, CH_3).

Anal. Calcd for $C_{15}H_{14}O$: C, 85, 68; H, 6.71. Found: C, 85.57; H, 6.74.

***trans*-1,10a-Dimethyl-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (*trans*-8a).** To a stirred solution of 1.30 g (3.30 mmol) of tetrakis-[(iodotri-*n*-butylphosphine)copper][40] in 9 ml of ether at 0° was added 2.19 ml of a 1.37 *M* ethereal methyllithium solution. A solution of 500 mg (2.38 mmol) of **9a** and 5 ml of dry ether was then added and the solution stirred at 0°. After 1 hr the yellow mixture was acidified with dilute hydrochloric acid and worked up to afford on preparative tlc 418 mg (78%) of *trans*-**8a** as a pale yellow oil that was evaporatively distilled (115° (0.03 mm)): λ_{max}^{neat} 6.06 μ; δ ($CDCl_3$) 6.57 (1 H, singl, C*H*=), 1.27 (3 H, singl, CH_3), 1.05 (3 H, doub, J = 7 Hz, CH_3CH); λ_{max}^{EtOH} 300 mμ (log ε 3.78), 224 (3.49); *m/e* 226.1355 (calcd for $C_{16}H_{18}O$: 226.1358). The 2,4-dinitrophenylhydrazone had mp 198–199.5°.

Anal. (2,4-DNPH) Calcd for $C_{22}H_{22}N_4O_4$: C, 65.01; H, 5.46. Found: C, 65.06; H, 5.44.

***trans*-1,10a-Dimethyl-1,2,3,9,10,10a-hexahydrophenanthrene (*trans*-7a).** Lithium aluminum hydride–aluminum chloride reduction of *trans*-**8a** as above afforded a 62% yield of *trans*-**7a**: δ ($CDCl_3$) 6.10 (1 H, tripl, J = 3.5 Hz, C*H*=), 1.05 (3 H, singl, CH_3), 0.94 (3 H, doub, J = 7 Hz, CH_3CH); λ_{max}^{EtOH} 286 (log ε 3.08); *m/e* 212.1565 (calcd for $C_{16}H_{20}$: 212.1556), 197 (base, P − CH_3), 170 (P − CH_3CH=CH_2).

***trans*-4a,10a-Dimethyl-3,4,4a,9,10,10a-hexahydrophenanthrene (14a).** A solution of 50 mg (0.443 mmol) of potassium *tert*-butoxide and 50 mg (0.131 mmol) of **1a** in 4 ml of dry 1,2-dimethoxyethane was stirred at reflux under a nitrogen atmosphere for 2 hr. The reaction mixture was diluted with water and extracted twice with ether. The ether extracts were worked up to afford on evaporative distillation 24 mg (87% yield) of **14a** as an oil (homogeneous by glpc): δ ($CDCl_3$) 5.58 (2 H, singl, C*H*=C*H*), 1.12 (3 H, singl, CH_3), 0.82 (3 H, singl, CH_3); *m/e* 212.1539 (calcd for $C_{16}H_{20}$: 212.1565).

Similarly, toluenesulfonate **1b** afforded in 94% yield **14b** as an oil that was homogeneous by glpc: δ ($CDCl_3$) 5.53 (2 H, singl, C*H*=C*H*), 3.77 (3 H, singl, OCH_3), 1.10 (3 H, singl, CH_3), 0.82 (3 H, singl, CH_3); *m/e* 242.1658 (calcd for $C_{17}H_{22}O$: 242.1681).

Kinetic Experiments. Ethanolysis rates were determined in buffered absolute ethanol (three- to fourfold excess fused sodium acetate) at a concentration of 6–11 × 10^{-4} *M* using standard sealed ampoule technique. The reaction was followed by observing the increase in optical density in the ultraviolet spectrum (295 mμ

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for **1a** and 269 mμ for **1b**). First-order rate plots were linear up to 5 half-lives and rate constants were calculated by the method of least squares. The error reported is the average of the standard deviation of each point from the calculated least-squares slope. Activation parameters were calculated from the Erying equation and the error reported is the maximum one[41] calculated from the uncertainty in k. Absolute ethanol was dried by distillation from sodium and diethyl phthalate. Karl–Fischer titration of the ethanol indicated less than 0.05% water to be present.

Acid-Catalyzed Equilibration of 12a. A solution of 150 mg (0.707 mmol) of **12a** and 150 ml of "stock" *p*-toluenesulfonic acid solution[42] was stirred under a nitrogen atmosphere at reflux for 20 hr. The reaction mixture was diluted with water and extracted with ether. The ether extracts was washed with water, aqueous sodium bicarbonate solution, and water, dried ($MgSO_4$), and concentrated to afford 146 mg (98%) of a yellow oil. Glpc analysis indicated a mixture of five major compounds (A, B, C, D, and E) in the ratio 58:27:8:3:4 (order of elution). By glpc peak enhancement A was identified as **13a**, B as **12a**, *C* as *trans*-**15a**, D as *trans*-**7a**, and E as *cis*-**7a**. Preparative glpc afforded in pure form A, a 4:1 mixture of B and C, and 3:4 mixture of D and E. The identity of A was established by direct comparison with authentic **13a** and of the two mixtures' components by comparison of the 100-MHz nmr spectra with those of the pure components.

For quantitative equilibration studies the reactions were carried out in sealed ampoules with added bibenzyl (1 mg/ml) as an internal glpc standard. Ampoules were removed periodically from a constant-temperature bath held at 120°, cooled, opened, and worked up, and the ether solution remaining was concentrated and analyzed by glpc. Material balances (95–105%) were high through 24 hr but then began to decrease. The results are shown in Figure 1.

Equilibration of 12a in Deuterioacetic Acid. A solution of 95 mg (0.45 mmol) of **12a** and 95 ml of deuterioacetic acid-d_1 solution (98% d_1 by nmr) 5.0 mM in *p*-toluenesulfonic acid monohydrate and 10 mM in acetic anhydride was stirred at reflux under a nitrogen atmosphere for 6 hr and worked up to afford 95 mg (100%) of a colorless oil which was separated into two fractions by preparative glpc.

Fraction 1 contained **13a** (85% pure by nmr). Using the angular methyl peak as internal standard the nmr spectrum showed that the aromatic ring of **13a** was undeuterated and that the vinyl hydrogen was 75% exchanged. The mass spectrum (10 eV) showed that an average of 2.3 deuterium atoms had been incorporated: 3% d_0, 27% d_1, 30% d_2, 22% d_3, 12% d_4, 5% d_5, 1% d_6.

Fraction 2 contained a 4:1 mixture of **12a** and *trans*-**15a**. The nmr spectrum showed that the aromatic ring was undeuterated, that the C_{10}-vinyl hydrogen of *trans*-**15a** was 17% exchanged, and that one deuterium atom had been incorporated at C-1 of *trans*-**15a** (the 1-methyl appeared as a singlet at δ 1.09). The mass spectrum (10 eV) showed that 2.3 deuterium atoms had been incorporated: 6% d_0, 28% d_1, 26% d_2, 19% d_3, 12% d_4, 7% d_5, 2% d_6.

Acid-Catalyzed Equilibration of 13a. A solution of 22.2 mg of **13a** in 23 ml of stock[42] *p*-toluenesulfonic acid solution was stirred under a nitrogen atmosphere at reflux for 18 hr, and worked up to afford 23.1 mg (104%) of a pale yellow oil. Glpc analysis indicated (average of two determinations): 55% **13a**, 31% **12a**, 9% *trans*-**15a**, and 5% of a mixture of *trans*-**7a** and *cis*-**7a**.

Acid-Catalyzed Equilibration of *trans*-7a. Heating *trans*-**7a** in stock[42] acid solution converted it very slowly into **12a**. After 6 hr in refluxing stock *p*-toluenesulfonic acid ~5% of **12a** was formed. The amount did not increase with time, however, and a peak that cochromatographed with **13a** reached a maximum intensity of *ca.* 4%. Neither compound was isolated.

Equilibration of *trans*-7a in Deuterioacetic Acid. A solution of 30.1 mg (0.142 mmol) of *trans*-**7a** (96.5% purely glpc) and 30 ml of a deuterioacetic acid solution (98% d_1 by nmr) 5.0 mM in *p*-toluenesulfonic acid monohydrate and 10 mM in acetic anhydride was stirred at reflux under a nitrogen atmosphere for 4 hr and worked up to afford 30.1 mg (100%) of a light yellow oil. Purification by glpc afforded 18.7 mg of *trans*-**7a** as a colorless oil. The nmr spectrum showed that the olefinic hydrogen was completely exchanged, and the mass spectrum (10 eV) showed 6% d_0, 93% d_1, 0.4% d_2, 0.3% d_3.

A similar experiment was run using a 1-hr reflux period. The mass spectrum showed 16% d_0, 84% d_1, 0.2% d_2.

Equilibration of a Mixture of 12a and *trans*-7a in Deuterioacetic Acid. A solution of 17.1 mg (0.081 mmol) of *trans*-**7a** and 13.1 mg (0.062 mmol) of **12a** in 30 ml of a deuterioacetic acid solution (91% d_1 by nmr) 5.0 mM in *p*-toluenesulfonic acid monohydrate and 10 mM in acetic anhydride was refluxed under nitrogen for 6 hr. The reaction was worked up to afford 28 mg (93%) of a dark yellow oil. Glpc of this indicated 55.8% *trans*-**7a**, 29.2% **13a**, 11.9% **12a**, and 3.0% *trans*-**15a** (the starting mixture contained 56.6% *trans*-**7a** by weight). This mixture was separated into three fractions by preparative glpc.

Fraction 1 contained a 9:1 mixture of **13a** and **12a**. The mass spectrum (10 eV) showed that 2.0 (2.3 after correcting for the isotopic purity of the solvent) deuterium atoms had been incorporated: 10% d_0, 28% d_1, 31% d_2, 19% d_3, 8% d_4, 3% d_5, 1% d_6.

Fraction 2 contained a 6:71:23 mixture of **13a**, **12a**, and *trans*-**15a**. The mass spectrum (10 eV) showed that 2.0 (2.3 after correcting for the isotopic purity of the solvent) deuterium atoms had been incorporated: 16% d_0, 26% d_1, 27% d_2, 16% d_3, 9% d_4, 4% d_5, 2% d_6.

Fraction 3 was pure *trans*-**7a**. The mass spectrum (10 eV) showed that 0.86 (0.94 after correcting for isotopic purity of the solvent) deuterium atom had been incorporated: 32% d_0, 58% d_1, 5% d_2, 3% d_3, 2% d_4.

Acknowledgment. Partial support of this work by the National Science Foundation and the National Institutes of Health is acknowledged.

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(42) An acetic acid solution 5.0 mM in *p*-toluenesulfonic acid monohydrate and 10 mM in acetic anhydride was used for all equilibration experiments.