

# Localized Activation in Bond-Forming Reactions under Electron Impact. Internal Solvation in Isolated Molecules

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**Abstract:** Bond making in unimolecular reactions under electron impact often involves hydrogen migration from any of several positions on an alkyl chain. We employed a phenyl substituent as a means of introducing selectivity into such processes. Specifically, we have studied the loss of water from the molecular ions of 6-phenylhexanol, 5-phenylpentanol, and 5-phenylpentanoic acid, in the mass spectra of the unlabeled and variously deuterated species. In each case, hydrogen migration from the activated position is greatly enhanced. The distribution of positions from which hydrogen migrates in processes of this kind is apparently determined by the interplay of localized activation with such other factors as ring size and charge exchange. These intramolecular effects seem best accounted for in terms of coiling of alkyl chains, stemming from attempts of isolated molecules to solvate themselves.

Since the earliest studies of the reactions of organic compounds under electron impact in the mass spectrometer, researchers have found a special fascination in the bond-making processes that so often accompany bond breaking even in these unimolecular systems.<sup>2a,b</sup> In the course of formulating a systematic organic chemistry peculiar to this context,<sup>3</sup> a substantial effort has been devoted to identifying and defining the roles of factors important in controlling such processes. In particular, much of this effort has focused on ring size in the transition state, where six-membered rings seem generally favored over those with three, four, five, or seven members,<sup>4</sup> although the preferred ring size certainly depends on the particular atoms constituting the ring.<sup>4,5</sup> For the moment, we exclude from consideration molecules with two heteroatom-containing functional groups that can interact directly with each other.<sup>6-9</sup>

McLafferty has emphasized that molecules containing a functional group characteristically undergo highly "specific" rearrangement reactions leading to a single discrete ionic product in high abundance, in contrast to the large array of products arising *via*

"random" rearrangements of alkanes.<sup>4,10</sup> Perhaps the classic example of such a specific rearrangement has been that consisting of  $\gamma$ -hydrogen migration and  $\beta$  cleavage in acyclic aliphatic carbonyl compounds.<sup>11,12</sup> However, recent studies of the mass spectra of aliphatic aldehydes by us<sup>13,14</sup> and others<sup>15,16</sup> appear at odds with such a simplified classification. First, the dominant reaction path, which leads to vinyl alcohol and the complementary 1-alkene, is subject to palpable competition from other rearrangement paths leading to  $[M - C_2H_4]^+$ ,  $[M - H_2O]^+$ , and  $C_3H_5O^+$ . This array of products might be regarded as arising by a variety of secondary reaction steps following hydrogen migration to the oxygen atom as a more nearly all-inclusive primary reaction of aldehydes. But even this view does not remove the discrepancy because, at least in the paths leading to  $[M - C_2H_4O]^+$ ,  $[M - H_2O]^+$ , and  $C_3H_5O^+$ , hydrogen migration occurs not solely from C-4, but from a range of positions along the chain. Overall, there does seem to be a preference for a six-membered cyclic transition state (or intermediate, as the case may be), but by no means to the exclusion of other ring sizes. A measure of such nonspecificity is associated with  $H_2O$  elimination from *n*-alkanols also, though the extent is small. About 10% of the alkyl hydrogens lost in hexanol, for example, *via* this route originate elsewhere than on C-4.<sup>17,18</sup> A number of other systems have been found to undergo hydrogen migration from multiple positions.<sup>19</sup>

A few literature reports point to localized activation, resulting from appropriate structural features, as a

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(1) (a) American Oil Co.; (b) National Research Council.

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(4) F. W. McLafferty in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, Chapter 2.

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(8) J. A. McCloskey and M. J. McClelland, *J. Amer. Chem. Soc.*, **87**, 5090 (1965); R. E. Wolff, M. Greff, and J. A. McCloskey, *Advan. Mass Spectrom.*, **4**, 193 (1968); G. H. Draffan, R. N. Stillwell, and J. A. McCloskey, *Org. Mass Spectrom.*, **1**, 669 (1968).

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(16) A. G. Harrison, *Org. Mass Spectrom.*, **3**, 549 (1970).

(17) W. Benz and K. Biemann, *J. Amer. Chem. Soc.*, **86**, 2375 (1964).

(18) S. Meyerson and L. C. Leitch, *ibid.*, **86**, 2555 (1964).

(19) C. Djerassi and C. Fenselau, *ibid.*, **87**, 5747 (1965); S. D. Sample and C. Djerassi, *ibid.*, **88**, 1937 (1966); J. K. McLeod and C. Djerassi, *ibid.*, **88**, 1840 (1966); A. M. Duffield, W. Carpenter, and C. Djerassi, *Chem. Commun.*, 109 (1967); M. Katoh and C. Djerassi, *ibid.*, 1385 (1969).

factor in determining the distribution of positions from which hydrogen migration occurs.<sup>9,20-22</sup> For example, in H<sub>2</sub>O elimination from 6-phenylhexanoic acid, about 64, 21, and 10%, respectively, of the hydrogen atoms lost with the hydroxyl group originate on C-6, C-5, and C-4, and phenyl activation seems clearly a contributing factor.<sup>20</sup> However, 1,6 elimination in this acid, as well as in the derived methyl ester, is assisted by an apparently highly favorable bicyclic transition state and by conjugation of a newly forming double bond with the aromatic ring, in a reaction path uniquely dependent on hydrogen activation on C-6.<sup>20</sup> Thus, 6-substituted alkanolic acids and esters may constitute a special case.

To throw further light on the effects of localized activation on the competition among similar reactions involving hydrogen migration from multiple positions, we chose for study the loss of H<sub>2</sub>O from the molecular ions of alkanols and alkanolic acids, using a phenyl substituent as the activating agent and deuterium labeling as a probe to observe the effects. Specifically, we have examined H<sub>2</sub>O loss from the molecular ions of 6-phenylhexanol unlabeled, -4-d<sub>2</sub>, -5-d<sub>2</sub>, and -6-d; 5-phenylpentanol unlabeled, -4-d<sub>2</sub>, and -5-d<sub>2</sub>; and 5-phenylpentanoic acid unlabeled and -5-d<sub>2</sub>.

## Results and Discussion

Isotopic distributions of the [M]<sup>•+</sup> (molecular) and [M - H<sub>2</sub>O]<sup>•+</sup> ions derived from the various isotopic species of the three compounds are listed in Table I.

Table I. Isotopic Composition of [M]<sup>•+</sup> and [M - H<sub>2</sub>O]<sup>•+</sup> Ions

Compd	Iso- topic species	[M] <sup>•+</sup>			[M - H <sub>2</sub> O] <sup>•+</sup>		
		% d <sub>2</sub>	% d <sub>1</sub>	% d <sub>0</sub>	% d <sub>2</sub>	% d <sub>1</sub>	% d <sub>0</sub>
6-Phenylhexanol	6-d		96	4	58	42	
	5-d <sub>2</sub>	98.5	1.5		83.4	13.5	3.1
	4-d <sub>2</sub>	97.1	2.9		94.5	4.7	0.8
5-Phenylpentanol	5-d <sub>2</sub>	88.7	11.3		22.6	60.4	17.0
	4-d <sub>2</sub>	98	2		84	16	
5-Phenylpentanoic acid	5-d <sub>2</sub>	88.6	11.4		39.4	51.1	9.5

Straightforward calculations from these data yield the per cent of [M - H<sub>2</sub>O]<sup>•+</sup> ions derived from the isotopically pure molecular ions with no loss of label and, by difference, the per cent that have lost a deuterium atom or, in some cases, two. For example, retention of both labels in [M - H<sub>2</sub>O]<sup>•+</sup> from 5-phenylpentanol-5-d<sub>2</sub> equals 22.6/0.887 = 25.5%; therefore, 74.5% of the molecular ions undergoing dehydration lose at least one label in the process. The per cents of [M - H<sub>2</sub>O]<sup>•+</sup> ions losing deuterium, so estimated from the spectra of the various labeled compounds, are listed in Table II.

(20) S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, **88**, 56 (1966).

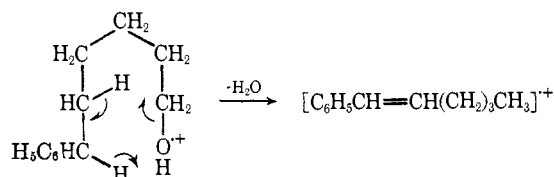
(21) N. C. Rol, *Recl. Trav. Chim. Pays-Bas*, **84**, 413 (1965).

(22) S. Meyerson, *Int. J. Mass Spectrom. Ion Phys.*, **1**, 309 (1968); J. Deutsch and A. Mandelbaum, *J. Amer. Chem. Soc.*, **91**, 4809 (1969); **92**, 4288 (1970); A. F. Thomas, B. Willhalm, and R. Müller, *Org. Mass Spectrom.*, **2**, 223 (1969); P. Brown, A. H. Albert, and G. R. Pettit, *J. Amer. Chem. Soc.*, **92**, 3212 (1970); W. J. Richter and A. L. Burlingame in "Recent Developments in Mass Spectroscopy," K. Ogata and T. Hayakawa, Ed., University Park Press, Baltimore, Md., 1970, p 1227.

Table II. Per Cent of [M - H<sub>2</sub>O]<sup>•+</sup> Ions That Have Lost Deuterium

	6-d	5-d <sub>2</sub>	4-d <sub>2</sub>
6-Phenylhexanol	40	15	3
5-Phenylpentanol		75	14
5-Phenylpentanoic acid		56	

The calculated loss of deuterium from 6-phenylhexanol-6-d is doubled to give the total hydrogen loss from C-6 (possible isotope effects are ignored). The summed losses from the positions labeled account essentially quantitatively—80 + 15 + 3 = 98%—for the alkyl hydrogens lost in the dehydration step, and an even larger fraction of the total comes from C-6 than in 6-phenylhexanoic acid. Here again, 1,6 elimination may be promoted by a mechanism paralleling that of the acid,<sup>20</sup> leading to a 1-phenyl-1-hexene ion



In 5-phenylpentanol, positions 5 and 4 contribute at least 89% of the alkyl hydrogens lost as H<sub>2</sub>O. The actual figure is, in fact, higher than this, because in an appreciable fraction of the H<sub>2</sub>O molecules both hydrogens come from C-5, as evidenced by the yield of unlabeled [M - H<sub>2</sub>O]<sup>•+</sup>. Clearly, the great bulk of the alkyl hydrogens lost come from C-5. Loss from the benzylic carbon of 5-phenylpentanoic acid is less than in the alcohols, but it is still greater than 50%. Even if the remaining alkyl hydrogen lost comes solely from C-4, the "normal" process receives severe competition from 1,5 elimination.

The distribution of positions from which hydrogen atoms are lost as H<sub>2</sub>O from aliphatic alcohols and acids is altered drastically by benzylic activation on C-6 or C-5, and probably on farther removed carbons as well.<sup>23</sup> Activation greatly increases the probability of hydrogen loss from the selected position. At the same time, despite the sharp decrease in carbon-hydrogen bond dissociation energy—from about 98 kcal/mol for a primary alkyl hydrogen or 95 for a secondary one to about 85 for a benzylic one<sup>24</sup>—competitive hydrogen loss from other positions persists.

**A Proposed Model. Internal Solvation.** The present results, taken in conjunction with earlier ones, seem best accounted for in terms of coiling of the alkyl chain,<sup>25,26</sup> which apparently occurs even in long-chain

(23) This extrapolation is supported by preliminary results from a similar study of the loss of H<sub>2</sub>O from ω-benzyloxyalkan-1-ols labeled with two deuteriums on the benzylic carbon, C<sub>6</sub>H<sub>5</sub>CD<sub>2</sub>O(CH<sub>2</sub>)<sub>n</sub>OH, under electron impact (M. M. Green, personal communication). However, this work incorporates an element of ambiguity in that the labels are located on a carbon adjacent to an ether oxygen and charge exchange is therefore a likely contributing factor.

(24) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(25) R. Ryhage and E. Stenhagen, *J. Lipid Res.*, **1**, 361 (1960); ref 3a, pp 179-180.

(26) (a) S. Meyerson, I. Puskas, and E. K. Fields, *Chem. Ind. (London)*, 1845 (1968). (b) A referee has emphasized, correctly, that our data do not distinguish between coiling and flailing of the flexible molecule. Either would be expected to lead to random abstraction from all sterically accessible positions subject to a measure of selectivity stemming from such factors as ring size and localized activation. Either

*n*-alkanes with no functional groups.<sup>27</sup> Such coiling very likely occurs in the neutral molecule, although it may be enhanced by ionization. The role of electron impact may well be chiefly to trigger a sequence of reactions the precise paths of which depend upon and thus reflect the preexisting orientation of the molecule.

Coiling most probably arises as an attempt by the isolated molecule to attain internal solvation, paralleling the postulated random coiling into a tight ball of long flexible polymers in dilute solution in poor solvents.<sup>28</sup> In this context, the isolated molecules in the rarefied atmosphere of the mass spectrometer might be considered as an infinitely dilute solution in an infinitely poor solvent.<sup>29</sup> The analogy can perhaps be extended to embrace the formation of spherical drops of liquid or of gas bubbles in a liquid and of circular islands in monomolecular films,<sup>30</sup> extrapolated again to the limiting case of a single molecule.

The widespread occurrence of intramolecular processes—often accounting for surprisingly large fractions of the total products—in competition with intermolecular processes in a variety of contexts gives further evidence of a tendency of flexible molecules to coil back on themselves. Such behavior is observed, for example, in the reactions of carbenes,<sup>31</sup> in a great many pyrolysis reactions,<sup>32</sup> and in the formation of alicyclic<sup>33</sup> and aromatic<sup>34</sup> products in hydrocarbon synthesis by the hydrogenation of carbon monoxide over an iron catalyst.

Ubbelohde and his associates have invoked a variety of physical measurements as evidence for extensive "crumpling" or coiling of flexible molecules, even as short as *n*-pentane and perhaps *n*-butane, in the gas phase.<sup>35</sup> They have proposed that such coiling, by shielding hydrogens on internal carbons more effectively than those on terminal ones, is responsible for the observed decrease, with increasing chain length, in reactivity of secondary relative to primary hydrogens in gas-phase chlorination of *n*-paraffins.<sup>36</sup> This proposal is supported by a recent report of a similar, but intermolecular, steric effect in a close-packed rigid array of adsorbed alkanolic acid molecules with their axes perpendicular to the adsorbing surface; such orienta-

tion sharply increases the relative probability of chlorination on the exposed terminal and next-to-terminal carbon atoms over that obtained in a homogeneous but otherwise similar reaction system.<sup>37</sup>

model would thus stand in contrast to the much higher selectivity associated with a more rigidly oriented charge-exchange complex.

(27) N. Dinh-Nguyen, R. Ryhage, S. Stållberg-Stenhagen, and E. Stenhagen, *Ark. Kemi*, **18**, 393 (1961).

(28) See, for example, C. Tanford, "Physical Chemistry of Macromolecules," Wiley, New York, N. Y., 1961, Chapters 2 and 3, and references cited there; M. Kurata, and W. H. Stockmayer, *Fortschr. Hochpolym.-Forsch.*, **3**, 196 (1963), and references cited there.

(29) The tendency to coil can be counteracted by a strong electrical field, as in field-ionization mass spectrometry, where linear molecules appear to be extended parallel to the field. This effect probably applies to neutral molecules adsorbed on the emitter surface as well as to gaseous ionized molecules. See H. D. Beckey, *Angew. Chem., Int. Ed. Engl.*, **8**, 623 (1969), and references cited there. Although the mechanisms are, of course, different, the effect of the electrical field in this environment is roughly analogous to that of Flory solvents in polymer solutions.<sup>28</sup>

(30) H. E. Ries and W. A. Kimball, *Nature (London)*, **181**, 901 (1958).

(31) R. A. Moss, *Chem. Eng. News*, **50** (June 30, 1969).

(32) C. D. Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, N. Y., 1929.

(33) A. W. Weitkamp, H. S. Seelig, N. J. Bowman, and W. E. Cady, *Ind. Eng. Chem.*, **45**, 343 (1953).

(34) W. E. Cady, P. J. Launer, and A. W. Weitkamp, *ibid.*, **45**, 350 (1953).

(35) A. R. Ubbelohde and J. C. McCoubrey, *Discuss. Faraday Soc.*, **10**, 94 (1951); J. C. McCoubrey, J. N. McCrea, and A. R. Ubbelohde, *J. Chem. Soc.*, 1961 (1951); G. A. McD. Cummings, J. C. McCoubrey, and A. R. Ubbelohde, *ibid.*, 2725 (1952); G. A. McD. Cummings and A. R. Ubbelohde, *ibid.*, 3751 (1953).

(36) G. Chambers and A. R. Ubbelohde, *ibid.*, 285 (1955).

In the mass spectrometer, the presence of a second functional group able to interact with the first such group, as by charge exchange,<sup>6</sup> may strongly favor a particular molecular configuration and thereby introduce a high degree of selectivity into the ensuing reactions.<sup>6-9,38</sup> Such charge-exchange, or charge-resonance, complexes presumably resemble the dimer cations of olefins and arenes, and especially the corresponding intramolecular complexes of bifunctional molecules such as norbornadiene and paracyclophane, formed by  $\gamma$  irradiation in glassy solvents at 77°K and detected by esr and visible absorption spectra.<sup>39-41</sup> A further analogy might be drawn with the charge-transfer complexes that have been proposed to account for transfer of charge and excitation between the aryl rings of the molecular ions of substituted bibenzyls in the mass spectrometer.<sup>42</sup> In the absence of an appropriate second functional group, the coiled molecule may well have more than one alkyl hydrogen bridged to a heteroatom and thus poised to make the jump when conditions are right, as has been suggested<sup>14</sup> for acids and nitriles.<sup>21</sup> Localized activation and preferred ring size might then influence the competition among closely similar reactions by introducing a measure of site selectivity. Such a model could also accommodate processes in which two hydrogens migrate to the carbonyl group, as observed in ketones,<sup>43,44</sup> especially at reduced ionizing voltage,<sup>44</sup> and in acids.<sup>21</sup>

Localized activation alters markedly the course of events in some photochemical reactions that seem closely analogous to reactions induced by electron impact. For example, certain  $\Delta^3$ -unsaturated 1,2-diketones have given 5-hydroxycyclopent-2-enones<sup>45</sup> in place of the 2-hydroxycyclobutanones obtained from

(37) N. C. Deno, R. Fishbein, and C. Pierson, *J. Amer. Chem. Soc.*, **92**, 1451 (1970).

(38) These effects may be considered as analogous to the attractive forces, such as electrostatic interactions and hydrogen bonds, between formally nonadjacent segments of a polymer molecule that are reflected in the crystal structures of cellulose, polypeptides, proteins, and nucleic acids. See, for example, ref 28 and H. A. Scheraga, *Advan. Phys. Org. Chem.*, **6**, 103 (1968). For a model for alkaloid biosynthesis via the interaction of nonadjacent functional groups along peptide chains, see G. E. Krejcarek, B. W. Dominy, and R. G. Lawton, *Chem. Commun.*, 1450 (1968).

(39) See, for example, B. Badger, B. Brocklehurst, and R. D. Russell, *Chem. Phys. Lett.*, **1**, 122 (1967); B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, **65**, 2576, 2582, 2588 (1969).

(40) Similarly, charge exchange is believed to be the first step in the reaction between a benzene molecule and an excited  $C_6H_6^+$  ion in the mass spectrometer at high pressures to produce the dimer cation  $C_{12}H_{12}^+$ . See S. Wexler and L. G. Pobo, *J. Phys. Chem.*, **74**, 257 (1970).

(41) The unexpectedly low ionization potential of *cis,cis,cis*-1,4,7-cyclononatriene has prompted a suggestion that the lowering of ionization potential due to proper juxtaposition of nonadjacent olefinic groups may be a general phenomenon [S. Winstein and F. P. Lossing, *J. Amer. Chem. Soc.*, **86**, 4485 (1964)]. A similar lowering of the ionization potential in bicyclo[2.2.1]heptadiene-2,5, bicyclo[3.2.1]octadiene-2,6, and bicyclo[2.2.2]octadiene-2,5 has been attributed to the interaction of favorably oriented nonconjugated olefinic groups [D. A. Demeo and M. A. El-Sayed, *J. Chem. Phys.*, **52**, 2622 (1970); P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969); R. Hoffmann, E. Heilbronner, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 706 (1970)].

(42) S. Meyerson, H. Hart, and L. C. Leitch, *ibid.*, **90**, 3419 (1968).

(43) G. Spittler, "Massenspektrometrische Strukturanalyse organischer Verbindungen," Verlag Chemie, Weinheim/Bergstr., 1966, p 127.

(44) W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, **90**, 160 (1968).

(45) R. Bishop and N. K. Hamer, *Chem. Commun.*, 804 (1969).

saturated 1,2-diketones.<sup>46</sup> The photoinduced hydrogen migration from the alkyl chain to the ketonic oxygen in *n*-alkyl *p*-benzophenonecarboxylates<sup>47</sup> closely resembles the electron impact induced hydrogen migration from the alkyl chain to the anhydride group of 4-*n*-alkyl esters of trimellitic anhydride.<sup>26</sup> 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.<sup>48</sup> 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.<sup>49</sup> The 6-phenylhexanol-6-*d* and 5-phenylpentanol-4-*d*<sub>2</sub> were intermediates in the preparation of 6-phenylhexanoic acid-6-*d* and -5-*d*<sub>2</sub>, reported earlier.<sup>22</sup> In both cases, the

(46) W. H. Urry and D. J. Trecker, *J. Amer. Chem. Soc.*, **84**, 118 (1962); W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Lett.*, 609 (1962).

(47) R. Breslow and M. A. Winnik, *J. Amer. Chem. Soc.*, **91**, 3083 (1969).

(48) S. Meyerson, I. Puskas, and E. K. Fields, unpublished results.

(49) L. C. Leitch and S. Meyerson, to be published.

isotopic compositions found for the alcohols are essentially the same as those of the acids prepared from them and of the derived methyl esters.<sup>20</sup>

**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,<sup>50</sup> made with the repellers at an average potential of 3 V, the exact values being selected to give maximum sensitivity. Isotopic compositions of the  $[M - H_2O]^+$  ions were estimated from 70-eV spectra. For 6-phenylhexanol-5-*d*<sub>2</sub> and -4-*d*<sub>2</sub>, 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.

(50) D. P. Stevenson and C. D. Wagner, *J. Amer. Chem. Soc.*, **72**, 5612 (1950).

## Solvolytic Rearrangements Accompanied by Multiple Alkyl Shifts

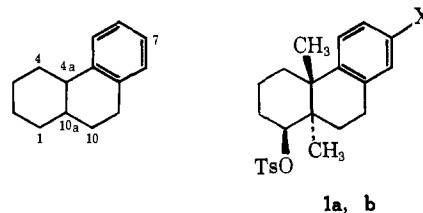
H. W. Whitlock, Jr.,\* and L. E. Overman<sup>1</sup>

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 4 $\alpha$ ,10 $\alpha$ -dimethyl-1 $\alpha$ ,2,3,4,4 $\alpha$ -, 9,10,10 $\alpha$ -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,<sup>2,3</sup> a series of methyl and hydrogen 1,2 shifts, are an integral part of currently accepted biosynthetic pathways to multicyclic triterpenes.<sup>4,5</sup> 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**.<sup>6</sup> We conclude below that solvolytic rearrangement of the carbon skeletons of



(1) NIH Predoctoral Fellow, 1966-1969.

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

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