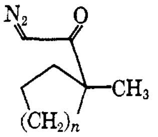
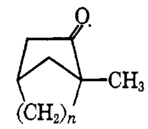
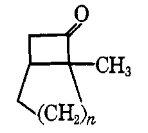
tion of diazomethyl α-methylcycloheptyl ketone (Xa)[16] led to 1-methyl-8-bicyclo[4.2.1]nonanone (XIa) [72% yield; liquid; infrared (neat): 5.75 μ (C=O, s); nmr ($CDCl_3$): three-proton singlet at δ 1.02 (Me)] and 1-methyl-9-bicyclo[5.2.0] nonanone (XIIa) [9%; liquid; infrared ($CCl_4$): 5.63 μ (C=O, s); nmr ($CDCl_3$): three-proton singlet at δ 1.23 (Me), three-proton multiplet at 2.2–3.5 (bridgehead H and α-ketomethylene)].[7] Decomposition of diazomethyl α-methylcyclohexyl ketone (Xb) produced a 62% yield of 1-methyl-7-bicyclo[3.2.1]octanone (XIb).[7] Decomposition of diazomethyl α-methylcyclopentyl ketone (Xc) afforded 1-methyl-2-bicyclo[2.2.1]heptanone (XIc;[17,18] 19%; semicarbazone mp and mmp[17] 212–214°) and 1-methyl-7-bicyclo[3.2.0]heptanone (XIIc) [3%; liquid; infrared ($CCl_4$): 5.63 μ (C=O, s); nmr ($CDCl_3$): three-proton singlet at δ 1.24 (Me), three-proton multiplet at 2.2–3.5 (bridgehead H and α-ketomethylene); semicarbazone mp 176–178°; 2,4-dinitrophenylhydrazone mp 93–95°].[19–21]



X



XI



XII

a, $n = 4$; b, $n = 3$; c, $n = 2$; d, $n = 1$

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(16) The authors are indebted to Dr. S. Shulman for his preparation of the precursor, α-methylcycloheptanecarboxylic acid, mp 43–45°.

(17) H. Toivonen, *Suomen Kemistilehti*, **33b**, 66 (1960); T. Gibson and W. F. Erman, *J. Org. Chem.*, **31**, 3028 (1966).

(18) The authors are indebted to Dr. T. Gibson for a sample of this substance.

(19) The solvent insertion product, hexahydrobenzyl α-methylcyclopentyl ketone (bp 87° (0.45 mm); semicarbazone mp 174°), was obtained in 9% yield.

(20) Decomposition of diazomethyl α-methylcyclobutyl ketone (Xd) has yielded *inter alia* 1-methyl-2-bicyclo[2.1.1]hexanone (XId) [liquid; infrared ($CCl_4$): 5.68 μ (C=O, s); nmr ($CDCl_3$): three-proton singlet at δ 1.18 (Me), two-proton multiplet at 2.05–2.25 (α-ketomethylene), one-proton multiplet at 2.72 (bridgehead H)].

(21) The authors are indebted to the National Science Foundation for support of this work.

(22) National Science Foundation Undergraduate Research Participant, summer 1967.

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## Distinguishing Diastereotopic Hydrogens by Mass Spectrometry. A Direct Probe into the Transition State of an Electron-Impact-Induced Elimination Reaction

*Sir:*

It has been recognized for some time that acyclic diastereomers exhibit mass spectral differences which are usually small and difficult to interpret.[1] While consistent differences are found for the intensities of ions formed in the fragmentation of double-bond stereoisomers they are also minor and not easily rationalized.[2] Cyclic diastereomers on the contrary have been the subject of many varied and continuing studies on the effect of stereochemistry on mass spectral fragmentations.[3]

We now report that two acyclic diastereomers, which are isomers *only* by virtue of isotopic substitution, can be distinguished by a stereoselective electron-impact-induced elimination reaction.

Racemic 2,4-pentanediol[4] was allowed to react with 1 equiv of *p*-toluenesulfonyl chloride in pyridine. Reduction of the derived tosylate with lithium aluminum deuteride in ethyl ether leads by stereospecific reaction[5,6] to (*S*,*R*)-2-deuterio-4-hydroxypentane (I).[7] Treatment of *meso*-2,4-pentanediol in exactly the same manner leads to (*S*,*S*)-2-deuterio-4-hydroxypentane (II). Conversion of I and II to their chlorosulfite esters and subsequent heating in dioxane produces III and IV, respectively.[8] Dissolution of I and II in pyridine and treatment with 1 equiv of thionyl chloride leads, respectively, by inversion of configuration,[9] to the chlorides IVa and IIIa. The reaction sequences are summarized in Scheme I while the mass spectral data are shown in Table I.

Table I.[a] Mass Spectral Data for Loss of HCl, DCl, and Cl from the Molecular Ions of III, IIIa, IV, and IVa[b]

| | III | IIIa | IV | IVa |
|---|---|---|---|---|
| *A* | 29.5 | 30.2 | 25.8 | 26.0 |
| *B* | 4.3 | 4.1 | 4.3 | 4.2 |

[a] Data were taken on a CEC-103-C mass spectrometer at a nominal 9-eV ionizing voltage with inlet at ambient temperature and ion source at ~28°. The molecular ion is undetectable under these conditions. The low source temperature was attained by scanning the region of interest immediately after starting the filament. The temperature was measured just before and after the run. The spectra were indistinguishable on various runs. At 130° and 70 eV the relative difference between III (IIIa) and IV (IVa) is close to 50% of that shown in table. [b] $A = \{(M - DCl)/[(M - DCl) + (M - HCl)]\}10^2$; $B = \{(M - Cl)/[(M - DCl) + (M - HCl) + (M - Cl)]\}10^2$.

It is apparent from the results shown in Table I that the two chlorides produced from I (Scheme I) eliminate different amounts of DCl. Further, the chlorides from

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(1) K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 144–151. See, though, H. E. Audier, H. Felkin, M. Fétizon, and W. Vetter, *Bull. Soc. Chim. France*, 3236 (1965).

(2) For a comprehensive review, see P. Natalis in "Mass Spectrometry," R. I. Reed, Ed., Academic Press Inc., New York, N. Y., 1965, p 379 ff. See also S. W. Staley and D. W. Reichard, *J. Am. Chem. Soc.*, **90**, 816 (1968).

(3) For a review of early work see ref 1. For more recent reviews see J. M. Wilson, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **63**, 275 (1966); H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 110 ff. More recent publications with leading references are: W. M. Bryant, III, A. L. Burlingame, H. O. House, C. G. Pitt, and B. A. Tefertiller, *J. Org. Chem.*, **31**, 3120 (1966); H. E. Audier, M. Fétizon, H. B. Kagan, and J. L. Luche, *Bull. Soc. Chim. France*, 2297 (1967); V. I. Zarettskii, N. S. Wulfson, and V. G. Zaikin, *Tetrahedron*, **23**, 3683 (1967); J.-L. Imbach, E. Doomes, N. H. Cromwell, H. E. Baumgarten, and R. G. Parker, *J. Org. Chem.*, **32**, 3123 (1967); M. Shamma and K. F. Foley, *ibid.*, **32**, 4141 (1967); L. Dolejš and V. Hanuš, *Collection Czech. Chem. Commun.*, **33**, 332 (1968).

(4) The diols were prepared following the procedure of J. G. Pritchard and R. L. Vollmer, *ibid.*, **28**, 1545 (1963). We are grateful to Professor C. G. Overberger for a sample of *d,l*-2,4-pentanediol.

(5) G. K. Helmkamp and B. F. Rickborn, *ibid.*, **22**, 479 (1957).

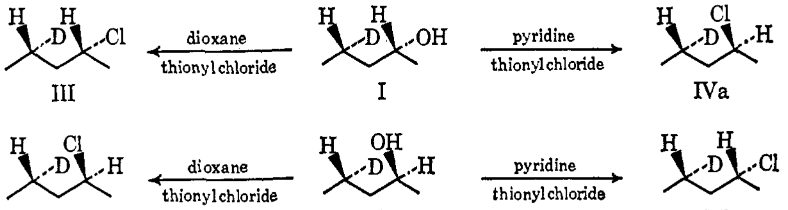
(6) Anchimeric assistance is not involved in this reaction; see H. B. Henbest and B. B. Millward, *J. Chem. Soc.*, 3575 (1960). Assistance through four-membered rings has been shown to be poor or nonexistent; see B. Capon, *Quart. Rev.* (London), **18**, 45 (1964).

(7) Unless otherwise specified all compounds are racemic mixtures. All deuterated compounds were found to be identical with authentic protium materials by vapor phase chromatography.

(8) This reaction is known to occur with retention of configuration; see C. E. Boozer and E. S. Lewis, *J. Am. Chem. Soc.*, **75**, 3182 (1953).

(9) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman, and A. D. Scott, *J. Chem. Soc.*, 1252 (1937).

Scheme I[10]

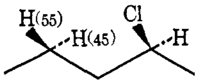


III I IVa

IV II IIIa

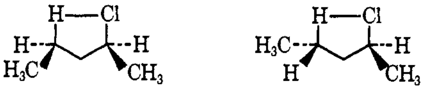
II lead to essentially the same results from the opposing reactions. Concurrently the intensity of the M − Cl ion is independent of stereochemistry. It follows from the data that the over-all stereospecificities, and deuterium incorporation,[11] for the reaction sequences outlined in Scheme I are the same. More important is the fact that the loss of the diastereotopic deuterium atoms[12] as deuterium chloride takes place to unequal extent. Since the deuteriums are related to each other in III and IV (or IIIa and IVa) exactly as the two C-4 hydrogens are related in 2-pentyl chloride (of a single configuration), the results can be summarized as shown in Scheme II.

Scheme II[10,13]



These results are compatible with a concerted elimination of hydrogen chloride (in contrast to loss of Cl· followed by H·). The simplest manner to envision such a reaction would be through a five-membered cyclic transition state. If this is so, the *mass spectral difference* between the diastereotopic hydrogens is remarkable since the competing transition states would be expected to differ by substantially less than 1 kcal![17] It is noteworthy that the favored thermochemical isomer of 1,3-dimethylcyclopentane (*i.e.*, *cis*) corresponds to the favored transition state for this elimination (Scheme III).

Scheme III



55% 45%

Further significance for these findings rests in the fact that an electron-impact-induced reaction occurring in compounds of widely variant structure has been shown to be sensitive to subtle structural features, and, in addition, this sensitivity is *only* a function of the transition state of the reaction.[18] It follows that studies along these lines will act as a probe into the effects of structure on these activated complexes as well as a means of correlating similar and dissimilar transition states of related electron-impact and condensed-phase processes.[22]

**Acknowledgment.** We are grateful for support of this research to the Petroleum Research Fund of the American Chemical Society (Grant No. 1104-Gl) and to Research Corporation for a Frederic Gardner Cottrell grant in aid.

[10] The diagrams in Schemes I and II are not designed to suggest conformation but rather to display convenient representations of the stereochemistry.

[11] The deuterium incorporation was quantitative as evidenced by the mass spectrum of the ketone derived by oxidation of a mixture of I and II. Further, this ketone was reduced with lithium aluminum hydride and the product was converted to chloride by reaction in dioxane and pyridine as described above. The two chlorides gave identical mass spectra.

[12] K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, p 1 ff.

[13] The numbers correspond to the relative loss of DCl from III (IIIa) and IV (IVa). The values given have been corrected for the expected 10–20% nonspecific[5,14] displacement of tosylate by deuterium in the reduction step. This will be an accurate reflection of the relative hydrogen loss if the isotope effect for loss of DCl in III and IV is the same (not necessarily one). A referee has alternatively suggested that the observed effect may be due to different isotope effects for each isomer (III and IV). We do not favor this explanation because it is difficult to understand why the two isomers should show such a difference especially in view of the only small over-all discrimination against deuterium observed in closely related reactions.[15,16] At any rate the fundamental difference must ultimately reside in the differing stereochemical environments of the two deuterium atoms, and the following discussion is couched in these terms.

[14] W. A. Sanderson and H. S. Mosher, *J. Am. Chem. Soc.*, 88, 4185 (1966).

[15] A. M. Duffield, S. D. Sample, and C. Djerassi, *Chem. Commun.*, 193 (1966), and references included therein.

[16] M. M. Green and J. Schwab, *Tetrahedron Letters*, 2955 (1968).

[17] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 202. This assumes a puckered ring and relief of equivalent eclipsing interactions in the isomers by replacement of the two $CH_2$ groups in cyclopentane by H and Cl. Lack of puckering would lower the energy difference. See also the discussion of E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 250.

[18] This study presents the first detection of a mass spectrometric difference between two compounds with identical ground states (it is reasonably assumed that the configuration at the deuterated carbon has essentially no effect on the ground-state properties of these compounds). There are two previous cases of electron-impact-induced competitive reactions which take place at different rates only by virtue of transition-state differences.[19,20] The alternative possibility in this case, that the elimination is a function of the conformer populations of 2-pentyl chloride, seems unlikely especially in the light of the conformational changes which are prerequisites for elimination of hydrogen chloride and water in cyclohexyl compounds.[16,21]

[19] P. Brown and C. Djerassi, *J. Am. Chem. Soc.*, 89, 2711 (1967).

[20] E. P. Smith and E. R. Thornton, *ibid.*, 89, 5079 (1967).

[21] C. G. Macdonald, J. S. Shannon, and G. Sugowdz, *Tetrahedron Letters*, 807 (1963).

[22] The Barton reaction[23] and the mass spectral elimination of water, processes which we propose obey similar driving forces, are being compared in detail by the present technique.

[23] M. Akhtar, "Advances in Photochemistry," Vol. 2, Interscience Publishers, New York, N. Y., 1964, pp 263–303.

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## The Molecular Geometry of Vanadyl Deoxophylloerythroetioporphyrin. An Analog of Chlorophyll

*Sir:*

The crystal and molecular structure of vanadyl deoxophylloerythroetioporphyrin (VO-DPEP) has been solved by three-dimensional X-ray techniques and is in the latter stages of analysis. The weighted *R* factor is