that tetrahydrofuran was used as the extractant for unreacted $NaAlH_4$. However, the analyses were inconclusive.

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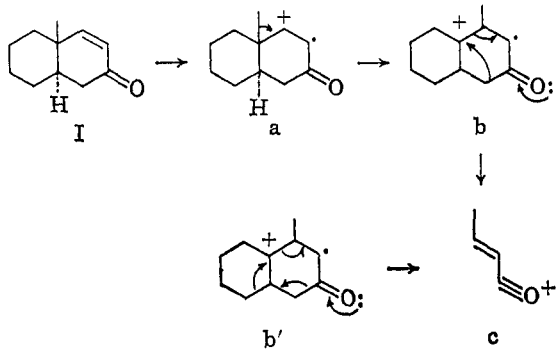
Mass Spectrometry in Structural and Stereochemical Problems. CIII.[1] Electron Impact Induced Methyl Migration in Some 2-Arylidene-1-decalones[2]

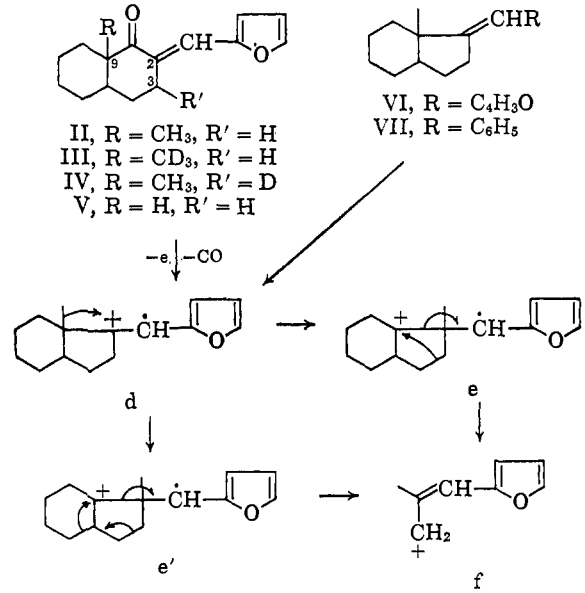
Sir:

Increasing attention is being paid to the electron impact induced rearrangement of substituents other than hydrogen in mass spectrometric fragmentation reactions. This is due to the intrinsic mechanistic interest that such rearrangements possess and the possible limitation that their occurrence may impose on the use of the "element mapping" technique.[3] One such rearrangement is typified by the elimination of stable neutral fragments such as formaldehyde, carbon monoxide, carbon dioxide, and diimide from the nonterminal portion of some linear molecules.[4] Another type is represented by authentic 1,2 migrations, which have been of particular concern to us because of their potential for comparison with carbonium ion rearrangements and for an evaluation of the hitherto unexamined field of relative migratory aptitudes in mass spectrometry. Such a methyl migration has recently been described[5] in *trans*-Δ^3-10-methyl-2-octalone (I) and related compounds, which give rise to an abundant ion which may be depicted as c.



We describe now a second example of such a methyl migration, which in spite of the structural dissimilarity of the starting compounds (I *vs.* II) seems to be mechanistically identical with the octalone rearrangement (a → c).[5] The base peak in the mass spectrum of *trans*-2-furfurylidene-9-methyl-1-decalone (II)[6] as well as in the analogous steroid ketones occurs at *m/e* 121 and by high-resolution mass spectrometry was shown to correspond to $C_8H_9O^+$. This peak is shifted to *m/e* 124 in the 9-d_3 analog III and to *m/e* 122 in the 3-d_1 derviative IV,[7] while it occurs at *m/e* 107 in the unmethylated precursor V. Appropriate mass shifts were encountered in the benzylidene (*m/e* 131), *p*-chlorobenzylidene (*m/e* 165/167), and *p*-methylbenzylidene (*m/e* 145) derivatives, and no significant change was observed in the mass spectrum of the *cis* isomer of II.

These results are only compatible with the assumption that the intense $C_8H_9O^+$ ion (*m/e* 121) of II retained the furfurylidene moiety together with carbon atoms 2 and 3 as well as the angular methyl group. We formulate its genesis through initial loss of carbon monoxide to species d,[8] followed by concerted methyl migration and subsequent bond cleavages (e or e') to the resonance-stabilized ion f (*m/e* 121). It should



(1) Paper CII: P. Potier, C. Kan, J. Le Men, M.-M. Janot, H. Budzikiewicz, and C. Djerassi, *Bull. Soc. Chim. France*, in press.

(2) Financial support (Grants No. CA-07195 and AM-04257) from the National Institutes of Health of the U. S. Public Health Service is gratefully acknowledged.

(3) K. Biemann, *Pure Appl. Chem.*, **9**, 95 (1964); K. Biemann, P. Bommer, and D. M. Desiderio, *Tetrahedron Letters*, 1725 (1964).

(4) For recent examples see P. Brown, C. Djerassi, G. Schroll, H. J. Jakobsen, and S.-O. Lawesson, *J. Am. Chem. Soc.*, **87**, 4559 (1965); J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson, and G. Schroll, *Chem. Commun.*, 403 (1965); A. Bhati, R. A. W. Johnstone, and B. J. Millard, *J. Chem. Soc.*, in press.

(5) F. Komitsky, Jr., J. E. Gurst, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 1398 (1965). In this paper we postulated conversion of b to c, which implies the elimination of the cyclopropyl radical i. Dr. W. J. Richter (Hoffman-LaRoche, Basel) has pointed out to us that a series of 1,2 cleavages as indicated in b' are equally feasible, the principal difference being the nature of the expelled radical (ii). Experiments are under way in our laboratory which may differentiate between these two subtle but important alternatives.

(6) W. S. Johnson, B. Bannister, and R. Pappo, *ibid.*, **78**, 6331 (1956). We are indebted to Professor Johnson for supplying us with starting materials for the d_3-labeled substrates, which were obtained by substituting methyl-d_3 iodide in the appropriate methylation steps in the decalone and steroid series.

(7) This substance was prepared by lithium aluminum deuteride reduction of (+)-*trans*-1-methoxy-9-methyl-$\Delta^{1,6}$-3-hexalone, followed by acid cleavage to *trans*-9-methyl-$\Delta^{2,6}$-1-decalone-3-d_1, catalytic hydrogenation of the two double bonds, and finally condensation with furfuraldehyde.

(8) The M − 28 peak at *m/e* 216 amounts to 40% of the intensity of the base peak (f, *m/e* 121) and by high-resolution mass spectrometry was shown to correspond to the expulsion of carbon monoxide rather than of ethylene. No metastable peaks were encountered in this work to substantiate the postulated intermediacy of the M − CO species in the formation of ion f, nor were any observed which would correspond to the direct production of f from the molecular ion.

be noted that the methyl migration and concomitant bond fissions (e or e′) are completely analogous to those (b or b′) encountered[5] in the octalone I and that the same radical (i or ii in ref 5) is produced in each case The postulated intermediate ion d formally corresponds to the molecular ion of 1-furfurylidene-8-methylhydrindane (VI). We have synthesized its benzylidene analog VII by treatment of benzylmagnesium chloride with 8-methylhydrindan-1-one followed by dehydration, and found in its mass spectrum an *m/e* 131 peak (f, furfuryl replaced by phenyl) of virtually the same relative intensity as encountered in 2-benzylidene-9-methyl-1-decalone,[9] thus offering support (though not proof[10]) for the intermediacy of an ion such as d.

Further work on the scope and other mechanistic implications of this and related[5] methyl migrations is under way in our laboratory.

(9) W. S. Johnson, *J. Am. Chem. Soc.*, **65**, 1317 (1943).
(10) *Cf.* W. H. Pirkle, *ibid.*, **87**, 3023 (1965).
(11) National Institutes of Health Postdoctoral Fellow, 1964–1965.

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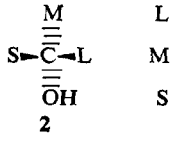
Configurational Correlation of Alcohols by Asymmetric Synthesis of Sulfinate Esters[1]

Sir:

The asymmetric synthesis of menthyl sulfinates by the reaction of *l*-menthol with sulfinyl chlorides has been developed as a general method for use in the assignment of absolute configurations to sulfinate esters and derived sulfoxides.[2] It has now been established that, conversely, the asymmetric synthesis of alkyl *p*-toluenesulfinates provides a rapid, convenient, and highly stereoselective general method for the configurational correlation of alcohols.

Reaction of *p*-toluenesulfinyl chloride with a variety of optically active secondary alcohols at −78° in the presence of pyridine gives a mixture of diastereomers which can be directly converted to optically active methyl *p*-tolyl sulfoxide (**1**) in 80–90% yields by reaction with methylmagnesium iodide. We find that the sign of the predominant enantiomer of **1** is uniquely related to the absolute configuration of the inducing alcohol: alcohols corresponding to stereoformula **2** yield an excess of the (−)-(*S*) enantiomer of **1**.[3]



2

L = large group
M = medium-sized group
S = small group

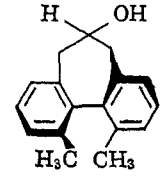
(1) This work was supported by the National Science Foundation under Grant No. GP-3375.
(2) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **87**, 1958 (1965).
(3) Alcohols of configuration **2** induce formation of an excess of the (−)-(*R*) enantiomer of atrolactic acid by the method of Prelog,[4] and of the (+)-(*S*) enantiomer of α-phenylbutyric acid by the method of Horeau.[5]
(4) V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953); V. Prelog and H. L. Meier, *ibid.*, **36**, 320 (1953).
(5) A. Horeau, *Tetrahedron Letters*, **No. 15**, 506 (1961); **No. 21**, 965 (1962); A. Horeau and H. B. Kagan, *Tetrahedron*, **20**, 2431 (1964).

Table I. Asymmetric Synthesis of Methyl *p*-Tolyl Sulfoxide (**1**)

Inducing Alcohol	Produced Sulfoxide **1** Obsd $[\alpha]^{25}D$ (ethanol), degrees	Calcd optical yield, %[c]
(−)-Methanol	−39	25.0
(−)-Isoborneol[a]	−60	50.2
(−)-Borneol[b]	−22	22.7
(+)-2-Butanol	+16	10.0
(+)-3-Methyl-2-butanol	+28	18.0
(+)-3,3-Dimethyl-2-butanol	+29	18.6

[a] A mixture of 84% (−)-isoborneol and 16% (+)-borneol. [b] A mixture of 88% (−)-borneol and 12% (+)-isoborneol. [c] Calculated on the basis of $[\alpha]^{25}D$ +156° (ethanol) for optically pure **1** (*cf.* K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 4958 (1965), ref 13). The optical yields calculated for (−)-isoborneol[a] and (−)-borneol[b] have been corrected and refer to the pure stereoisomers (*i.e.*, the major components in the respective mixtures).

Representative results are collected in Table I. The three levorotatory terpene derivatives have the (*R*) configuration at the asymmetric carbinol carbon,[4] fit stereoformula **2**, and preferentially induce the formation of (−)-(*S*)-**1**. Dextrorotatory methylethyl-, methylisopropyl-, and methyl-*t*-butylcarbinols have the (*S*) configuration at the asymmetric carbinol carbon,[6] fit the enantiomer of stereoformula **2**, and preferentially induce the formation of (+)-(*R*)-**1**. Since the ratio of enantiomeric sulfoxides produced in the Grignard reaction equals the ratio of diastereomeric precursor sulfinates,[2] it follows that the optical yield is an accurate measure of the stereoselectivity of the esterification reaction. The high optical purities of the sulfoxides produced in the Grignard reactions (Table I) therefore reflect the high stereoselectivity of the asymmetric esterifications. High stereoselectivity is also demonstrated by the finding that (+)-(*S*)-2-propanol-1-d_3 (**3**)[6] functions as an inducing alcohol to give (−)-(*S*)-**1** of 0.26% optical purity. The sign of rotation indicates that **3** fits stereoformula **2** and that, accordingly, CH_3 exceeds CD_3 in effective steric bulk. This result is consistent with previous conclusions to the same effect.[7] Finally, use of (+)-(*S*)-4′,1″-dimethyl-1,2,3,4-dibenz-1,3-cyclohepta-diene-6-ol (**4**)[6,8] as the inducing alcohol affords (+)-(*R*)-**1**, 6% optically pure. The sign of rotation of **1** indicates that **4** corresponds to the enantiomer of stereoformula **2**, a result which is consistent with the finding[9] that (*R*)-binaphthyl **5** gives a preponderance of (−)-(*R*)-atrolactic acid and thus corresponds to stereoformula **2**.[3]



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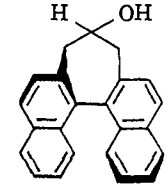

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(6) K. Mislow, R. E. O'Brien, and H. Schaefer, *J. Am. Chem. Soc.*, **84**, 1940 (1962), and references cited therein.
(7) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *ibid.*, **86**, 1733 (1964); A. Horeau, A. Nouaille, and K. Mislow, *ibid.*, **87**, 4957 (1965).
(8) K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, and C. Djerassi, *ibid.*, **82**, 1455 (1962).
(9) K. Mislow, V. Prelog, and H. Scherrer, *Helv. Chim. Acta*, **41**, 1410 (1958).