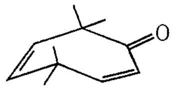
These data clearly point to singlet excited VI as the principal precursor to both the 1,3 and 3,3 migration processes.

Preliminary results paralleling those of Table I indicate that the photochemistry of the simple bicyclononatrienone XVII also proceeds through competitive [3,3] and [1,3] sigmatropic rearrangements, the former predominating. An extension of this study to other "homocyclohexadienones" (XVIII) is in progress.



XVIII

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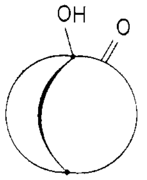
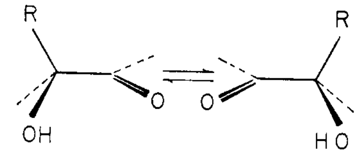
## Bridgehead Ketols

*Sir:*

We wish to draw attention to a class of compounds (bridgehead ketols,**1**) that offers a variety of novel ways to enrich our knowledge and understanding of skeletal rearrangements in bridged molecules. This communication (a) points out some of the special features of the bridgehead $\alpha$-ketol unit, (b) reports the synthesis and characterization of the norbornyl representative **8**, which is a key member of the class, and (c) presents evidence that **8** undergoes the essential degenerate alkali-induced rearrangement that underscores the utility of these compounds for mechanistic studies.



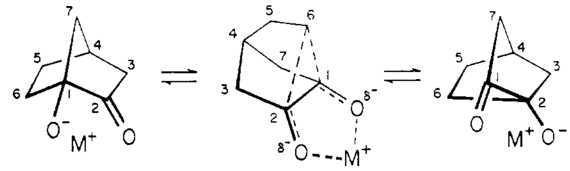
1



R=H,ALKYL OR ARYL

2

Isomerizations of $\alpha$-hydroxy carbonyl compounds (see **2**) can often be induced by acidic and basic reagents and are well documented, especially in the steroid field.[1] If the ketol unit were at a bridgehead (**1**) of a suitably bridged system, the rearrangement could be degenerate, and the midway stage would have geometry like that in Wagner–Meerwein shifts. Equation 1 illustrates the interconversion of the norbornyl analog *dextro*-**3** $\rightleftarrows$ *levo*-**3** by alkali (M = cation). Whether the delocalized species *meso*-**3** is a transition state or an intermediate is as pertinent a consideration in this *anionic* rearrangement as it is in its cationic counterpart, the norbornyl cation. However, unlike the elusive cation, which scrambles by hydrogen shifts, the anion **3** should be largely stable in alkaline medium, and complications due to hydrogen scrambling are precluded by involvement of the two oxygens.[2]



(1)

dextro-3 meso-3 levo-3

Nmr and X-ray crystallographic investigations of metal salts (or perhaps even metaloid complexes[3]) could be used to learn whether classical (*e.g.*, *dextro*-**3**) or nonclassical (*e.g.*, *meso*-**3**) structures prevail. Various $\pi$ routes and $\Delta$ routes[4] to **3** can be envisaged, as can structural modifications (*e.g.*, replacement of oxygen by other heteroatoms) that might enhance the relative stability of the delocalized form. Since ways are available[5] for conversion of HOR to ·OR, bridgehead ketols are also potentially useful to study rearrangements, electron delocalization, etc., in alkoxy radicals. In addition, the 1,2-dioxygenated array can be used to set up specialized features in *cationic* shifts. For example, products and rates in solvolyses of *exo* and *endo* C-2 brosylates with an oxygen function at C-1 (*e.g.*, OH, OR, etc.) are of high interest in their own right and will be reported separately. The accompanying communication reveals still a different application in an nmr study of equilibrating tertiary cations.[6]

Our synthetic scheme to ketol **8** involved hydrolysis of 2-bromonorbornane-1-carboxylic acid (**4**)[7] in acid and oxidation of the crude hydroxy acids with Jones reagent. The derived keto acid **5** ($C_8H_{10}O_3$; mp 128.5–129.5°;

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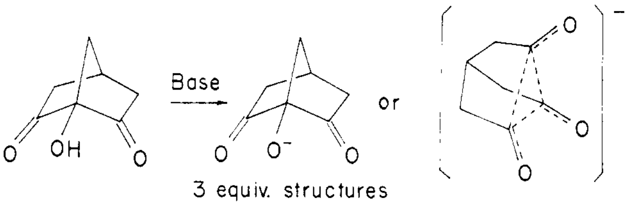
[1] (a) For leading references to steroidal examples, see a review by N. L. Wendler in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 16; (b) Y. Mazur and M. Nussim, *Tetrahedron Letters*, 817 (1961); (c) H. O. House and H. W. Thompson, *J. Org. Chem.*, **28**, 164 (1963); (d) D. Y. Curtin and S. Leskowitz, *J. Amer. Chem. Soc.*, **73**, 2633 (1951); (e) J. F. Eastham, J. E. Huffaker, V. F. Ramen, and C. J. Collins, *ibid.*, **78**, 4323 (1956); (f) M. J. Frearson and D. M. Brown, *J. Chem. Soc., C*, 2909 (1968).

[2] Intriguing variants are "sesquiketols" (*e.g.*, i) in which the corresponding alkoxide could adopt three degenerate structures (ii), each with a plane of symmetry, or a single mesomeric structure with $C_{3v}$ symmetry (iii).



3 equiv. structures

i ii iii

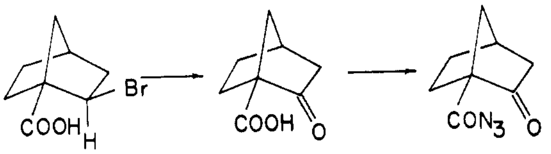
[3] Ordinarily $\alpha$-hydroxy ketones do not form isolable metal chelates, but the stability of cupric tropolone and of chelates of dithiotropolone indicate that specialized features can alter this: J. M. Robertson, *J. Chem. Soc.*, 1222 (1951); C. E. Forbes and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 6884 (1968).

[4] A. Nickon and G. D. Pandit, *Tetrahedron Letters*, 3663 (1968).

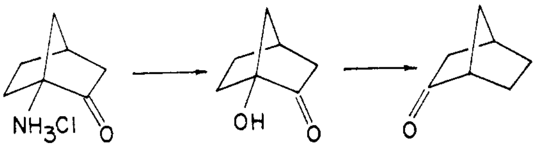
[5] For leading references see: (a) A. L. Nussbaum and C. H. Robinson, *Tetrahedron*, **17**, 35 (1962); (b) M. Akhtar, P. Hunt, and P. B. Dewhurst, *J. Amer. Chem. Soc.*, **87**, 1807 (1965); (c) A. Padwa, *Tetrahedron Letters*, 3465 (1964); (d) D. B. Denney and J. W. Hanifin, Jr., *J. Org. Chem.*, **29**, 732 (1964); (e) F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz, and W. N. Smith, *J. Amer. Chem. Soc.*, **83**, 2196 (1961); (f) D. Rosenthal, C. F. Lefler, and M. E. Wall, *Tetrahedron Letters*, 3203 (1965); (g) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957; (h) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

[6] A. Nickon and Y.-i Lin, *J. Amer. Chem. Soc.*, **91**, 6861 (1969).

[7] (a) W. Boehme, *ibid.*, **81**, 2762 (1959); (b) H. Kwart and G. Null, *ibid.*, **81**, 2765 (1959).



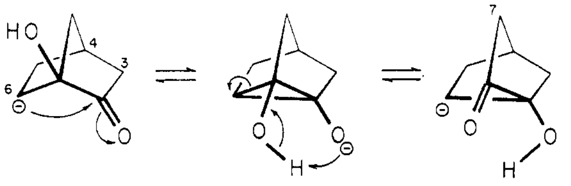
4 5 6



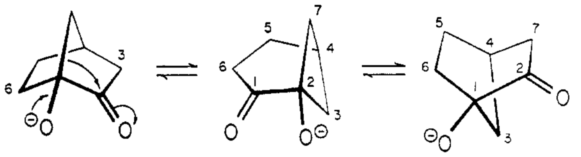
7 8 9

$\nu$ 1760, 1720 cm$^{-1}$; $\delta$ 10.1)[8] was converted by a modified Curtius sequence[9] *via* azide **6** ($\nu$ 2140, 1760, 1710 cm$^{-1}$) to the amino ketone hydrochloride **7** ($C_7H_{12}ClNO$; mp 211 dec; $\nu$ (KBr) 1760 cm$^{-1}$). Deamination ($NaNO_2$) in acid gave ketol **8**: $C_7H_{10}O_2$; mp 146–147° (sealed tube); $\nu$ 3520, 1755, 1410 cm$^{-1}$; $\delta$ 2.5 (bridgehead H) and 2.6 (OH, exchangeable by $D_2O$), no low-field $\alpha$-H signal; 2,4-DNP ($C_{13}H_{14}N_4O_5$) mp 173–175.5°. Independent structure proof was obtained by $LiAlH_4$ reduction of **8** to a diol mixture,[10] which, when brosylated and solvolyzed in aqueous acetone, gave norbornan-2-one (**9**), identical (glpc, ir, nmr) with an authentic sample.

Ketol **8** (1.6 mmol) in $D_2O$ (440 mmol) containing $K_2CO_3$ (0.58 mmol) was warmed at 80° for 145 hr. After work-up and a wash with 0.78 mmol of $H_2O$ (to exchange OD) ketol **8** was recovered ($\nu$ 2135, 2232 cm$^{-1}$) and its mass spectrum showed 1% $d_2$, 9% $d_3$, 89% $d_4$, 1% $d_5$[11] (total 3.91 deuteriums per molecule). This maximum of four carbon-bound deuteriums is expected if *dextro*-**3** and *levo*-**3** interconvert *via meso*-**3** because C-3 and C-7 become equivalent enolizable sites. The results exclude two alternative mechanisms for multiple deuterium entry. One of these involves abstraction of a C-6 proton to give a homoenolate ion (eq 2)[12] in which the two oxygenated carbons can easily become equivalent.[13] In this way C-6 as well as C-3 and C-7 can exchange their protons, and this requires incorporation of six deuteriums without a leveling off at four deuteriums. The second alternative mechanism reasonably excluded involves migration of the C-1–C-7 bond (eq 3) to give a *meso intermediate* with a bicyclo[3.1.1]heptane skeleton.[14] This path allows C-3, C-6, and C-7 to become enolizable, and species with up to six deuteriums would be expected after the prolonged treatment.[15]



(2)



(3)

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(8) Satisfactory analytical data were obtained for all new compounds whose empirical formulas are given. Solution ir spectra refer to $CCl_4$ and nmr to $CCl_4$ or $CDCl_3$.

(9) W. Feller, Ph.D. Dissertation, Johns Hopkins University, 1968. We are grateful to Drs. Murr and Feller for these details.

(10) For separate kinetic studies we have separated and characterized the individual *exo* and *endo* diols.

(11) We attach no significance to the 1% $d_5$ in view of the accuracy limits of the mass analysis and the expectation that a small amount of OD remains after the $H_2O$ wash. In a separate run we checked that mass spectral and combustion techniques give the same deuterium assay (*cf.* 3.91 and 3.95 deuteriums, respectively).

(12) A. Nickon and J. L. Lambert, *J. Amer. Chem. Soc.*, **84**, 4604 (1962); A. Nickon J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *ibid.*, **88**, 3354 (1966), and references cited there.

(13) We are investigating other routes to bridgehead ketols including bifunctional reduction of 1,3-diketones followed by opening of the cyclopropane diols: V. T. C. Chuang, J. Frank, and D. Covey, unpublished results; N. J. Cusack and B. R. Davis, *J. Org. Chem.*, **30**, 2062 (1965); M. L. Kaplan, *ibid.*, **32**, 2346 (1967); E. Wenkert and E. Kariv, *Chem. Commun.*, 570 (1965); K. M. Baker and B. R. Davis, *Chem. Ind.* (London), 768 (1966); T. J. Curphey, C. W. Amelotti, T. P. Layloff, R. L. McCartney, and J. H. Williams, *J. Amer. Chem. Soc.*, **91**, 2817 (1969); W. Reusch and D. B. Preddy, *ibid.*, **91**, 3677 (1969).

(14) This path produces a different type of carbon scrambling than do the other paths and suggests ways of probing subtle details of these anionic isomerizations. Interconvertibility of [3.1.1] and [2.2.1] systems is of considerable interest in *cationic* rearrangements [W. Kirmse and R. Siegfried, *ibid.*, **90**, 6564 (1968)].

(15) Known chemistry of bicyclo[3.1.1]heptane systems indicates no particular difficulty in enolization [*e.g.*, R. Lelande, J. Feugas, and C. Colette, *Compt. Rend.*, **251**, 2972 (1960); J. Meinwald and P. G. Gassman, *J. Amer. Chem. Soc.*, **82**, 5445 (1960)].

(16) Supported by the National Science Foundation and by the Petroleum Research Fund administered by the American Chemical Society. We are grateful to the donors for this financial aid and to David Roodman for technical assistance.

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## Observation and Energy Barrier of Equilibrating 1,2-Dimethoxy-2-norbornyl Cations[1]

*Sir:*

The synthesis of the bridgehead ketol 1-hydroxynorbornan-2-one[2] has made possible the study of the 1,2-dimethoxy-2-norbornyl cation, which is of special interest because of effective skeletal symmetry attainable by carbon bridging or by degeneracy of a classical structure. We report the preparation of ketal **3** and the temperature-dependent nmr of its cation ($3^+$) derived by methoxy loss in $FSO_3H$–$CH_2Cl_2$.[3–6] Parallel studies with the norbornyl ketal **1**[3] and with the 1-methylnorbornyl ketal **2** substantiated the nmr assignments and revealed additional pertinent information. Cation $3^+$ represents the first clear case of a Wagner–Meerwein *degenerate* cation sufficiently stable to permit observations of its "frozen" classical structure and measurement of the barrier for rearrangement to its enantiomer.[7]

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(1) Supported by the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society. We are grateful to the donors for this financial aid.

(2) A. Nickon, T. Nishida, and Y.-i Lin, *J. Amer. Chem. Soc.*, **91**, 6860 (1969).

(3) T. G. Traylor and C. L. Perrin, *ibid.*, **88**, 4934 (1966).

(4) B. G. Ramsay and R. W. Taft, *ibid.*, **88**, 3058 (1966).

(5) (a) H. Hart and D. Tomalia, *Tetrahedron Lett.*, 3383, 3389 (1966); (b) K. Kimroth and P. Heinrich, *Angew. Chem.*, **78**, 714 (1966); (c) S. Kabuss, *ibid.*, **78**, 714 (1966); (d) D. N. Brouwer, E. L. Mackor, and C. MacLean, *Rec. Trav. Chim. Pays-Bas*, **85**, 114 (1966).

(6) (a) M. Brookhart, R. K. Lustgarten, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6354 (1967); (b) M. Brookhart, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1968.

(7) An earlier study with the 1,2-di(*p*-anisyl)-2-norbornyl cation was only partially informative: P. von R. Schleyer, D. C. Kleinfelter, and