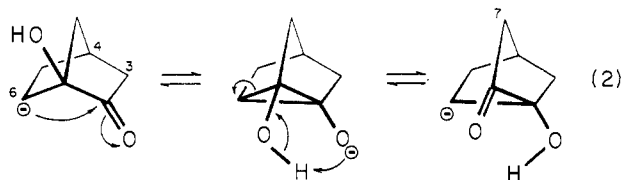


ν 1760, 1720 cm^{-1} ; δ 10.1)⁸ was converted by a modified Curtius sequence⁹ via azide 6 (ν 2140, 1760, 1710 cm^{-1}) to the amino ketone hydrochloride 7 ($\text{C}_7\text{H}_{12}\text{ClNO}$; mp 211 dec; ν (KBr) 1760 cm^{-1}). Deamination (NaNO_2) in acid gave ketol 8: $\text{C}_7\text{H}_{10}\text{O}_2$; mp 146–147° (sealed tube); ν 3520, 1755, 1410 cm^{-1} ; δ 2.5 (bridgehead H) and 2.6 (OH, exchangeable by D_2O), no low-field α -H signal; 2,4-DNP ($\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}_3$) mp 173–175.5°. Independent structure proof was obtained by LiAlH_4 reduction of 8 to a diol mixture,¹⁰ which, when brosylated and solvolized 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 (ν 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 ex-

(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.

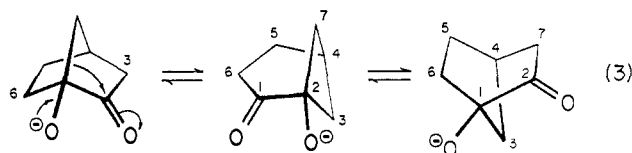
(10) For separate kinetic studies we have separated and characterized the individual *exo* and *endo* diols.

(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

change 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

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 Cations¹

Sir:

The synthesis of the bridgehead ketol 1-hydroxy-norbornan-2-one² 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 $\text{FSO}_3\text{H}-\text{CH}_2\text{Cl}_2$.^{3–6} Parallel studies with the norbornyl ketal 1³ 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

(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).

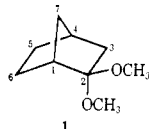
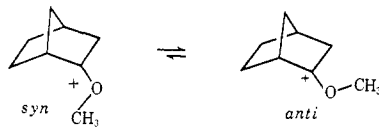
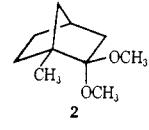
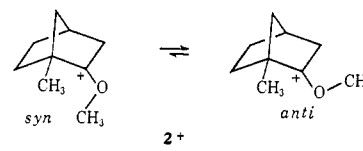
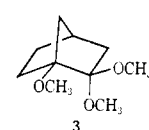
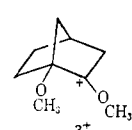
(4) B. G. Ramsay and R. W. Taft, *ibid.*, **88**, 3058 (1966).

(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

Table I. Nmr of Ketals and Derived Cations^a

Room temperature (CCl ₄) ^b				Low temperature (FSO ₃ H-CH ₂ Cl ₂) ^c			
δ	Pattern ^d	Integration	Assignment	δ	Pattern	Integration	Assignment
 1				 1 ⁺			
3.10	s	3 H	endo OCH ₃ ^e	4.71	s	1/5 × 3 H	syn OCH ₃
3.07	s	3 H	exo OCH ₃ ^e	4.65	s	4/5 × 3 H	anti OCH ₃
2.4-2.0	Two b pk	2 H	C-1, C-4	3.74	d ^f	1/5 × 1 H	C-1 syn form
2.0-0.9	m	8 H	C-3, C-5, C-6, C-7	3.50	d ^f	4/5 × 1 H	C-1 anti form
				3.2-1.2	m	9 H	C-3, C-4, C-5, C-6, C-7
 2				 2 ⁺			
3.16	s	3 H	endo OCH ₃ ^e	4.66	s	3 H	anti OCH ₃
3.11	s	3 H	exo OCH ₃ ^e	2.84	b	3 H	C-3, C-4
1.20	s	12 H	C-CH ₃	1.35	s	9 H	C-CH ₃
2.3-0.8	m		Remainder	2.4-1.1	m		C-5, C-6, C-7
 3				 3 ⁺			
3.36	s	3 H	C-1 OCH ₃ ^g	4.90	s	3 H	C-2 OCH ₃ ^h
3.24	s	3 H	endo OCH ₃ ^g	3.77	s	3 H	C-1 OCH ₃ ^h
3.16	s	3 H	exo OCH ₃ ^g	3.06	s, b	3 H	C-3, C-4
2.1-1.1	m	9 H	Remainder	2.8-1.2	m	6 H	C-5, C-6, C-7

^a All chemical shifts (δ) are in ppm downfield from internal TMS. ^b Recorded at 60 MHz. ^c Recorded at 100 MHz at -68° with internal CH₂Cl₂ (δ 5.30) as a standard. ^{db} The spectrum of 1⁺ was essentially unchanged at room temperature, but 2⁺ was not examined. All spectra of cations also showed a methyl singlet at δ 4.10-4.13 (3 H) due to the protonated CH₂OH released. ^d s = singlet, d = doublet, b = broad, pk = peak, m = unresolved multiplets. ^e Assignments are based on those of Traylor³ but are not critical to our work. ^f J (C-1, C-6 *exo*) \sim 5 Hz (cf. D. G. Farnum and G. Mehta, *J. Amer. Chem. Soc.*, **91**, 3256 (1969); P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964)). ^g When the ketal was dissolved at room temperature in methanol-*d*₄ containing a trace of acetic acid the 3.16 peak (*exo* OCH₃) initially decreased at a faster rate than the 3.24 peak (*endo* OCH₃), while the 3.36 peak was least altered of all (cf. ref 3). ^h The methoxyls are probably *anti,anti*, but this point is not critical.

Table II. Nmr of 1,2-Dimethoxy-2-norbornyl Cation in FSO₃H-CH₂Cl₂ at 38.5^o

δ	Pattern	Integration	J , Hz	Assignment	Results of irradiation at *			
					C-4	C-3 + C-7	C-6	C-5
4.35	s	6 H		OCH ₃				
3.10	m	1 H		C-4	*	s	Nil	m ^b
2.76	d	4 H	2.2	C-3, C-7	s, b ^c	*	Nil	Nil
2.37	m	2 H	6.5	C-6	Nil	b	*	s, b ^c
2.02	m	2 H	6.5	C-5	s, b ^d	b	s, b	*

^a Solution prepared from 0.080 ml of ketal **3**, 0.30 ml of CH₂Cl₂, and 0.30 ml of FSO₃H. With time, decomposition gradually sets in. ^b Better resolved than without decoupling. ^c The expected small splittings are unresolved. ^d With higher resolution a pentuplet is expected with $J \sim 2.2$ Hz.

1-Methoxynorbornan-2-one [C₈H₁₂O₂, ν 2838, 1752 cm⁻¹; nmr δ 3.38, (OCH₃)] was synthesized by deamination of 1-aminonorbornan-2-one² in methanol and also by methylation of 1-hydroxynorbornan-2-one² with CH₃I-Ag₂O. The three ketals **1**,³ **2** (C₁₀H₁₈O₂, ν 2865 cm⁻¹), and **3** (C₁₀H₁₈O₃, ν 2838 cm⁻¹) were prepared from their parent ketones,³ and the nmr of their corre-

H. G. Richey, Jr., *J. Amer. Chem. Soc.*, **85**, 479 (1963); for norbornyl nmr studies see: G. A. Olah and A. M. White, *ibid.*, **91**, 3954, 3956 (1969).

sponding cations (**1**⁺, **2**⁺, **3**⁺) were observed by extraction of CH₂Cl₂ solutions into FSO₃H at -68° . The data are summarized in Table I.

The 2-methoxy-2-norbornyl cation (**1**⁺) showed two singlet methoxyl resonances in a 1:4 ratio, whose mean position (δ 4.68) is 1.6 ppm downfield ($\Delta\delta$) relative to the mean methoxyl position (δ 3.08) in the covalent precursor **1**. Such shifts are typical for methoxyls at-

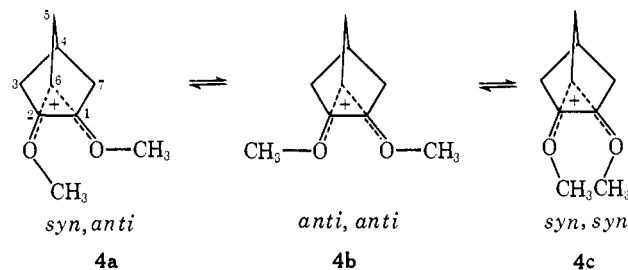
(8) L. Claisen, *Ber.*, **26**, 2729 (1893); *Ann.*, **297**, 76 (1897).

tached to cationic centers and reveal that C-2 is essentially trigonally hybridized.^{4,5,6} The small separation (0.06 ppm) in the two methoxyl peaks in **1**⁺ indicates existence of *syn* and *anti* forms due to restricted rotation about the C–O bond or to restricted oxygen inversion. This interpretation is confirmed by the existence of two signals for the C-1 proton in the same ratio, 1:4. The *anti* structure appears less congested and is assigned to the predominant form. Cation **2**⁺ shows only one methoxyl peak, which is very likely the *anti* form because of hindrance by the CH₃ group at C-1.⁹

In the conversion of **2** → **2**⁺ the large shift ($\Delta\delta = 1.53$) in the C-2 methoxyl and the small shift ($\Delta\delta = 0.15$) in the C-1 methyl resonances are in accord with the classical formulation for **2**⁺ in which C-2 is essentially sp² while C-1 is sp³ hybridized.

The nmr of the 1,2-dimethoxy-2-norbornyl cation (**3**⁺) showed temperature dependence. The spectrum at –68° (Table I) persisted until ca. –15° at which stage line broadening began and at 7°, among other changes, the two methoxyl signals coalesced. Importantly, the original spectrum was regenerated when the temperature was lowered to –60°. At coalescence (7°) the first-order rate constant⁴ for exchange of the OCH₃ magnetic environment is 251 sec⁻¹, and $\Delta G^\ddagger = 13.2$ kcal/mol. Table II shows that at 38.5° the spectrum of cation **3**⁺ is completely averaged. The signals fall into five distinct groups whose assignments are supported by the decoupling results. As expected, the single methoxyl peak (δ 4.35) is at the mean position (δ 4.33) of the two methoxyl signals in the low-temperature spectrum.

That **3**⁺ does not possess a carbon-bridged structure **4** which could exist in three distinct geometric forms (**4a–c**) is clear from the following considerations, among others. (i) Substrates **1** and **2** (Table I) as well as others



in the literature^{6b} reveal that a methoxyl signal moves downfield ($\Delta\delta$) by ca. 1.5–1.6 ppm when a ketal is converted to a tertiary cation by OCH₃ loss.¹⁰ For **3** → **3**⁺ $\Delta\delta$ is 1.70 for the C-2 methoxyl and 0.41 for the C-1 methoxyl. Clearly, the cation has one oxygen attached to a trigonal cationic center while the other remains bound to an sp³ carbon which is only slightly perturbed electronically. (ii) The large separation (1.13 ppm) between the two methoxyl peaks in **3**⁺ (Table I) is not understandable in terms of *syn,anti* differences (**4a–c**).¹¹ (iii) Symmetry requires that for the nonclassical structure to show two *equal intensity* methoxyl peaks, **4b** and

(9) Alternatively, a very low *syn,anti* barrier could produce a single "averaged" methoxyl peak but this possibility is ruled out by the results with **1**⁺ and by published data on barriers of this sort.^{6b}

(10) We have also examined camphor dimethyl ketal and found $\Delta\delta = 1.58$.

(11) Compare **1**⁺. Also in other known *syn,anti* situations (e.g., R–C⁺–(OCH₃)₂; R = CH₃ or OH) the two methoxyls are less than 0.3 ppm from each other.^{4,6b}

4c would have to contribute equally or not at all to the low-temperature conformational population, a situation that is hardly likely.

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Do Aromatic Pinacols Oxidize at a Mercury Electrode?

Sir:

Michielli and Elving¹ recently put in doubt the reality of the anodic oxidation of benzpinacol previously described by us.^{2,3} They report under the heading "Reputed Benzpinacol Oxidation"¹ an unsuccessful attempt to reproduce the anodic polarographic wave of benzpinacol in alkaline aqueous ethanol solutions.

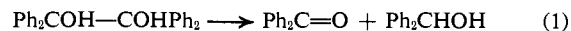
Nevertheless, our conclusion on the anodic oxidation of benzpinacol is well founded experimentally. We have examined not only benzpinacol but also fluorenopinacol, xanthopinacol, and 4-chlorobenzpinacol, which behave quite analogously.^{4–6} Anodic oxidation in alkaline or neutral solutions seems to be a general property of aromatic pinacols.

We have prepared the pinacols by several methods: controlled-potential electrolysis, photoreduction, or chemical reduction of ketones. The compounds were thoroughly purified and checked as to their identity and purity before use.

The anodic oxidation follows quantitatively the kinetics of a slow electron-transfer reaction with pinacol monoanion as a depolarizer. Oxidation proceeds with a C–C bond rupture, to ketone as a product. The electron-transfer step is preceded by a protolytic dissociation of a pinacol to its monoanion. The rate of this proton-transfer step determines the oxidation current near pH 7.

The oxidation wave is proportional to the pinacol concentration. This wave was quantitatively interpreted in terms of the kinetics and thermodynamics of dimerization of ketyl free radicals,^{5,6} and the values obtained were confirmed independently. In the course of dimerization, or at varying pH of the solution, the pinacol oxidation wave appears at the cost of the anodic wave of ketyl free radicals.

In alkaline solutions pinacols undergo dismutation, e.g., eq 1. In the course of reaction 1 the anodic



pinacol wave slowly disappears (its kinetics were quantitatively studied),⁶ while the current of the first cathodic wave of ketone increases about 1:2 with respect to the decrease of the anodic wave (see Figure 1).

(1) R. F. Michielli and P. J. Elving, *J. Am. Chem. Soc.*, **90**, 1989 (1968).

(2) W. Kemula, Z. R. Grabowski, and M. K. Kalinowski, *Collection Czech. Chem. Commun.*, **25**, 3306 (1960).

(3) W. Kemula, Z. R. Grabowski, and M. K. Kalinowski, *Naturwissenschaften*, **47**, 514 (1960).

(4) Z. R. Grabowski and M. K. Kalinowski, The Fifth International Symposium on Free Radicals, Almqvist & Wicksell, Publishers, Stockholm, 1961, paper 22.

(5) M. K. Kalinowski, Z. R. Grabowski, and B. Pakula, *Trans. Faraday Soc.*, **62**, 918 (1966).

(6) M. K. Kalinowski and Z. R. Grabowski, *ibid.*, **62**, 926 (1966).