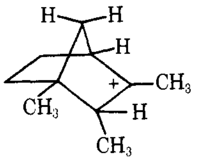
Table I. Nmr Chemical-Shift Positions[a] of the Carbonium Ions

Ion	Description
I and II	At −95°, 5.26 (d, J = 7 Hz), 5.34 (d, J = 7 Hz), the C-1 protons of the two ions; 6.12 and 6.34 (broad), the C-6 exo protons; 6.59, the C-2 methyl protons of both isomers; 6.79, probably the C-3 protons; 8.69 and 8.94, the nonequivalent *gem*-dimethyl groups of one isomer and 8.69 and 8.87, these same groups in the other isomer
IIIa ⇄ IIIb	At −40°,[b] 6.945, C-6 exo proton of IIIa (C-6 endo of IIIb); 7.300, probably C-4 proton; 7.49 (from decoupling experiments), C-3 proton of IIIa (C-7 of IIIb); 7.695, C-2 methyl protons of IIIa (C-1 of IIIb); 7.795, C-1 methyl protons of IIIa (C-2 of IIIb); 8.480 (d, J = 6.0 Hz), C-3 methyl protons of IIIa (C-7 of IIIb); 8.1–8.4, C-5 exo and endo protons[c]
IIIc ⇄ IIId	At −40°,[b] 7.655, C-1 methyl group of IIIc (C-2 of IIId); 7.97, C-2 methyl group of isomer IIIc (C-1 of isomer IIId); 7.55 (from decoupling experiments), C-3 proton of IIIc (C-7 of IIId); 8.95 (d, J = 7.2 Hz), C-3 methyl protons of IIIc (C-7 of IIId)[c]
IV	7.00 (very broad), averaged C-6 exo and endo protons; an AB pair centered at 7.51 and 7.72 (J = 15.0 Hz), the averaged C-3 exo-C-7 syn and C-3 endo-C-7 anti protons; 7.612, averaged C-1 and C-2 methyl protons; 8.415 (t, J = 6.0 Hz), this coupling with C-6 protons confirmed by double irradiation, the averaged C-5 exo and endo protons; 8.556, the C-4 methyl protons
V	2.36, C-2 proton; 6.82 (t, J = 6.0 Hz), the methylene protons at C-4 and C-6; 7.14, C-1 methyl protons; 7.68 (q, J = 6.0 Hz), the C-5 protons; 8.595 (d, J = 7 Hz), the isopropyl methyl protons[c]

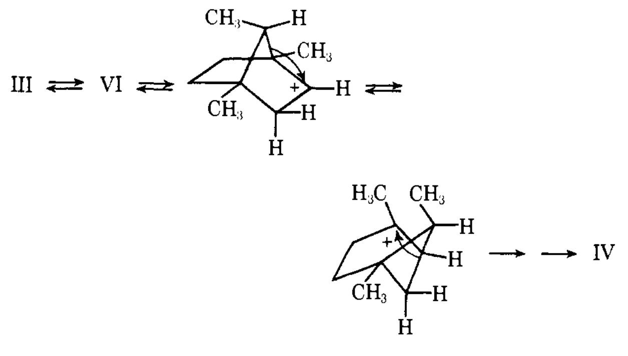
[a] In τ (parts per million) relative to internal tetramethylammonium cation; τ 6.90 in this and the following paper. [b] The chemical shifts are very temperature dependent, showing that the proportions of IIIa and IIIb or IIIc and IIId are changing with temperature. This is, of course, expected if the equilibrium constants are something other than unity. [c] Only peaks which could be assigned with reasonable certainty are included in the table. There are, in addition, broad absorptions in the regions expected for the protons not included in the table.

10) and ions such as III exist predominantly in the forms indicated, in spite of the easy accessibility of cation VI.



VI

The order in which the ions appear in the rearrangements is not an indication of sequential reactions since each step is certainly reversible. We believe, for example, that ion V is actually derived from I. The mechanism of the ion III → IV rearrangement is the only one not reasonably obvious and may involve a bicyclo[3.1.1]heptyl cation intermediate.



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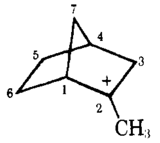
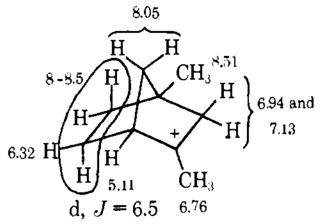
Observable Degenerate Rearrangements in 2-Methyl-2-norbornyl and Related Cations

Sir:

The 2-methyl-2-norbornyl cation I and 2,4-dimethyl-2-norbornyl cation II, in acidic solvents,[1] show



I



II

nmr spectra at −80° appropriate for the static structures, but, at higher temperatures, line broadening is readily apparent. The results are complementary. In I, the C-1 proton doublet broadens above −80°[2] and the high-field peaks for the C-5, C-6-endo, and C-7 protons also broaden in a nondescript manner. The C-2 methyl peak remains unchanged and the C-6-exo peak becomes *less* broad. Beyond the coalescence temperature, the high-field region resembles an AB quartet and a coalesced peak (τ 6.71) develops under the C-2 methyl group (confirmed using 2-CD_3 derivative). Double irradiation spin saturation transfer (DISST) experiments[6,7] show that the C-1 proton is exchanging with a complex peak centered at *ca.* τ 8.30, assigned to the C-6-endo proton.

Cation II was prepared from 1,4-dimethyl-2-*endo*-norbornanol and is unreported. As the temperature is raised, the C-1 proton peak broadens but *both* methyl peaks *and* the C-6-exo proton peak remain nearly unchanged. The C-3-exo and endo proton peaks coalesce. DISST experiments at temperatures (−60°) where line broadening is just observable, in the region

(1) For example, FSO_3H, FSO_3H–SO_2ClF, SbF_5–SO_2, FSO_3H–SbF_5. The rearrangement rates are virtually identical.

(2) The spectrum of I at −95° has been published by Olah, *et al.*[3,4] Their assignments were based on the earlier work of Farnum and Mehta[5] on the 2-phenyl analog. Our results show that the C-6-endo and a C-5 proton assignment should be interchanged. Olah, *et al.*, have referred vaguely to nmr line broadening for I but the results described, particularly in the later paper, are quite contrary to our own.

(3) G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3958 (1969).

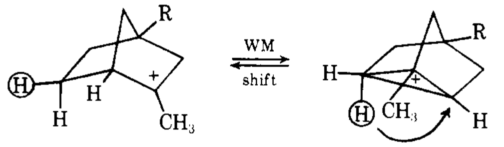
(4) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970).

(5) D. G. Farnum and G. Mehta, *ibid.*, **91**, 3256 (1969).

(6) S. Forsén and R. A. Hoffman, *J. Chem. Phys.*, **39**, 2892 (1963).

(7) F. A. L. Anet and A. J. R. Bourns, *J. Amer. Chem. Soc.*, **89**, 760 (1967).

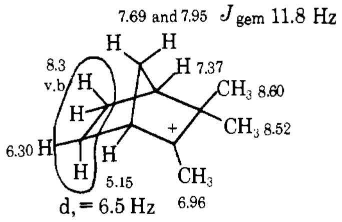
expected for the C-6-endo proton (τ 8.30), result in a marked decrease in the C-1 proton area and *vice versa.* At the same temperature, irradiation of the C-6-exo proton simply decouples the C-1 proton doublet. A summary is provided by the following: (1) groups on C-2, C-4, and C-6-exo remain essentially unchanged except for averaging of coupling effects; (2) C-3-exo and endo interchange; (3) C-5-exo and endo interchange with C-7-syn and anti (the 2(AB) peak in I showing an averaged J_{gem} coupling constant of 11.5 Hz); (4) C-1 and C-6-endo interchange. These results are due to a symmetrization which in traditional terms would be explained by a Wagner–Meerwein shift in I or II, followed by a stereospecific endo-6,2-hydride shift (as expected[8,9]) in the intermediate[10] (6-exo in I or II) and then the reverse WM shift (abbreviated WM-6,2-WM shift).



I or II, R = H or CH_3

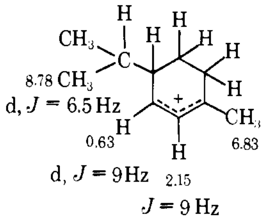
The rate of the degenerate rearrangement in I was measured both by following the initial broadening of the C-1 doublet and comparing to computer calculated curves (at $-53.3°$, $k = 100$ sec^{-1}, $\Delta F^{\ddagger} = 11.1$ kcal/mol, $\Delta H^{\ddagger} = 10.9 \pm 2$ kcal/mol) and by using the DISST technique (at $-87.0°$, $k = 1$ sec^{-1}, *cf.* value of 0.85 sec^{-1} calculated from the line broadening). The rate for II is slightly slower. Ion I is reasonably stable to 30°[15] but ion II rearranges at $-19°$ to the 1,2-dimethyl-2-norbornyl cation[16] ($k = 1.2 \pm 0.2 \times 10^{-4}$ sec^{-1}, $\Delta F^{\ddagger} = 18.9$ kcal/mol).

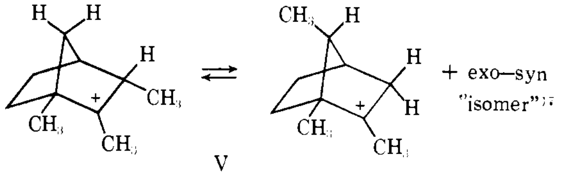
This WM-6,2-WM process has been directly observed in three other systems, the α-fenchyl–β-fenchyl cation interconversion,[17] the *exo*-2,3-dimethyl-*endo*-2,3-dimethyl-2-norbornyl cation interconversion (these ions also rearrange at *ca.* $-20°$ to the 1,2-dimethyl-2-norbornyl cation), and in the *tert*-camphenehydro cation. At $-120°$, the solution obtained by adding camphene or tricyclene to 4:1 SO_2ClF–FSO_3H shows an nmr spectrum of the static structure III.



III

As the temperature is raised, all peaks except one methyl group and an AB pair broaden. The rate of this process was calculated from the broadening of the lower field methyl peak (comparison with computer calculated curves, at $-104.2°$, $k = 59.2$ sec^{-1}, $\Delta H^{\ddagger} = 7.8 \pm 0.3$ kcal/mol, $\Delta F^{\ddagger} = 8.3$ kcal/mol, $\Delta S^{\ddagger} = 1.5$–$4.5$ eu). At still higher temperatures, the remaining sharp methyl peak broadens. However, before this coalescence temperature is reached, a rearrangement of ion III into ion IV (38%) and ion V (62%) occurs; rate constant for the disappearance of III, $9.8 \pm 0.2 \times 10^{-4}$ sec^{-1} at $-30.0°$ ($\Delta F^{\ddagger} = 17.5$ kcal/mol). Ion IV is formed from many terpenes, on addition to FSO_3H, *e.g.*, α-terpineol, β-pinene, sabinene, etc. The two-methyl exchange is due to an exo-3,2-methyl shift, from classic experiments on the racemization of camphene.[18,19] The slower three-methyl exchange could most reasonably be either an endo-3,2 shift or the WM-6,2-WM process.[18,19] These processes can be nicely distinguished by the DISST technique; thus, irradiation of the averaged C-5-endo–C-6-endo protons signal causes the almost complete loss of the averaged C-1–C-4 protons signal. A quantitative treatment is difficult but a minimum estimate of the C-1–C-4, C-5-endo-C-6-endo exchange (which must be the WM-6,2-WM shift) is 2–5 sec^{-1} at $-65°$ ($\Delta F^{\ddagger} = 11.5$–$12$ kcal/mol). Using the observed three-methyl exchange broadening, the rate constant for this process was 31.4 sec^{-1} at $-64.1°$ ($\Delta H^{\ddagger} = 8.0 \pm 0.2$ kcal/mol, $\Delta F^{\ddagger} = 10.7$ kcal/mol, $\Delta S^{\ddagger} = -13 \pm 2$ eu). The agreement is tolerable and we believe that the three-methyl exchange and the WM-6,2-WM process are the same. The exo-





V

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(8) J. A. Berson and P. W. Grubb, *J. Amer. Chem. Soc.*, 87, 4016 (1965).

(9) B. M. Benjamin and C. J. Collins, *ibid.*, 88, 1556 (1966).

(10) Elegant work of Olah, *et al.*,[4] has shown the 2-norbornyl cation to be corner-protonated nortricyclene, which undergoes an extremely rapid 6,2-hydride shift. We see no conceptual difficulty in picturing an intermediate in the WM-6,2-WM process as a methyl-substituted analog which likewise undergoes rapid 6,2-hydride shifts, probably *via* an edge-protonated transition state. If the first step is an equilibrium, then one can estimate the value (1×10^{-3}, $\Delta F = 4.1$ kcal/mol at 25°) using Olah's rate for the unsubstituted ion (this assumes the methyl group will not affect this rate significantly). One can also compare $\Delta F^{\ddagger}$, 5.9[4] and 11.5 kcal/mol for the two 6,2-hydride shifts. If the transition states are similar (*e.g.*, edge-protonated, above assumption) then the difference (5.6 kcal mol) is the added stabilization due to the 2-methyl substituent in I or II. This value is less than half the classical secondary–tertiary cation difference[11–13] and implies a stability of the bridged *vs.* classical secondary norbornyl cation, *ca.* 6–8 kcal/mol (*cf.* comparable estimates of >5.8 and 8–9.[4,14]

(11) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, 90, 2436 (1968).

(12) D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, 87, 210 (1968).

(13) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 92, 2540 (1970).

(14) H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, 89, 74 (1970).

(15) Above 0°, further broadening occurs. The high-field AB quartet peaks broaden as do the C-3–C-4 protons peak. DISST experiments show that proton exchange is occurring between these groups.

(16) G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *J. Amer. Chem. Soc.*, 93, 1442 (1971).

(17) See part I of this series: E. Huang, K. Ranganayakulu, and T. S. Sorensen, *ibid.*, 94, 1779 (1972).

(18) J. D. Roberts and J. A. Yancey, *ibid.*, 75, 3165 (1953).

(19) W. R. Vaughan and R. Perry, Jr., *ibid.*, 75, 3168 (1953).

3,2 shift in III is considerably faster than the WM-6,2-WM rearrangement (*cf.* ref 18 and 19).

The $\Delta F^{\pm}$ values (kcal/mol) for the WM-6,2-WM processes are: I, 11.1; II, *ca.* 11.1; 2,7,7-trimethyl-2,5,5-trimethyl-2-norbornyl, *ca.* 11.2; and III, 10.7. This rearrangement is therefore not sensitive to extra methyl substitution. The rapidity of the WM rearrangement allows one to understand more clearly why camphene hydrochloride can *rapidly* rearrange to the thermodynamically more stable isobornyl chloride, a reaction of immense historical importance.[20]

Acknowledgment. The authors wish to thank the National Research Council of Canada for generous financial support.

(20) H. C. Brown, *Chem. Eng. News*, 87 (Feb 13, 1967).

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An Electron Spin Resonance Study of Dialkoxyphosphonyl Radicals, $(RO)_2\dot{P}O$

Sir:

Dialkoxyphosphonyl radicals **2** are recognized to be intermediates in some reactions of dialkyl phosphonates (dialkyl phosphites, **1**),[1] but the esr spectra of the radicals in solution have never been observed. We report here an esr study of the formation and reactions of these radicals, which have been derived from two different sources.

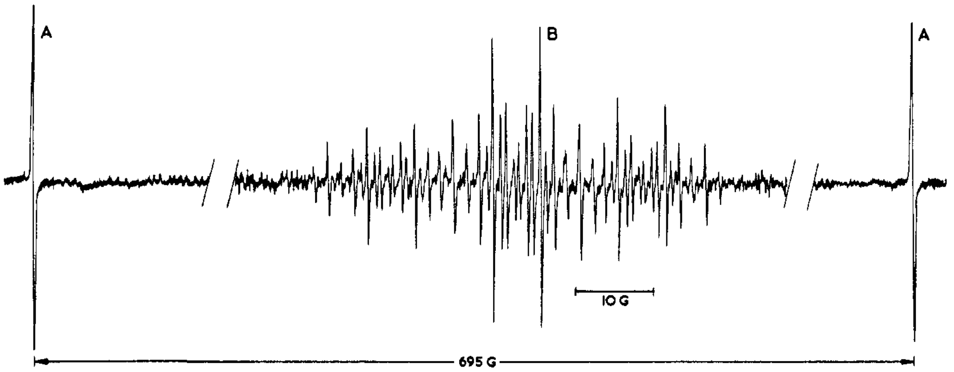

Figure 1. Esr spectrum (at 9.158 GHz) of the diethoxyphosphonyl radical (A), which is replaced by the spectrum of the benzyl radical (B) when benzyl bromide is added to the reaction system.

If di-*tert*-butyl peroxide is photolyzed in an esr cavity[2] in the presence of a dialkyl phosphonate (**1**; R^1 = Me, Et, *i*-Pr, or *n*-Bu, 10–20% (v/v) in peroxide as solvent), alkoxyl radicals abstract the hydrogen which is bonded to phosphorus, and the doublet spectra of the corresponding phosphonyl radicals, **2**, are observed (Figure 1).[3]

$$\textit{tert}\text{-BuOO-}\textit{tert}\text{-Bu} \xrightarrow{h\nu} 2\textit{tert}\text{-BuO}\cdot \qquad (1)$$

$$\textit{tert}\text{-BuO}\cdot + \underset{\mathbf{1}}{(R^1O)_2P(O)H} \longrightarrow \textit{tert}\text{-BuOH} + \underset{\mathbf{2}}{(R^1O)_2\dot{P}O} \qquad (2)$$

The identical but more intense spectrum of the diethoxyphosphonyl radical was also obtained when di-*tert*-butyl peroxide was photolyzed in the presence of tetraethyl pyrophosphite (**3**). This represents a novel bimolecular homolytic substitution[6] reaction at a phosphorus center (eq 3). In contrast to the reaction

$$\begin{array}{l} \textit{tert}\text{-BuO}\cdot + \underset{\mathbf{3}}{(EtO)_2POP(OEt)_2} \longrightarrow \\ \quad \textit{tert}\text{-BuOP(OEt)}_2 + O\dot{P}(OEt)_2 \\ \quad \Big\downarrow \textit{tert}\text{-BuO}\cdot \\ \quad \underset{\mathbf{4}}{(\textit{tert}\text{-BuO})_2\dot{P}(OEt)_2} \longrightarrow \textit{tert}\text{-Bu}\cdot + OP(OEt)_2(O\text{-}\textit{tert}\text{-Bu}) \end{array} \qquad (3)$$

of *tert*-butoxyl radicals with trialkyl phosphites,[7] no phosphoranyl radical derived from the pyrophosphite could be detected, but, on prolonged photolysis, the spectrum of the phosphoranyl radical **4** ($a(^{31}P)$ = 892 G) derived from *tert*-butyl diethyl phosphite, and of the *tert*-butyl radical which is formed from **4** by β scission,[7] were apparent.

g values and ^{31}P hyperfine splitting constants for the phosphonyl radicals between −10 and −50°, cal-

Table I. Esr Spectra of Dialkoxyphosphonyl Radicals

	g^a	$a(^{31}P)$, G^a
$(MeO)_2\dot{P}O^b$	2.004	700
$(EtO)_2\dot{P}O$	2.005	687
$(i\text{-PrO})_2\dot{P}O$	2.004	685
$(n\text{-BuO})_2\dot{P}O$	2.005	688

[a] g values ±0.001; hyperfine splitting, ±1.0 G. [b] Dichloromethane was added to maintain one liquid phase.

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(1) J. I. G. Cadogan, *Advan. Free Radical Chem.*, 2, 203 (1967); C. Walling and M. S. Pearson, *Top. Phosphorus Chem.*, 3, 1 (1966).

(2) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. B*, 1823 (1971).

(3) When hydroxyl radicals, generated from the Ti^{III}–H_2O_2 couple, were caused to react with dialkyl phosphonates in an aqueous flow system the only radicals detected were those formed by abstraction of hydrogen from the alkoxy groups.[4,5] The spectra obtained under our conditions indicate that abstraction of hydrogen from the alkoxy groups was much slower than abstraction of the hydrogen bound to phosphorus.

(4) E. A. C. Lucken, *J. Chem. Soc. A*, 1354 (1966).

(5) A. R. Metcalfe and W. A. Waters, *ibid.*, *B*, 340 (1967).

(6) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971; A. G. Davies and B. P. Roberts, *Nature Phys. Sci.*, 229, 221 (1971).

(7) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed. Engl.*, 10, 738 (1971).