The phosphoranylperoxy radicals appear to exist in equilibrium with a diamagnetic dimer in this temperature range since a sudden increase in temperature from −100 to −60° during the course of a decay (in the dark) produces a temporary increase in the radical concentration. By analogy with the behavior of tertiary alkylperoxy radicals[13–15] it seems likely that this dimer is a tetroxide.

$$2\textit{tert}\text{-BuO(R'O)}_3\text{POO}\cdot \rightleftharpoons \textit{tert}\text{-BuO(R'O)}_3\text{POOOOP(OR')}_3\text{O-}\textit{tert}\text{-Bu} \quad (12)$$

At temperatures from −45 to −70° the phosphoranylperoxy radicals decay with first-order kinetics. The measured rate constants depend slightly on the phosphite concentration. Thus, a tenfold increase in phosphite almost doubled the first-order decay constant. With initial phosphite concentrations of 0.3 *M* the rate constants at −50, −60, and −70° were 2.6, 1.5, and 0.9 sec^{-1} for R′ = Me; 0.9, 0.4, and 0.2 sec^{-1} for R′ = Et; and 2.3, 0.8, and 0.2 sec^{-1} for R′ = *i*-Pr. The differences in rate constants between the three radicals are not significant, particularly as it is uncertain which process is being measured under conditions where a chain reaction is certainly occurring. Quite probably the rate-controlling step for chain termination involves some cross reaction such as

$$\text{RO(R'O)}_3\text{POO}\cdot + \text{RO}\dot{\text{P}}\text{(OR')}_3 \longrightarrow \text{RO(R'O)}_3\text{POOP(OR')}_3\text{OR} \quad (13)$$

so that the peroxy radicals decay with first-order kinetics. At lower temperatures the rate of attack of the phosphoranylperoxy radical on phosphite (reaction 8) will be reduced. In consequence, the concentration of phosphoranylperoxy radicals relative to that of the other radicals in the system will rise and hence the bimolecular self-reaction 11 will predominate.

(13) P. D. Bartlett and G. Guaraldi, *J. Amer. Chem. Soc.*, **89**, 4799 (1967).

(14) K. Adamic, J. A. Howard, and K. U. Ingold, *Chem. Commun.*, 505 (1969); *Can. J. Chem.*, 47, 3803 (1969).

(15) J. E. Bennett, D. M. Brown, and B. Mile, *Chem. Commun.*, 504 (1969).

(16) NRCC Postdoctoral Fellow, 1970–1972.

G. B. Watts,[16] K. U. Ingold*
Division of Chemistry, National Research Council of Canada
Ottawa, Canada

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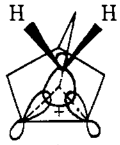
Electron Spectroscopy of Organic Ions. II.[1a] Carbon 1s Electron Binding Energies of the Norbornyl, 2-Methylnorbornyl, and Related Cations. Differentiation between "Nonclassical" Carbonium and "Classical" Carbenium Ions[1b]

Sir:

We have recently demonstrated in the case of the *tert*-butyl cation that in going from a neutral hydrocarbon to the corresponding trivalent carbocation (carbenium ion), intensive positive charge localization on the electron-deficient carbenium center increases the 1s electron binding energy of that atom by *ca.* 5 eV.[1,2] The less-affected methyl carbon atoms experience an increase of only 1.5 eV or less. Extensive charge delocalization, as in the trityl and tropylium cations, results only in a small and relatively uniform increase of the 1s orbital energy of all the carbon atoms which share the formal positive charge. Separate peaks cannot, therefore, be observed.

Since in electron spectroscopy the time scale of the measured ionization processes is on the order of 10^{-16} sec, definite ionic species are characterized, regardless of their possible intra- and intermolecular interactions (*e.g.*, Wagner–Meerwein rearrangements, hydride shifts, proton exchange, etc.). Thus, electron spectroscopy can give an unequivocal, direct answer to the long debated question of the "classical" or "nonclassical" nature of the norbornyl cation, independent of any possible equilibration process.

We wish to report new evidence for the nonclassical carbonium ion nature of the norbornyl cation **1**, as given by the electron spectroscopic study of this ion, compared to a series of related model ions with varying degrees of charge localization. These model ions are the cyclopentyl **2**, methylcyclopentyl **3**, and 2-methylnorbornyl **4** cations as well as the previously studied *tert*-butyl cation (see Table I). The carbon 1s electron spectra have been measured under similar conditions to those reported for the *tert*-butyl cation.[1a] However, we found that AsF_3 is, in many cases, a preferred solvent which, due to its higher freezing point, diminishes the probability of water condensation and ice formation on the surface of the samples. Thus, the probability of quenching of the ions in the surface layer during the measurement is greatly reduced. The carbon 1s spectrum of the cyclopentyl **2** and methylcyclopentyl **3** cations clearly exhibits two distinct carbon 1s electron lines with relative separations of electron binding energy ($\text{d}E_\text{b}$) values of 4.3 ± 0.5 and 4.2 ± 0.2 eV and approximate intensity ratios of 1:4 and 1:5, respectively.[3] These separations are characteristic of cationic species with intensive charge localization (*cf.* the relative chemical shift of 3.9 eV in *tert*-butyl cation[1a,2]). The 2-methylnorbornyl cation **4** (Figure 1, upper trace) shows a



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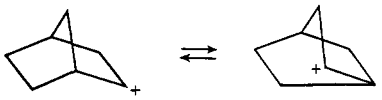
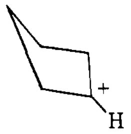


1a **1b**



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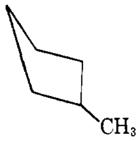

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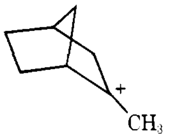

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(1) (a) Part I: G. A. Olah, G. D. Mateescu, L. A. Wilson, and M. H. Gross, *J. Amer. Chem. Soc.*, **92**, 7231 (1970). (b) For the definition of carbocations differentiating trivalent *carbenium ions* from penta- or tetracoordinated *carbonium ions* see G. A. Olah, *ibid.*, **94**, 808 (1972).

(2) Corrected value in reference to methane. Spectrum measured in a frozen solution of $\text{(CH}_3\text{)}_3\text{C}^+\text{SbF}_6^-$ in AsF_3.

(3) The lower binding energy lines corresponding to four and five carbon atoms, respectively, are somewhat broadened, without showing any possibility of estimating the relative carbon 1s E_b values of these atoms.

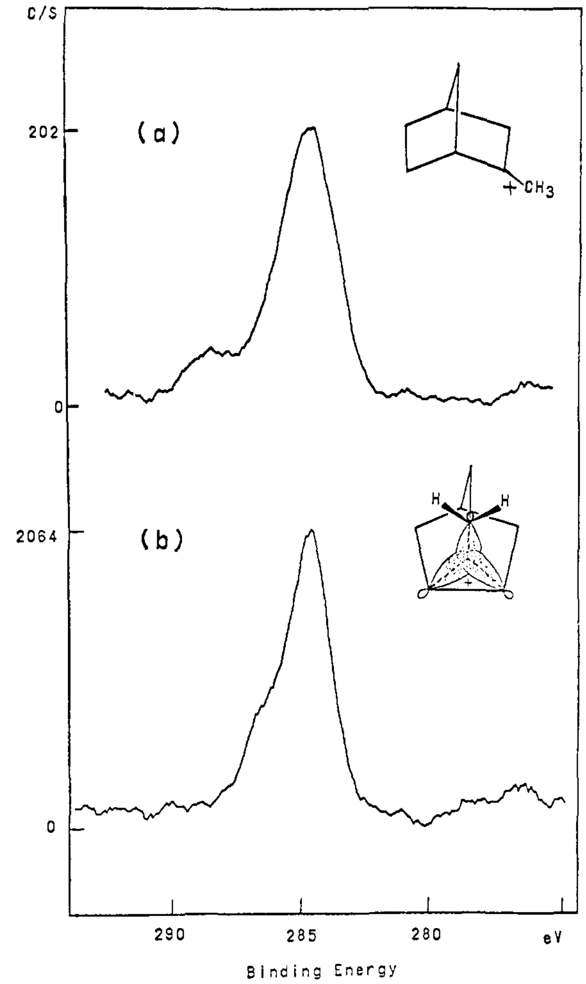
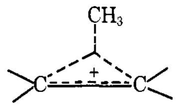


Figure 1. Carbon 1s electron spectrum of norbornyl cation **1** (lower trace) and 2-methylnorbornyl cation **4** (upper trace).

smaller separation of 3.7 eV (with an intensity ratio of ~1:7) which indicates that in spite of the stabilizing effect of the methyl group, there is some σ delocalization in the bicyclo[2.2.1]heptyl system.

An essentially different carbon 1s electron spectrum is obtained for the parent norbornyl cation **1** (Figure 1, lower trace). There is a single broad line with a pronounced shoulder on the higher binding energy side (corresponding to C_2 and C_6). A curve resolver analysis gave an approximate intensity ratio of 2:5 and a maximum separation of 1.7 eV. These results clearly suggest that the ion **1** is of "nonclassical" carbonium ion nature since no high-binding energy line characteristic of a carbenium center is found. An equilibrating classical structure **1a** $\rightleftarrows$ **1b** should give an electron spectrum identical with a static "classical" carbenium ion, even under conditions of extremely rapid equilibration. For example, the rapidly equilibrating, degenerate cyclopentyl cation clearly shows the carbenium center line separated from the methylene carbons. The results obtained for the norbornyl cation are in excellent agreement with reported carbon-13 and proton magnetic resonance, as well as Raman spectroscopy data on the long-lived norbornyl cation, which all strongly support the methylene-bridged pentacoordinated carbonium ion or "nonclassical" nature of the norbornyl cation.[4]

Moreover, *ab initio* calculations[5] on model $C_3H_7^+$ ions show that in structure **6** the difference in carbon 1s



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electron binding energy between the bridged methyl and adjacent methylene groups is *ca.* 1.1 eV. This value is consistent with our experimental results.

Table I. Binding Energy Differences of Carbocation Centers from Neighboring Carbon Atoms (dE_{b^+C-C})

Ion	dE_{b^+C-C}	Approximate rel C^+/C intensity
$(CH_3)_3C^+$	3.9 ± 0.2	1/3
5		
3	4.2 ± 0.2	1/5
4	3.7 ± 0.2	1/7
2	4.3 ± 0.5	1/4
1	1.7 ± 0.2	2/5

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(4) (a) G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3958 (1969), and references cited therein. (b) For a correlation between nmr and electron spectroscopy, see G. D. Mateescu, Abstracts, Papers of the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 1972, No. 237; G. D. Mateescu and J. L. Riemenschneider, Abstracts of Papers, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, No. ORGN-115.

(5) We thank Professor J. Pople, Dr. L. Radom, and Professor P. v. R. Schleyer for communicating their results prior to publication.

(6) NIH postdoctoral fellow.

George A. Olah,* Gheorghe D. Mateescu
J. Louise Riemenschneider[6]
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

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Anomerization of Glycosyl Azides in a Two-Step 1,3-Dipolar Cycloaddition Reaction

Sir:

We wish to report the first instance in which a substituted azide has been demonstrated to undergo a two-step 1,3-dipolar cycloaddition. The synthesis of *vic*-triazoles by an azide cycloaddition to cyanoacetamide has been known for many years.[1-3] The mechanism of these 1,3-dipolar cycloaddition reactions has, however, remained obscure. Recent investigations in our laboratory of an unusual rearrangement of glycosyl azides have provided evidence to clarify the cycloaddition mechanism of substituted azides with 2-substituted acetonitrile derivatives.

The preparation[4] of 2,3,5-tri-*O*-benzyl-β-D-arabino-

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(1) O. Dimroth, *Ber.*, **35**, 1029 (1902).

(2) J. R. E. Hoover and A. R. Day, *J. Amer. Chem. Soc.*, **78**, 5832 (1956).

(3) A. Dornow and J. Helberg, *Chem. Ber.*, **93**, 2001 (1960).

(4) All new compounds reported gave elemental analyses consistent with assigned structures; the complete physical, spectral, and optical properties will be reported in the full paper.