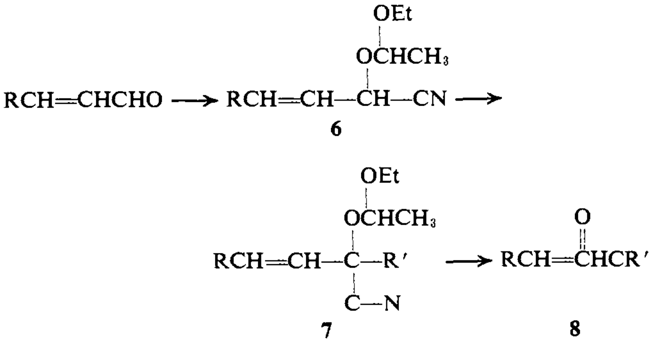
also be used. The protected cyanohydrin[5] from hexanal (3, R = *n*-pentyl) thus gave, with butyl bromide, 70% of **4** (R = *n*-pentyl; R′ = butyl, bp 87–90° (0.05 mm)) hydrolyzed essentially quantitatively, as usual, to 5-decanone (**5**, R = *n*-pentyl; R′ = butyl).[6]

A particularly interesting case is that of the synthesis starting with α,β-unsaturated aldehydes. The sequence then leads to α,β-unsaturated ketones.



$$\mathrm{RCH{=}CHCHO} \longrightarrow \underset{\mathbf{6}}{\mathrm{RCH{=}CH{-}\overset{\begin{array}{c}OEt\\|\\OCHCH_3\\|\end{array}}{C}H{-}CN}} \longrightarrow$$

$$\underset{\mathbf{7}}{\mathrm{RCH{=}CH{-}\underset{\begin{array}{c}|\\C{-}N\end{array}}{\overset{\begin{array}{c}OEt\\|\\OCHCH_3\\|\end{array}}{C}}{-}R'}} \longrightarrow \underset{\mathbf{8}}{\mathrm{RCH{=}CH\overset{\overset{O}{\|}}{C}R'}}$$

Terminal vinyl ketones can thus be made from the readily available acrolein cyanohydrin.[7] Alkylation of the ethyl vinyl ether adduct[8] **6** (R = H) with *n*-hexyl bromide gave an ~75% yield of **7** (R = H; R′ = *n*-hexyl; bp 87–88° (0.07 mm)), easily hydrolyzed, as usual, to 1-nonen-3-one (**8**, R = H; R′ = —*n*-hexyl), identical with an authentic sample.

Obviously, since the cyanohydrins derived from aromatic aldehydes are considerably more acidic than those from their aliphatic counterparts, alkylation by this method also gives excellent yields with these substances. The protected cyanohydrin of benzaldehyde thus gave overall conversions to valerophenone, isobutyrophenone, and 1,3-diphenyl-1-propanone ranging from 71% for the latter after crystallization (mp 69–71°; lit.[9] 72°) to 94% for the other two.[10] Furfural similarly gave 1-furyl-1-pentanone in ~90% yield.

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(5) Aldehyde cyanohydrins can be made easily by a variety of methods; *cf.*, *inter alia*, E. Pierson, M. Giella, and M. Tishler, *J. Amer. Chem. Soc.*, **70**, 1450 (1948).

(6) This and other ketones were produced essentially quantitatively (**4** → **5**) as shown by vpc. The identity of the ketones was established by ir and nmr spectra and/or comparison with authentic samples.

(7) R. Rambaud, *Bull Soc. Chim. Fr.*, 1317 (1934).

(8) The procedure of ref 3 was used but without heating initially or at the end of the reaction. The low boiling material was removed at the water pump and the residue was distilled under vacuum, bp 42–45° (0.1 mm) (60% overall from acrolein). Redistillation through a short Vigreux column gave bp 58–59° (0.3 mm). This is a mixture of two diastereoisomers (54% A, 46% B; A, 8.9 min retention time, and B, 9.9 min on SE-30 at 130°). The mixture is used as such in the alkylation sequence.

(9) N. H. Cromwell and R. H. Johnson, *J. Amer. Chem. Soc.*, **65**, 316 (1943).

(10) The higher acidity of the protected cyanohydrins from aromatic aldehydes allows, in some cases, the use of sodium hydride in dimethoxyethane as base; the α-ethoxyethyl ether of benzaldehyde cyanohydrin thus gave 88% yield on alkylation with *n*-amyl bromide.

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Theoretical ^{13}C Nuclear Magnetic Resonance Chemical Shifts in CH_5^+ and $C_2H_5^+$

Sir:

At the present time there is considerable experimental and theoretical interest in the structure of small carbonium ions.[1] One of the main experimental techniques used to determine such molecular structures is nmr spectroscopy (^{1}H and ^{13}C).[2] Theoretically, both semiempirical[3,4] and *ab initio*[5–9] methods have been used to predict the equilibrium structures of carbonium ions. Recently we developed a theory of ^{13}C nmr chemical shifts, and applications to neutral molecules have led to results which are in good agreement with experimental values.[10,11] The theory is particularly successful in describing ^{13}C chemical shifts in molecules of comparable size and in which the carbon nucleus has a similar position relative to the origin of the vector potential describing the magnetic field. This suggests that the theory may give a good description of the relative ^{13}C chemical shift between a neutral molecule and the associated carbonium ion with the same number of electrons, *e.g.*, CH_4 and CH_5^+, C_2H_4 and $C_2H_5^+$. If successful, this would provide a useful link between theoretical studies of equilibrium geometries and the experimental nmr data. The aim of this note is to present calculated ^{13}C magnetic shielding constants for the equilibrium structures of CH_5^+ and $C_2H_5^+$ determined by Lathan, Hehre, and Pople.[7–9] While these systems have never been obtained experimentally, the calculated results can be compared with simulated experimental data derived from similar systems.[2]

The method used is Hartree–Fock perturbation theory formulated within the molecular orbital framework, each molecular orbital being written as a linear combination of a small extended basis set (4-31G)[12] of atomic functions φ_μ (LCAO)

$$\psi_i = \sum_\mu c_{\mu i}\varphi_\mu$$

The equilibrium geometries for CH_5^+ and $C_2H_5^+$ are taken from the work of Lathan, Hehre, and Pople.[9]

The calculated results are shown in Table I together with the energies reported in ref 9. Since there are no experimental values available for the ethyl cation (it has never been observed experimentally), we have attempted to estimate chemical shift values for the

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(1) For recent reviews, see C. C. Lee, *Progr. Phys. Org. Chem.*, **7**, 129 (1970); J. L. Fry and G. J. Karabatsos in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1970, Chapter 14.

(2) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3954 (1969); **91**, 5801 (1969).

(3) G. A. Olah, G. Klopman, and R. H. Schlosberg, *ibid.*, **91**, 3261 (1969).

(4) R. Sustman, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969).

(5) W. Th. A. M. Van der Lugt and P. Ros, *Chem. Phys. Lett.*, **4**, 389 (1969).

(6) H. Kollmar and H. O. Smith, *ibid.*, **5**, 7 (1970).

(7) W. A. Lathan, W. J. Hehre and J. A. Pople, *Tetrahedron Lett.*, 2699 (1970).

(8) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2141 (1970).

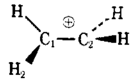
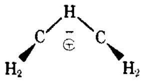
(9) W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 808 (1971).

(10) R. Ditchfield, D. P. Miller, and J. A. Pople, *Chem. Phys. Lett.*, **6**, 573 (1970).

(11) R. Ditchfield, D. P. Miller, and J. A. Pople, *J. Chem. Phys.*, **54**, 4186 (1971).

(12) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).

Table I. Calculated Carbon Chemical Shifts

Molecule		σ, ppm	$\Delta\sigma^{a}$ (calcd)	$\Delta\sigma$ (exptl)	Energy,[b] hartrees
CH_4		222.1	0.0	0	−40.13976
CH_5^+ (D_{3h})		253.4	31.3		−40.31506
CH_5^+ (C_{4v})		250.2	28.1		−40.31891
CH_5^+ (C_s)		173.1	−49.0		−40.32206
C_2H_4		105.5	0.0	0.0	−77.92189
	C_1	173.6	+68.1	+49[c]	−78.19498
	C_2	−127.3	−232.8	−193[c]	
		73.2	−32.3		−78.18414

[a] CH_5^+ shifts are relative to CH_4; $C_2H_5^+$ shifts are relative to C_2H_4. [b] Taken from ref 9. [c] Estimated from data on similar systems given in ref 2.

classical form of the ethyl cation from experimental data reported by Olah and White[2] on other stable classical cations. We report these estimates under the "experimental" entry of the table.

The problem for $C_2H_5^+$ is one of determining whether the actual structure may be represented by a rapidly equilibrating pair of ions or by a static ion with a hydrogen bridge. It can be seen from the table that the results for the CH_3 and CH_2 resonances of the classical form of the ethyl cation are in moderately good agreement with the experimental estimates. If the ion may be represented by a rapidly equilibrating pair of ions, then the ^{13}C shift will be the average of $\sigma(C_1)$ and $\sigma(C_2)$. This average is calculated to be −82.3 ppm (relative to C_2H_4), in good agreement with the value of −72 ppm estimated from the results of Olah and White.[2] The ^{13}C shift in the hydrogen-bridged structure, on the other hand, is predicted to be about 50 ppm to high field of this average value. Thus if the ethyl cation could be observed directly, ^{13}C chemical shift measurements would be capable of distinguishing between the possible structures. The calculated results also support the conclusions of Olah and White[2] on similar types of ions (*e.g.*, the 2-butyl cation).

Carbon chemical shifts were also calculated for the trigonal-bipyramidal (D_{3h}), square-pyramidal (C_{4v}), and less symmetrical (C_s) structures of CH_5^+ given in ref 7. All three forms show sizable shifts from CH_4. The ^{13}C resonance of the C_s structure is shifted 49 ppm downfield from CH_4, while the C_{4v} and D_{3h} structures are predicted to give upfield resonances of 28.1 and 31.3 ppm, respectively. Estimation of experimental results for CH_5^+ is less straightforward. However, as Olah has pointed out, "onium-type" carbons are to be found in bridged species, *e.g.*, the 2-norbornyl, 7-norbornenyl, and 7-norbornadienyl cations.[13] In these three cations, the bridging carbon chemical shifts range from −43 to −23 ppm relative to CH_4.[13] It is perhaps worthy of note that these values are quite close to the calculated value for CH_5^+ (C_s). Thus, if CH_5^+ exists as a static ion these results suggest that ^{13}C nmr would be able to distinguish between the less symmetrical (C_s) and the other two (C_{4v} and D_{3h}) structures. However, it should be noted that the activation energy for hydrogen rearrangement within the ion is only about 2 kcal/mol.

It is of interest to briefly examine the origin of the shifts in these systems. Decreasing the negative charge on carbon usually leads to an overall contraction of the carbon valence atomic orbitals. Such contraction results in an increased paramagnetic contribution to magnetic shielding and a low-field shift. Although there is a contraction of carbon orbitals as we go from the D_{3h} to the C_s structure, the total charges (as measured by Mulliken[14] gross populations) on carbon in CH_5^+ and CH_4 are in the order

$$CH_5^+\ (D_{3h}) > CH_5^+\ (C_{4v}) > CH_5^+\ (C_s) > CH_4$$

and thus it appears that the shifts cannot be rationalized in terms of such charge effects alone.

In addition to charge effects, the shielding at a nucleus will also depend upon the extent to which the electrons can be perturbed by the magnetic field. Some measure of this is given by the availability of excited singlet states. It is likely that all four systems have excited states of approximately the same (relatively high) energy. However, it is important to note that for CH_4, CH_5^+ (D_{3h}), and CH_5^+ (C_{4v}), contributions from many of these excited states are zero by symmetry. In contrast, contributions from all excited singlet states of CH_5^+ (C_s) will have finite values and this together with the more contracted carbon valence functions in the C_s structure may explain the larger paramagnetic value.

Similar ideas may be used to explain the shifts in the various structures for the ethyl cation. The carbon orbitals of the CH_2 center are rather more contracted than those of the CH_3 group due to the greater positive charge on this center. However, all the trends cannot be explained in terms of charge effects alone. It is worthy of note that some excitations are mainly localized on the CH_2 center and will probably further increase the paramagnetic contribution for C_2 while leaving that for C_1 almost unchanged.

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The Reactions of *exo*- and *endo*-8-Carbenatricyclo[3.2.1.$0^{2,4}$]octane[1]

Sir:

Several years ago we reported on the methoxide ion induced decomposition of the tosylhydrazone of

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