

In the case of **4b**, this process initially places the methyl group on the outside of the ring. For conformational reasons, the initially formed ion must be **5a**. Should the transoid species be the thermodynamically stable conformer under these conditions, then **5a** is considered to be the correct structure since double bridge inversion to place methyl in the sterically less favorable inner position does not operate (*vide infra*). If, on the other hand, the ion is cisoid, the structure must be **5b** (inversion of the methylene bridge) rather than the sterically more demanding ion with the methyl inside. It is important to note that **5** is a static structure and that rapid exchange between **5a** and **5b** is not important. Deuteration of **4b** as before led in this case to stereoselective ($75 \pm 10\%$)⁶ deuterium incorporation at the 9i site.

Numerous attempts to protonate **4c** and **4d** in various media at low temperatures have proved unsuccessful. Not unexpectedly,^{2,3} the 9,9-dimethyl derivative **4e** likewise did not give rise to a bishomotropylum ion.

Comparison of the nmr data for the two 1,3-bishomotropylum ions reveals, *inter alia*, that the average chemical shift of H_{8i} and H_{9i} (τ 8.08) in **5** compares well with that of the corresponding protons in **2** (8.09). The unsymmetrical nature of **5** does, however, reveal for the first time the magnitude of $J_{6,7}$ (8.0 Hz). Although this finding can be readily accommodated by **5a** in which significant twisting of the C_{6,7} bond is necessary to maximize overlap across the methylene bridges, the attendant decrease in C₆-C₇ overlap could so affect J that a clearcut distinction between **5a** and **5b** is unfortunately not possible on this basis.

When consideration is given to the stereochemistry of the deuteration process as revealed by the spectra of the long-lived cations, a greater *net* endo positioning of deuterium is seen in **5**. Unfortunately, the stereoselectivity of H⁺ (or D⁺) attack cannot be determined unambiguously. Consequently, these observations may be satisfied by one of several options: (a) random deuteration to give trans ions **2b** and **5a** with no flipping of either bridge atom, (b) stereoselective exo electrophilic attack followed by a single flip of either bridge in **2b** to give **2a** and by inversion of only the methylene bridge in **5a** with formation of **5b**, (c) in the unsubstituted example, the first inversion (trans \rightarrow cis), when operative, is followed by a rapid flip of the other bridge (cis \rightarrow trans).

Since the type c sequence in the case of **4b** would position methyl in an endo orientation (not reconcilable with the measured coupling constants), operation of this mechanism can be discounted in this instance. Its generality can consequently be questioned. Also, examination of models indicates that the methyl group in **4b** is sufficiently remote from the sites (two equivalent positions are available) of initial electrophilic bonding not to cause the sizable selectivity difference noted upon deuteration of **1** and **4b**. Therefore, ran-

(6) The rather large uncertainty quoted for this inner/outer deuterium ratio arises from several factors. First, partial overlap of the H_{9i} and methyl absorptions renders integration of this peak difficult. The H_{9o} multiplet is clearly separated from all other resonances, but the *total* amount of entering deuterium is unknown (the DSO₃F has 2-3% proton contamination). As a consequence of an unknown isotope effect, the amount of H at C₆ could vary from 1.0 to 1.1. It follows then that if the H_{9o} peak comprises 75% of 1.0 hydrogen, the ratio is 75:25, but if 1.1 hydrogens are present the ratio now becomes 83:17.

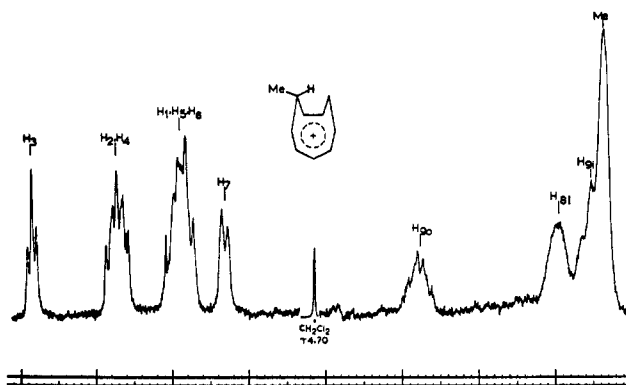


Figure 1. Nmr spectrum of protonated **4b**.

dom deuteration is seemingly not a suitable mechanistic hypothesis.

Thus, the protonation of *cis*-bicyclo[6.1.0]nonatrienes under conditions of long life would appear to involve initial formation of a trans cation which subsequently experiences conformational inversion of a (less substituted) methylene bridge. Molecular models show that the trans ion is reasonably rigid, fairly strain free, and certainly less demanding than a comparable 1,4-bishomotropylum ion.⁷ Nevertheless, although the transoid intermediates are capable of interception under presumed kinetic control conditions,^{2,3} they transmuted to their *cis* counterparts when thermodynamic control can operate. This can be interpreted to mean that **2b** (or **2c**) resides closer to the transition state for bridge inversion than does **2a**. A number of important questions still remain to be answered about the electronic nature of the trans ion⁸ and about the possible differences which may arise in solvent systems other than superacids.

(7) H. A. Corver and R. F. Childs, *J. Amer. Chem. Soc.*, **94**, 6201 (1972).

(8) Preliminary calculations suggest that **2a** and **2b** may be nearly isoenergetic. However, the lack of strong dependence on molecular geometry requires highly refined calculations before this point may be assessed accurately (J. Clardy, personal communication).

(9) Holder of a NATO Postdoctoral Fellowship (1970-1972) administered by the Science Research Council.

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Leo A. Paquette,* Michael J. Broadhurst⁹

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Philip Warner*

Department of Chemistry, Iowa State University
Ames, Iowa 50010

George A. Olah,*¹⁰ Gao Liang

Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

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Stable Carbocations. CLV.¹ The Ethylenechloronium and Methylchlorocarbenium Ions

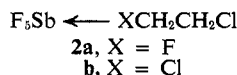
Sir:

Alkenehalonium ions have long been suggested as intermediates in electrophilic halogen addition and

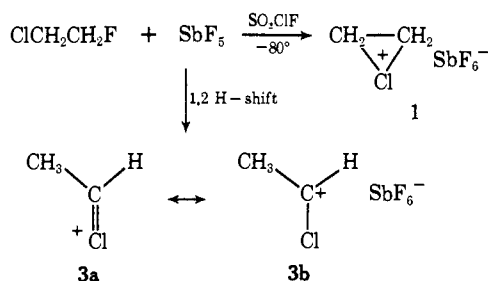
(1) Stable Carbocations. CLIV: G. A. Olah and Y. K. Mo, *J. Org. Chem.*, in press.

substitution reactions.² In our previous work,³ we have reported the preparation and study of a number of halonium ions under long-lived conditions. A notable exception so far among the directly observed halonium ions was the ethylenechloronium ion (1) which presented a long standing challenge. We now report the preparation and nmr spectral study of this ion, the last unreported of the parent alkenehalonium ions.

When 1,2-dichloroethane or 1-chloro-2-fluoroethane is added to an excess of antimony pentafluoride in sulfur dioxide, only a donor-acceptor complex (2) is formed.



If instead of SO₂, sulfuryl chloride fluoride is used as the solvent the reaction of antimony pentafluoride with 1-chloro-2-fluoroethane at -80° gives a solution whose 60-MHz proton nmr spectrum consists of three absorptions, a doublet (δ 4.6, 3 H, *J* = 6 Hz), a quartet (δ 13.3, 1 H, *J* = 6 Hz), and a singlet (δ 5.9), consistent with the presence in solution of the ethylenechloronium ion (1) and the methylchlorocarbenium ion (3), respectively.



The observation of a static methylhalocarbenium ion such as (3) has also not previously been reported; although in our preceding studies, we showed that the methylfluorocarbenium ion, prepared from 1,1-difluoroethane and antimony pentafluoride, undergoes rapid fluoride ion exchange with its SbF₆⁻ counterion, resulting in a set of temperature-dependent pmr spectra.⁴ The line shape and position of ion (3) are temperature independent in the range studied (-80° to -50°; however, see subsequent observations).

The assignment of the singlet absorption at δ 5.9 to the ethylenechloronium ion is consistent with our previous observations on the corresponding ethylenebromonium and -iodonium ions.^{3c} Additional proof of these assignments, however, follows from the cmr spectrum of the above solution. Singlets at +140.7 and -107.8 ppm (from ¹³CS₂), which become a quartet and doublet, respectively, on "off-resonance" decoupling, were observed and assigned to the methylchlorocarbenium ion (3). The chemical shift of the carbenium ion center in ion 3 is shielded by approximately 17 ppm from the corresponding shift in the isopropyl cation.

(2) I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, **59**, 947 (1937); for a review, see B. Capone, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964); G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **92**, 718 (1970).

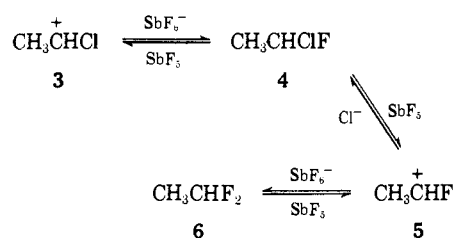
(3) (a) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4774 (1967); (b) G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 947 (1968); (c) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968); (d) G. A. Olah and P. E. Peterson, *ibid.*, **90**, 4675 (1968).

(4) G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Org. Chem.*, **37**, 1169 (1972).

This suggests that resonance form 3a is a substantial contributor to the structure of 3, since a deshielding of approximately 20 ppm occurs in a hydrocarbon on replacement of a methyl group by a chlorine atom.⁵ However, it is possible that the shielding is brought about by the presence of a small amount of 1-fluoro-1-chloroethane (4) in equilibrium with 3. The measured carbon-hydrogen coupling constants of 139.8 (*J*¹³CH₃) and 196.4 Hz (*J*¹³CH) are also consistent with the assigned structure (3).

A singlet at δ 119.7 in the cmr spectrum which becomes a triplet on "off-resonance" decoupling was assigned to the ethylenechloronium ion (1). The carbon-hydrogen coupling constant of 188 Hz is comparable to the corresponding coupling constant in the ethylenebromonium ion (185 Hz).⁶ Such a large value for a tetrahedrally hybridized carbon atom is indicative of a highly strained three-membered ring. The slightly larger coupling constant in 1 is most likely a result of the greater electronegativity of chlorine compared with bromine. Both carbon-hydrogen and carbon-carbon coupling constants have been observed to increase with increasing electronegativity of substituents.^{7,8}

The ratio of ions 1 and 3 depends on the conditions under which they are prepared. If care is taken to keep the reactants below -80°, the ethylenechloronium ion (1) predominates. However, the available data show that ions 1 and 3 are not interconvertible. As the temperature is raised to -50°, the doublet and quartet of 3 disappear and a new set of signals (*J* = 18 Hz) appear upfield at δ 4.3 (3 H) and 10.3 (1 H). At the same time, the signal from the ethylenechloronium ion (1) does not change in position or intensity. We suggest this is due to formation of methylfluorocarbenium ion (5), which is in equilibrium with 1,1-difluoroethane (6)



under the reaction conditions.⁴ As proof of this, a 1:1 (m/m) mixture of 1,1-difluoroethane and 1-chloro-1-fluoroethane was ionized in SbF₅-SO₂ClF at -80°. The pmr spectrum of the resulting solution displayed four signals: those attributed to the methylchlorocarbenium ion (3) and a broad doublet at δ 4.3 and a broad multiplet at δ 10.3. On warming to -50°, 3 disappeared and the other signals (attributed to the equilibrium 5 ⇌ 6) increased. If to a fresh portion of this solution (held at -80°) HF was added, no signals attributable to 3 could be seen! Instead, a sharp doublet (3 H, *J* = 4.2 Hz, δ 1.78) and an equally sharp quartet (1 H, *J* = 4.2 Hz, δ 6.20) were observed. The equilibrium 5 ⇌ 6 and consequently the proton chem-

(5) G. C. Levy and G. L. Nelson, "Carbon 13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972, p 47.

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

(7) Reference 5, pp 28, 58.

(8) For a review of the use of cmr chemical shifts and coupling constants in evaluating carbocation structure, see G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

ical shifts and coupling constants were found⁴ to be dependent on the concentration of HF. Addition of HF results in a shift⁴ to higher field for both the doublet and quartet and at the same time an increase in the vicinal H-H coupling constant. We have previously reported that addition of HF to the equilibrating system $5 \rightleftharpoons 6$ produces just such a spectrum.⁴ In this case, swamping the system with fluoride ion destroys ion **3** by the formation of **4**, which rapidly produces **5** at the higher temperature (-50°).

The observations of the ethylenechloronium ion (**1**) as a stable, well defined ion has substantial importance not only in regard with its intermediacy in electrophilic chlorine addition to ethylene, but ion (**1**) also may play an important role in the mechanism of β -chloroethylation reactions,⁹ as well in biological alkylating systems involving precursors to incipient β -chloroethyl cations. These aspects will be discussed separately.

Acknowledgment. Support of our work by the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

(9) G. A. Olah and S. J. Kuhn, *J. Org. Chem.*, **29**, 2317 (1964).

(10) Postdoctoral research associate, 1971-1973.

George A. Olah,* David A. Beal, Philip W. Westerman¹⁰
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106
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Evaluation of Lanthanide-Induced Carbon-13 Contact vs. Pseudocontact Nuclear Magnetic Resonance Shifts¹

Sir:

The apparent pseudocontact nature of the dispersal of proton resonances of molecules in the presence of lanthanide chelates is proving quite useful as a tool for structure identification,² and criteria for testing the validity of signal assignments have been devised.³ The utilization of the pseudocontact model for lanthanide-separated carbon-13 spectra is complicated for amine⁴ and pyridine base⁵ adducts of $\text{Eu}(\text{DPM})_3$ by the presence of a large Fermi contact contribution to the observed, induced chemical shifts. Since carbon-13 spectra contain unique information about carbocyclic molecular structure, we have investigated methods to obviate the "contact shift effect." Our initial approach has been to assay the magnitude of the problem by obtaining correlated carbon-13 and proton nmr spectra of isoquinoline in the presence of eight of the non-isotropically paramagnetic tris(dipivaloylmethane)-lanthanide chelates and to factor the apparent contact and pseudocontact contributions.

Correlation of carbon and proton spectra was effected by performing both measurements on the same solutions of a lanthanide-DPM chelate and isoquinoline. Experimental details as well as the computational pro-

(1) Part IV of the series "Interpretation of the Pseudocontact Model for Nuclear Magnetic Resonance Shift Reagents."

(2) M. R. Willcott, III, R. E. Davis, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, **94**, 1742 (1972). Programs are available on request from the authors (R. E. D.).

(3) R. E. Davis and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **94**, 1744 (1972).

(4) G. E. Hawkes, C. Marzin, S. R. Johns, and J. D. Roberts, *J. Amer. Chem. Soc.*, **95**, 1661 (1973).

(5) O. A. Gansow, P. A. Loeffler, R. E. Davis, M. R. Willcott, III, and R. E. Lenkinski, *J. Amer. Chem. Soc.*, **95**, 3390 (1973).

cedure for analyzing the induced chemical shift data may be summarized.

Lanthanide-induced ^{13}C and ^1H shifts are treated as follows: (i) the europium location is mapped vs. the agreement factor R for the ^1H data;^{2,3} (ii) the scale factor K , used to match experimental to calculated ^1H shifts, was recorded; (iii) the carbon pseudocontact shift values for each europium location are computed using K ; (iv) a difference spectrum ($^{13}\text{C}_{\text{obsd}} - ^{13}\text{C}_{\text{calcd}} = ^{13}\text{C}_{\text{diff}}$) was generated for the carbon spectrum. A survey of the carbon difference maps for the eight lanthanides revealed differences in the internal contact shift ratios, but no reversal of the sign ordering pattern of the shifts. For present purposes, it is convenient to ameliorate these differences by calculating, for each metal chelate, an average $\delta_{\text{contact}}/\delta_{\text{pseudocontact}}$ for the heterocyclic ring carbons proximate to the lanthanide (C-1,3,4,9,10), the contact shifts in the distal aromatic fragment (C-5,6,7,8) being small. These average terms, recorded in Table I, are indices of the contact shift

Table I. Average Values for $\delta_{\text{contact}}/\delta_{\text{pseudocontact}}$ in the Nitrogen Ring of Isoquinoline vs. $\text{LAN}(\text{DPM})_3$

Eu = 0.80	Er = 0.25	Ho = 0.19	Dy = 0.13
Nd = 0.70	Tb = 0.21	Pr = 0.15	Yb = 0.05

induced by a particular lanthanide and provide a basis for ranking the reagents as usable heteronuclear shift reagents.

Several assumptions bear on the validity of this evaluation. First, the McConnell-Robertson⁶ equation on which we base our analysis requires axial symmetry of the lanthanide paramagnetism, a condition which is only approximately correct.⁷ Second, our computational procedure for locating the lanthanide and constructing the difference map places the heterocyclic nitrogen on the principal symmetry axis of the chelate, a situation which is also nearly correct, *a fortiori*.⁸ Finally, the pseudocontact description of the induced proton shifts is not rigorously justified.⁹ The combined inaccuracies introduced by these assumptions are manifest as imprecision in the location of the lanthanide (Table II). The variations of the locations are not of great concern since we are able, in our simple scheme, to note that the magnitude of the "contact shift effect" on lanthanide-dispersed ^{13}C spectra is not a sensitive function of the lanthanide position.

From Table II it is perceived that the lanthanides can be grouped into several sets according to their aptitude at inducing contact shifts. Isoquinoline complexed to $\text{Eu}(\text{DPM})_3$ has by far the largest contact shifts, followed by the $\text{Nd}(\text{DPM})_3$ adduct. The chelates of Dy, Ho, Tb are intermediate in this contribution, while Er, Pr spectra are less affected by spin delocalization induced chemical shifts. It is abundantly clear that to obtain lanthanide-dispersed spectra, certainly for nitro-

(6) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(7) W. D. Horrocks and J. D. Sipe, III, XIIIth Experimental NMR Conference, 1972, Abstract 5.2, p 32.

(8) J. D. Roberts, R. A. Smith, M. Christl, D. Leibfritz, C. Marzin, G. E. Hawkes, S. R. Johns, R. A. Cooper, and D. W. Roberts, ref 7, Abstract 6.1.

(9) The present authors will soon publish an analysis of contact vs. pseudocontact shifts induced by lanthanides in proton nmr.