

Stable Carbonium Ions. XII.¹ Direct Observation of the Allyl and 2-Methylallyl Cations

Sir:

Allylic carbonium ions are thought to be important intermediates in various acid-catalyzed reactions involving allyl halides and 1,3-dienes. While there is considerable kinetic evidence for their transient existence, direct methods of detection do not appear to have been used till very recently.

Rosenbaum and Symons² reported in 1961 that solutions of a series of allylic compounds and 1,2-dienes in sulfuric acid gave ultraviolet spectra thought to be those of the corresponding allylic carbonium ions. Deno and his collaborators³ identified for the first time a series of alkylated cyclopentenyl and cyclohexenyl cations through their n.m.r., infrared, and ultraviolet spectra, and also established linear alkenyl cations: the 2,4-dimethylpentenyl, and the 2,3,4-trimethylpentenyl, cation.



It was found by Deno that the mode of addition of the diene to the sulfuric acid is critical in order to produce stable solutions of the monomeric ion. The

with excess antimony pentafluoride, serving both as strong Lewis acid and as solvent, is applicable to observe directly the elusive allyl and methylallyl cations.

Allyl and 2-methylallyl fluoride (obtained from allyl and 2-methylallyl *p*-toluenesulfonates with potassium fluoride) form with antimony pentafluoride complex layers which are less stable however than those obtained with propyl and butyl fluorides. Carrying out the complex formation at around 0° (the lowest temperature obtainable with neat antimony pentafluoride) results in highly colored solutions and n.m.r. spectra of these solutions show, besides the expected ions, substantial cyclization, similar to the observation of Deno³ on the behavior of sulfuric acid solutions of allylic carbonium ion precursors. When SO₂-SbF₅ solutions of the allyl fluorides were obtained at -60°, the spectra of these solutions indicated the expected allyl (I) and 2-methylallyl cations (II). Table I summarizes the chemical shifts of the ions and their fluoride precursors. The spectrum of the allyl cation is shown in Fig. 1.

The four methylene protons in I show a rather broad doublet (with some indication of further coupling) at -8.97 p.p.m. The CH proton is broad and not well-resolved at -9.64 p.p.m. The relative peak areas are 4.17:1. There are secondary product peaks also observable at -3.93, -3.42, -3.08, and -1.70 p.p.m. (all

TABLE I
N.M.R. SHIFTS OF THE ALLYL AND METHYLALLYL CATIONS AS HEXAFLUOROANTIMONATE COMPLEXES IN SO₂-SbF₅ SOLUTION AT -60°^a

	=CH ₂		-CH-	-CH ₂ F	-CH ₃
CH ₂ =CH-CH ₂ -F (in SO ₂)	-5.14 (<i>trans</i>)	-5.01 (<i>cis</i>)	-5.52	-4.56 (<i>J</i> _{HF} = 47.5)	
[CH ₂ =CH-CH ₂]+SbF ₆ ⁻		-8.97	-9.64		
CH ₂ =C(CH ₃)-CH ₂ -F (in SO ₂)	-4.81	-4.69		-4.32 (<i>J</i> _{HF} = 46)	-1.47
[CH ₂ =C(CH ₃)-CH ₂]+SbF ₆ ⁻		-8.95			-3.85

^a P.p.m. from external (CH₃)₄Si.

preferred way of addition is that from the end of a capillary into vigorously stirred 96% H₂SO₄ at 0°. Otherwise dimerization, polymerization, and rearrangement take place preferentially during dispersion of the

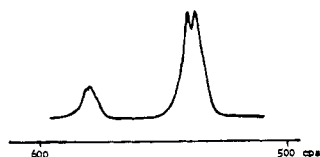


Fig. 1.—Proton magnetic resonance spectrum of the allyl cation in SbF₅-SO₂ at -60° (60 Mc., external TMS).

diene into the sulfuric acid. In view of this observation and the presented data it must be assumed that the bulk of the reported absorption maxima in the work of Rosenbaum and Symons was not due to the simple monomeric ions, like the allyl cation, [CH₂=CH=CH₂]⁺.

We wish to report now that the antimony pentafluoride method⁴ for obtaining stabilized carbonium ion complexes by the interaction of alkyl fluorides

broadened), indicating the presence of cycloalkenyl cation formation. The four methylene protons in II are again broadened at -8.95 p.p.m., whereas the methyl protons are at -3.85 p.p.m., not very different in deshielding from the methyl protons of the *t*-butyl cation. There is considerably less secondary cyclized ion formation than in the case of the allyl cation, indicating the enhanced stability of a methylallyl cation.

F¹⁹-Resonance spectra of the allyl hexafluoroantimonate system, which according to the proton resonance spectra was completely ionized in SbF₅-SO₂, showed no evidence of aliphatic fluorine, only equivalent SbF₆⁻ fluorines and those of the excess solvent. This observation, however, could be equally well-explained by a fast exchanging -F → SbF₅ system, and therefore should not in itself be considered as evidence for the formation of the allyl cation.

Quantum mechanical calculation of electron distribution of the allyl cation was carried out by Hirst and Linnett⁵ and by Simonetta and Heilbronner.⁶ The valence bond (VB) treatment of the latter authors gave the following distribution of the excess positive charge of I.

(1) Part XI: M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5680 (1964).

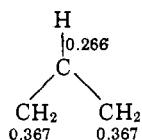
(2) J. Rosenbaum and M. C. R. Symons, *J. Chem. Soc.*, 1 (1961).

(3) N. C. Deno, *et al.*, *J. Am. Chem. Soc.*, **85**, 2991, 2995, 2998 (1963); **86**, 1871 (1964).

(4) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *ibid.*, in press.

(5) D. M. Hirst and J. W. Linnett, *J. Chem. Soc.*, 1035 (1962).

(6) M. Simonetta and E. Heilbronner, *Theoret. Chim. Acta* (Berlin), **2**, 228 (1964).

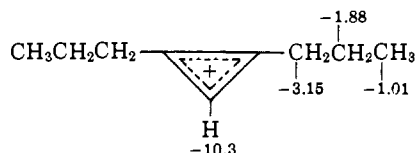


This treatment had taken into account the contribution of 1,3- π -interactions between the terminal centers. In contrast, the traditional resonance argument or the simple Hückel treatment of the two odd alternant terminal allyl cations would put the excess positive charge predominantly on the terminal carbon atoms.

The large experimentally observed deshielding effect of the $>\text{CH}$ proton in the allyl cation and similarly that of the methyl protons in the 2-methylallyl cation indicate the strong contribution of 1,3- π -interactions.⁶



This suggestion is supported by observations of Breslow and co-workers⁷ on the proton magnetic resonance shifts of the dipropylcyclopropenyl cation



Katz and Gold⁸ recently put forward strong evidence for 1,3- π -interactions in cyclobutenyl cations and demonstrated from the observed proton magnetic resonance shifts of these ions that the charge densities are about halfway between those in simple alkenyl cations and the fully symmetrical cyclopropenyl cations, where the charge density must be one-third of a unit charge on each ring carbon atom.

We are extending our investigations to precursors which potentially should yield the cyclopropyl and cyclopropenyl cations in our carbonium ion formation method, and hope to report these data and their comparison with those of the allyl cations in a subsequent publication.

(7) R. Breslow, H. Hover, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962); R. Breslow and H. Hover, *ibid.*, **82**, 2644 (1960).

(8) T. J. Katz and E. H. Gold, *ibid.*, **86**, 1600 (1964).

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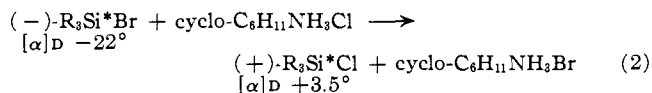
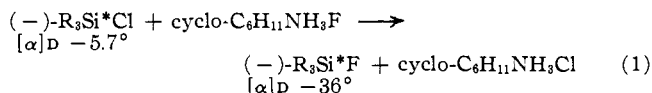
Halide-Halide Exchange at Asymmetric Silicon

Sir:

We wish to report the first stereochemical studies of halide-halide exchange reactions at asymmetric silicon in optically active α -naphthylphenylmethylsilanes,¹ $\text{R}_3\text{Si}^*\text{X}$.

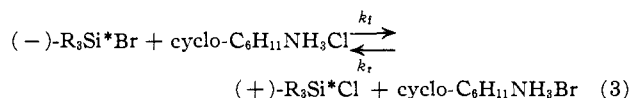
In the following reactions (1 and 2), which take place with predominant inversion of configuration, based on previous assignments of relative configuration,¹ the entering nucleophile is a stronger base and (for silicon) a better nucleophile than the leaving group, X. Both reactions were carried out in pure, dry chloroform.

(1) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964).



Reaction 1 proceeds with at least 90% inversion of configuration. Reaction 2 proceeds with predominant inversion of configuration and a minimum stereospecificity of 80%.

For reaction 2 which was homogeneous (no solid salt present), infrared spectra showed that equimolar concentrations of $\text{R}_3\text{Si}^*\text{Br}$ and $\text{cyclo-C}_6\text{H}_{11}\text{NH}_3\text{Cl}$ give a product which contains a maximum of 2% of $\text{R}_3\text{-Si}^*\text{Br}$. Thus, for the equilibrium formulation



it is possible to assign a minimum value for the equilibrium constant, which also provides the ratio $k_f/k_r \geq 2.4 \times 10^3$.

A linear plot of $1/C$ vs. time for reaction 2 during the first half-life was obtained from polarimetric rate data and gave the second-order rate constant for reaction 2 as $k_2 = 6.7 \text{ l. min.}^{-1} \text{ mole}^{-1}$. In view of the above equilibrium formulation for k_f/k_r , this means that the second-order rate constant for the backward reaction in (3), k_r , has a maximum value of $k_2 \leq 2.8 \times 10^{-3} \text{ l. min.}^{-1} \text{ mole}^{-1}$.

In Table I are given the first- and second-order rate constants for the salt-induced racemization of $\text{R}_3\text{Si}^*\text{Cl}$ by cyclohexylammonium chloride, bromide, and iodide. In each case the product was racemic chlorosilane, the racemizations were approximately first-order in added salt over the range from 0.04 to 0.09 M salt, and the rate law is rate = $k_2[\text{R}_3\text{Si}^*\text{Cl}][\text{cyclo-C}_6\text{H}_{11}\text{-NH}_3\text{X}]$.

Two aspects of the data in Table I are noteworthy. First, k_2 (inversion) for racemization of $\text{R}_3\text{Si}^*\text{Cl}$ by RNH_3Br exceeds the rate of displacement of Cl by Br by a factor of at least 15: $k_2(\text{inversion})/k_2(\text{displacement}) = (4.2 \times 10^{-2}/\leq 2.8 \times 10^{-3}) \geq 15$. Furthermore, the insensitivity of rate of racemization to variation in the halide ion component of the salt (less than a factor of four is involved) is also quite suggestive. Taken together the data suggest operation of mechanism² $\text{SN}_1\text{-Si}$ for racemizations (1), (2), and (3) in Table I, which involves salt-promoted formation of siliconium ion pairs in the rate-controlling step.

TABLE I

RATE CONSTANT DATA FOR THE RACEMIZATION OF $\text{R}_3\text{Si}^*\text{Cl}$ (0.0872 M) AT 25.0° IN CHLOROFORM WITH CYCLOHEXYLAMMONIUM SALTS (0.0872 M)

Reaction	Halide	$k_1(\text{rac.})$, min. ⁻¹	$k_2(\text{rac.})$, l. min. ⁻¹ mole ⁻¹	$k_2(\text{inv.})$, l. min. ⁻¹ mole ⁻¹
1	Cl	1.2×10^{-2}	1.4×10^{-1}	6.9×10^{-2}
2	Br ^a	7.2×10^{-3}	8.4×10^{-2}	4.2×10^{-2}
3	I ^a	2.6×10^{-2}	3.0×10^{-1}	1.4×10^{-1}

^a The product is racemic chlorosilane.

(2) For a discussion of the meaning of symbol $\text{SN}_1\text{-Si}$ and other examples of siliconium ion pair mechanisms, see L. H. Sommer, "Stereochemistry. Mechanism and Silicon," McGraw-Hill Book Co., New York, N. Y., in press.