Stable Carbocations. CXLVII.[1a] Carbon-13 Nuclear Magnetic Resonance Study of the Rapidly Equilibrating Bridgehead Bicyclo[4.4.0]decyl, Bicyclo[4.3.0]nonyl, and Bicyclo[3.3.0]octyl Cations and Related Model Ions

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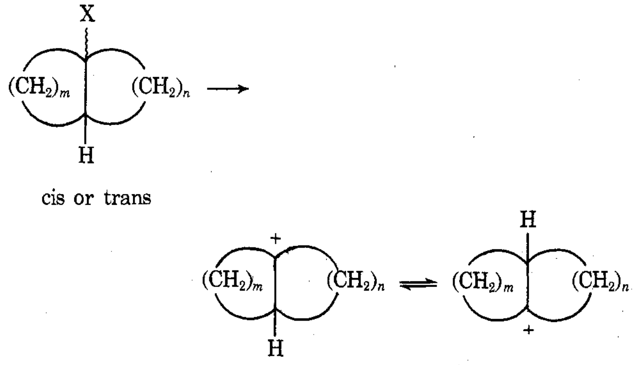
Carbon-13 nmr spectroscopic study reveals that the bridgehead 9-decalyl (1), 8-hydrindanyl (2), and 7-perhydropentalenyl (3) cations are all rapidly equilibrating ions. This necessitates revision of previous assignments in the pmr spectrum of ion 3. The 1,2-hydrogen shift between the bridgehead carbon atoms is extremely fast and cannot be "frozen out" even at very low temperature. Quenching solutions of the cations either with $NaBH_4$ or MeOH–NaOMe gives predominantly trans products, which confirms the rapid equilibration process. The 7-perhydropentalenyl cation shows an unexpectedly large deshielding effect of the β protons which is not observed in the six-membered-ring cations and which led in previous work, when considering only pmr data, to wrong assignment. The power of cmr spectroscopy is demonstrated in elucidating the structure of rapidly equilibrating carbocations.

Solvolytic studies at the bridgehead positions of condensed ring systems have been reported[2] and recently reviewed.[3] Although the solvolytic carbenium ion intermediates derived from the cis and trans isomers of bicyclo[4.4.0]decyl (9-decalyl), bicyclo[4.3.0]nonyl (8-hydrindanyl), and bicyclo[3.3.0]octyl (7-perhydropentalenyl) derivatives are different,[2,3] the stable carbenium ions obtained in superacids in each of the above three cases are identical regardless of the isomeric form of the precursors.[4] During our studies we have directly observed the bridgehead bicyclo[4.4.0]decyl (9-decalyl, 1),[4] bicyclo[4.3.0]nonyl (8-hydrindanyl, 2),[5] and bicyclo[3.3.0]octyl (7-perhydropentalenyl, 3)[6] cations by pmr spectroscopy. Ions 1 and 2 have been characterized as equilibrating carbenium ions with a rapid 1,2 hydrogen shift between the bridgehead positions,[4,5] while ion 3 was regarded as a static ion.[6]



1, $m = n = 4$
2, $m = 4$; $n = 3$
3, $m = n = 3$

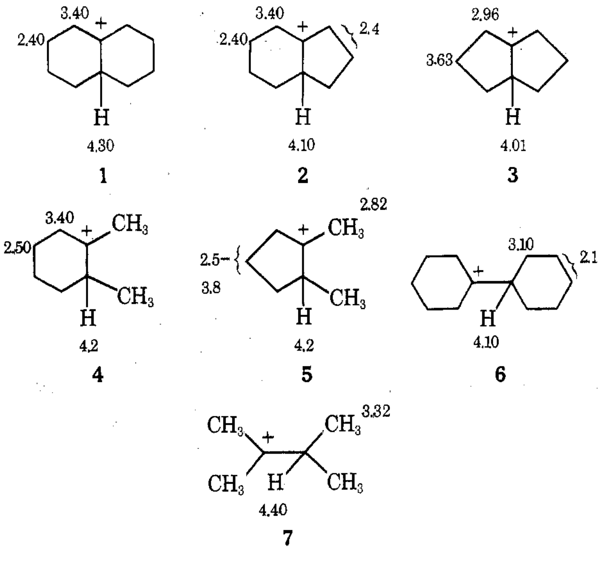
We wish now to report the cmr spectroscopic study of the ions, which shows that *all* three carbenium ions are rapidly equilibrating and have a fast equilibrating bridgehead proton. Conclusions obtained from these spectroscopic data are also supported by results of quenching experiments, carried out under carefully controlled experiments and quantitatively analyzed by gas–liquid chromatography, using for comparison authentic synthetic samples for all products.

Results and Discussion

The 9-decalyl (1), 8-hydrindanyl (2), and 7-perhydropentalenyl (3) cations were generated by previously described procedures. Ions 1 and 2 are stable up to room temperature, while ion 3 is only stable to −35°, whence it rearranges to the 2-methyl-2-norbornyl cation.[6b,7]

Parameters derived from the pmr (60 MHz) spectra of ions 1 and 2 as well of ion 3 (220 MHz) are summarized in Scheme I. For comparison several model ions with rapidly equilibrating bridgehead protons were also observed and their data are included. The bridgehead proton absorptions in ions 1, 2, and 3 are found at δ 4.30, 4.10, and 4.01, respectively.[6c] The slightly shielded proton resonances for the latter ions might suggest that more of the positive charge is shared by the fused five-membered ring(s). Similar proton absorptions have also been observed for ions 4–8, which have equilibrating but *not* bridgehead protons.[8]

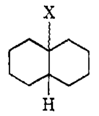
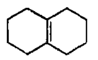
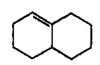
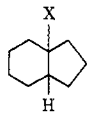
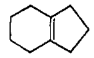
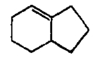
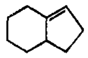
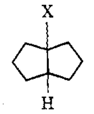
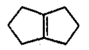
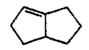
Scheme I



The proton-coupled cmr (25.16 MHz) spectra for ions 1, 2, and 3 were obtained at −70° using the fast Fourier transform method. Cmr parameters are summarized in Scheme II together with assignments. Multiplicities and coupling constants (J_{CH}, in hertz) are given in parentheses. The carbon-13 nmr spectra of the three ions are shown in Figure 1.

The two equivalent bridgehead-carbon ^{13}C resonances for ions 1, 2, and 3 were observed as doublets at δ −7.6 ($J_{C\text{-}H}$ = 50.8 Hz), −10.7 ($J_{C\text{-}H}$ = 55.3 Hz), and −24.1 ($J_{C\text{-}H}$ = 51.3 Hz), respectively. The greater deshielding for the ion 3 may be a result of the greater ring strain existing in this ion, compared to ions 1 and 2. The same reason may also account for greater shielding of the α-C shift

Table I
Quenching Products Distribution of 9-Decalyl, 8-Hydrindanyl, and 7-Perhydropentalenyl Cations

Cation	Condition	Substituent	Product (%)				
9-Decalyl							
			cis	trans			
	A. NaBH$_4$, −70°	X = H	<2	69	18	11	
	B. MeOH–NaOMe, −78°	X = OMe	<1	74	12	13	
8-Hydrindanyl							
			cis	trans			
	A	X = H	0	62	24	4	10
	B	X = OMe	<2	48	21	2	17
7-Perhydropentalenyl							
			cis	trans			
	A	X = H	0	0	64	36	
	B	X = OMe	<2	0	42	56	

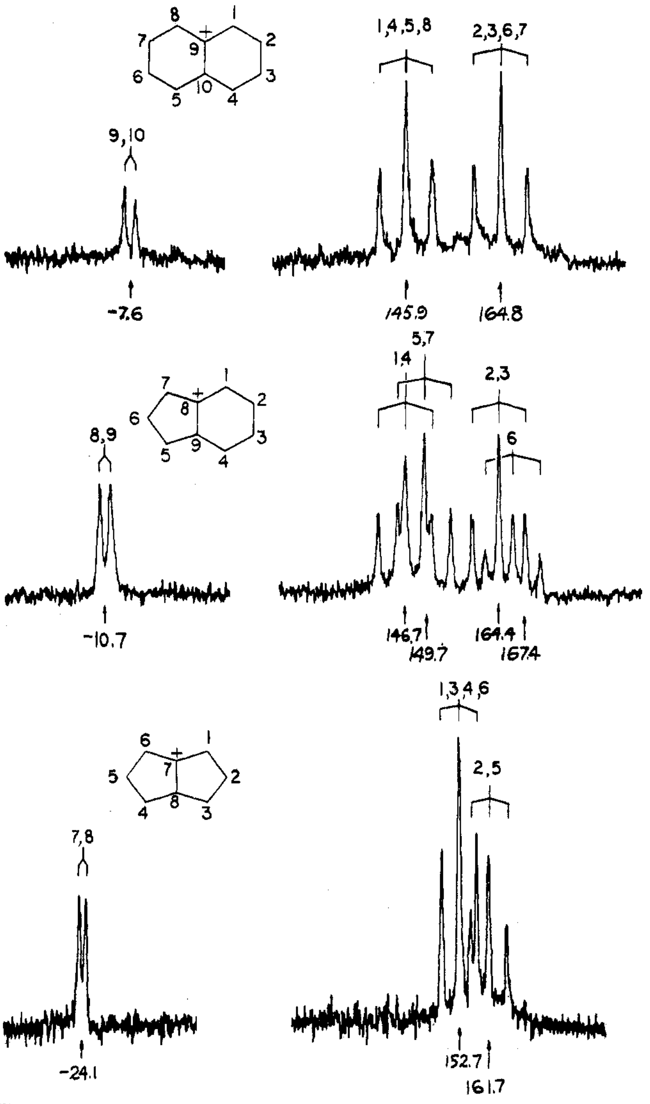
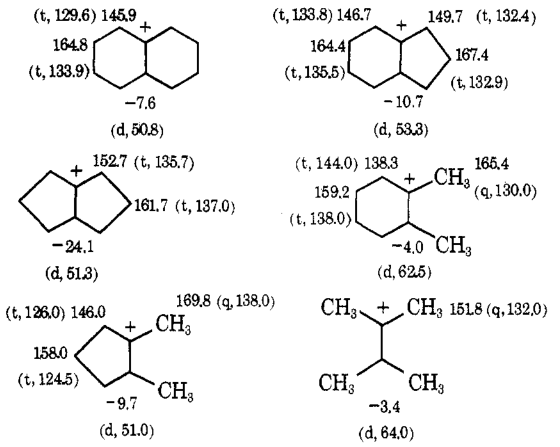


Figure 1. Carbon-13 nmr spectra (25.16 MHz) of the bicyclo[4.4.0]decyl, bicyclo[4.3.0]nonyl, and bicyclo[3.3.0]octyl cations in FSO$_3$H-SbF$_5$-SO$_2$ClF at −70°

Scheme II



(about 55 ppm) in ion **3** as well as the greater deshielding of the β-C (about 3 ppm) shift. The presence of greater positive charge at the β position of the five-membered ring than at the α position most likely is the reason for the reversal of the normal deshielding order of the α- and β-methylene proton absorptions (Scheme I). Since there are only three carbon absorptions in the cmr spectrum of ion **3**, and the coupling constant between the bridgehead carbons and the equilibrating proton ($J_{\text{C-H}}$ = 51.3 Hz) is characteristic for rapidly equilibrating systems, we conclude that ion **3** itself is a rapidly equilibrating bridgehead ion. If ion **3** were static, there would be five carbon absorptions instead of the observed three. Consideration of models suggest that ion **3** has a geometry which is favorable for the 1,2-hydrogen shift without the rings having to undergo too much deformation. It can be inferred from similar models that the corresponding shift in ions **1** and **2** occurs with more ring deformation than in ion **3**. Unfortunately, we have been unable to measure the rate of such processes, since they are still extremely fast at −145°.

Quenching experiments confirm the spectroscopic observations.[9] The results of the quenching experiments for ions **1**, **2**, and **3** are summarized in Table I. Both 9-decalyl and 8-hydrindanyl cations yielded (as analyzed by glc) almost exclusively trans products (with only trace amounts of cis products). In accordance with solvolytic results,[2c] the 7-perhydropentalenyl cation gave only olefins, owing to the instability of the trans products. In no case, under the reaction conditions used, did isomerization between the cis and trans products take place.

Experimental Section

Preparation of the bridgehead cations was carried out as previously described.[4-6]

Quenching of solutions of bridgehead cations was carried out in either MeOH-NaOMe or $NaBH_4$-SO_2ClF by the previously described procedure.[5] Products were extracted with carbon tetrachloride and the combined extracts were washed, dried ($MgSO_4$), concentrated, and then analyzed by glc using comparison with authentic samples.[2c] Data of parallel experiments are summarized in Table I.

Carbon-13 nuclear magnetic resonance spectra were obtained using a Varian Associates Model XL 100 nmr spectrometer equipped with a Fourier transform accessory, a spin decoupler, and a variable-temperature probe. The pulse width used was 15–20 μsec, and the need to provide multichannel excitation over the range of interest (10,000 Hz) limited the data acquisition time to 0.4 sec. Approximately 500–1000 accumulations were made for satisfactory spectra, depending on the ion concentration. A Varian 620L computer was used to accumulate data. The external lock used was fluorobenzene. Fourier transformation of the accumulated free induction signal gave the frequency spectrum, from which was obtained the chemical shift of each signal relative to the external signal of a 5% ^{13}C enriched TMS capillary. Coupling constants (in hertz) were directly obtained from the coupled cmr spectra. However, in these cases longer accumulation times were required. Pulse delay and pulse width used were 0.5 sec and 35 μsec, respectively.

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References and Notes

(1) (a) Part CXLVI: G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **95**, 194 (1973). (b) Taken in part from the Ph.D. Thesis of G. Liang, Case Western Reserve University, Cleveland, Ohio, 1971. (c) Postdoctoral Fellow, 1971–1973.

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(5) (a) G. A. Olah, G. Liang, J. R. Wiseman, and J. A. Chong, *J. Amer. Chem. Soc.*, **94**, 4927 (1972).

(6) (a) G. A. Olah, J. M. Bollinger, and D. P. Kelly, *J. Amer. Chem. Soc.*, **92**, 1432 (1970). (b) G. A. Olah and G. Liang, *ibid.*, **93**, 6873 (1971). (c) Previous comparison[6a] of the 60-MHz pmr spectrum of ion **3** with that of the decalyl ion **1** and the hydrindanyl ion **2** misled us to conclude that ion **3** did not have a rapidly equilibrating bridgehead proton. Comparison of the cmr spectrum of **3**, however, with that of **1** and **2** clearly indicates that the former is also a rapidly equilibrating ion. The correct assignments in the pmr spectrum of ion **3** are the bridgehead proton at δ 4.01, eight methylene protons α to the positive charge at δ 2.96, and four methylene protons β to the positive charge at δ 3.63.

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

(8) (a) Ions **6** and **7** have been previously reported. See ref 4a and references cited therein. (b) For ions **4** and **5**, see G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **96**, 189 (1974).

(9) We have carefully repeated all the previously reported quenching experiments using glc analysis (compared with authentic samples) and the results shown in Table I are considered the correct products.

Remote Anodic Acetamidation of Esters *via* Carbonium Ions

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The anodic oxidation of several acyclic esters has been performed in acetonitrile solution. A platinum anode, a divided cell, and potentiostat were employed. When lithium perchlorate was the electrolyte, a very clean conversion of ester to monoacetamidated ester took place. Ethyl butanoate, for example, produced ethyl 3-acetamidobutanoate in 70% yields when 3 faradays/mol of electricity was passed. Selectivity for ω-1 substitution was also found with other substrates. Although tetraethylammonium fluoroborate as electrolyte provides the same product it is shown that electrolyte oxidation processes are intimately involved in this acetamidation process. Thus, it is required that the potential be high enough [$LiClO_4$, 2.74, and $(CH_3CH_2)_4NBF_4$, 3.10] to oxidize the electrolyte in order to get good yields of product. The intermediacy of a carbonium ion is proposed to explain the formation of acetamides and the formation of rearranged products from the oxidation of methyl pivalate.

This study commenced as a survey of the anodic chemistry of aliphatic compounds. Our primary goal was to establish the common reactions of simple molecules.[2] Additionally, we hoped that the energetic intermediates generated at high potentials would lead to unique and useful reactions. We report here on the anodic products from esters in acetonitrile solvent. Although the reaction conditions (other than potential) are very mild, this process generates aliphatic carbonium ions from ordinary alkyl groups. It also provides a method for acetamidation at remote positions, a reaction which cannot be directly accomplished by other means.

Anodic substitution of acetamide for an activated (allylic, benzylic) hydrogen is well documented.[3] Of particular importance to this study is the extension of this reaction to certain saturated hydrocarbons. The oxidation of adamantane in acetonitrile–lithium perchlorate, for example, produces 1-adamantylacetamide in 90% yield.[2] The oxidation of octane in acetonitrile–tetraethylammonium fluoroborate gives an equal mixture of 2-, 3- and 4-octyl acetamides in 40% yield.[4] In contrast to the esters studied here each of these hydrocarbons oxidizes at a potential below that which is necessary for oxidation of the electrolyte.

Results

Oxidations were performed potentiostatically in a three-compartment cell at a platinum anode. The reference electrode was a silver wire immersed in 0.1 *M* $AgNO_3$ in acetonitrile. The anolyte and catholyte were acetonitrile–0.1 *M* lithium perchlorate. Background current without added substrate varied in individual experiments from 120