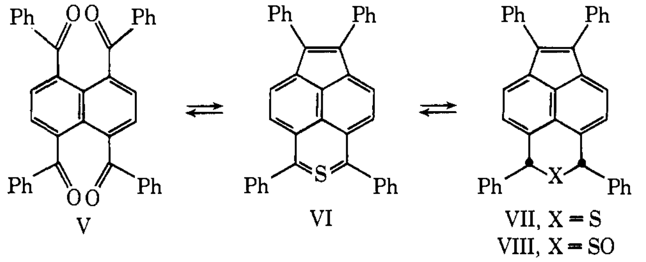
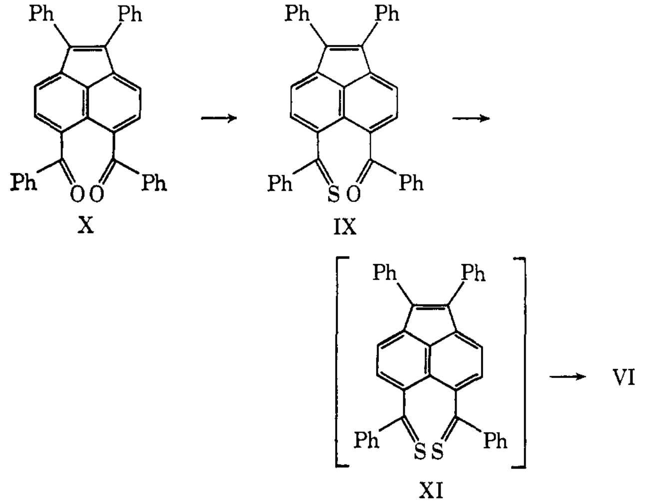
m/e 512 (100%, parent ion of VI) and 480 (22%, ion of 1,2,5,6-tetraphenylpyracylene).

Oxidative degradation of heterocycle VI using sodium dichromate[9] gives rise to the tetraketone V in 71% yield. Catalytic reduction (palladium on carbon) of VI occurs sluggishly (100 hr) to give the *cis*-sulfide VII. Conversion of VII into its corresponding sulfoxide VIII followed by dehydration of VIII regenerates heterocycle VI in good over-all yield.[10]



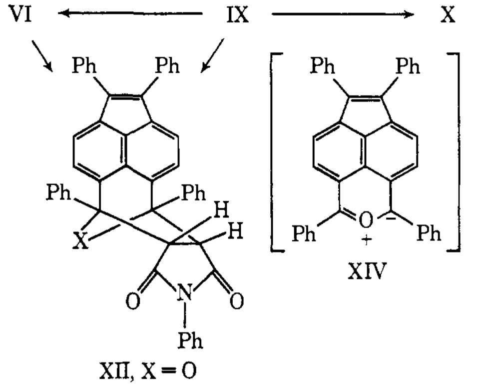
A remarkable reaction occurs on oxidation of VI with Sarett's reagent.[11] Brief treatment of VI with chromium trioxide in pyridine gives rise to a mixture of the brown monothiodiketone IX (68%, mp 235–238°)[12] and the red diketone X (32%, mp 296–297°). Prolonged oxidation of either VI or IX under these conditions affords diketone X as the sole reaction product. Both IX and X along with heterocycle VI are formed when the reaction of tetraketone V with phosphorus pentasulfide is carried out over brief periods (100°, 10 min). Treatment of either IX or X with the phosphorus pentasulfide–pyridine mixture gives VI in high yield. However, no reaction occurs on treatment of IX with pyridine alone (100°, 6 hr). These results suggest that the formation of VI from X probably occurs by stepwise conversion of the diketone *via* the monothiodiketone into the dithiodiketone XI followed by collapse of XI into the heterocycle.



An interesting series of interconversions between the monothiodiketone IX and compounds VI and X have been found. Compound IX smoothly gives heterocycle VI on treatment with gaseous hydrogen chloride in freshly distilled ether solvents. In addition, either *p*-toluenesulfonyl chloride or triphenylphosphine in degassed xylene solution (110°) converts IX into VI in high yield. However, when these reactions are carried out in the presence of dissolved oxygen, diketone X is the predominate product and only small amounts of heterocycle VI are formed. The dramatic influence of oxygen on the course of these reactions is not yet clearly understood.

Upon heating above its melting point (240°), the monothiodiketone IX suffered extensive decomposition. The only isolable product from this reaction was heterocycle VI (27%). Surprisingly, thermolysis of IX at 240° in the presence of N-phenylmaleimide gave a mixture of the oxide adduct XII (70%, mp 320–322°) and the sulfide adduct XIII (10%, mp >360°). A 94% yield of adduct XIII was obtained by reaction of heterocycle VI with the dienophile. Adducts XII and XIII show ultraviolet and visible absorption typical of diphenylacenaphthylene derivatives. The nmr spectra of XII and XIII exhibit resonance for the two protons α to the imide carbonyls at δ 4.55 and 5.10, respectively, a position compatible with *exo* geometry. Both adducts undergo *retro*-Diels–Alder fragmentation on electron impact. Adduct XII (75 eV) shows peaks at *m/e* 669 (35%, parent ion of XII) and 496 (100%, ion of pyran XIV) while adduct XIII shows peaks at 685 (25%, parent ion of XIII) and 512 (100%, ion of heterocycle VI). It is not yet known whether the oxygen heterocycle XIV is involved in the formation of adduct XII from IX.

A thorough examination of the manifold chemical and physical properties of heterocycle VI hopefully will allow a detailed description of this interesting system.



Acknowledgment. We wish to thank the National Science Foundation for funds to purchase the Hitachi mass spectrometer.

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[9] The oxidation procedure used was similar to that described by H. C. Brown and C. P. Carg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

[10] For examples of similar transformations, see ref 1 and 6.

[11] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

[12] Unlike most thioketones, the monothiodiketone IX is remarkably stable and presents no problems with respect to isolation and purification.

The Carbon-13 Nuclear Magnetic Resonance Spectrum of the Stable Nonclassical Norbornyl Cation. Incompatibility with the Equilibrating Classical Ion Conception and Further Proof for the Protonated Nortricyclene Structure[1]

Sir:

The stable norbornyl cation has been shown by Raman spectroscopy[2] to be closely related to nortricy-

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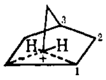
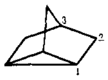
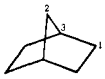
[1] Stable Carbonium Ions. LXXXVI. Part LXXXV: G. A. Olah, A. Commeyras, J. R. DeMember, and J. L. Bribes, *J. Amer. Chem. Soc.*, in press.

clene, and in accordance with the related pmr spectroscopic studies[3] the protonated structure **1** was proposed. This structure is also of considerable interest because it is an example of a stable, long-lived cation that has been shown to contain a protonated cyclopropane ring. To obtain further insight into the nature of this carbonium ion we have obtained its ^{13}C magnetic resonance spectrum. This spectrum was obtained in natural abundance from 2-*exo*-norbornyl chloride in SbF_5–SO_2 solution at −70° using the INDOR technique, observing the ^{13}C satellites in the proton spectrum of the ion at 100 MHz, and locating connected ^{13}C transitions by irradiation at 25 MHz.[4] Details of the proton and carbon nmr spectra of the ion are given in Table I, and the carbon resonance spectrum obtained is shown in Figure 1.

Table I. ^{13}C and ^{1}H Nmr Chemical Shifts and Coupling Constants in the Norbornyl Cation, Cyclopentyl Cation, Nortricyclene, and Norbornane

	Solvent		$\delta_{^{13}C}$[a]	$\delta_{^{1}H}$[b]	J_{CH}[c]
	SbF_5–SO_2 −70°	C_1	+101.8	5.01	53.3
		C_2	+162.5	1.86	140.2
		C_3	+156.1	2.82	153
	SbF_5–SO_2ClF −70°		+95.4	4.48	28.5
		C_1	+183.6	0.99	175
	CCl_4 35°	C_2	+161.8	1.19	133
		C_3	+165.2	1.89	148
		C_1	+164.2[d]	. . .	(130 ± 2)
	CCl_4 35°	C_2	+155.4[d]	1.20	(130 ± 2)
		C_3	+157.6	2.18	140

[a] In ppm from $^{13}CS_2$. [b] In ppm (δ) from internal TMS. [c] In hertz. [d] Assignment of C_1 and C_2 carbon shifts uncertain.

The 53.3-Hz pentuplet observed at 101.8 ppm (from $^{13}CS_2$) on irradiation of the satellites of the lowest field proton peak is due to three equivalent carbons associated with the four equivalent protons. These carbons are assigned to the cyclopropane ring, being equivalent due to the fact that the equilibrium **1a** ⇄ **1b** ⇄ **1c** or **1d** ⇄ **1e** ⇄ **1f**)[5] (asterisk denoting a ^{13}C label) is fast with respect to the time scale of the nmr experiment. For the corner-protonated equilibrium **1a** ⇄ **1b** ⇄ **1c**, the observed carbon–hydrogen coupling constant will be the average of the four direct carbon–hydrogen coupling constants (neglecting long-range coupling which will be small).[5,6] Assuming sp^3 hybridization for the two carbon–hydrogen bonds in the bridged group (J_{CH} = 125 Hz) would give values for the remaining two coupling constants of 195 Hz. Alternatively for the edge-protonated equilibrium **1d** ⇄ **1e** ⇄ **1f**, assuming that the coupling constant of the edge-proton to the carbons is zero, the direct carbon–hydrogen coupling constant for the remaining three protons will be four times that observed (53.3 Hz) or 213 Hz.

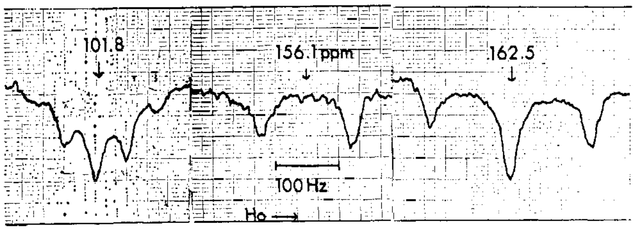
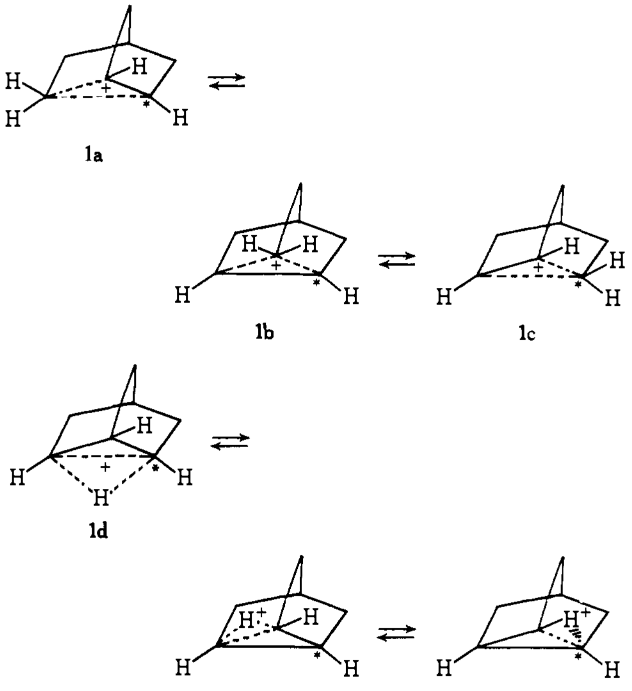


Figure 1. ^{13}C INDOR spectrum of the norbornyl cation generated in SbF_5–SO_2 solution from *exo*-2-chloronorbornane and recorded at −70°. The spectrum was obtained by observing the ^{13}C satellites in the proton spectrum at 100 MHz while irradiating the sample with a swept 25-MHz frequency. ^{13}C shifts indicated are with respect to $^{13}CS_2$.



The effect of increasing positive charge on the carbon atoms in three-membered rings is to cause an increased deshielding of the carbon resonance and an increase in the carbon–hydrogen coupling constant. This effect is demonstrated by the series cyclopropane (δ +196.9 ppm, J = 162 Hz),[7] ethylene oxide (δ +154.6 ppm, J = 176 Hz),[8] and the ethylenebromonium ion (δ +120.8, J = 185 Hz).[4] Thus the deshielding of the ^{13}C resonance and the increase in J_{CH} for the cyclopropane ring protons in either the edge- or corner-protonated molecule as compared to nortricyclene (see Table I) are completely consistent with the protonated nortricyclene structure of the cation. The chemical shift of the equivalent methylene carbons is not much changed in ion **1** as compared to nortricyclene. The bridgehead carbon in ion **1** is, however, deshielded by 10 ppm as compared to its position in nortricyclene, indicating a cage effect on the methine group sitting directly above the charged

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(2) G. A. Olah, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, in press.

(3) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964).

(4) For experimental details of the INDOR method used, see G. A. Olah and A. M. White, *ibid.*, in press.

(5) Theoretical calculations show little preference for either edge- or corner-protonation although face-protonation can be ruled out on these grounds: G. Klopman, *ibid.*, **91**, 89 (1969).

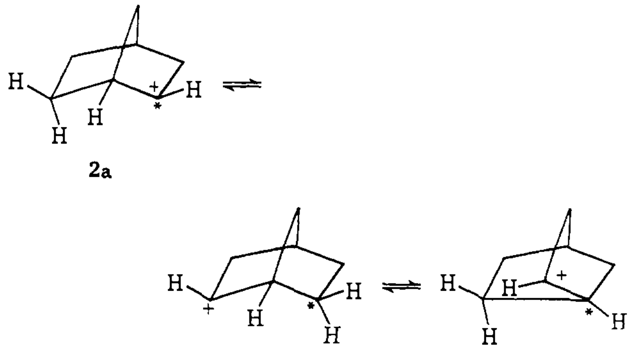
(6) A value of 0.0 Hz was found in the bridged ethylene bromonium ion.[4]

(7) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **86**, 1870 (1964).

(8) (a) G. E. Maciel and G. B. Savitzky, *J. Phys. Chem.*, **69**, 3925 (1965); (b) E. Lippert and H. Prigge, *Ber. Bunsenges. Phys. Chem.*, 67, 415 (1963).

cyclopropane ring. This effect is also evident in the comparison of the proton spectra.

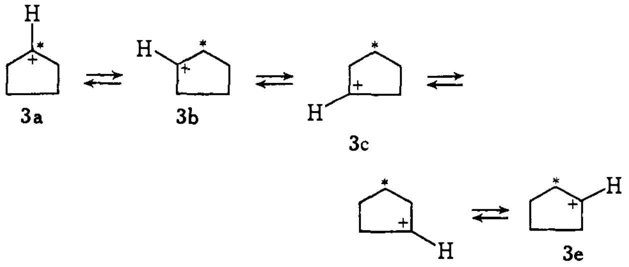
To account for both the proton and carbon nmr spectra in terms of a classical ion, the 1,2 Wagner–Meerwein rearrangement and the 6,2-hydride shift have to be fast with respect to the nmr time scale, **2a** $\rightleftarrows$ **2 b** $\rightleftarrows$ **2c**.[9] The observed shift will thus be the average of the shifts for the carbon bearing the positive charge and carbons one and two bonds removed. Using the isopropyl cation[4] as a model for the positively charged carbon and norbornane for the bridgehead methine and methylene shifts (see Table I) gives a calculated average shift of 65 ppm. An analogous calculation gives a calculated coupling constant of 47 Hz. This approach makes no allowance for the effect of the positive charge one and two bonds removed from the carbonium ion center, and if such corrections are made (from shifts observed in alkyl carbonium ions), the calculated shift is reduced to 50 ppm. Clearly the observed shift is incompatible with the equilibrating classical structure of the ion.



2a **2b** **2c**

As confirmation that the isopropyl cation is a reasonable model for estimating the chemical shift and coupling constant in the classical norbornyl cation, we obtained the ^{13}C spectrum of the closely related cyclopentyl cation **3**.[10]

The ion was prepared from chlorocyclopentane in SbF_5–SO_2ClF solution, and the proton spectrum of the ion at −70° consists of a single resonance at δ 4.48 (from internal TMS). The intensity of the ^{13}C satellites ($\sim$5% of the main peak) shows that complete equilibration of the nine protons among the five carbon atoms is occurring through equilibria **3a** $\rightleftarrows$ **3b** $\rightleftarrows$, etc., interconversions proceeding *via* the rapid 1,2-hydride shifts. The ^{13}C INDOR spectrum is a ten-line multiplet centered at +95.4 ppm with a coupling constant of 28.5 Hz.



3a **3b** **3c** **3d** **3e**

The coupling constant observed is the average of one sp^2 and four sp^3 carbon–hydrogen coupling constants. This neglects long-range couplings which, however, will not only be small but should cancel out because of the opposing signs. Using the isopropyl cation (J = 169 Hz) and cyclopentane (J = 131 Hz)[7] as models gives a calculated coupling constant of $(169 + 8 \times 131/(9 \times 5)$ or 27 Hz, in excellent agreement with the observed value. Similarly the chemical shift will be the average of the isopropyl cation shift (−125 ppm) and four methylene shifts (cyclopentane 167 ppm)[7] giving a calculated value of 109 ppm. If allowance is made for the methylenes being one and two bonds removed from the cation center (using data for alkylcarbonium ions), this value is reduced to 95 ppm, again in excellent agreement with the observed value.

Protonated nortricyclene is the only structure in accordance with the low-temperature Raman, proton, and carbon nmr spectra of the stable norbornyl cation. The question still remains, however, as to whether it is edge- or corner-protonated and which of these forms represents an intermediate or transition state in the equilibrium observed. Both corner- and edge-protonated forms could be compatible with both the ^{13}C and Raman spectroscopic observations (see, however, the following communication). What we feel is the more important point, however, is that the "norbornyl cation" corresponds much more closely in geometry to nortricyclene than to norbornane, and in our view the observed stable, long-lived nonclassical norbornyl cation can be properly described as protonated nortricyclene (rather than implying a structural relationship to norbornane).

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[9] M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 5680 (1964).

[10] The pmr spectrum of this degenerate ion was known previously: G. A. Olah and J. Lukas, *ibid.*, **90**, 933 (1968).

The Proton Magnetic Resonance Spectrum of the Nonclassical Norbornyl Cation and Its Identity with Corner-Protonated Nortricyclene, a Stable Protonated Cyclopropane Containing a Pentacoordinated Carbon Atom[1]

Sir:

Since the first pmr observation of the 2-norbornyl cation,[2] various approaches have been used to elucidate its structure. Raman spectroscopy demonstrated that the cation has a geometry corresponding to that of nortricyclene rather than that of a 2-norbornyl derivative,[3] and it was proposed that the stable ion observed was protonated nortricyclene. In the preceding communication we have reported the complete ^{13}C nmr spectrum of the ion at −70° which is consistent only

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[1] Stable Carbonium Ions. LXXXVII. Part LXXXVI: G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3954 (1969).

[2] (a) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964); (b) M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964).

[3] G. A. Olah, A. Commeyras, and C. Y. Lui, *ibid.*, **90**, 3882 (1968).