Stable Carbocations.[1] CXXXVII. Cycloheptenyl, Cyclooctenyl, and Cyclononenyl Cations

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Abstract: ^1H and ^{13}C nuclear magnetic resonance spectral studies of cycloheptenyl, cyclooctenyl, and cyclononenyl cations and some of their derivatives are reported and compared with those of cyclopentenyl and cyclohexenyl cations. All the cycloallylic cations were studied in two different superacid solvents, FSO_3H-SbF_5 and SbF_5 diluted with SO_2ClF (SO_2) at low temperature. The parent cycloheptenyl cation was observed, while the parent cyclooctenyl and cyclononenyl cations were found to be unstable even in superacid media, although a series of substituted derivatives were obtained. The stabilities of cycloalkenyl cations decrease as the ring size increases. The equilibration of the stereoisomers of protonated 2-cyclohepten-1-one and the protonated 2-cycloocten-1-one in FSO_3H-SbF_5-SO_2ClF solution are also discussed.

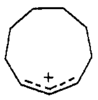
Various groups have investigated the generation of cycloallylic carbocations either in concentrated sulfuric acid or in much stronger superacid solvents.[2] The characteristic proton magnetic resonance band positions for cycloalkenyl cations have been very well demonstrated by Deno and others.[3] Cyclization of linear allylic cations into either cyclopentenyl or cyclohexenyl cations and the equilibrium between the latter two allylic cations have also been paid much attention.[4] However, among the reported cycloalkenyl cations only substituted cyclobutenyl,[5,6] cyclopentenyl, and cyclohexenyl cations have been directly observed: no unsubstituted derivatives and larger cycloalkenyl cations such as cycloheptenyl,[7] cyclooctenyl, and cyclononenyl cations have been observed.

1a

2a

3a

15a



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In our recently reported work,[3i] we demonstrated that the unsubstituted cyclopentenyl and cyclohexenyl cations were stable in superacid solutions at low temperature. No interconversion between substituted cyclopentenyl and cyclohexenyl cations was observed. Now we wish to report the direct observation of larger ring (C_7–C_9) cycloalkenyl cations by nuclear magnetic resonance spectroscopic studies in superacid solutions. Further the cycloalkenyl cations are also characterized by carbon-13 nuclear magnetic resonance spectroscopy using the fast Fourier transformation method.[8]

Results and Discussion

Formation of Cycloalkenyl Cations. Cyclopentenyl Cations. The parent and monomethylcyclopentenyl cations have been successfully generated from their appropriate precursors 2-cyclopenten-1-yl (**1a**) and 1-methyl-2-cyclopenten-1-yl (**1b**). The method of generation of these two ions and their characterization have been recently reported,[3i] and they are not subject to further discussion save their carbon-13 nmr study, which is discussed subsequently.

1a, R = H
b, R = CH_3

Cyclohexenyl Cations. The parent 2-cyclohexen-1-yl cation (**2a**) and its four methyl-substituted derivatives (**2b–2e**) have been prepared. Their generation and characterization (by pmr) have also been recently re-

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(1) Part CXXXVI: G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, in press.

(2) For review, see N. C. Deno in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, Chapter 18; N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 160, 1964.

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(5) (a) I. Lillien and L. Handloser, *ibid.*, **93**, 1682 (1971); (b) K. B. Wiberg and G. Szdimies, *ibid.*, **92**, 571 (1970); (c) Z. Majerski and P. v. R. Schleyer, *ibid.*, **93**, 665 (1971); (d) U. Schollkpof, *Angew. Chem., Int. Ed. Engl.*, 7, 588 (1968); (e) P. v. R. Schleyer, G. W. V. Dine, U. Schollkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

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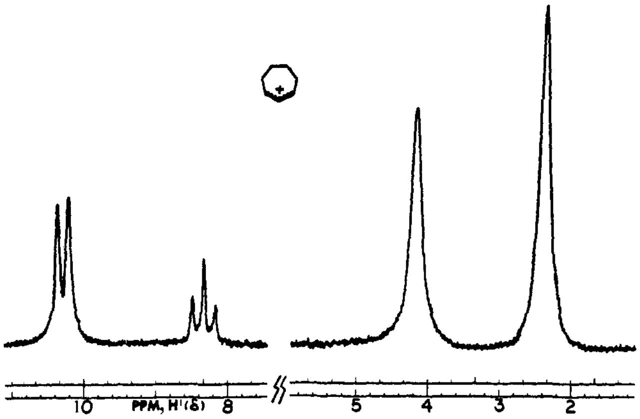


Figure 1. Pmr spectrum (60 MHz) of 2-cyclohepten-1-yl cation.

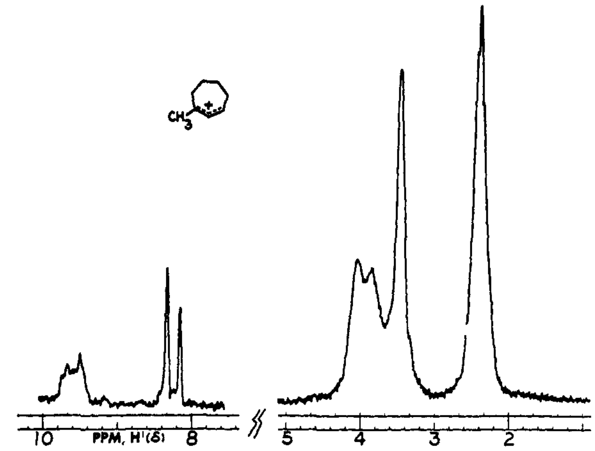


Figure 2. Pmr spectrum 60 MHz of 1-methyl-2-cyclohepten-1-yl cation.

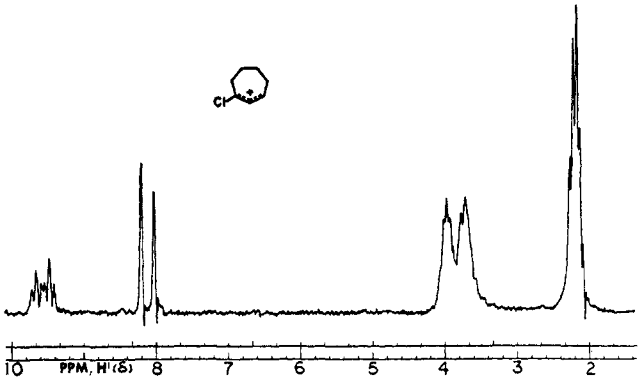
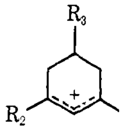


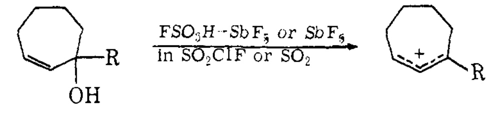
Figure 3. Pmr spectrum (60 MHz) of 1-chloro-2-cyclohepten-1-yl cation.



2a, $R_1 = R_2 = R_3 = H$
b, $R_1 = CH_3$; $R_2 = R_3 = H$
c, $R_1 = R_2 = CH_3$; $R_3 = H$
d, $R_1 = R_3 = CH_3$; $R_2 = H$
e, $R_1 = R_2 = R_3 = CH_3$

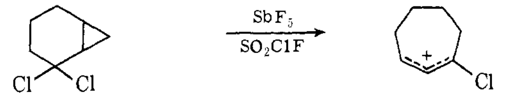
ported along with those of the cyclopentenyl cations.[3i] We have now obtained their carbon-13 nmr spectra, which are discussed subsequently in comparison with the cyclopentenyl cations and the presently studied larger ring cycloalkenyl cations.

Cycloheptenyl Cations. Three cycloheptenyl cations (**3a–c**), including the parent, have been generated according to the procedure described in the Experimental Section from appropriate precursors **4a**, **4b** and **5**. The formation of 2-cyclohepten-1-yl (**3a**) and 1-methyl-2-cyclohepten-1-yl (**3b**) cations from 2-cyclohepten-1-ol (**4**, R = H) and 1-methyl-2-cyclohepten-1-ol (**4**, R = CH_3), respectively, take place in either FSO_3H–SbF_5–SO_2ClF (SO_2) or SbF_5–SO_2ClF solutions at −78°. Both cations were characterized by comparison with the pmr spectra of cyclohexenyl cations as discussed in the subsequent section (Figures 1–3).



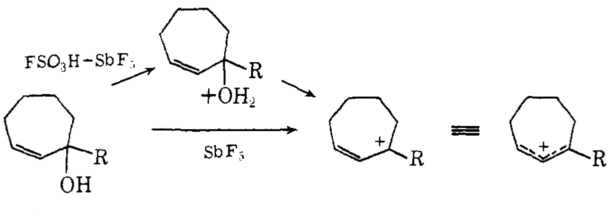
4a, R = H
b, R = CH_3

3a, R = H
b, R = CH_3



5

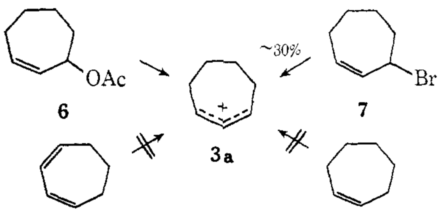
3c



4

3a or 3b

Although the parent cycloheptenyl cation **3a** was successfully generated from the allylic alcohol **4** (R = H) in FSO_3H–SbF_5 diluted with SO_2ClF at −78°, in SbF_5–SO_2ClF solution, a considerable amount of uncharacterized materials were formed. We also treated 1-acetoxy-2-cycloheptene (**6**), 1-bromo-2-cycloheptene (**7**), 1,3-cycloheptadiene (**8**), and cycloheptene (**9**) with either FSO_3H–SbF_5 or SbF_5 in SO_2ClF at −78° (or lower temperatures). Only compounds **6** and **7** give ion **3c** (~30% in the latter case, and polymeric materials). As we have found that cyclopentene reacted with Cl_2–SbF_5–SO_2ClF at low temperature to give the cyclopentenyl cation,[3i] we also attempted the same reaction with cycloheptene. Unfortunately, only unidentifiable materials were obtained under all experimental conditions used.



6

7

3a

8

9

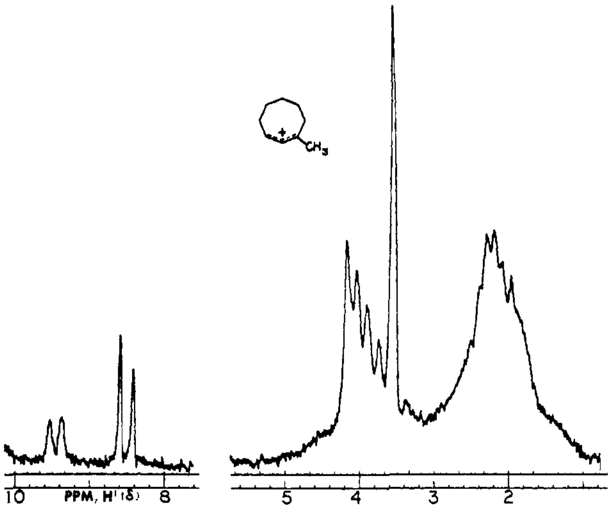
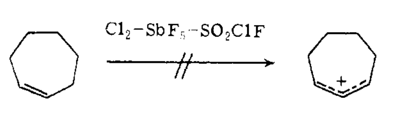
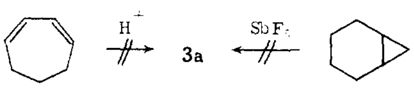


Figure 4. Pmr spectrum (60 MHz) of 1-methyl-2-cycloocten-1-yl cation.



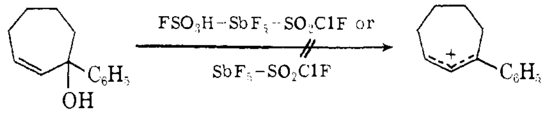
9 3a

Protonation of cycloheptadiene **8** and ionization of bicyclo[4.1.0]heptane at −78° were also unsuccessful; again only uncharacterized materials which gave rise to broad peaks in the pmr were obtained.



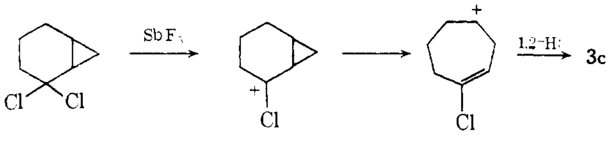
8 10

Both 2-cyclohepten-1-yl (**3a**) and 1-methyl-2-cyclohepten-1-yl (**3b**) cations are stable in superacid solutions at temperatures below −50°. We also have attempted to generate 1-phenyl-2-cyclohepten-1-yl cation (**3d**) (R = C$_6$H$_5$–) under the same reaction conditions, but only unidentifiable materials were obtained. Phenyl substitution has been noticed to decrease the stability of allyl cations relative to methyl substitution.



11 3d

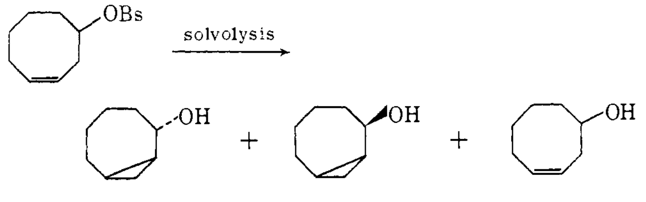
The 1-chloro-2-cyclohepten-1-yl cation (**3c**) is generated from 2,2-dichlorobicyclo[4.1.0]heptane (**5**) in SbF$_5$-SO$_2$ClF solution at −78°. The formation of **3c** must involve the ionization of one of the two chlorine atoms followed by cyclopropyl ring opening to give **13** (*via* **12**), and finally a 1,2-hydride shift to give the allylic cation.



5 12 13

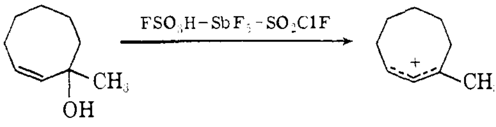
The stabilizing effect of methyl groups on carbocationic centers has long been established.[2] It is found true in the case of ion **3b**. A chloro substituent has also been noticed to increase the stability of allyl cations and is about half as effective as a methyl substituent.[2,4b,9] However, the chloro-substituted cycloheptenyl cation **3c** is only stable at temperatures below −50°.

Cyclooctenyl Cations. Although much work has been done on the solvolysis of cyclooctenyl derivatives,[7c,10] including bicyclooctyl systems, most of the reported results include only investigation of the reactivities of carbenium centers being generated remote from the participating olefinic double bond, such as and allylic type cyclooctenyl carbenium ions have received scant notice. We thus prepared and studied several cyclooctenyl cations.



Preparation of 2-cycloocten-1-yl cation (**15a**), the parent ion, has been attempted from 2-cycloocten-1-ol (**16**), 1-acetoxy-2-cyclooctene (**17**), and 1-bromo-1-cyclooctene (**18**) in either FSO$_3$H-SbF$_5$-SO$_2$ClF or SbF$_5$-SO$_2$ClF solutions at −78° or even lower temperatures. None was successful in giving ion **15a**. As the ring size increases, the stability of cycloalkenyl cations is expected to decrease.[2,3g] A similar trend of stability is also found in simple cycloalkyl carbenium ions.[11]

We also have attempted to generate ion **15a** by protonation of cyclooctadiene **19** and ionization of cyclooctene **20**, without success. As we have previously found that methyl substitution increases substantially the stability of cycloalkenyl cations in five-, six-, and seven-membered rings, we hoped that the terminal methylated cyclooctenyl cation would be stable enough to be observed under long-lived ion conditions. Thus 1-methyl-2-cycloocten-1-ol (**21**) was synthesized from 2-cyclooctenone, and was carefully ionized in FSO$_3$H-SbF$_5$-SO$_2$ClF at −78°. Surprisingly enough, the 1-methyl-2-cycloocten-1-yl cation (**15b**) is stable even at −40°. The ion is characterized by its proton nuclear magnetic resonance spectrum, which is discussed in the following section (Figure 4).



21 15b

Cyclononenyl Cations. Solvolysis of cyclopropyl derivatives and bicyclo[*n*.1.0]alkyl derivatives generally

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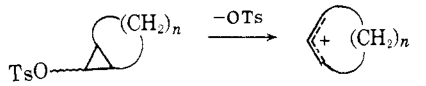
(9) G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Amer. Chem. Soc.*, **94**, 3551 (1972), and the references therein.

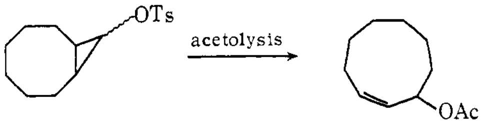
(10) (a) P. G. Gassman, J. Seter, and F. J. Williams, *ibid.*, **93**, 1673 (1971); (b) L. E. Friedrich and F. R. Wight, *ibid.*, **92**, 1807 (1970); (c) K. B. Wiberg and J. G. Pfeiffer, *ibid.*, **92**, 553 (1970); (d) K. B. Wiberg and A. de Meijere, *Tetrahedron Lett.*, 519 (1969); (e) A. C. Cope, R. W. Gleason, S. Moon, and C. H. Park, *J. Org. Chem.*, **32**, 942 (1967); (f) A. C. Cope, S. Moon, and P. E. Peterson, *J. Amer. Chem. Soc.*, **84**, 1935 (1962); (g) A. C. Cope and P. E. Peterson, *ibid.*, **81**, 1643 (1959).

(11) G. A. Olah, D. P. Kelly, and R. G. Johanson, *ibid.*, **92**, 4137 (1970).

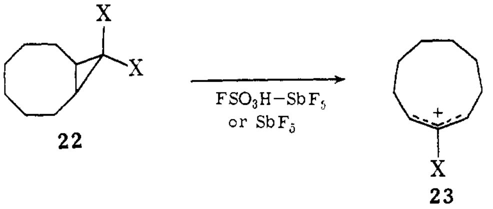
lead to allylic products.[3] Experimental results verifying the theoretical predictions of the cyclopropyl ring-opening mechanism have been extensively discussed. *cis*-2-Cyclononen-1-yl acetate has been found as the major product in the solvolysis of *exo*- and *endo*-



bicyclo[6.1.0]nonyl *p*-toluenesulfonates.[4,6,12] In the light of these results, we have attempted to ionize 9,9-



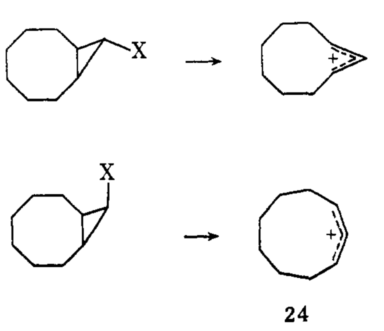
dihalobicyclo[6.1.0]nonane (**22**, X = Cl or Br) in both



$FSO_3H–SbF_5–SO_2ClF$ and $SbF_5–SO_2ClF$ solutions at −78°.

When 9,9-dibromobicyclo[6.1.0]nonane (**22**, X = Br) was carefully added to the superacid solutions at −78°, a dark solution was formed immediately and the nmr spectrum showed only uncharacterized materials. However, when 9,9-dichlorobicyclo[6.1.0]nonane (**22**, X = Cl) was ionized in $SbF_5–SO_2ClF$ (SO_2) at −78° (or lower temperature), a light brown solution was formed. The pmr spectrum is as expected for 2-chloro-2-cyclononen-1-yl cation (**23**, X = Cl) (Figure 5). This ion is not stable above −60°, at which temperature the solution of the ion quickly darkens and a considerable amount of unidentifiable materials are formed.

According to the solvolysis data of *cis*- and *trans*-2-bicyclo[6.1.0]nonyl derivatives,[6] two distinct reaction pathways to the allylic products are possible, depending on whether the leaving group is cis or trans to the cyclopropyl ring. However, under long-lived ion conditions, the thermodynamically preferred product should be obtained.



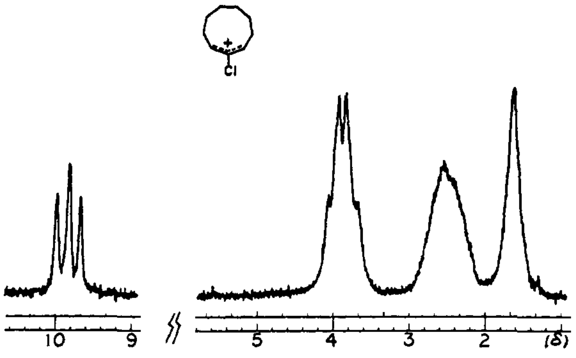


Figure 5. Pmr spectrum (60 MHz) of 2-chloro-2-cyclononen-1-yl cation.

Proton Nuclear Magnetic Resonance Spectroscopic Studies. The 60-MHz pmr spectra of the cyclopentenyl and cyclohexenyl cations were previously reported.[3i] Table I summarizes the 60-MHz pmr spectral data obtained for the cyclopentenyl, cyclohexenyl, cycloheptenyl, cyclooctenyl, cyclononenyl, and their derivative cations either in $FSO_3H–SbF_5–SO_2ClF$ or in $SbF_5–SO_2ClF$ solutions at −78°. For comparison, two bicyclic cyclohexenyl cations (1-methyl- and 3-methyl-$\Delta^{1,9}$-decal-2-yl) and two protonated ketones (2-cycloheptenone and 2-cyclooctenone) are also reported.

Examination of the pmr parameters of the ions in Table I reveals several interesting features: (a) the deshielding of the terminal allylic protons decreases as the ring size increases; (b) the coupling constants between the central and the terminal protons ($J_{2,3}$) in the allylic system increase as the ring size increases; (c) a methyl or chloro substituent substantially alters the charge distribution of the two terminal allylic carbon atoms; and (d) the charge in the allylic system is distributed heavily on the terminal carbons, as can be seen by the chemical shifts of the methyl signals connected to either terminal or central carbon atoms. Although the methyl (or chlorine) group anisotropic shielding effects have been noticed in organic molecules,[13a] the same is believed to be a minor effect according to the substantial change of the allylic carbon chemical shifts discussed below (*vide infra*). The vicinal allylic proton coupling constants ($J_{2,3}$) in the observed cyclopentenyl cations ($J_{2,3}$ = 4.2 Hz) are about half as large as those in cyclohexenyl cations ($J_{2,3}$ = 8.0), which in turn are much smaller than those in cycloheptenyl, cyclooctenyl, and cyclononenyl cations ($J_{2,3}$ = 9.8 Hz). This is in agreement with the well-established dependence of $J_{HC=CH}$ on ring size, observed in simple cycloolefins.[13b]

Carbon-13 Nuclear Magnetic Resonance Spectroscopic Studies. The ^{13}C nmr spectra of cycloalkenyl cations were obtained by the fast Fourier transformation method.[8] For simplicity, only chemical shifts of the allylic part in the ions are summarized in Table II. Due to the instability of the 1-methyl-2-cycloocten-1-yl (**15b**) and 2-chloro-2-cyclononen-1-yl (**23**) cations, their ^{13}C nmr spectra were not obtained.

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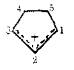
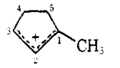
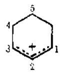
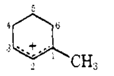
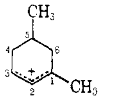
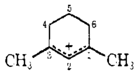
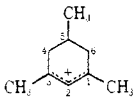
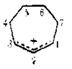
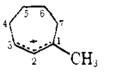
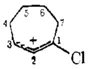
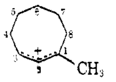
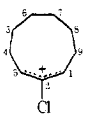
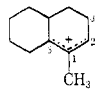
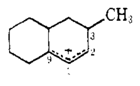
(12) (a) K. B. Wiberg and T. Nakahira, *J. Amer. Chem. Soc.*, **93**, 5193 (1971); (b) P. G. Gassman, E. A. Williams, and F. J. Williams, *ibid.*, **93**, 5199 (1971); (c) C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, **92**, 4274, 4282 (1970); (d) K. B. Wiberg, and T. Nakahira, *Tetrahedron Lett.*, 3759 (1970); (e) C. H. DePuy and J. L. Marshall, *J. Org. Chem.*, **33**, 3326 (1968).

(13) (a) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966; (b) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 2017 (1963).

Table I. Pmr Parameters (δ) of Cycloalkenyl Cations at 60 MHz in $FSO_3H–SbF_5–SO_2ClF$ Solutions at −78° [a]

Cations	H_1 H_3	H_2	H_4	H_5 or H_6	H_7	H_8	H_9	CH_3	$J_{2,3}$[b]	$J_{3,4}$	$J_{4,5}$
 **4a**	11.26 (d)ii	8.65 (t)	4.23 (s)iii						4.2		
 **4b**	10.60 (d)	8.36 (d)	4.05 (s)iii					3.61 (s)	4.2		
 **3a**	10.25 (d)	8.32 (t)	3.81 (t)	2.40 (p)					8.0		6.8
 **3b**	9.73 (d)	8.08 (d)	3.60 (m)	2.42 (p)				3.36 (s)	8.0		6.4
 **3c**	9.61 (d)	8.04 (d)	3.51 (m)	2.82 (m)				1.43 (d) 3.34 (s)	8.0		6.0
 **3d**		8.04 (s)	3.60 (t)	2.60 (p)				3.14 (s)			6.0
 **3e**		7.97 (s)	3.3–3.6 (m)	2.80 (m)				1.45 (d) 3.14 (s)			6.0
	10.18 (d)	8.34 (t)	4.19	2.38	4.19				9.8		
	9.58 (d–t)	8.05 (d)	3.82 (m)	2.39	4.02 (m)			3.45 (s)	10.4	4.0	
	9.50 (d–t)	8.05 (d)	3.62 (m)	2.10	3.90 (m)				11.0	4.4	
	9.42 (d–t)	8.50 (d)	4.00 (m)	2.22	1.90	2.22	4.00	3.56 (s)	10.4	3.8	
	9.82 (t)		3.85 (d–t)	2.50	1.65	1.65	2.50	3.85 (d-t)		8.6	
		9.30 (m						2.60 (s)			
	8.06 (d)	9.42 (d-t)						1.8 (m)	$J_{1,3}$ = 8.8		

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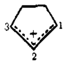
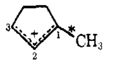
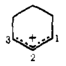
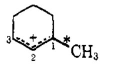
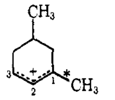
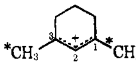
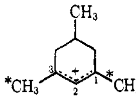
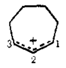
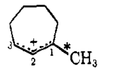
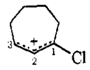
[a] External TMS was used for reference: d = doublet, t = triplet, s = singlet, m = multiplet, d-t = doublet-triplet. [b] Measured in hertz.

Examination of cmr parameters for the cycloalkenyl cations in Table II shows several interesting features. First, in unsubstituted allylic cyclopentenyl, cyclohexenyl, and cycloheptenyl cations the charges are equally and densely populated at two terminal carbon atoms. This is revealed from the identical carbon-13 chemical shift of the two terminal allylic carbon atoms in cyclopentenyl, cyclohexenyl, and cycloheptenyl cations with a value of −24, −41, and −12.1 ppm, respectively. Second, the difference of the carbon chemical shifts between the central allylic carbon and the terminal allylic carbon(s) ($\Delta_{C_1–C_2}$) in cycloheptenyl cations is about 27 ppm smaller than those in cyclohexenyl ($\Delta_{C_1–C_2}$ = +89 ppm) and cyclopentenyl ($\Delta_{C_1–C_2}$ = +81 ppm) cations. We believe that more significant 1,3-orbital interaction[3h] is observed in the seven-membered ring system. Third, when one of the terminal protons is replaced by a methyl (or chlorine) group, the charge distribution is substantially changed. In case of cyclopentenyl cations, a decrease of 10.2

Table II. Cmr Parameters (in ppm) of Cycloalkenyl Cations at 25.4 MHz in $FSO_3H–SbF_5–SO_2ClF$ Solutions at −60° [a]

Cations	C_1	C_2	C_3	CH_3[b]	$\Delta_{C_2-C_1}$	$\Delta_{C_1-C_3}$
	−24.0	−24.0	+57.0		+81	0
	−67.0	−24.4	+46.8	+146.0		−42.6
	−41.0	−41.0	+48.0		+89	0
	−52.5	−11.3	+54.1	151.9		−41.2
	−50.4	+9.5	+55.3	+150.3		−40.9
	−33.9	−33.9	+55.9	+161.0		0
	−33.7	−33.7	+56.7	+161.0		0
	−12.1	−12.1	+42.3		+54.4	0
	−60.7	−16.4	+53.8	+147.8		−54.3
	−42.7	−21.1	+52.3			−21.6

[a] Carbon-13 shifts are in parts per million from CS_2 (external). For simplicity, only the carbon shifts of the allylic part are shown. [b] Only the carbon shift(s) of the methyl carbon indicated by an asterisk is shown.

ppm is observed for the central allylic carbon chemical shift, where increases of 6–8 and 10 ppm are observed in case of cyclohexenyl and cycloheptenyl cations, respectively. The charge delocalization of cyclobutenyl cations has been postulated[3h,14] to involve significant 1,3-orbital interaction, thereby placing charge at the central position. As the ring size increases, overlap between C_1 and C_3 is expected to decrease. The carbon-13 chemical shift difference between the two terminal allylic carbons ($\Delta_{C_1-C_3}$) of the four monomethyl-substituted cyclopentenyl **1b**, cyclohexenyl **2b** and **2d**, and cycloheptenyl **3b** are −42.6, −41.2, −40.9, and −54.3 ppm, respectively. The large difference of the carbon shifts ($\Delta_{C_1-C_2}$) indicates that significant amount of positive charge has been moved toward the carbon atom at 1 position. Although methyl substitution deshielding effect has been demonstrated in both aromatic and olefinic systems,[14c] having a deshielding of *ca.* 9 ppm at the carbon upon replacement of hydrogen by methyl, the origin of large values of $\Delta_{C_1-C_2}$ cannot be attributed entirely to the methyl (or chlorine) neighbor anisotropy effect. For ion **3c**, a large neighboring chlorine anisotropic shielding effect is observed ($\Delta_{C_1-C_3}$ = −21.6). However a discussion of the neighboring halogen anisotropic shielding effect on the ring size is impossible on the basis of the limited data presented in Table II. Finally, the methyl ^{13}C shift has been shown to reflect the changing charge density of the adjacent, electron-deficient carbenium center,[15] except in certain cases.[14] The carbon-13 chemical shifts of the methyl group of ion **1b**, **2b**, and **3b** are +146.0, +151.9, and +147.8 ppm, respectively. The similar values for both ion **1b** and **3b** shows that the electron charge density distribution in the five-membered ring allylic cation is similar to that in the seven-membered ring. A detailed analysis of the geometry of the cycloalkenyl cations is not possible at the present time.

Protonation of 2-Cyclohepten-1-one and 2-Cycloocten-1-one. Evidence has been recently presented that protonation of α,β-unsaturated cyclic ketones leads to an equilibrium mixture of stereoisomers observable by pmr spectroscopy.[16] Carbon-13 nuclear magnetic resonance studies of protonated α,β-unsaturated ketones have also recently been reported,[17] including protonated 2-cyclopenten-1-one and 2-cyclohexen-1-one. These data indicate that the charge density at C_3 is greater than at C_1 and that there is practically no positive charge at C_2. We also protonated 2-cyclohepten-1-one and 2-cycloocten-1-one in $FSO_3H–SbF_5–SO_2ClF$ at −78°, and the equilibration of the two stereoisomers was followed by proton and carbon-13 nmr spectroscopy at different temperatures.

Protonated 2-cyclohepten-1-one gives rise to two stereoisomers, **25a** and **25b**. The protons on oxygen appear as two singlets at δ 12.18 and 12.38 at −60°,

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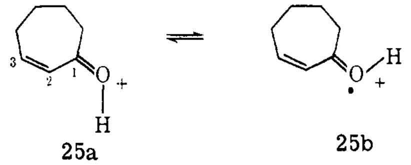
[14] (a) T. S. Sorensen, *J. Amer. Chem. Soc.*, **91**, 6398 (1969); (b) T. J. Katz and E. H. Gold, *ibid.*, **86**, 1600 (1964); (c) J. B. Stothers, *Quart. Rev., Chem. Soc.*, 144 (1965).

[15] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 580 (1969).

[16] G. A. Olah and M. Calin, *ibid.*, **90**, 938 (1968).

[17] G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *ibid.*, **94**, 3554 (1972).

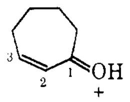
and as a sole singlet at δ 12.24 when observed at 0°. The rest of the pmr chemical shifts are summarized as shown



25a **25b**

Temp, °C	H_2	H_3
−60	7.30,d, 7.48,d, $J_{2,3}$ = 12 Hz	doublet of triplets centered at δ 8.82, $J_{3,4}$ = 5.2 Hz

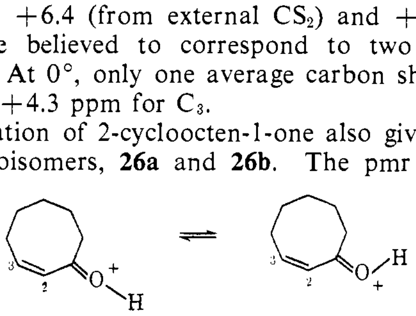
At 0°, the two sets of doublets of H_2 centered at δ 7.30 and 7.48 became one set of doublets. The rest of the proton absorptions were not changed except the two singlets of the protons on oxygen. Interestingly, when the cmr spectra of protonated 2-cyclohepten-1-one were followed at different temperatures, the C_3 carbon was found to have different carbon shifts for the two different stereoisomers. The carbon shifts of C_1, C_2, and C_3 are summarized as



Temp, °C	$\delta_{^{13}C_1}$	$\delta_{^{13}C_2}$	$\delta_{^{13}C_3}$
−60	−27	+44.6	+6.4 and +7.4
0	−30	+66.3	+4.3

At −60°, two carbon shifts are observed for the C_3 carbon at +6.4 (from external CS_2) and +7.4 ppm, which are believed to correspond to two different isomers. At 0°, only one average carbon shift is observed at +4.3 ppm for C_3.

Protonation of 2-cycloocten-1-one also gives rise to two stereoisomers, **26a** and **26b**. The pmr chemical shifts are shown in the following scheme. The protons on oxygen appear as two singlets at δ 12.22 and 12.44 at −60°, and one singlet at δ 12.36 at 0°. The doublet of doublets of C_2 proton also becomes one set of doublets centered at δ 7.48 at 0°, indicating that rotation about the carbon–oxygen double bond occurs.



26a **26b**

Temp, °C	H_2	H_3
−60	doublet of doublets centered at δ 7.48, $J_{2,3}$ = 11 Hz	doublet of triplets centered at δ 8.62, $J_{3,4}$ = 9.0 Hz

In summary, allylic cycloalkenyl cations can be observed in superacid solutions at low temperature by nuclear magnetic resonance spectroscopy. The stability of these ions decreases as the ring size increases. Both ^1H and ^{13}C nmr spectroscopy studies show that the positive charge is equally distributed on the two terminal allylic carbon atoms, with practically no charge on the central carbon atom for the unsubstituted or symmetrically disubstituted cycloalkenyl cations. When one of the terminal allylic protons is replaced by a methyl substituent, the positive charge is more concentrated on the carbon atom to which the methyl group is attached. Both methyl and chloro substituents stabilize the cycloalkenyl cations. A greater degree of stabilization is found in the case of methyl substitution. There is practically no interconversion between cyclopentenyl and cyclohexenyl cations in superacid solutions. The order of stability of allylic cycloalkenyl cations based on their reactivity in superacid solutions is as follows: cyclopentenyl > cyclohexenyl > cycloheptenyl > cyclooctenyl > cyclononenyl. It should be noticed that all the directly observed stable cycloalkenyl cations are believed to be the thermodynamically most stable intermediates in superacid solvents (low nucleophilicity media). This does not mean that other relatively unstable intermediate ions are not involved in solvolytic systems (high nucleophilicity media).

Experimental Section

Nuclear Magnetic Resonance Spectra. Proton nuclear magnetic resonance spectra were obtained by using a Varian Associates Model A56/60A nmr spectrometer equipped with a variable-temperature probe. External TMS (capillary tube) was used as reference. Carbon-13 nuclear magnetic resonance spectra were obtained by the Fourier transform method, using a Varian HA-100 nmr spectrometer equipped with a variable temperature probe. External methyl iodide was used as reference (capillary tube). Carbon shifts were obtained with respect to the external CH_3I as reference and converted to the CS_2 standard. A value of 208.7 ppm is used for $\delta_{^{13}CH_3I}$ (SO_2ClF, −60°).

Preparation of Ions. The procedure for the preparation of cycloalkenyl cations is essentially the same as that previously reported.[35]

Materials. The preparation of cyclopentenyl and cyclohexenyl derivatives has been previously reported.[35]

2-Cyclohepten-1-yl bromide (7), 2-cyclohepten-1-yl acetate (6), 1,3-cycloheptadiene (8), and 2-cyclohepten-1-ol (4, R = H) were prepared according to literature procedures,[18] and had bp 57 (5.0 mm) (lit.[18] 59° (5.2 mm)), 75 (7.5 mm) (lit.[18] 70° (6 mm)), 50 (65 mm) (lit.[18] 55° (75 mm)), and 62.2° (2.4 mm) (lit.[18] 72° (7 mm)), respectively.

Oppenhauer oxidation of 2-cyclohepten-1-ol (**4**, R = H) according to Hodgkins and Flores' procedure gave a 45% yield of **2-cyclohepten-1-one (25)**: bp 65° (8.5 mm) (lit.[18] bp 73–73° (11 mm)).

1-Methyl-2-cyclohepten-1-ol (4, R = CH_3). This alcohol was prepared in 85% yield from 5.6 g (0.05 mol) of **25** and excess of methyllithium (1.8 mol in ether) at room temperature: bp 50–51° (1.7 mm). *Anal.* Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 76.00; H, 10.98.

1-Phenyl-2-cyclohepten-1-ol (11). This alcohol was prepared in 90% yield from 5.6 g of **25** and excess of phenyllithium (2.3 mol in 70:30 benzene–ether) at gentle reflux temperature: bp 90–92° (0.1 mm). The alcohol solidified in receiver upon standing. *Anal.* Calcd for $C_{13}H_{16}O$: C, 92.98; H, 8.51. Found: C, 93.05; H, 8.44.

2-Cycloocten-1-yl bromide (18), 2-cycloocten-1-yl acetate (17), 2-cycloocten-1-one (26), and 2-cycloocten-1-one (16) were prepared according to literature procedures and had bp 61.0° (0.9 mm) (lit.[19] 65° (1.2 mm)), 52° (0.8 mm) (lit.[20] 57° (1 mm)), 32° (0.15 mm) (lit.[20] 89° (14 mm)), and 42° (0.3 mm) (lit.[20] 74° (2 mm)), respectively.

1-Methyl-2-cycloocten-1-ol (21). This alcohol was prepared in 65% yield from 2-cycloocten-1-one (**26**) in the same way as **4** (R = CH_3), bp 50° (0.8 mm); nmr (external TMS, $CDCl_3$) 1.8 (s, 3 H), 2.5 (s, 1 H), 1.9–2.85 (m, 10 H), and 6.0 (m, 2 H). *Anal.* Calcd for $C_9H_{16}O$: C, 78.58; H, 11.42. Found: C, 18.22; H, 11.75.

2,2-Dichlorobicyclo[4.1.0]heptane (5), cycloheptene (9), cyclooctene (20), 1,3-cyclooctadiene (19), 9,9-dibromobicyclo[6.1.0]nonane (22,

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(18) A. C. Cope, T. A. Liss, and G. W. Wood, *J. Amer. Chem. Soc.*, **79**, 6287 (1957).

(19) A. C. Cope and L. L. Estes, Jr., *ibid.*, **72**, 1129 (1950).

(20) A. C. Cope, M. R. Kinter, and R. T. Keller, *ibid.*, **76**, 2757 (1954).

X = Br), and 9,9-dichlorobicyclo[6.1.0]nonane (22, X = Cl) were all commercially available (Aldrich Chemical Co.).

Acknowledgment. Support of our work by the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

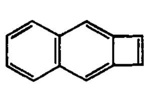
Naphtho[*b*]cyclobutadiene

M. P. Cava* and An-Fei C. Hsu

Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104. *Received February 22, 1972*

Abstract: Reaction of naphtho[*b*]cyclobutene (**6**) with 1 equiv of NBS gives crude 1-bromonaphtho[*b*]cyclobutene (**7**), which could be purified only chemically by hydrolysis to naphtho[*b*]cyclobuten-1-ol (**8**) followed by treatment of the latter with hydrogen bromide. Reaction of bromide **7** with potassium *tert*-butoxide generates the unstable naphtho[*b*]cyclobutadiene (**1**). The observed reactions of **1** include (a) addition of *tert*-butyl alcohol to give 1-*tert*-butoxynaphtho[*b*]cyclobutene (**12**), (b) formation of the dimer 1,2:5,6-dinaphtho[*b*]cycloctatetraene (**19**), and (c) addition of 1,3-diphenylisobenzofuran to give a mixture of endo and exo adducts **14** and **15**. The reactions of naphtho[*b*]cyclobutadiene are contrasted with those of benzocyclobutadiene (**11**).

Naphtho[*b*]cyclobutadiene (**1**) is a molecule of considerable theoretical interest. It is a closely related isomer of the much studied biphenylene (**2**) and is one of the simplest of all possible fully unsaturated condensed benzenoid systems.[1,2] The 1,2-diphenyl and 1,2-dibromo-3,8-diphenyl derivatives (**3** and **4**) have been isolated and characterized,[3,4] but attempts to isolate 3,8-diphenylnaphtho[*b*]cyclobutadiene (**5**) were unsuccessful.[5,6]



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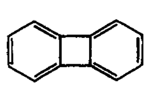
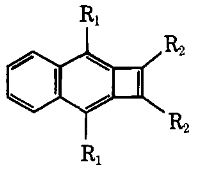


2



3, $R_1 = H; R_2 = Ph$
4, $R_1 = Ph; R_2 = Br$
5, $R_1 = Ph; R_2 = H$

In this paper, we report a method of generation of the parent naphtho[*b*]cyclobutadiene (**1**), as well as some simple chemical reactions of this hydrocarbon.

Results

Naphtho[*b*]cyclobutene (**6**)[7] reacts readily with 1 equiv of *N*-bromosuccinimide to give a crude product which was shown by nmr analysis to consist of about 35% unchanged hydrocarbon **6**, 60% 1-bromonaphtho[*b*]cyclobutene (**7**), and 5% of dibrominated derivatives of **6**. Attempts to separate pure bromide **7** from this mixture chromatographically were unsuccessful, but pure **7** was obtained indirectly in the following manner. Treatment of the bromination mixture with silver trifluoroacetate in aqueous acetonitrile gives the readily purified naphtho[*b*]cyclobuten-1-ol (**8**); reaction of **8** with hydrogen bromide affords pure **7**, mp 82–83.5°. In practice, impure **7** obtained by the bromination of **6** was satisfactory for further transformations.

The reaction of 1-bromobenzocyclobutene (**9**) with an excess of potassium *tert*-butoxide is known to afford a high yield of 6a,10b-dihydrobenzo[*a*]biphenylene (**10**), a product derived from benzocyclobutadiene (**11**) by angular dimerization.[8] Under similar conditions, dehydrobromination of 1-bromonaphtho[*b*]cyclobutene (**7**) gave no isolable hydrocarbon product. There was formed instead, in 72% yield, a crystalline product assigned the structure of 1-*tert*-butoxynaphtho[*b*]cyclobutene (**12**) on the basis of spectral and analytical data.

It seemed mechanistically unlikely that ether **12** was the product of a displacement reaction involving *tert*-butoxide ion; a mechanism involving dehydrobromination of **7** to napththo[*b*]cyclobutadiene (**1**), followed by addition of *tert*-butoxide ion to the cyclobutadienoid 1,2 bond of **1**, appeared more likely. Indeed, treatment of bromide **7** with excess potassium *tert*-butoxide in the presence of 1,3-diphenylisobenzofuran (**13**) gave a product consisting of ether **12** and the endo and exo adducts **14** and **15** in the ratio 2:2:5. It was found, however, that adducts **14** and **15** were not formed when a solution of ether **12** was refluxed with furan **13** and potassium *tert*-butoxide, showing that the alkoxide-catalyzed addition of *tert*-butyl alcohol to naphtho[*b*]cyclobutadiene is not a reversible process.

The stereochemistry of adducts **14** and **15** was assigned on the basis of their nmr spectra. The benzylic hydrogens of the endo adduct **14** appear at δ 4.63, compared with the value 4.30 for the corresponding hydrogens of the exo adduct **15**. This effect is attributable to a deshielding of these hydrogens in **14** by the

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