Protonation of Some Norcaradienes

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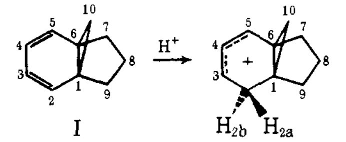
Abstract: This paper reports the fluorosulfonic acid protonation of two norcaradienes (tricyclo[4.3.1.0^{1,6}]deca-2,4-diene and tricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene) and the direct nmr observation of the resulting allylcyclopropyl ions (wherein protonation occurred at the 2 or 5 position). From the nmr data, it is concluded that the six-membered ring of both ions exists in a boat conformation, with C_2 and C_5 bent away from the cyclopropane ring. This allows the conjugation with the cyclopropane ring to be nearly symmetrically bisected.

The study of the structural factors affecting the norcaradiene–cycloheptatriene equilibrium has been of interest to chemists for some time.[4] We have been interested in the stability[5] and reactivity of norcaradienes. In this latter connection, we now report the protonation of two related norcaradienes, which resulted in the formation of allylcyclopropyl ions.[6] As will be shown, these ions provide a unique opportunity for the direct comparison of allyl and cyclopropylcarbinyl interactions. Furthermore, we will remark on the failure of ion IV to exist as the bishomotropylium ion, IVa.

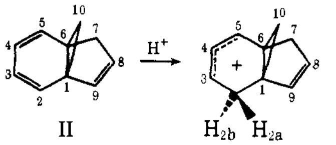
Results and Discussion

When either tricyclo[4.3.1.0^{1,6}]deca-2,4-diene (I)[11] or tricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene (II)[12] was extracted from a CD_2Cl_2 solution into a 1:3 (v/v) mixture of FSO_3H-SO_2ClF at −78°, a light yellow-orange solution was formed. These solutions remained unchanged indefinitely at −78°, but rapid darkening and decomposition took place, in both cases, at −25°. Several attempted quenches in MeOH–NaOMe at −78° yielded complex product mixtures (of which I and II were but minor components). The 100-MHz nmr spectra of the ion derived from I (*i.e.*, III) and that derived from II (*i.e.*, IV) are shown in Figures 1 and 2, respectively.



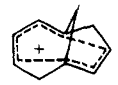
I

III



II

IV



IVa

That protonation occurred, as expected, at C_2 of both I and II is readily seen from an analysis of the nmr spectra. The spectral assignments were all confirmed *via* the appropriate decoupling experiments (only the methylene protons of the five-membered ring of III could not be fully assigned) and are summarized in Tables I and II.

Table I. Nuclear Magnetic Resonance Data for Protonated Tricyclo[4.3.1.0^{1,6}]deca-2,4-diene (III)[a]

Proton	Chem shift,[b] τ	Coupling constants, Hz
H_{2a}	6.06	$J_{2a,3} = 4.0 \pm 0.5$
H_{2b}	6.62	$J_{2a,2b} = -23 \pm 0.5$
H_3	3.35	$J_{2b,3} =$ *ca.* 0
H_4	2.93	$J_{3,4} = 9.0 \pm 0.5$
H_5	1.15	$J_{4,5} = 4.2 \pm 0.2$
$2H_7$, $2H_8$, $2H_9$	7.0–8.1	
$H_{10\alpha}$, $H_{10\beta}$	5.38, 7.50	$J_{10\alpha,10\beta} = \pm 3.2 \pm 0.2$ $J_{5,10\alpha} \cong J_{5,10\beta} \cong J_{2a,5} =$ small

[a] Spectrum of a solution in FSO_3H-SO_2ClF (1:3, v/v) at *ca.* −80° was measured on a Varian HA100 nmr spectrometer, frequency sweep. [b] Chemical shifts measured relative to internal $CHDCl_2$ (τ 4.70).

Within the framework of structure III, two ambiguities exist in the assignment of the resonances. The first is the differentiation between H_{2a} and H_{2b} (exo and endo protons), while the second concerns distinguishing $H_{10\alpha}$ from $H_{10\beta}$. Furthermore, with respect to IV, the alternate structure V must be excluded.

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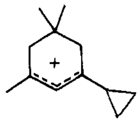
[2] National Science Foundation Predoctoral Fellow, 1966–1970.

[3] Deceased Nov 23, 1969.

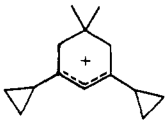
[4] For a review, see G. Maier, *Angew. Chem., Int. Ed. Engl.*, 6, 402 (1967). See also M. Jones, Jr., *ibid.*, **8**, 76 (1969); G. Sargent, N. Lowry, and S. Reich, *J. Amer. Chem. Soc.*, **89**, 5985 (1967); and R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970).

[5] For a review of the evidence for the monohomobenzenoid character of norcaradienes, see P. Warner, Ph.D. Dissertation, University of California at Los Angeles, 1970, p 96.

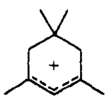
[6] Directly observed ions of this type are rare. In addition to X[7] and the bicyclohexenyl ions,[8,9] Deno[10] has studied the set of ions, i–iii, from which it may be concluded that the first cyclopropyl ring (as in i) has a greater stabilizing effect than the second one (as in ii). However, in both i and ii the cyclopropyl groups are not conformationally rigid.



i



ii



iii

[7] M. Roberts, H. Hamberger, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 6346 (1970).

[8] (a) R. F. Childs, M. Sakai, and S. Winstein, *ibid.*, **90**, 7144 (1968); (b) R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968); (c) R. F. Childs and B. Parrington, *Chem. Commun.*, 1540 (1970).

[9] P. Vogel, M. Saunders, N. M. Hasty, and J. A. Berson, *J. Amer. Chem. Soc.*, **93**, 1551 (1971).

[10] N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965).

[11] E. Vogel, W. Wiedemann, H. Kiefer, and W. Harrison, *Tetrahedron Lett.*, 673 (1963).

[12] (a) P. Radlick and W. Rosen, *J. Amer. Chem. Soc.*, **88**, 3461 (1966); (b) W. Grimme, M. Kaufhold, U. Dettmeier, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **5**, 604 (1966).

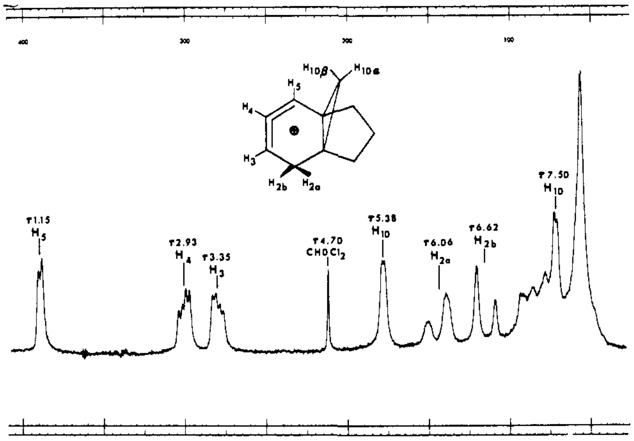


Figure 1. Nmr spectrum (100 MHz) of protonated tricyclo[4.3.-1.0^{1,6}]deca-2,4-diene (III) in FSO_3H-SO_2ClF (1:3, v/v) at *ca.* −120°.

The nmr spectra of both III and IV showed that only one of the protons attached to C_2 was appreciably coupled to H_3. This means the virtually uncoupled proton at C_2 bears a *ca.* 90° dihedral angle relationship with H_3.[13] Examination of models indicates that there are two possible conformations of the six-membered ring which fulfill this requirement; both are boats and are depicted in VI and VII. In VI, the cyclopropane ring is symmetrically oriented with respect to the substituents at C_5, just the incorrect orientation for cyclopropyl conjugation.[14] However, the orientation of C_5 with respect to the cyclopropane ring in VII is the symmetrical bisected conformation, required for effective conjugation.[14] Since, as we show below, the charge is distributed into the cyclopropane ring, we take VII to be the correct conformation,[15] whereby H_{2a} is the coupled exo proton.[16]

Table II. Nuclear Magnetic Resonance Data for Protonated Tricyclo[4.3.1.0^{1,6}]deca-2,4,7-triene (IV)[a]

Proton	Chem shift,[b] τ	Coupling constants, Hz
H_{2a}	5.97	$J_{2a,3} = 4.0 \pm 0.5$
H_{2b}	6.46	$J_{2a,2b} = -22.5 \pm 0.5$
H_3	3.27	$J_{2b,3} =$ *ca.* 0
H_4	2.87	$J_{3,4} = 9.0 \pm 0.5$
H_5	1.25	$J_{4,5} = 5.0 \pm 0.2$
H_{7a}, H_{7b}	6.58, 6.99	$J_{7a,b} = -18.0 \pm 0.5$
H_8[c]	3.61	$J_{8,9} = 8.0 \pm 0.5$
H_9[c]	3.43	
$H_{10\alpha}$, $H_{10\beta}$	5.60, 7.40	$J_{10\alpha,10\beta} = \pm 3.4 \pm 0.4$
		$J_{5,10\alpha} \cong J_{5,10\beta} \cong J_{2a,5} =$ small

[a] Spectrum of a solution in FSO_3H-SO_2ClF (1:3, v/v) at *ca.* −80° was measured on a Varian HA100 nmr spectrometer, frequency sweep. [b] Chemical shifts measured relative to internal $CHDCl_2$ (τ 4.70). [c] The differentiation between H_8 and H_9 was based on the plausible assumption that the proton next to the cyclopropane would resonate at lower field, as is the case in uncharged species, where conjugation is probably less severe.

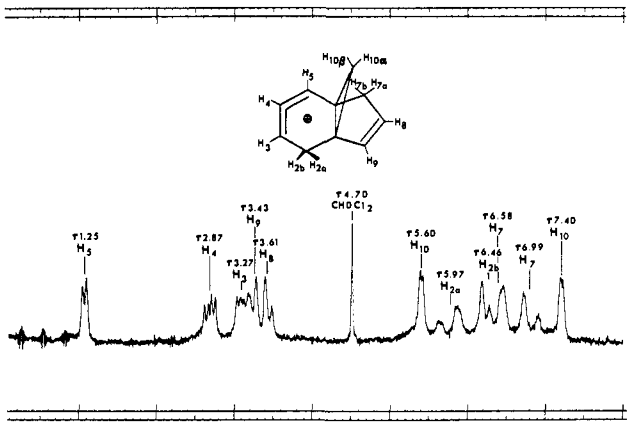
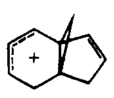
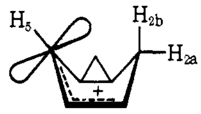


Figure 2. Nmr spectrum (100 MHz) of protonated tricyclo-[4.3.1.0^{1,6}]deca-2,4,7-triene (IV) in FSO_3H-SO_2ClF (1:3, v/v) at *ca.* −120°.

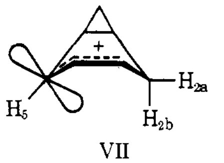
The assignments of $H_{10\alpha}$ and $H_{10\beta}$ in III and IV are difficult to make. Both are long range coupled to H_5. Also, the variously substituted bicyclo[3.1.0]-hexenyl ions,[8,9] which are possible model systems,



V



VI



VII

show differences with respect to which the cyclopropyl proton (exo or endo) appears at lower field. Therefore, in the absence of deuterium labeling experiments, we cannot make a firm assignment. However, it is interesting to note the rather large chemical shift difference between $H_{10\alpha}$ and $H_{10\beta}$.[18] Clearly, the assignments of $H_{10\alpha}$ and $H_{10\beta}$ could be cleared up *via* the appropriate deuterium labeling experiments.

How can structure V be eliminated from consideration? To the extent charge leaks through the cyclopropane ring to the double bond of the five-membered ring (from the chemical shifts, this leakage seems small, but real; *i.e.*, the downfield shifts of H_8 and H_9 are too large to be accounted for on the basis of inductive effects alone), V is poor in that it is cross-conjugated, whereas IV is linearly conjugated (this effect must already be felt in the late transition state). Admittedly,

(13) E. Garbisch, Jr., *J. Amer. Chem. Soc.*, 86, 5561 (1964).

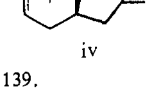
(14) (a) C. U. Pittman, Jr., and G. Olah, *ibid.*, 87, 5123 (1965); (b) D. S. Kabakoff and E. Namanworth, *ibid.*, 92, 3234 (1970).

(15) It is important to note that only one conformation is possible since deuteration of either I or II takes place stereospecifically to place the deuteron at D_{2a} (topside attack in, most likely, a late transition state, since bottomside attack takes place in other more exothermic reactions, such as the Diels-Alder reaction of I). Since this deuteron remains in its initial position, no equilibration between VI and VII is occurring. Yet models would indicate no great barrier to their interconversion, which means one of the conformations (VII) must be more stable.

(16) It is interesting to note that the chemical shift of H_{2a}, the proton syn to the cyclopropane ring, is an average of 0.55 ppm lower in field than that of H_{2b}, the proton anti to the cyclopropane ring. This relative field position is just reversed for neutral compounds. In fact, calculations based on empirical cyclopropane shielding parameters[17] indicate that the syn proton should be about 0.1 ppm to higher field than the anti proton. The failure of the correlation to hold for III and IV is not unexpected, since there has been a considerable loss of electron density from the cyclopropane rings of III and IV, as well as a change in electron distribution.

(17) Calculations based on empirical cyclopropane shielding values (P. Warner, ref 5, p 114) indicate the shielding by the cyclopropane ring can account for no more than a 0.25-ppm upfield shift of the allylic protons of III and IV. Clearly this is far below the observed values (but this may not be a factor at all).[16]

(18) This large difference also holds for the protonated ketone iv[19] (Δδ 1.88 ppm).

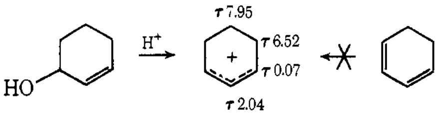


iv

(19) P. Warner, ref 5, p 139.

however, this argument does not rigorously exclude V. Although experimentally difficult, ^{13}C nmr spectroscopy could solve this problem.

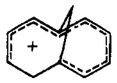
What is the evidence for charge distribution into the cyclopropane rings of III and IV? First of all, it is necessary to demonstrate that the allyl portions of III and IV (C_3, C_4, C_5) contain less charge than expected. For this purpose, the model cyclohexenyl cation VIII[20] was generated from cyclohex-2-en-1-ol (it could not be successfully generated from 1,3-cyclohexadiene) in FSO_3H–SO_2ClF (1:3, v/v). The chemical shifts of the allyl portion of the cyclohexenyl cation,



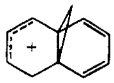
VIII

τ 0.07 and 2.04, are far lower than the corresponding shifts of either ion III or IV,[17] particularly with respect to the shifts of H_3 (τ 3.35 and 3.27 *vs.* 0.07). Thus, clearly, a considerable amount of charge (which, due to the conformation of the six-membered ring, could not be allylically delocalized)[21] has been transferred to the cyclopropane ring. The shifts of $H_{10\alpha}$ and $H_{10\beta}$, as well as the small $J_{10\alpha,10\beta}$, indicate charge is present at C_{10}. The small leakage of charge onto C_8 and C_9 of IV, as well as the increase in $J_{8,9}$ (from 6 to 8 Hz) on going from II to IV (indicating a release in strain in the five-membered ring caused by loosening of the 1,6 bond), points to the presence of charge at C_1. Thus the ions are best described as nearly symmetrical bisected, as opposed to homoallylic (static bicyclobutonium) type ions.[23]

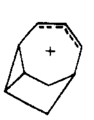
A priori, one of the intriguing aspects of the protonation of II is that the resulting ion may exist as a bishomotropylium ion (IVa).[24] The failure of IV to do so has already been mentioned. On the other hand, IX exists as the open ion, rather than the closed IXa.[26]



IX



IXa



X

This would seem to indicate that to forego charge delocalization to the 1-bridge carbon, an ion such as IV or IX must gain conjugation with at least two additional double bonds. This means that conjugation with each cyclopropane α–β bond is worth somewhat more than conjugation with one double bond (this conclusion is further indicated by the greatly decreased allylic interaction of C_5 with C_4 and C_3, as discussed below).

Allycyclopropyl ions such as III and IV are peculiar in that they cannot, because of steric restraints, be both flat allyl systems and symmetrically bisected cyclopropylcarbinyl ions. However, they could have reasonably flat allyl systems if they adopted a bicyclobutonium (homoallyl) structure where charge would be delocalized to mainly C_{10} of the cyclopropane ring. That the allyl systems of III and IV are not flat is seen from the small $J_{4,5}{}^{III} = 4.2$ Hz and $J_{4,5}{}^{IV} = 5.0$ Hz (compare the corresponding $J = 9$ Hz for the symmetrical ion, X).[7] As a result of this bending of the allyl system, considerably less charge resides at C_3 of III and IV relative to the corresponding position of X (*viz.*, chemical shifts of τ 3.35 and 3.27 *vs.* 1.37). That the preference of ions III and IV for the nearly symmetrical bisected with bent allyl conformation, as opposed to the bicyclobutonium with flat allyl conformation, is a reflection of the relative efficiency of the two neighboring groups is not immediately obvious, because of the substituents on these groups. However, judging from solvolysis data, the allylic substitution pattern[27] is more favorable (relative to unsubstituted allyl) than the cyclopropylcarbinyl substitution pattern[28] (relative to unsubstituted cyclopropylcarbinyl). Also, examination of models reveals little strain difference between the two conformations. Therefore, we conclude that the nearly symmetrical bisected conformation allows the better neighboring group—cyclopropyl—to play its best role.

Experimental Section

The syntheses of I[11,29] and II[12,29] have been reported. Cyclohex-2-en-1-ol was commercially obtained (Aldrich Chemical Co.). Generation of the ions was achieved at −78° (for ions III and IV) and at −116° (for ion VIII) by standard literature procedures.[30]

Acknowledgment. We are grateful to Dr. David L. Harris for help in obtaining the 100-MHz nmr spectra and for valuable discussions regarding their interpretation.

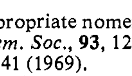
(20) An erroneous report of the cyclohexenyl cation has previously been made: G. A. Olah and W. S. Tolgyesi, *J. Amer. Chem. Soc.*, **83**, 5031 (1961). However, Professor Olah has restudied this ion in detail, and his results support ours: G. A. Olah, G. Liang, and Y. K. Mo, submitted for publication.

(21) This idea is also vividly seen by comparing vicinal vinyl coupling constants in I, III, and VIII. These are, respectively, $J_{3,4} = 5.9$ Hz,[22] $J_{3,4} = 9.0$ Hz, $J = 7.0$ Hz, $J_{4,5} = 9.3$ Hz,[22] $J_{4,5} = 4.2$ Hz, $J = 7.0$ Hz. Clearly, the protonation has converted the 3,4 bond from "single" to "double," with the opposite effect on the 4,5 bond. Since the double bond in III is now effected mainly by induction (as opposed to resonance), H_4 is at slightly lower field than H_3.

(22) H. Günther, *Tetrahedron Lett.*, 2967 (1967).

(23) P. Warner, D. Harris, C. H. Bradley, and S. Winstein, *ibid.*, 4013 (1970).

(24) If V is the correct structure for protonated II, it, too, could exist as the bishomotropylium ion, v, which would then be of the 1,2- variety.[25]



v

(25) For a review of the appropriate nomenclature, see (a) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 1284 (1971); (b) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

(26) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 7785 (1969).

(27) Andrew Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 78.

(28) P. v. R. Schleyer and G. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966).

(29) W. Rosen, *Diss. Abstr.*, **28**, 4506-B (1968). We thank Professor Radlick for a copy of the thesis.

(30) J. M. Bollinger, J. M. Brinich, and G. A. Olah, *J. Amer. Chem. Soc.*, **92**, 4025 (1970).