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THE 8-TETRACYCLO[4.3.0.0^{2,4}.0^{3,7}]NONYL CARBONIUM ION[1]

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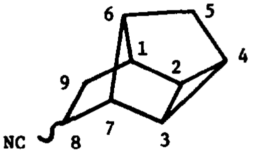
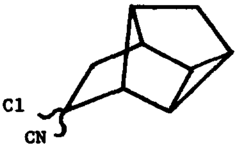
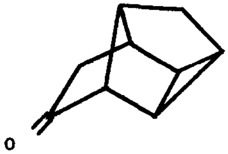
The interesting tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane ring system, which serves as the basic structural unit for the mixture of nitrile epimers (I) obtained in the homo-Diels-Alder condensation of acrylonitrile with norbornadiene, has not been extensively studied due to the low yields previously encountered in the synthesis of useful intermediates.[2] We have developed a facile synthesis of ketone III in two steps: chlorination of the nitriles I (exo and endo)[3] with phosphorus pentachloride in refluxing carbon tetrachloride,[4] followed by treatment of chloronitrile II with sodium hydroxide in dimethylsulfoxide gives III in yields of up to 47% based on nitriles I. The structure of tetracyclic ketone III was confirmed by infrared and n.m.r. spectral comparison with an authentic sample.[5]



I

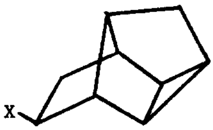


II

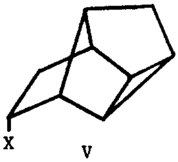


III

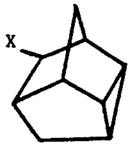
An investigation of the solvolyses of suitable derivatives of <u>exo</u>- and <u>endo</u>-8-tetracyclo/4.3.0.$0^{2,4}$.$0^{3,7}$/nonane(IV and V) seemed especially interesting, since, due to the incorporation of both nortricyclene (carbons 1, 2, 4, 3, 7, 6 and 5) and norbornane (carbons 1, 2, 3, 7, 8, 9 and 6) ring systems into structures IV and V, a double norbornonium ion VIII, as well as the more traditional norbornonium ions VII are possible intermediates.



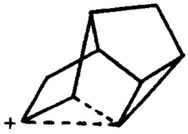
IV



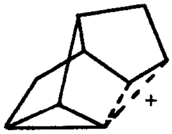
V



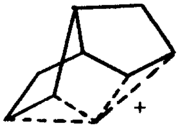
VI



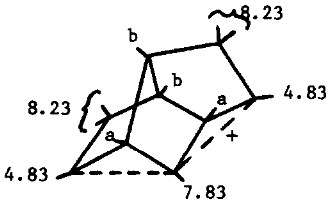
VIIa



VIIb



VIII



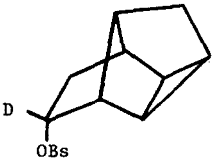
IX

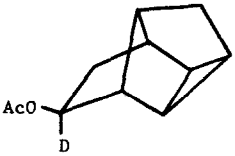
a protons: 7.08 or 7.50

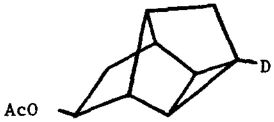
b protons: 7.50 or 7.08

<u>endo</u>-V-OBs (m.p. 63-64°) was prepared from V-OH, which, in turn, was synthesized by sodium borohydride reduction of ketone III.[6] The epimeric IV-OBs[7] (m.p. 59-60°) was prepared from IV-OH, which was generated by hydrolysis of a mixture of IV-Cl and V-Cl, which in turn was prepared by hydrolysis of nitriles I to acids IV-COOH and V-COOH, followed by chlorodecarboxylation.[8] The Hofmann rearrangement of a mixture of amides prepared from nitriles I gave a mixture of IV-NH_2 and V-NH_2.[9] The epimeric nature of IV-OH and V-OH was demonstrated by oxidation of IV-OH to III with chromium trioxide-pyridine.

Acetolyses of IV-OBs and V-OBs, as well as deamination of a mixture of IV-NH_2 and V-NH_2 in acetic acid, result in only one acetate, IV-OAc. Structural verification was accomplished by base catalyzed hydrolyses of the solvolysis products to IV-OH. In each case v.p.c. analysis of the IV-OH obtained demonstrated that no detectable V-OH ($<0.5\%$) was present. Acetolysis of labeled brosylate X (synthesized from the <u>endo</u> alcohol obtained by lithium aluminum deuteride reduction of III) produces <u>exo</u>-acetate which exhibits an infrared absorption at 3067 cm.$^{-1}$ (cyclopropane C-H) diminished relative to that of the unlabeled acetate (IV-OAc). The ratio of the 3067 cm.$^{-1}$ peak in the labeled acetate relative to that of the unlabeled acetate (IV-OAc) is 5.0:6.0. The n.m.r. spectrum of the labeled acetate exhibits a quartet at τ 5.11 (hydrogen α to acetoxy) which is diminished in intensity by one-half relative to the unlabeled acetate (IV-OAc). These results are consistent with the formation of an equimolar mixture of acetates XIa and XIb in which the deuterium is distributed between C-8 and C-4.


X


XIa


XIb

The nature of the deuterium scrambling and the lack of formation of VI-OAc, the Wagner-Meerwein rearrangement product, clearly exclude VIIa as the product determining intermediate and raise doubts concerning ion VIII.

Dissolution of IV-OH or V-OH in FSO_3H-SO_2 at -78° produces a light yellow solution which does not decolorize when warmed to at least -10°. The n.m.r. spectrum of this solution does not change significantly from -55° to -10° and is characteristic of a carbonium ion,[10] showing absorptions at τ 4.83, 7.08, 7.50, 7.83 and 8.23 (internal reference, $CHCl_3$) in the ratio 2:2:2:1:4, respectively. Neutralization of the n.m.r. sample in aqueous potassium hydroxide yields IV-OH. The two proton absorption at τ 4.83 is inconsistent with the n.m.r. spectrum expected for VIII or for a rapid equilibrium of equivalent norbornonium ions VIIa and VIIb, since these two situations would give a four proton absorbance near τ 4.83. A third possibility is a moderately rapid equilibrium of ions VIIa and VIIb ($k_{equilibration} < 30$ sec.$^{-1}$),[11] and a fourth possibility is represented by structure IX. Carbonium ion IX is preferred over a moderately rapid equilibrium of norbornonium ions, since no Wagner-Meerwein rearrangements were observed, and the relatively simple n.m.r. spectrum is more consistent with that anticipated for IX than for VIIa or VIIb. Carbonium ion IX possesses five pairs of equivalent protons and one unique proton and the assignments can be made as indicated in IX, whereas, carbonium ion VII has no equivalent protons and would be expected to exhibit a more complex spectrum.

Rate constants for the acetolysis of IV-OBs and V-OBs at 25° show good first-order behavior and are 2.79×10^{-4} sec.$^{-1}$ and 4.74×10^{-6} sec.$^{-1}$, respectively. Table 1 allows a comparison of estimated rate constants (relative to cyclohexyl brosylate), calculated for non-assisted acetolysis by the method of Schleyer,[12] with the observed values.

TABLE 1

ROBs	k^{25} (sec.$^{-1}$)	log k_{rel}[a] calc.	exp.	log anchimeric assistance
IV-OBs	2.79×10^{-4}	-2.7[b]	3.21	5.9
V-OBs	4.74×10^{-6}	-2.3[b,c]	1.44	3.7

[a] Relative to cyclohexyl brosylate. [b] The carbonyl stretching frequency for ketone III is 1756 cm.$^{-1}$, measured in dilute CCl_4 and calibrated against a polystyrene spectrum. [c] Nonbonded interaction strain was taken as an average of that for _endo_-2-norbornenyl and _endo_-2-norbornyl tosylate (0.9 kcal.).[12]

Thus one finds a large degree of anchimeric assistance for the _exo_-isomer IV-OBs and, surprisingly, a substantial amount of assistance in the case of the _endo_ epimer V-OBs.[13] On the basis of all the experimental evidence, it seems most reasonable to rationalize the enhanced rate of the _exo_-brosylate as a result of direct formation of the non-norbornonium, norbornyl ion IX. The anchimeric assistance observed for _endo_ V-OBs is atypical, being greater than that for _exo_-2-norbornyl ($10^{3.3}$), and tends to rule out direct formation of a classical ion, followed by rearrangement to IX. The precise nature of the rate enhancement observed for V-OBs is presently under investigation.

REFERENCES

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5. We express our appreciation to Professor A. Nickon for providing us with n.m.r. and infrared spectra of a sample of ketone III prepared by Dr. H. K. Hall.
6. Sodium borohydride reduction of ketone III yields V-OH and IV-OH in a 84:16 ratio. The stereochmical assignment is based upon the expected predominance of *endo* and the n.m.r. absorption patterns for hydrogen α to hydroxyl. IV-OH exhibits a doublet of doublets at τ 5.72 (Js = 2.0, 6.6 c.p.s.) and V-OH a more complex multiplet at τ 5.60.
7. The IV-OH used to prepare IV-OBs contained no detectable *endo* V-OH ($<$ 0.5% by v.p.c.) and n.m.r. analysis of IV-OBs and V-OBs indicated no intercontamination of epimers.
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13. A similar pattern is found for the *exo-exo*- and *exo-endo*-tricyclo-[3.2.1.$0^{2,4}$]octan-6-yl brosylates studied by K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965) and A. K. Colter and R. C. Musso, *ibid.*, **30**, 2462 (1965) (log anch: *exo-exo*, 4.8; *exo-endo*, 1.2; ν_{co} = 1757 cm.$^{-1}$ for the related ketone), although the anchimeric assistance calculated for the *exo-endo* isomer is boderline.