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TRIAXANE[1]

Alex Nickon and Gopalkrishna D. Pandit
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

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We wish to describe the preparation and characterization of a novel tetracyclic hydrocarbon that along with its ring opened tricyclic derivatives possesses symmetry features like those in the nortricyclane-norbornane series and that can afford new opportunities to probe the enigmatic behavior of norbornyl systems.

The parent hydrocarbon is tetracyclo$[3.3.1.0^{2,4}0^{3,7}]$nonane (1), descriptively called "triaxane".[2] It has C_{3v} symmetry and cleavage of any cyclopropyl bond with HZ produces the noradamantane skeleton 2. The bonds in 2 are arranged such that ionization of Z (with or without anchimeric assistance) can produce a degenerate ion 3, whose classical equivalent can convert to its enantiomer by a Wagner-Meerwein rearrangement, by a 1,3-hydride shift, or by a blend of these processes as might occur in a more highly symmetrical "nortricyclonium"-like ion.[3] Importantly, however, triaxane and noradamantane lack much of the ground state strain[4] of their nortricyclane and norbornane counterparts and so these higher homologs are of immediate interest. Furthermore, because C-Z is flanked by bridgehead carbons, vicinal hydride shifts are discouraged and olefin formation is precluded. These last features are particularly attractive for a variety of mechanistic studies (e.g. 1,3-eliminations, cyclopropyl ring cleavages, homoenolization etc.) where olefin production introduces experimental and interpretative complications.[7] If carbon bridging facilitates ionization in 2, a faster ionization rate is possible for equatorial Z (see 2c) than for axial Z and this would be of special interest because the opposite order is commonly found in cyclohexyl systems.[8] The bridged ion 3 (or its classical equivalent) is not only accessible by the σ-route (e.g. 2→3) and by the Δ-route (1→3),[9] but also by the π-route (e.g. 5a→3). We now report the synthesis and characterization of triaxane and show that acid opens it solvolytically to the noradamantyl system 2 (Z=equatorial) thus illustrating the potential usefulness of these substrates for detailed mechanistic study.

Noradamantan-2-one (4a) was obtained as reported[5] and although its structure was reasonably certain it was unambiguously established by Haller-Bauer cleavage with sodium amide in benzene to give a mixture of amides. Methanolysis of this mixture produced two pure liquid methyl esters, one of which was identical (ir, glpc) with the ester produced by hydrogenation of bicyclo[3.2.1]hept-6-ene 3-exo-carboxylic acid[10] (5b) followed by treatment with diazomethane. This Haller-Bauer product from a cyclopentanone could have arisen only from structure 4a or from brendan-8-one,[11] and the latter ketone is excluded because its symmetry precludes existence of epimeric alcohols.[5]

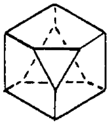
Pyrolysis of the sodium salt of the p-toluenesulfonylhydrazone 4b gave triaxane (C_9H_{12}; mp 183.5-184.5°), which showed cyclopropyl C-H stretch (CCl_4) at 3031 cm^{-1}, prominent mass spectral peaks at 120,105, 91, 79, and 66, and no olefinic hydrogens (nmr). Four cyclopropyl structures are in principle possible from a C-2 carbene and these involve insertion towards C-4, C-9, C-8, and C-7. Proton and ^{13}C magnetic resonance spectra[12] uniquely support structure 1, which contains only three types of carbon nuclei (ratio 3:3:3) and four types of protons (ratio 3:3:3:3).

The ^{13}C resonance spectrum (with proton decoupling) consisted only of three peaks of equal intensity (at 144.0, 150.5, and 154.5 ppm from CS_2). The pmr peaks of triaxane (in CCl_4) fell into four equal intensity groups, viz the bridgehead hydrogens (H_b) as a broad peak ($W_{\frac{1}{2}} \sim 11$ Hz) at δ 2.46; the cyclopropyl hydrogens (H_c) as a closely spaced doublet at δ 2.01 ($J_{bc} \sim 1.5$ Hz);the equatorial hydrogens (H_e) as two overlapping triplets at δ 1.61; and the axial hydrogens (H_a) as a doublet at δ 1.28. The distortion in the 6-membered ring of 1 decreases the H_eH_b dihedral angle and increases the H_aH_b dihedral angle from those in a normal cyclohexane ring, and the vicinal couplings are modified as expected.[13] Double resonance confirmed the assignments and provided more accurate coupling constants. Thus saturation of the H_b protons converted H_c to a singlet and transformed H_a and H_e to a typical AB quartet ($J_{ae} \sim 10.5$ Hz); and saturation of H_c left H_b as a triplet ($J_{be} \sim 5$ Hz).

Ring opening with $HOAc/H_2SO_4$ at 25° converted triaxane (1) to a monoacetate (>98% 2, Z=OAc), which was saponified to noradamantanol (2, Z=OH) and oxidized to noradamantan-2-one (4a). These ring opened products were identical (ir, nmr, glpc) with samples obtained other ways.[5] Cleavage of 1 with D_2SO_4/acetic acid-d_4 ultimately gave the corresponding monodeuterated alcohol and ketone (98.5%-d_1). Bamford-stevens reaction on the tosylhydrazone of the deuterated ketone provided pure triaxane-*d* (98.5%-d_1), whose ir showed cyclopropyl C-D at 2270 cm^{-1} and whose nmr showed a one-third intensity drop of the H_c signal at *δ* 2.01, thus confirming the cyclopropyl proton assignment in the nmr.[14] The absence of polydeuterated species and the retention of all the label on oxidation of the deuterated alcohol to the ketone are additional noteworthy features of these compounds. The synthesis of functionalized triaxanes and various mechanistic studies are in progress.

REFERENCES

1. Supported by the National Science Foundation.
2. Three axial bonds (*tri*, *ax*ial) of the cyclohexane ring are joined to the cyclopropane ring. This name (kindly suggested by D. Covey) anticipates future synthesis of the heptacyclic homolog "peraxane" (i) in which the remaining axial bonds lead to a second cyclopropyl ring. Conceptually, peraxane is cubane with two opposite corners truncated.



(i)

3. (a) S. Winstein and D.S. Trifan, *J. Amer. Chem. Soc.*, **74**, 1154 (1953); (b) J.D. Roberts, C.C. Lee and W.H. Saunders, *ibid.*, **76**, 4501 (1954).
4. That noradamantane systems may possess a degree of "adamantanoid" stability is indicated by their formation in acid isomerizations of deltacyclane, brendane, and brexane systems.[5,6]
5. A. Nickon, G.D. Pandit, and R.O. Williams, *Tetrahedron Letters*, 2851 (1967).
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8. E.L. Eliel, N.L. Allinger, S.J. Angyal, and G.A. Morrison, "Conformational Analysis", Interscience Publishers, New York, New York, 1965, p 84.
9. We suggest the term Δ-route (delta-route) for paths that produce cations by cleavage of three-membered rings (*cf* ref 7b).

10. We thank Professor J. Baldwin and Mr. W.D. Foglesong for an authentic sample of this unsaturated acid [J.E. Baldwin and W.D. Fogelsong, Tetrahedron Letters, 4089 (1966)].

11. A. Nickon, H. Kwasnik, T. Swartz, R.O. Williams, and J.B. DiGiorgio, J. Amer. Chem. Soc., **87**, 1613, 1615 (1965).

12. We are grateful to Professor J.B. Stothers and Mr. G.W. Buchanan for the ^{13}C spectra done at 15.1 MHz on a CS_2 solution (containing 300 mg/ml) with proton decoupling, and also to Dr. R. Highet for the decoupled pmr spectra (in CCl_4 on a Varian HA-100 MHz instrument).

13. N.S. Bhacca and D.H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry", Holden-Day, Inc., San Francisco (1964), p 49.

14. Interestingly the cyclopropyl protons are at unusually low field for a hydrocarbon (*cf* corresponding hydrogens in nortricyclane are at *ca* δ 1.0).