Stereospecific π- *versus* σ-Participation in Solvolysis of Tricyclononadienyl *p*-Nitrobenzoates

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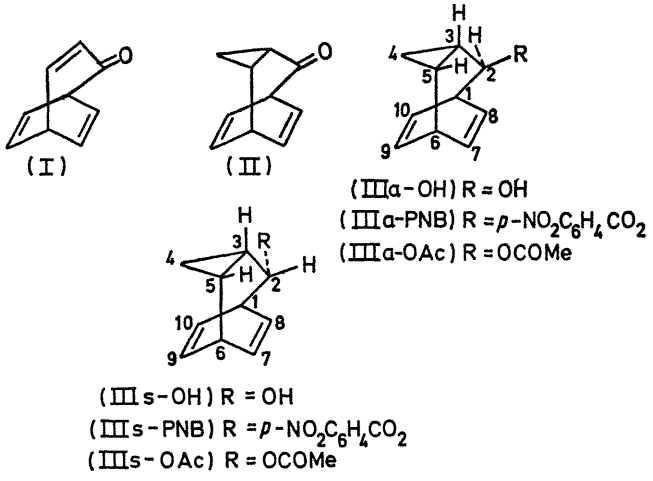
Summary Acetolysis of the tricyclic *p*-nitrobenzoate (IIIs-PNB) yields exclusively the unrearranged (IIIs-OAc), whereas the less reactive epimer (IIIa-PNB) undergoes stereospecific and complete rearrangement to acetates (IV-OAc) and (VI-OAc); solvolysis in the (IIIs) series may be aided by cyclopropyl σ-participation, whereas that in the (IIIa) series involves back-side homoallylic π-participation during C–O heterolysis.

PARTICIPATION by a double bond or cyclopropyl ring in delocalizing positive charge frequently accompanies solvolytic rearrangements of bridged alicyclic systems.[1] We now report striking stereospecificity in acetolysis of the epimeric tricyclo[4,2,2,$0^{3,5}$]deca-7,9-dien-2-yl esters (IIIa-PNB) and (IIIs-PNB) which may involve competition between alternative modes of participation at the developing cationic centre. Homologation[2] of ketone (I)[3] gave 60% of the cyclopropyl ketone (II), ν_{max} (CCl_4) 1690 cm^{-1}; 2,4-dinitrophenylhydrazone: m.p. 192—193°,† which on $LiAlH_4$ reduction at −70° gave a 6 : 1 ratio of *anti*-alcohol (IIIa-OH), m.p. 123—125°, and *syn*-alcohol (IIIs-OH), m.p. 137—138°. Configurational assignments were based on n.m.r. vicinal couplings to the C-2 proton, which in (IIIa-OH) is a doublet at δ3·83 with $J_{1,2}$ 3·8 Hz, whereas in (IIIs-OH) the corresponding signal at δ3·87 is a doublet of doublets having $J_{1,2}$ 4·3 Hz and $J_{2,3}$ 7·7 Hz.



Acetolysis of (IIIs-PNB)‡ in refluxing HOAc buffered by 1 equiv of NaOAc proceeded with a half-life of *ca.* 1·5 h to give as kinetic product only (>95%) the corresponding acetate (IIIs-OAc).§ In contrast, (IIIa-PNB) underwent acetolysis with a half-life of *ca.* 11 h to give three volatile products: a preparatively inseparable mixture of two

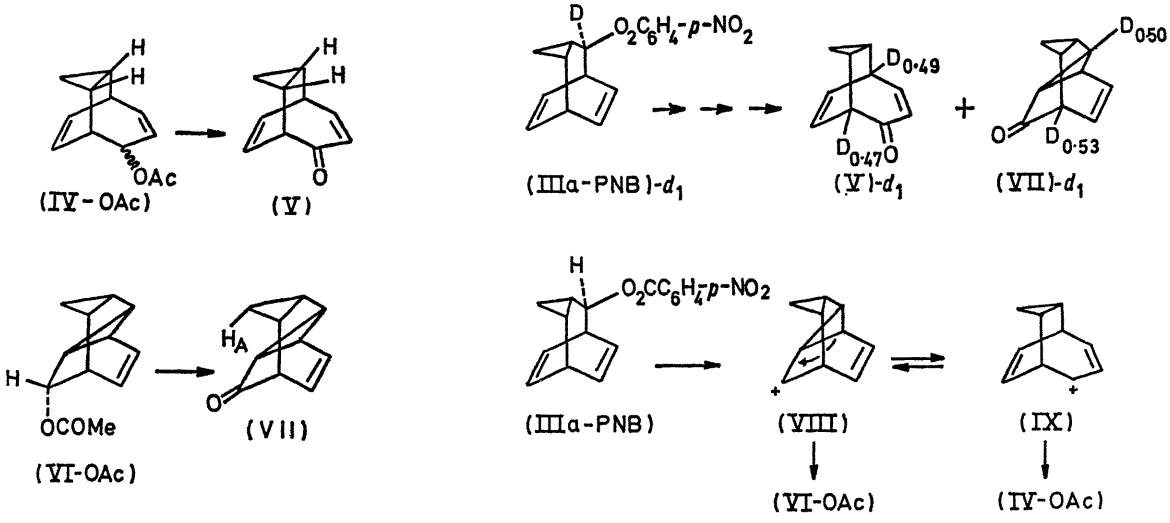
† All new compounds were characterized by i.r. and n.m.r. spectra and gave combustion analyses or mass spectra in agreement with the reported structures.

‡ The *p*-nitrobenzoates (IIIs-PNB) (m.p. 122—123°), (IIIa-PNB) (m.p. 96—97°). (VI-PNB) (m.p. 119—120°), and (IV-PNB) (m.p. 112—114°, two epimers) were prepared from the corresponding alcohols using *p*-nitrobenzoyl chloride in dry pyridine, crystallized to constant m.p., and satisfactory isomeric purity by n.m.r.

§ An analytical 1/8 in. × 20 ft. column of 10% FFAP on ABS (Anakrom, 100—110 mesh) at 165—170° permitted nearly quantitative, determination of five acetolysis components according to the following retention times: (IIIs-OAc) (22 min); (IV-OAc), minor epimer (23 min); (IV-OAc), major epimer (24 min); (IIIa-OAc) (25 min); (VI-OAc) (29 min).

epimeric tricyclic acetates (IV-OAc) (74%) and a single tetracyclic acetate, (VI-OAc) (22%). Control studies showed that (IIIs-OAc) or (IIIa-OAc) could have been detected if formed under these reaction conditions.¶

The dramatic stereospecificity in these acetolyses and complete absence of crossover products (under kinetic control)¶ clearly exclude any role by the sp^2-hydridized

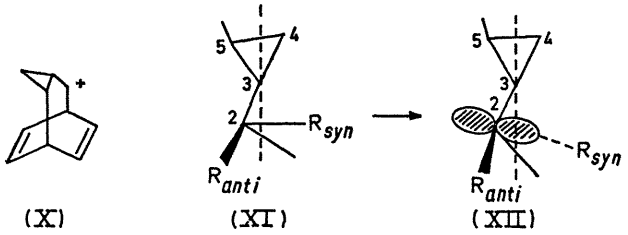


Structure (IV-OAc) was established by hydrolysis and MnO_2 oxidation of the mixed epimeric alcohols to dienone (V) ν_{max} (CCl_4) 1670 cm^{-1}, in which proton topology and configuration could be rigorously assigned by 100 MHz n.m.r. decoupling and europium shift studies.[4] Hydrolysis of (VI-OAc) in turn gave the alcohol, m.p. 69—71°, oxidized by CrO_3–C_5H_5N to the tetracyclic ketone (VII), ν_{max} (CCl_4) 1707 cm^{-1}. Structure (VII) was fully consistent with n.m.r. studies whereby H_A was characterized by its highly shielded position (δ −0·16) and its high slope in europium shift analysis, as required by its proximity to the carbonyl group.[5]

When labelled monodeuterio (IIIa-PNB) was acetolysed for 16 h and the products were oxidized to the corresponding ketones as described above, the deuterium distribution in the ketones could be established by n.m.r. as follows: monodeuterio-(V) equally labelled at both bridgehead carbons, monodeuterio-(VII) labelled equally at the bridgehead and the cyclopropyl position as shown.

On this evidence, the acetolysis of (IIIa-PNB) appears to involve stereospecific homoallylic participation to yield the presumed tetracyclic intermediate (VIII) which undergoes twofold symmetrization (as required by the deuterium distribution) probably by rapid equilibration with the tricyclic allylic cation (IX) prior to discharge by solvent. This hypothesis is in accord with the finding that *both* (VI-PNB) and (IV-PNB) yield on kinetically controlled acetolysis substantially the same distribution of three acetates as that observed from (IIIa-PNB).

cation (X) in these solvolyses and directly implicate π- or σ-participation prior to product formation. Although homoallylic π-participation appears sterically as feasible for (IIIa-PNB) as for (IIIs-PNB), such participation alone cannot account for the contrasting behaviour observed. We suggest that the differing reaction pathways may originate from greater cyclopropyl σ-participation in solvolysis of (IIIs-PNB) than in that of the *anti*-epimer, (IIIa-PNB). If one projects the substituents on C-2 relative to a plane normal to and bisecting the plane of the cyclopropyl ring (*cf.* XI) it becomes clear that the ionization of the *syn*-substituent R_{syn} produces a vacant orbital (shaded in XII) in optimum steric relationship for cyclopropyl participation.[6] For ionization of an *anti*-substitutent, R_{anti}, the geometry is less favourable for cyclopropyl interaction and a major role in charge delocalization is then assumed by back-side participation of the homoallylic π-bond.



¶ Although more stable than the corresponding *p*-nitrobenzoates, both (IIIs-OAc) and (IIIa-OAc) slowly isomerize in refluxing acetic acid with half-lives of *ca.* 4·5 h and 12 h, respectively, to yield the characteristic mixture of (IV-OAc) (two epimers) and (VI-OAc) in approximately 3 : 1 ratio.

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[1] Examples of such participation in degenerate rearrangements are reviewed by R. E. Leone and P. von R. Schleyer, *Angew. Chem. Internat. Edn.*, 1970, **9**, 860.
[2] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1353.
[3] M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, 1967, **89**, 6356.
[4] J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, 1971, **93**, 641, and earlier references cited therein.
[5] See "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", by L. M. Jackman and S. Sternhall, 2nd edn., Pergamon, London, 1969, pp. 88—92.
[6] Recent work includes B. R. Ree and J. C. Martin, *J. Amer. Chem. Soc.*, 1970, **92**, 1660; C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, p. 4274; C. D. Poulter and S. Winstein, *ibid.*, p. 4282; earlier key references are given in these papers.