

POLYCYCLIC REARRANGEMENTS. A NOVEL, CARBONIUM ION MEDIATED,
 BICYCLO (4.2.0) OCTA-2,4-DIENE \longrightarrow 1,3,5-CYCLOOCTATRIENE
 ISOMERISATION IN A PROPELLANE FRAMEWORK

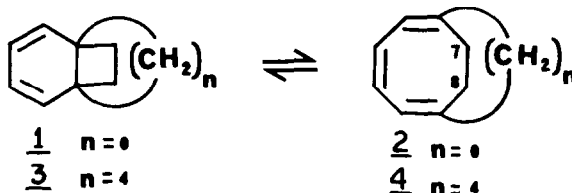
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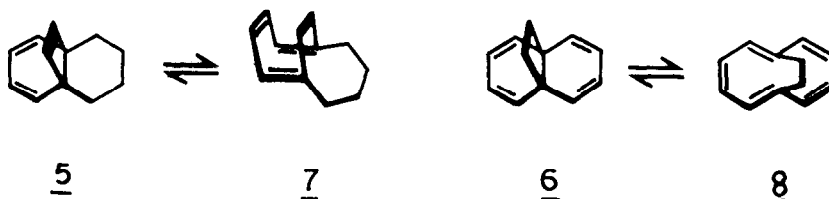
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Summary: A serendipitous cationic rearrangement of hexacyclic propellane 9 to its strained fluxional isomer, the bridged 1,3,5-cyclooctatriene 10 is described.

The equilibrium position in the symmetry allowed bicyclo (4.2.0) octa-2,4-diene 1 - 1,3,5-cyclooctatriene 2 valence isomerisation has been shown to be a function of the substituents at C₇ and C₈ positions¹. When constrained

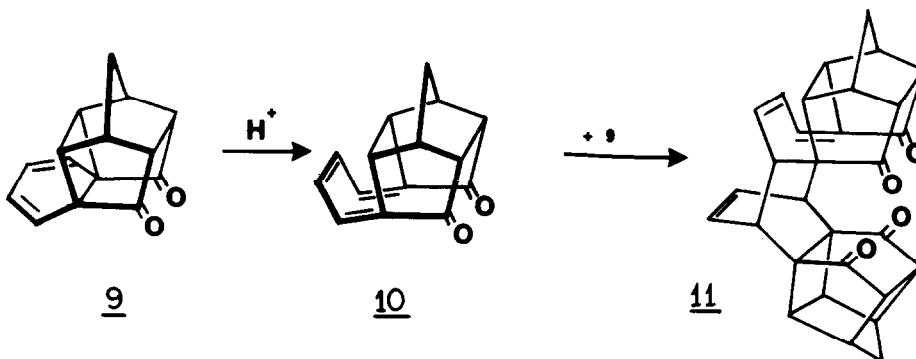


into a rigid polycyclic frame, such as the (4,4,2) propellane 3, the direction of $3 \rightleftharpoons 4$ equilibrium presents intriguing possibilities², particularly in view of the reports^{4,5} that closely related propellanes 5 and 6 show no tendency towards electrocyclic reaction to 7 and 8, respectively. Hexacyclo (7.4.2.0^{1,9}.0^{3,7}.0^{4,14}.0^{6,15}) pentadeca-10,12-diene-2,8-dione 9 is a unique, readily



accessible polycycle⁶ that embodies a (4.4.2)-propella-2,4-diene moiety 3 as part of its rigid architecture. In principle, 9 can valence isomerise to highly strained 10 as ordained by orbital symmetry rules, but, in practice

showed little inclination towards such a thermal electrocyclic process⁷. However, under acid catalysis 9 smoothly rearranges to highly reactive 10, which in turn is intercepted by 9 as $\pi^4_s + \pi^2_s$ adduct 11. The discovery of this unanticipated but remarkable rearrangement and the X-ray crystal structure determination of 11 is the object of this report.



Rapid dispersal of a CH_2Cl_2 solution of 9 into few drops of Conc. H_2SO_4 , stirring for 1 hr at $0-5^\circ$ and neutralisation with bicarbonate led to the isolation of a single crystalline compound, mp. $269-70^\circ$, in 50-60% yield. The dimeric nature of this product and its structural complexity were revealed through spectral parameters [$\text{C}_{30}\text{H}_{24}\text{O}_4$, UV: $\lambda_{\text{max}}^{\text{MeOH}}$ 282nm, broad ($\epsilon \sim 3000$); ir (KBr): 1750, strong (cyclopentanone), 1640 cm^{-1} , medium (conjugated carbonyl); ^1H nmr (270 MHz, $\text{DMSO}-d_6$); δ 6.71(1H, br s), 6.66(1H, t, $J=6\text{Hz}$),

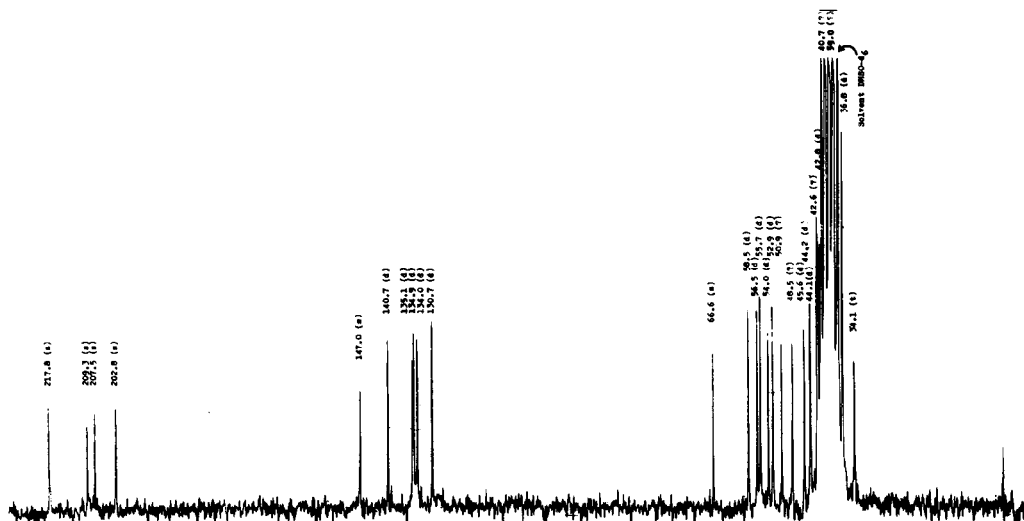
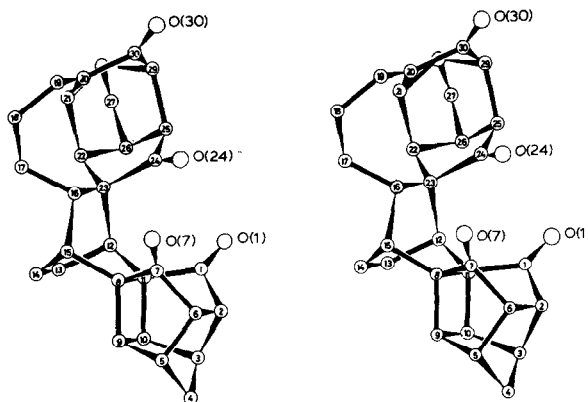


Fig. I. ^{13}C nmr spectrum at 22.64 MHz of 11 in $\text{DMSO}-d_6$

Fig.II. Stereoview of 11

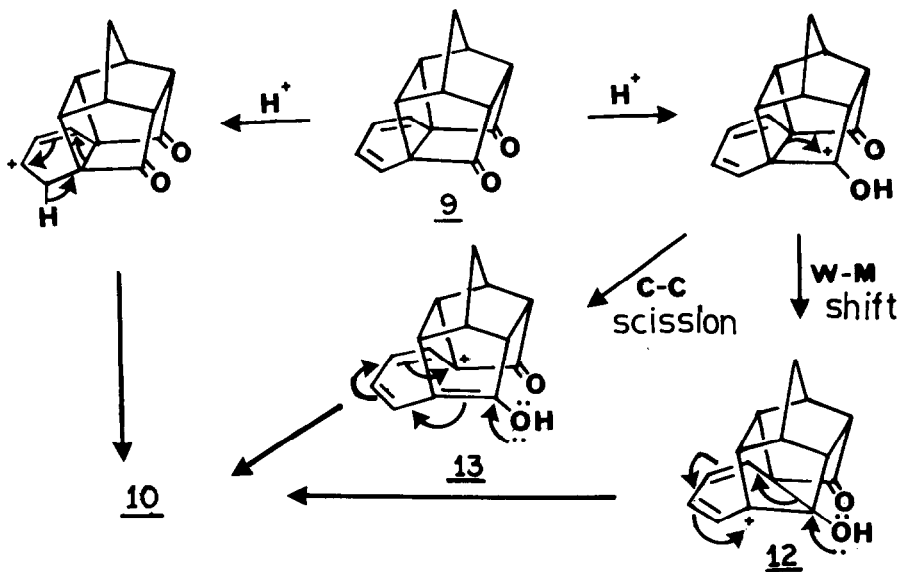
6.63(1H, t, $J=6\text{Hz}$), 6.21(1H, d with st, $J=10\text{Hz}$), 5.34(1H, dd, $J_1=10\text{Hz}, J_2=7\text{Hz}$), 3.24 (2H, t with st), 3.1(1H, d, $J=6\text{Hz}$), 2.2-2.98(12H, cluster of m), 1.78(1H, $\frac{1}{2}$ ABq, $J=11\text{Hz}$), 1.76(2H, br s), 1.58(1H, $\frac{1}{2}$ ABq, $J=11\text{Hz}$); ^{13}C nmr (22.64 MHz, DMSO- d_6): δ 217.8(s), 209.3(s), 207.5(s), 202.8(s), 147.0(s), 140.7(d), 135.1(d), 134.9(d), 134.0(d), 130.7(d), 66.6(s), 58.5(d), 56.5(d), 55.7(d), 54.0(d), 52.9(d), 50.9(?), 48.5(?), 45.6(d), 44.2(d), 44.1(d), 42.6(?), 42.0(?), 40.7(?), 39.0(?), 36.8(?), 34.1(t). The presence of four widely diverse carbonyl resonances (cf. 210.2 in 9) as well as presence of 6 olefinic C's, including a fully substituted one at 147.0 in the ^{13}C nmr spectrum (Fig.I) indicated deep seated structural change. Since preliminary degradative work on the structure proved to be of little diagnostic value, its structure was probed by direct single crystal X-ray analysis and established as 11.

The crystals of 11 used in the X-ray diffraction were monoclinic and belonged to the space group $P2_1/N$. The unit cell parameters were $a = 14.361(2)$, $b = 12.631(2)$, $c = 12.252(3)$ Å; $\gamma = 109.84(1)^\circ$ and there were four molecules per unit cell. From a total of 3271 independent reflections which were measured on a CAD4 four circle diffractometer with monochromatic Mo- K_α radiation 1912 reflections had net amplitudes greater than three times their standard deviation and these were used for the structure determination. The structure was solved by a multi solution tangent formula procedure which is part of the SHELDRICK X-ray system⁹. All the hydrogen atoms were located in the final structure (Fig.II) which was refined by least squares with anisotropic thermal parameters on the heavy atoms and individual isotropic thermal parameters on the hydrogen atoms to an R factor of 0.037 (R=0.06 for all 3271 reflections).

Formation of 11 requires an initial carbonium ion rearrangement of 9 to

the bridged 1,3,5-cyclooctatriene 10 followed by $\pi^4s + \pi^2s$ cycloaddition to another molecule of 9 in the preferred endo-mode. Several mechanisms can be speculated for the acid induced genesis of 10 from 9 and a few possible ones are depicted in Scheme I. Intermediates 12 & 13 do not look particularly favourable from stereo-electronic stability considerations but we have no firm evidence to discount them. Efforts are currently underway to elucidate the mechanism of this interesting reaction and establish the generality of 9→10 type rearrangement in model propellanes.

SCHEME 1



Acknowledgement: We are indebted to Dr.H.Duddeck, Ruhr University, for obtaining the ^{13}C nmr spectrum reported here.

References and Notes:

1. R.Huisgen, G.Boche, A.Dahmen and W.Hechtl, *Tetrahedron Letts.*, 5215 (1968).
2. Although, several (4.4.2) propella-2,4-dienes have been reported in literature³, their fluxional behaviour, to our knowledge has not been commented upon. However, under forcing conditions of thermal activation, fragmentation to aromatic products has been generally encountered^{4,5}.
3. D.Ginsberg, *MTP International Review of Science, Organic Chemistry, Series Two, Vol.5*, Butterworths, London (1976) and references cited therein.
4. L.A.Paquette, J.C.Phillips & R.E.Wingard, jr, *J.Amer.Chem.Soc.*, **93**, 4516 (1971).
5. a) E.Vogel, W.Maier and J.Eimer, *Tetrahedron Letts.*, 655 (1966);
b) J.J.Bloomfield and J.R.S.Irelan, *ibid*, 2971 (1966).
6. A.S.Kushner, *Tetrahedron Letts.*, 3275 (1971); N.Fillipescu and J.M.Menter, *J.Chem.Soc.*, B, 616 (1969).
7. For example, 9 could be recovered unchanged after refluxing in p-dichlorobenzene (bath temp. 190°) for 40 hr. At higher temperatures a very complex mixture of products was obtained. Study of these compounds will be reported in due course.
8. Off-resonance multiplicities in the ^{13}C nmr spectrum are given in parenthesis. Some of the carbon resonances are masked by the solvent peaks.
9. G.Sheldrick, X-ray system 1976, University Chemical Laboratory, Lensfield Road, Cambridge, England.

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