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ON THE FLUXIONAL BEHAVIOUR OF A POLYCYCLIC (4.4.2) PROPELLA-2,4-DIENE

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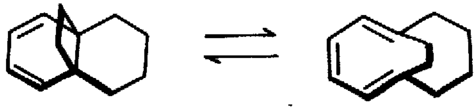
Summary: Existence of bicyclo (4.2.0) octa-2,4-diene $\rightleftharpoons$ 1,3,5-cyclooctatriene type of valence isomerisation in a polycyclic propellane framework has been demonstrated through cycloaddition and thermolysis reactions.

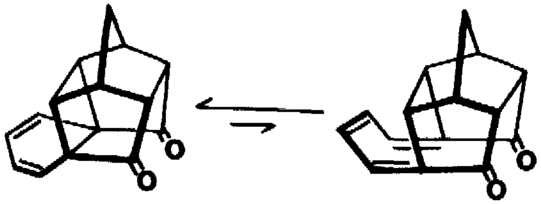
Although the symmetry allowed bicyclo (4.2.0) octa-2,4-diene 1 $\rightleftharpoons$ 1,3,5-cyclooctatriene 2 valence isomerisation has been extensively observed[1a,b], attempts to detect such an equilibrium in the propellane framework e.g., 3 $\rightleftharpoons$ 4 and congeners have not proved fruitful[1b-f]. We have recently reported[2] a novel acid catalysed rearrangement of the hexacyclic dione 5[3], embodying the propellanic framework of 3, to the novel dimer 14 and implicated the valence tautomer 6 as an intermediate. This observation provided the stimulus towards a direct search for the 5 $\rightleftharpoons$ 6 type of equilibrium process. In this communication, we report on the 5 $\rightleftharpoons$ 6 valence isomerisation as unravelled through cycloaddition reactions and thermal activation.

1 2

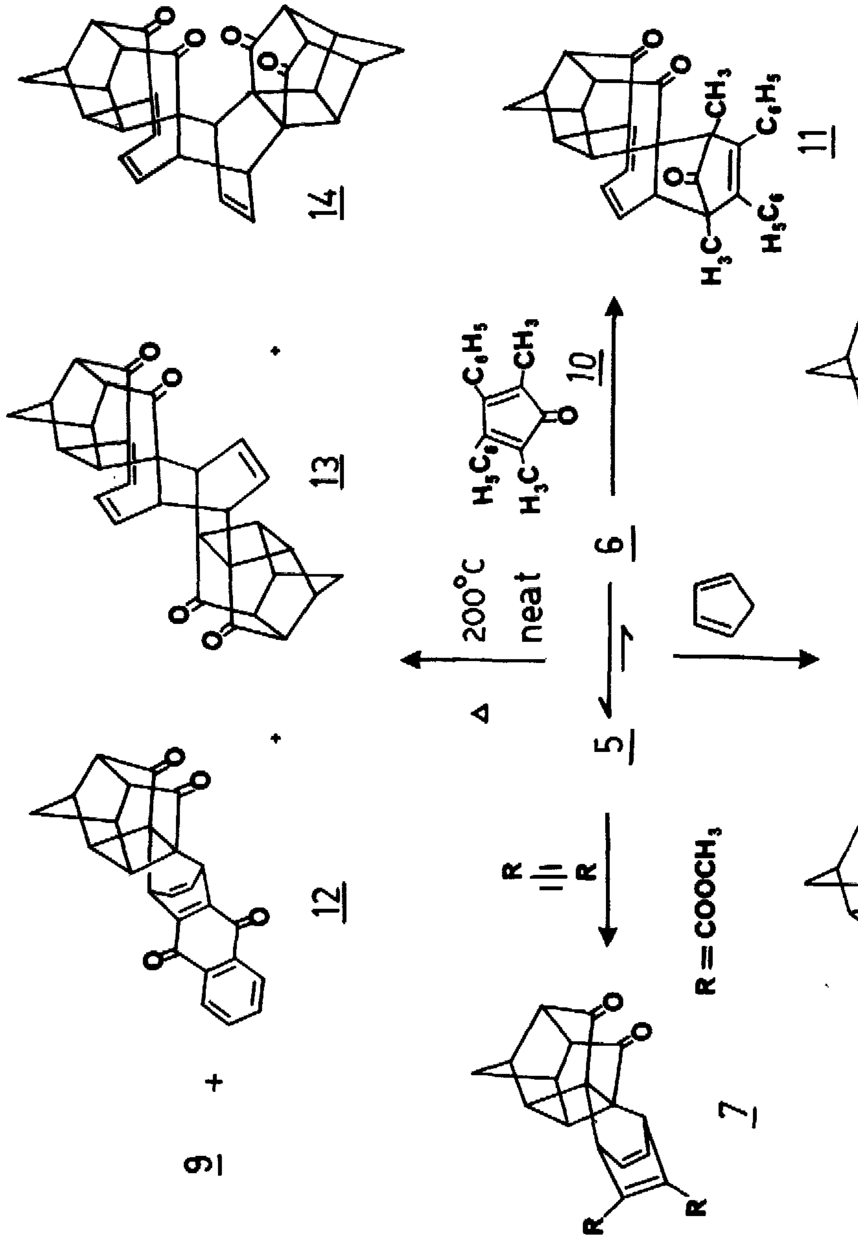


3 4

Previously, we have reported[2] that 5 exhibited appreciable thermal stability[4] and in conformity with this observation its ^{1}H nmr spectrum



5 6


5
6
200°C neat
Δ
10
R = COOCH₃
7
8
9
11
12
13
14
9 +
H₅C₆
C₆H₅
H₃C
CH₃
H₃C
H₅C₆
CH₃
C₆H₅
R

remained temperature invariant (+30 to +130°, DMSO-d_6, 2hr equilibration time) and gave no discernible clue to the presence of triene form 6. However, the response of 5 to cycloaddition reactions proved to be incisive and decisive. While dienophiles like dimethyl acetylenic ester reacted[3] with 5 to capture its 1,3-cyclohexadiene moiety and furnished $\pi 4_s + \pi 2_s$ adduct 7, mp.186-7°, in high yield; the reactive 1,3-dienes intercepted the highly strained, dienophilic valence tautomer 6 and furnished novel $\pi 4_s + \pi 2_s$ adducts. Thus, reaction of 5 with 1,3-cyclopentadiene (Cp) in refluxing toluene (7hr) and chromatography (SiO_2gel) furnished two crystalline 1:1 adducts in 80 and 4% yield. The major adduct, mp.138-39°, is formulated as 8 on the basis of spectral data: $C_{20}H_{18}O_2$, UV: λ_{max}^{MeOH} 283 nm (ε = ~2000) and 240 (ε = ~5000); ir (KBr): 1736 (strong, cyclopentanone), 1640 cm^{-1} (medium, conjugated carbonyl); ^{1}H nmr ($CDCl_3$): δ 6.92 (1H, br s), 6.4 (1H,m), 6.28 (1H,m), 6.1 (1H,d with st, J=10Hz), 5.28 (1H, dd, J_1=10Hz, J_2=6.5Hz); ^{13}C nmr ($CDCl_3$): δ 218.7(s), 203.4(s), 146.7 (s), 139.3(d), 139.1(d), 137.5(d), 135.4(d), 130.8(d), 72.7(s), 58.9(d), 55.7 (d), 54.1(d), 52.5(d), 47.3(d), 46.1(d), 44.6(?), 44.5(?), 44.4(d), 44.2(t), 35.1(t)[5]. In particular the presence of six olefinic C's, including a fully substituted one at δ 146.7, and the presence of widely separated carbonyls C's at 218.7 and 203.4 in the ^{13}C nmr provided convincing evidence for the structural assignment 8. The minor adduct 9, mp.258-59°, was readily formulated as the Diels-Alder adduct of 5 and Cp with the later participating as the 2π component. In an analogous manner, reaction of hemicyclone 10 with 5 in refluxing toluene (68hr) *furnished the 1:1 adduct* 11, *mp.*227-28° in ~20% yield [5-7].

When subjected to forcing conditions[4] of thermal activation (200°±10°, neat, 2hr) 5 yielded a complex mixture of products from which four products 9, 12, 13 & 14 could be isolated in 1:3:1:2 ratio through SiO_2 gel chromatography. *Structure of* 9 *was quickly recognised as it was found identical with* the minor product obtained in the reaction of Cp with 5. Similarly, 14 could be readily identified as the dimer obtained by us earlier[2]. The structure of 12 was indicated by its spectral characteristics[5,6] and further verified through its preparation via dehydrogenation of the Diels-Alder adduct of naphthoquinone and 5. Finally, the structure of the dimer 13 was tentatively *deduced from the similarity of its spectral data* (^{13}C nmr and ^{1}H nmr)[5,6] with the dimer 14 of firmly established stereostructure. Formation of products 9, 12, 13 & 14 in the thermolysis of 5 indicates that both the thermal fragmentation[1f] and valence isomerisation are operative under our reaction conditions. *On one hand, sequential 2+2 and 4+2 cycloreversion of* 5 *generates cyclo*pentadiene and naphthoquinone which re-add in $\pi 4_s + \pi 2_s$ fashion to 5 and furnish adducts 9 and 12. The other pathway from 5 leads to the strained, reactive valence isomer 6 and is further captured by 5 to form dimers 13 and 14.

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References and Notes:

1(a) R.Huisgen, G.Boche, A.Dahmen and W.Hechtl, Tetrahedron Letts., 5215(1968); (b) D.Ginsburg, MTP International Review of Science, Organic Chemistry Series 2, Vol.5, Butterworths, London (1976); (c) L.A.Paquette, J.C.Phillips & R.E.Wingard jr, J.Amer.Chem.Soc., 93, 4516 (1971); (d) E.Vogel, E.Maier and J.Eimer, Tetrahedron Letts., 655 (1966); (e) J.J. Bloomfield and J.R.S.Irelan, ibid., 2971 (1966), (f) L.A.Paquette and G.L.Thomson, J.Amer.Chem.Soc., 94, 7127 (1972).

2. G.Mehta, V.K.Singh, A.Srikrishna, T.S.Cameron & C.Chan, Tetrahedron Letts., 4595 (1979).

3. Hexacyclo (7.4.2.$0^{1,9}$.$0^{3,7}$.$0^{4,14}$.$0^{6,15}$) pentadeca-10,12-diene-2,8-dione 5 was prepared as reported by A.S.Kushner, Tetrahedron Letts., 3275 (1971).

4. In refluxing o-dichlorobenzene, 5 remained essentially unchanged for few hrs but prolonged reaction time led to complex mixture of products.

5. ^{1}H nmr and ^{13}C nmr spectra were recorded on a JEOL MH-100 and FX-100 instruments at 100 MHz and 25.0 MHz, respectively. Chemical shifts are with respect to internal TMS. Off-resonance multiplicities, when clearly discernible, in the ^{13}C nmr are given in parenthesis. Many of the ^{1}H nmr spectral assignments were confirmed by appropriate spin decoupling and LIS studies.

6. Compound 9: $C_{20}H_{18}O_2$, ir(KBr): 1725, 1740 cm^{-1} (cyclopentanone); ^{1}H nmr(CDCl$_3$): 6.34(2H,t,J=3.5Hz), 5.52(2H,m), 3.3(1H,m), 1.62-3.10(13H,m): ^{13}C nmr (CDCl$_3$):δ 212.6(s), 133.9(d), 132.5(d), 131.4(2c,d), 55.8(d), 45.9(d), 43.4(d), 41.9(d), 40.8(?), 38.9(s), 36.6(d), 34.6(d), 33.4(t). Some of the carbon resonances seem to be overlapping. Compound 11: $C_{34}H_{28}O_3$, ir(KBr): 1778(Bridge carbonyl), 1738(cyclopentanone), 1630(conjugated carbonyl); ^{1}H nmr(CDCl$_3$): δ6.8-7.4(11H, m), 6.26(1H,d,J=10Hz), 5.56(1H,dd,J_1=10Hz,J_2=6Hz), 3.3(3H,br s), 2.9(2H,m), 2.76(2H,m), 1.98(2H,br s), 1.34(3H,s), 1.16(3H,s). Compound 12: mp. > 300°, $C_{25}H_{16}O_4$, UV: λ_{max}^{MeOH} 330,270,250,244 & 240 nm; ir(KBr): 1736(cyclopentanone), 1672 cm^{-1}(conjugated carbonyl); ^{1}H nmr (TFA): δ 7.98(2H,m), 7.66(2H,m), 6.7(2H, t,J=3.5Hz), 4.56 (2H,t,J=3.5Hz), 3.14 (2H,m), 2.94 (2H,m), 2.82 (2H,br s), 2.1 (2H,br s). Compound 13: mp. > 300°, $C_{30}H_{24}O_4$, UV: λ_{max}^{MeOH} 276 ($\varepsilon \sim$ 2600) and 241 nm ($\varepsilon \sim$4200); ir(KBr): 1730, 1740 (cyclopentanone), 1645 cm^{-1} (conjugated carbonyl); ^{1}H nmr (CDCl$_3$): δ 6.84 (1H,br s), 6.15-6.7 (3H,m), 5.84(1H,dd,J_1=6.5,J_2=10Hz), 1.3-3.3, (19 H,m); ^{13}C nmr (CDCl$_3$): δ 218.7(s), 212.8(s), 212.4(s), 203.7(s), 145.1(s), 135.5(d), 134.7(d), 133.9(d), 133.2(d), 131.0(d), 68.3(s), 59.1(d), 56.1(d), 55.3(s), 55.3(d), 55.0(d), 51.1(d), 50.6(d), 46.4, 45.4, 45.3, 44.6, 43.6, 43.4, 41.9, 40.8, 35.3, 34.6, 34.2, 32.0(t).

7. We have not ventured to make any stereochemical assignment to adducts 8, 9, 11 & 12 as it was neither readily deducible from the spectral data nor quite germane to the main theme of this report.

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