ANIONIC (4+2)-CYCLOREVERSIONS LEADING TO THE
CYANOCYCLOPENTADIENIDE ION

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Cycloreversions become exothermic if they combine the formation of aromatic systems with the release of ring strain. The easy fragmentation of the (4+2)-adducts of benzene with cyclopentadiene[1] as well as with itself[2] illustrates this effect. Cycloreversions leading to charged aromatic systems should be favored similarly and the splitting of the 7-phenylnorbornenyl anion[3] into ethylene and the phenylcyclopentadienide ion at room temperature gives a first example. The cation of homobarrelene, on the other hand, does not revert to benzene and the cyclopropenium ion but rearranges instead to a homoaromatic ion[4]. We have prepared the formal Diels-Alder adducts 1 and 2 of 5-cyano-cyclopentadiene[5] to cyclopentadiene, in which the nitrile takes on the part of the diene and the ene, respectively, and find that the conjugate bases 1-cb and 2-cb of these adducts rapidly cyclorevert at room temperature.

Treatment of anti-5-hydroxy-endo-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene[6] with thionylchloride in boiling ether gives the chloride, which is subjected to the Kolbe synthesis with NaCN in boiling 85% ethanol. After separation from regenerated alcohol by column chromatography (alumina, ether-pentane 1:9) and from the corresponding ethyl ether by glpc (DEGS, 135°) nitrile 1 is obtained [19%; ir (neat) ν_{CN} 2245 cm^{-1}; ms (70 eV) m/e 157 (M$^+$, 0.4), 91 (C$_5$H$_5$CN$^+$, 4), 66 (C$_5$H$_6^+$, 100); pmr (CCl$_4$) δ 5.98 (m, H-8,9), 5.60 (AB-system, Δ_ν = 29.4 Hz,

J = 6 Hz, H-3,4), 3.4 (m, H-2), 3.1 (m, 2 H), 2.8 (m, 2 H), 1.53 (AB-system,

Δ_ν = 19.6 Hz, J = 7.5 Hz, H-10$_{s,a}$)]. The same reaction sequence when applied

to anti-10-hydroxy-endo-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene[7] yields the com-

plementary nitrile 2 [22%; mp 36°; ir (neat) ν_{CN} 2235 cm^{-1}; ms (70 eV) m/e 157

(M$^+_\cdot$ 2), 91 (C$_5$H$_5$CN$^+_\cdot$ 8), 66 (C$_5$H$_6^+_\cdot$ 100); pmr (CCl$_4$) δ 5.97 (t, H-8,9), 5.50 (m,

H-3,4), 3.5 (m, H-2), 3.1 (m, H-1,6,7), 2.50 (t, H-10$_s$), 2.00 (AB-system, Δ_ν

= 36.5 Hz, J = 18 Hz, H-5$_{s,a}$)]. Deprotonation of nitrile 1 or 2 with a twofold

excess of lithium 2,2,6,6-tetramethylpiperidide (LiTMP) in 1:1 hexane-THF

solution (0.8 M) containing 1 mole equiv of tetramethylethylenediamine at 0°

and warming the mixture to room temperature produces a red solution, the pmr

spectrum of which shows in the low field region (δ = 8-5 ppm) only the signals

of the cyanocyclopentadienide ion[5b] [δ benzene - 1.32 (A$_2$B$_2$-system, Δ_ν = 26

Hz, J = J' = 3 Hz, 4 H) and of the cyclopentadienide ion [δ benzene - 1.53

(s, 5 H)]. Obviously, the conjugate bases 1-cb and 2-cb of the nitriles readi-

ly undergo the (4+2)-cycloreversion to the cyanocyclopentadienide ion and to

cyclopentadiene, which in turn is deprotonated by the second mole equiv of Li-

TMP.
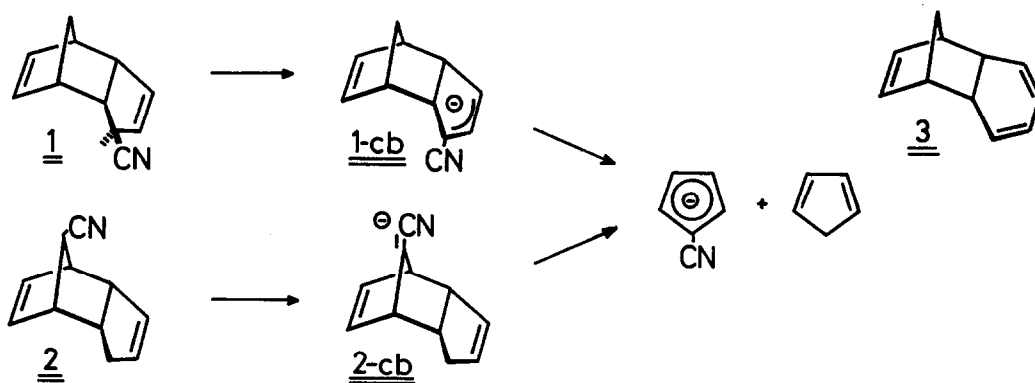
Compared with the benzenoid analogue, endo-tricyclo[6.2.1.0^{2,7}]undeca-3,5,9-

triene 3[1], the anion 1-cb cycloreverts at least 10^3 times faster. This is not

due to a higher exothermicity of the ionic reaction since the difference in the

heats of reaction of 3 and 1-cb is approximately equal to the difference in the

heats of hydrogenation of the dienophilic double bond. For benzene the heat of

hydrogenation of the first double bond is +5.7 kcal/mole[8] whereas for the cyanocyclopentadienide ion this value is that of the parent nitrile (ΔH_h = -23.7 kcal/mole[8])minus the heat of neutralization of the allylic anion with 5-cyano-cyclopentadiene, which according to the $\Delta pK_a \approx 12$[5b] amounts to ca.-16 kcal/mole The cycloreversion of the anion 1-cb is thus about 13 kcal/mole less exothermic than that of 3 and we rationalize the faster fragmentation of the former in terms of the FO-theory[9], since the HOMO of the cyclopentadienide ion (0.618) is closer in energy to the LUMO of cyclopentadiene (-0.618) than is that of benzene (1.000).

In the pair of 5-cyanocyclopentadiene adducts to benzene we find the same instability of the conjugate bases: Thermolysis of anti-9-cyano-bicyclo[6.1.0]-nona-2,4,6-triene[10] affords a mixture of the 1-cyano-cis-8,9-dihydroindene epimers[10a] to which maleic anhydride is added. Electrolytic bisdecarboxylation of the derived diacids gives after chromatography (alumina, ether-pentane 1:9) anti-5-cyano-tricyclo[5.2.2.0^{2,6}]undeca-3,8-10-triene 4 [23%; mp 29-31°; ir (neat) ν_{CN} 2240 cm^{-1}; ms (70 eV) m/e 169 (M$^+$, 0.15), 91 ($C_5H_5CN^+$, 66), 78 ($C_6H_6^+$, 100); pmr (CDCl$_3$) δ 6.4 (m, H-8,9,10,11), 5.62 (AB-system of t, Δ_ν = 26.3 Hz, J = 6 Hz, H-3,4), 3.77 (m, H-7), 3.58 (m, H-1), 3.0 (m, H-2,6), 2.8 (m, H-5)]. The complementary cycloadduct with exchanged roles of the partners, anti-11-cyano-endo-tricyclo[6.2.1.0^{2,7}]undeca-3,5,9-triene 5, is obtained from the corresponding alcohol (mp 77°)[11] via the same route as given for the nitriles 1 and 2 [20%; mp 73°; ir (KBr) ν_{CN} 2240 cm^{-1}; pmr (CDCl$_3$) δ 6.09 (t, H-9,10), 5.57 (s, H-3,4,5,6), 3.28 (m, H-1,2,7,8), 2.10 (t, H-11)].
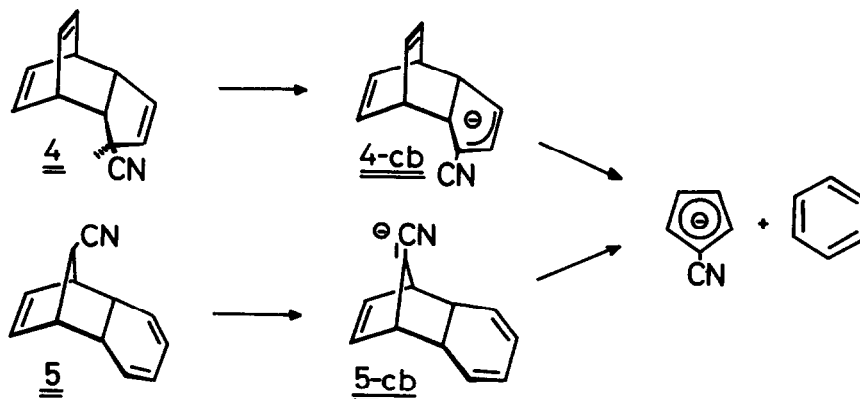
On deprotonation of $\underline{4}$ or $\underline{5}$ with 1 mole equiv of LiTMP under the standard conditions of above the conjugate bases $\underline{4\text{-cb}}$ and $\underline{5\text{-cb}}$ cyclorevert within min. to the cyanocyclopentadienide ion and benzene. In this case, the increased rate of the anion $\underline{5\text{-cb}}$ as compared with that of the parent nitrile $\underline{5}$ or of the hydrocarbon $\underline{3}$ cannot be explained by a narrowing of FO energies as the HOMOs of cyclopentadiene and of its anion are isoenergetic. The heat of reaction, however, is lowered in the case of $\underline{5\text{-cb}}$ by ca. 20 kcal/mole as follows from the difference in the pK_as of 4-cyanocyclopentene and of 5-cyanocyclopentadiene[5b] ($\Delta pK_a \approx 15$)by the reasoning given above and part of this energy loss should be felt in the transition state.

REFERENCES AND NOTES

[1]   A. R. Rye and D. Wege, Aust. J. Chem., $\underline{27}$, 1943 (1974).

[2]   W. Grimme and E. Schneider, Angew. Chem. Int. Ed. Engl., $\underline{16}$, 717 (1977).

[3]   E. S. Bowman, G. B. Hughes and J. B. Grutzner, J. Amer. Chem. Soc., $\underline{98}$, 8273 (1976).

[4]   R. M. Magid and G. W. Whitehead, Tetrahedron Lett., $\underline{1977}$, 1951.

[5]   (a) D. Peters, J. Chem. Soc., $\underline{1960}$, 1832; (b) O. W. Webster, J. Amer. Chem. Soc., $\underline{88}$, 3046 (1966).

[6]   K. Alder and F. H. Flock, Chem. Ber., $\underline{87}$, 1916 (1954).

[7]   R. B. Woodward and T. J. Katz, Tetrahedron,$\underline{5}$, 70 (1959).

[8]   J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London and New York, 1970.

[9]   For recent reviews on the potential of the FO-method see: (a) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", J. Wiley and Sons, London and New York, 1976; (b) K. N. Houk in A. P. Marchand and R. E. Lehr, Editors, "Pericyclic Reactions", Academic Press, 1977, Vol.II,Chap.4

[10] (a) A. G. Anastassiou and R. C. Griffith, Tetrahedron Lett., $\underline{1973}$, 3067; (b) G. Boche and G. Schneider, Tetrahedron Lett., $\underline{1974}$, 2449; we thank Professor G. Boche for experimental details.

[11] The synthesis of this alcohol will be published with H. LeBlanc in a forthcoming paper. Another preparation is given in the Ph.D. thesis of R. A. Kuhlmann-Taylor, Cornell University 1973; we thank Professor M. J. Goldstein for kindly sending us a copy of this work.