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[9]1,3-CYCLOPENTADIENIDOPHANE

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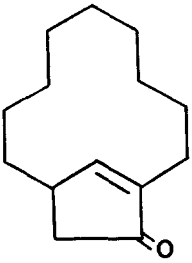
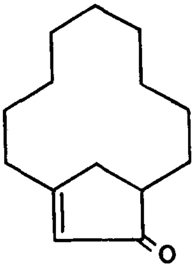
HMO calculations predict[2] and experiments (pK_a values,[3] chemical reactivity,[4] spectroscopic data,[5]) prove that ionic metal cyclopentadienides must be regarded as π excessive aromatic species: we now provide decisive evidence that, in accord with theory,[6] the cyclopentadienide ring is capable of sustaining a ring current.

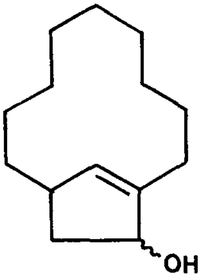
3-Acetylcyclododecanone[7] was cyclised (NaOEt-EtOH at reflux) to a mixture (70% yield) of the isomeric 1,3-bridged cyclopentenones [(Ia), b.p. 142-144/1mm, PMR ($CDCl_3$): 2.7τ, C=CH-] and [(Ib), b.p. 140-143/1mm, m.p. 43-45°, PMR ($CDCl_3$): 4τ, C=CH]. Separation of (Ia) from (Ib) was achieved by column chromatography



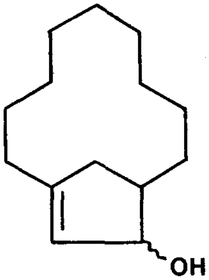
(Ia)



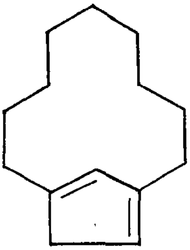
(Ib)



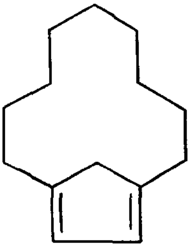
(IIa)



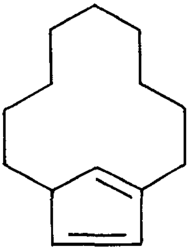
(IIb)



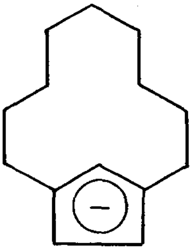
(IIIa)



(IIIb)



(IIIc)



(IV)

(SiO_2,Et_2O-pentane 1:1). Lithium hydride reduction in Et_2O of the crude mixture of (Ia) and (Ib) afforded a mixture (90% yield) of the corresponding four carbinols [(IIa), mixture of diastereoisomers, b.p. 130-135/0.1; (IIb), mixture of diastereoisomers, m.p. 96-100 from Et_2O-pentane]. Separation of (IIa) from (IIb) was performed by column chromatography (SiO_2, Et_2O-pentane, 1:1). Structural assignment to alcohols (II) was confirmed by Jones' oxidation of (IIa) and (IIb), which afforded the enones (Ia) and (Ib), respectively. Distillation in vacuum (0.1mm 110-115°) of (IIa,b) in the presence of traces of TsOH caused dehydration to a mixture of the three 1,3-bridged cyclopentadienes [(IIIa,c), b.p. 85-87/0.1]. Isomer ratio was (by vpc): (IIIa):(IIIb):(IIIc)=72:20:8. The following representative peaks were present in the PMR spectrum ($CDCl_3$): (IIIa): 3.6 and 4.1τ (=CH), 7.1τ (=C-CH_2-C=); (IIIb): 3.9τ (=CH), 7.3τ (=C-CH_2-C=); (IIIc): 6.75τ (=C-CH-C=); for all isomers, allylic CH_2 7.6τ, Chain CH_2 8.55-8.90τ. Sodium methylsulphinyl carbanion (sodium dimsyl) caused deprotonation of the three isomeric cyclopentadienes (IIIa-c) to the 1,3-bridged cyclopentadienide (IV). PMR (DMSO, 1M in (IV) 2M in dimsyl anion, 60°): 4.67τ,t,(1H); 4.98τ,d,(2H); 8.4-9τ,m,(12H); 9.45τ,m,(2H); other protons hidden by the solvent.

The high-field displacement of one methylene of the bridge is most reasonably accounted for by the diamagnetic effect due to the ring current sustained by the aromatic cyclopentadienide ring.

Evaluation of this effect as a diagnostic tool for assessment of aromaticity in related substrates containing the cyclopentadienide or cyclopentadienylidene moiety is being investigated.

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