Reduction of *cis*-Bicyclo[6,1,0]nona-2,4,6-triene in Ammonia and in Hexamethylphosphoramide–Tetrahydrofuran

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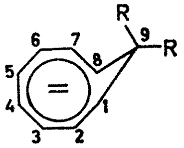
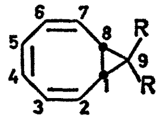
Summary Alkali-metal reduction, followed by protonation, of *cis*-bicyclo[6,1,0]nona-2,4,6-triene in polar media gives convenient yields of *cis,cis,cis*-cyclonona-1,3,6-triene in a highly selective manner as indicated by labelling experiments.

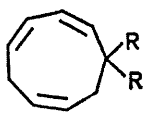


(I)

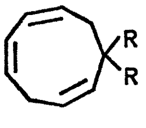


(II)

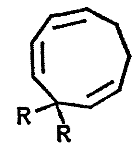
a; R = H b; R = D c; R = CH_3



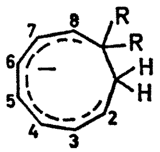
(IV)



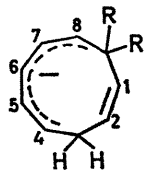
(V)



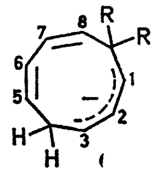
(VI)



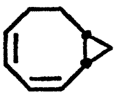
(VII)



(VIII)



(IX)



(III)

HOMOCYCLO-OCTATETRAENE dianion (Ia), the two-electron reduction product of *cis*-bicyclo[6,1,0]nona-2,4,6-triene (IIa), was reported by Winstein and Ogliaruso[1] to react with methanol in 1,2-dimethoxyethane (DME) to give *cis*-bicyclo[6,1,0]nona-2,4-diene (III) in $>$85% yield. Monocyclic substances derived from C-1—C-8 or C-1—C-9 cleavage of (IIa) were not observed. We now report the significantly different result that when (IIa) is reduced in more polar media, only C-1—C-8 cleavage products are formed.

The addition of (IIa)[2] to an excess of 2 g-atoms of alkali metal in ammonia at −78° under argon produces a deep orange solution of (Ia). The dilithium salt reverts to (IIa) in *ca.* 85% recovery on exposure to traces of air. Quenching of the sodium salt with solid ammonium chloride gave (IVa)[3] in 67% yield in addition to small amounts (*ca.* 5%) of *cis,cis*-cyclonona-1,5-diene.[4] Lithium or potassium reductions also gave (IVa). When the deuterium-labelled compound (IIb)[5] ($>$1·8 D/molecule by mass spectrometry) was reduced with sodium in the same way as (IIa), the corresponding labelled 1,3,6-triene produced ($>$1·6 D/molecule) was observed to possess a n.m.r. spectrum consistent with that expected for (IVb), (Vb), or a mixture of (IVb) and (Vb). The spectrum of (IVa)[3] exhibits a 2H triplet (*J ca.* 7 Hz) at τ 7·3 (bis-allylic methylene) and a 4H multiplet at τ 7·9 (monoallylic methylene). The spectrum of labelled triene (IVb–Vb) is similar to that of (IVa) except that the 4H multiplet at τ 7·9 is replaced by a two proton doublet (*J ca.* 7 Hz). The labelled monocyclic triene is likely to be an inseparable 1 : 1 mixture of (IVb) and (Vb) resulting from the suggested intermediate (VIIb) described below. A related separable pair of isomers analogous to (IVb) and (Vb) was obtained by reducing the methyl labelled (IIc)[2] in a similar way. The products from reducing (IIc) were (A) (55·6%) and (B) (21·3%), whose spectral properties are compatible with their assignments as (IVc) and (Vc) or (Vc) and (IVc), but not with (VIc). [Isomer A: n.m.r. (CCl_4), τ 4·0—4·9 (6H, m), 7·30 (2H, t, *J ca.* 6 Hz), 7·72 (2H, d, *J ca.* 6 Hz), and 8·98 (6H, s); u.v. (hexane), λ_{max} 218 nm (ϵ 3250). Isomer B: n.m.r. (CCl_4) τ 4·1—4·9 (6H, m), 7·15 (2H, t, *J ca.* 6 Hz), 7·78 (2H, d, *J ca.* 8 Hz), and 8·88 (6H, s); u.v. (hexane), λ_{sh} 219 nm (ϵ3600) and λ_{max} 234 nm (ϵ 4470). Both (A) and (B) lacked C–H out-of-plane bending bands characteristic of *trans*-olefins (900—1000 cm^{-1}) and revealed strong bands in the region (650—750 cm^{-1}) characteristic of *cis*-olefins in their i.r. spectra.]

Assuming a stepwise, irreversible protonation process, primary C-1 protonation of (I) leads to monoanion (VII), which upon competitive protonation at C-4 and C-6 leads to (IV) and (V) respectively, but not to (VI). This pathway explains the labelling results in a simple way, but the intermediacy of (VIII) (by C-3 protonation) or (IX) (by C-4 protonation) cannot be completely excluded. The difference between our results in ammonia and the previous results[1] in DME can tentatively be ascribed to ion-pairing differences between the two solvents. Although electronic and steric factors appear to be important in the reductive cleavage of cyclopropane rings, Walborsky has suggested recently that solvent can also play an important role in related cleavage reactions.[6]

In other experiments, we have observed that (IIa) can be reduced with 2 g-atoms of sodium at −30° in a 1 : 2 or 2 : 1 mixture of hexamethylphosphoramide–tetrahydrofuran (HMPA–THF).[7] The dianion (Ia) produced in this way gave (IVa) in 10—20% yield upon quenching with acetic acid–water. With deuteriated quenching agent (IV) is produced with one deuterium in the bis-allylic position and one in a monoallylic position. This result is consistent with the pathway described above. Interestingly, when (IIa) reacts with 1 g-atom of sodium in 1 : 19 THF–HMPA at 0° the cyclononatetraenyl anion (observed by n.m.r.) is produced.[5] Quenching the anion gave 40—80% yields of *cis,cis,cis,cis*-cyclonona-1,3,5,7-tetraene.[8] Further details of these and other experiments will be described in the full paper.†

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† Professors Staley and Ogliaruso have kindly informed us that they have also observed the formation of (IVa) from (IIa) in liquid ammonia.

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