

THE FACILE ($<-50^{\circ}\text{C}$) FORMATION OF cis-BICYCLO[6.1.0]NONA-2,4,6-TRIENES FROM
CYCLONONA-1,3,5,7-TETRAENES: A SYMMETRY-FORBIDDEN REACTION ?

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Summary: The formation of the cis-bicyclo[6.1.0]nona-2,4,6-trienes 4a-c is not due to the sequence $1 \rightarrow 2 \rightarrow 4$, which would involve the symmetry-forbidden reaction $2 \rightarrow 4$ even at -50°C . Rather, reaction of RX at C⁴⁻⁷ of 5, which is formed together with 1, leads (probably via 6a-c and 7a-c) to 4a-c.

Thermally symmetry-forbidden electrocyclic reactions ¹⁾ are normally reluctant to occur at any measurable rate below 0°C ²⁾. Thus, the facile ($<50^{\circ}\text{C}$) formation of substituted cis-bicyclo[6.1.0]nona-2,4,6-trienes (e.g. 4c) from cis-, cis,cis,cis-cyclonona-1,3,5,7-tetraenes (e.g. 2c) ³⁾, which seems to hurt the Woodward-Hoffmann rules ³⁾, would be quite exceptional. The properties and the protonation reaction of the all-cis-[9]annulene anion (1) and its trans-isomer 5 ⁴⁾, the electrophilic amination ⁵⁾ of these anions and a reexamination of the origin of 4c, however, lead to the conclusion that 4a-c are not formed via a forbidden reaction from 2a-c. Rather, the genesis of 4 traces back to some trans-anion 5, as shown below.

If all-cis-anion 1 is reacted with electrophiles RX, only all-cis-2 can arise (Fig.1.). Thus, the protonation of 1 ⁶⁾ gives 2a, which isomerizes at 35°C ($\tau_{1/2}=16$ min) to 3a ⁷⁾. Likewise, the amination of 1 ⁶⁾ with N,N-dimethyl-O-(oxo-diphenoxy-phosphoryl)-hydroxyl amine ⁸⁾ in tetrahydrofuran (THF) between -30 and 0°C , followed by workup (2n HCl, 2n NaOH) at 0°C , leads to 2b (¹H-nmr (CDCl₃): $\delta=2.27$ (s, 6H, N(CH₃)₂), 3.86 (m, 1H, H¹), 5.17-6.10 (m, 8H, H²-H⁹)). On warming to 30°C , 2b isomerizes to 3b ⁹⁾. A similar behavior is also observed if 1 ⁶⁾ is alkylated with α -bromobenzyl acetate ³⁾ in THF between -50 and 0°C : 4c ³⁾ is not detectable ¹⁰⁾, as this is the case with 4a in the protonation and 4b in the amination reaction of 1 ⁶⁾.

The reaction of the trans-anion 5, which is formed in the reaction of 9-anti-chloro-cis-bicyclo[6.1.0]nona-2,4,6-triene with lithium in addition to 1 ^{3,4ab)}, with electrophiles RX is also shown in Fig.1: depending on the site of the reaction not only all-cis-cyclononatetraenes 2 but also cis, trans, cis,cis- and/or trans,cis,cis,cis-isomers 6 and 8, respectively, can be formed. This is clearly demonstrated by the protonation of 5 ^{4a,11)}: 6a and 8a are trapped with tetracyanoethylene between -50 and 60°C and they isomerize already at around -30°C to 4a (!) and 2a, respectively; 2a leads to 3a at 30°C . Similar-

ly, in the amination of 5 between -30 and 0°C , followed by workup at 0°C , one observes ¹⁰⁾ the amine 4b ⁹⁾ in $40\pm 5\%$ yield. Again, the alkylation of 5 with α -bromobenzyl acetate ³⁾ in THF between -50 and 0°C is in accord with the protonation and amination reactions of 5: 4c ³⁾ is formed ¹⁰⁾ in $40\pm 5\%$ yield. Therefore, in analogy to 4a, 4b and 4c should result from 6b and 6c, respectively, which originate from the amination ⁸⁾ and alkylation ³⁾ at C^{4-7} of 5.

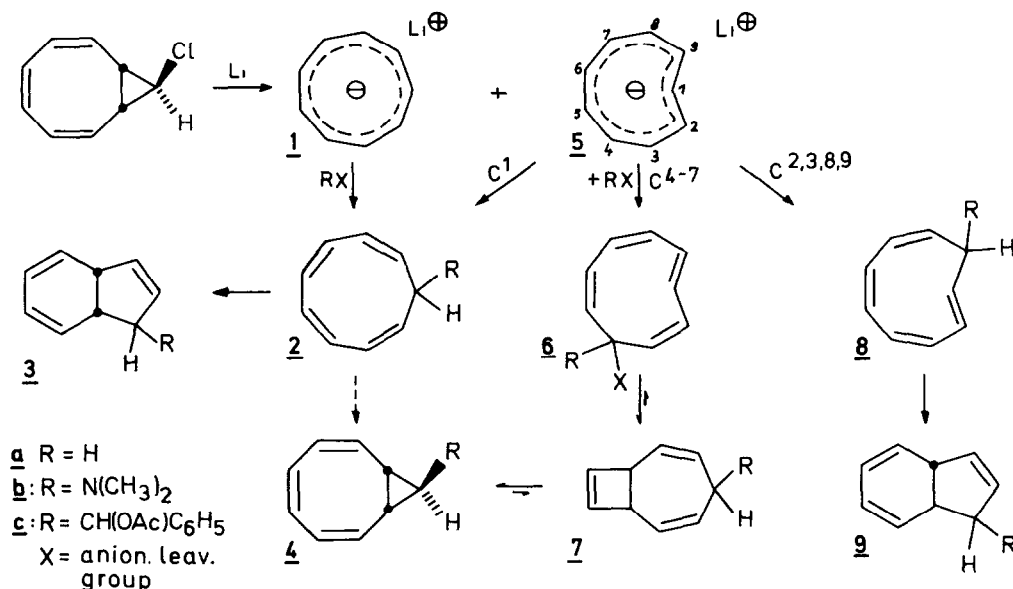


Fig. 1.: Reactions of anions 1 and 5 with electrophiles RX.

References and notes

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