

ALKALI-METAL INDUCED C,C-BOND CLEAVAGE, C,H-BOND CLEAVAGE, AND
CYCLOPOLYMERIZATION IN 1,5-HEXADIENES

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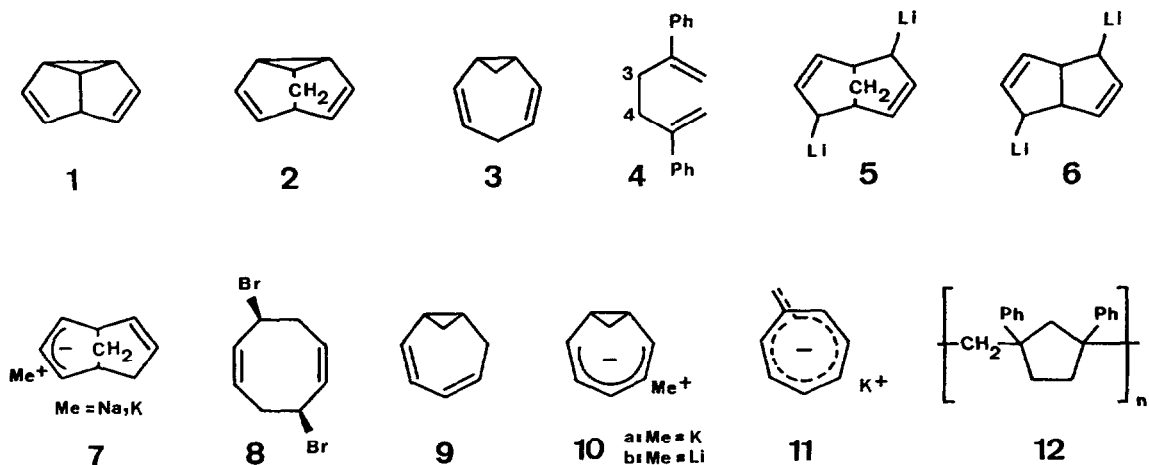
Abstract: Reaction of the 1,5-dienes 3,4-homotropilidene (3) and 2,5-diphenylhexa-1,5-diene (4) with alkali metals induces C,H-bond cleavage (hydride formation) and cyclopolymerization, respectively, in contrast to the C,C-bond cleavage observed in semibullvalene and barbaralane.

Reaction of semibullvalene (1) and barbaralane (2) with alkali metals induces reductive cleavage of the central cyclopropane bond.^{1,2,3} While the resulting dilithio species 5 and 6 persist in ethereal solutions the corresponding disodium and dipotassium derivatives obtained from 2 are not stable and undergo protonation to mono allyl-type systems such as 7.³ Cleavage of the σ -bond of 1 and 2 is facilitated (i) by the relief of ring strain and (ii) the formation of stable allyl-metal subunits. A related argument might hold in the (less strained) 3,4-homotropilidene (3) while in the acyclic diene analogue 4 a reductive σ -bond cleavage would only benefit from the formation of separate 2-phenyl allyl moieties. In order to compare the 1,5-hexadienes 1 - 4 we describe the reaction of 3 and 4 with alkali metals.

The starting compound 3 could be simply obtained by the reductive debromination of 8.⁴ Treatment of 8 with disodium tetraphenylethanedide in THF at -78°C gave 3 (37 %). Interestingly, the same reaction at -10°C afforded exclusively the isomeric 1,2-homotropilidene (9) (55 %). Contact of a solution of 3 (D_8)-THF, 25°C) with a potassium mirror gave rise to a single ionic product. The protonation of this anion with methanol afforded 9. The $^1\text{H-NMR}$ spectrum of the anion was identical to that obtained by Kloosterziel et al. upon deprotonation of 3 with potassium amide in liquid ammonia.⁵ Identification of the ionic product as 10a is thus straightforward. This outcome indicates that the reaction of 3 with potassium induces a reductive C,H-bond cleavage under hydride formation rather than a cleavage of the cyclopropane bond. Under our

experimental conditions species 11, which has been observed by Kloosterziel as rearrangement product of 10a, is not formed.

At -78°C the reaction of 3 with potassium caused quantitative isomerization to 9, even after prolonged reaction less than 5 % of 10a was formed. Lithiation of 3 at -78°C provided derivative 10b in addition to ethylbenzene which became the major product ($\approx 75\%$) when the metallation of 3 was carried out at room temperature. The role of the cyclopropane ring opening in the formation of ethylbenzene is not clear.



Reaction of 4 with alkali metals (Li, Na, K, Cs) induces a cyclopolymerization to 12. Products such as α -methylstyrene or cumene, which might have been formed by reductive cleavage of 4 to yield two equivalents of the 2-phenyl allyl anion, could not be detected. The "intra-intermolecular" formation of 12 has previously been described for the cationic polymerization of 4.^{6,7} The product we obtained upon attempted lithiation of 4 has a mean molecular weight $\bar{M}_n = 7.300 \text{ g/mol}$ (vapor pressure osmometry) and melts between 158 and 168°C .

It thus appears that the ready formation of allyl-type species upon reductive C_3, C_4 -bond cleavage in 1,5-hexadienes is a specific property of hydrocarbons such as 1 and 2; they differ from the related dienes 3 and 4 in that alternative metal induced reactions such as C,H-bond cleavage or cyclopolymerization are not possible.

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