

CYCLIC CUMULENES. THE SYNTHESIS AND
SOME REACTIONS OF 1,2,3-CYCLODECATRIENE

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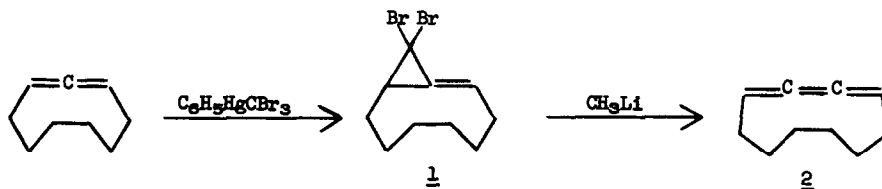
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The formation of allenes from the reaction of the dibromocarbene adducts of olefins with organolithium reagents has proved to be a reaction of considerable synthetic utility.^{1,2} Recently, extension of this reaction to the dibromocarbene adducts of allenes has led to the formation of several cumulenes.^{3,4} In this paper we report the conversion of the dibromocarbene adduct of a cyclic allene to a cyclic cumulene and some of the properties of the latter.

Treatment of 1,2-cyclononadiene with one equivalent of phenyl(tribromomethyl)mercury,⁵ in refluxing benzene followed by removal of phenylmercuric bromide and the solvent gives 10,10-dibromobicyclo[7.1.0]decene-1(2), 1, in nearly quantitative yield. Since extensive decomposition has occurred on distillation, usually this material has been employed without further purification; gas chromatographic analysis and subsequent reactions indicate a purity of at least 95%. Distilled samples of 1 have been obtained by use of a Hickman still ($\sim 40^\circ$ at 0.01 mm); nmr: δ multiplet 6.50 (0.9⁺H), broad bands centered at 2.20 and 1.50 (13H).

Treatment of 1 with methyllithium in ether at -80° followed by warming to 0° and hydrolytic work-up gives almost complete conversion to 1,2,3-cyclodecatriene, 2, (obtained as a solution in ether in at least 93% yield) along with a small amount ($\sim 5\%$) of an unidentified compound.^{6,7}



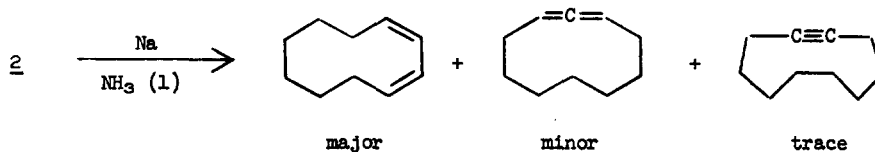
The cyclic cumulene reacts rapidly with oxygen to form a white solid insoluble in ether. When neat, 2 tends to polymerize, but pure samples have been collected (for spectral purposes) by glc.

A cold dilute solution of 2 in ether has been stored under nitrogen for several weeks without appreciable loss.

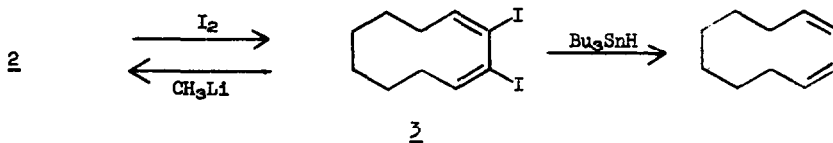
The mass spectrum of 2 shows a strong molecular ion peak at m/e 134 (44% of the base peak at 91) in agreement with the molecular formula $C_{10}H_{14}$. The nmr spectrum shows bands centered at δ 1.54 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$) and 2.30 (allylic CH_2) and a triplet at 5.53 ($J \sim 2.6$ cps, $=\text{C}-\text{CH}-$). Intense absorption in the ultraviolet characteristic of butatrienes⁴ is found; $\lambda_{\text{max}}^{\text{heptane}}$ 228 (log ϵ 4.09) and 256 μ (log ϵ 4.35), 286 sh (log ϵ 3.1)

Ozonolysis of 2 employing oxygen-free ozone in ether-methylene chloride at -80° followed by oxidation with hydrogen peroxide-acetic acid and esterification with methanol-sulfuric acid gave dimethyl suberate.⁵ Reduction of the ozonolysis product with sodium borohydride followed by methylation with sodium hydride-methyl iodide gave 1,8-dimethoxyoctane.⁵

Reduction of 2 with excess sodium in liquid ammonia occurred rapidly to give cis and trans-cyclodecene in a ratio of 61 to 1; in the presence of tert-butyl alcohol the ratio was lowered to 9.3 to 1. Reduction of excess 2 with sodium in liquid ammonia (to enable isolation of intermediate reduction products) gave cis, cis-1,3-cyclodecadiene as the major product (53%) along with 1,2-cyclodecadiene (18%) and a trace of cyclodecyne as well as cis cyclodecene (13%) from further reduction and two unidentified compounds (1% and 15%) which from glc retention times appear to be sodium amide-promoted isomerization products of 2. Formally then, the major reductive pathway is addition to the central double bond of 2.



Although the addition of bromine to 2 has given a complex mixture of products, the cumulene rapidly absorbs one equivalent of iodine to give a diiodide assigned structure 3 along with minor amounts of several unidentified compounds. Reduction of 3 with tributyltin hydride gave cis, cis-1,3-cyclodecadiene. Treatment of 3 with methyl lithium in ether resulted in regeneration of 2.



Further studies of the chemistry of 2 as well as the preparation of other cyclic cumulenes are in progress.

References

- (1) W. R. Moore and H. R. Ward, J. Org. Chem., 25, 2073 (1960); 27, 4179 (1962).
- (2) L. Skattebøl, Tetrahedron Letters, 167 (1961); Acta Chemica Scand., 17, 1683 (1963).
- (3) L. Skattebøl, Tetrahedron Letters, 2175 (1965).
- (4) W. J. Ball, S. R. Landon and N. Punja, J. Chem. Soc., 194 (1967).
- (5) D. Seyferth and J. M. Burlitch, J. Organometal. Chem., 4, 127 (1965).
- (6) The results are similar if the reaction is carried out at 0° except that at this temperature traces of several other materials result.
- (7) The yield estimates are based on glc employing naphthalene as an internal standard. The minor compound has the same retention time as one of the base-catalyzed isomerization products of 2; it may be 1,2,4-cyclodecatriene.
- (8) Identified by comparison with an authentic sample.