

NOVEL CONJUGATED ENE-ALLENES VIA CYCLOPROPYLIDENE INTERMEDIATES:

A CYCLOPENTADIENE FROM TWO INDEPENDENT ROUTES

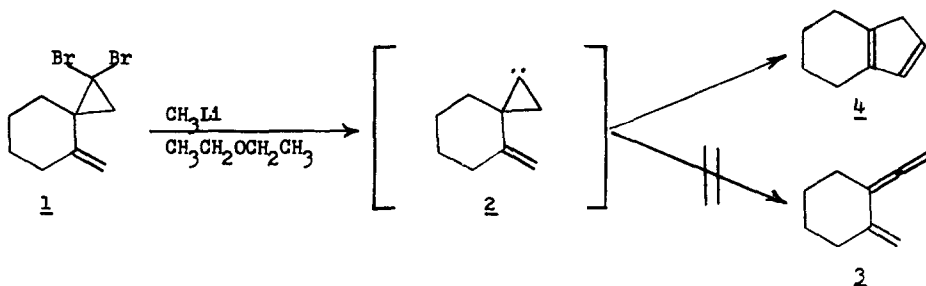
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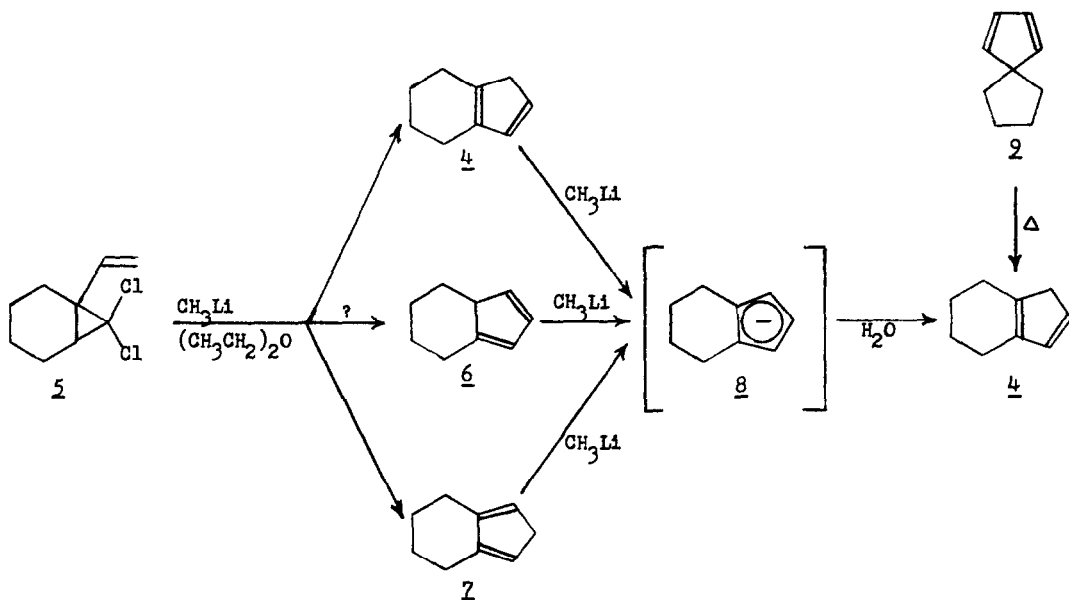
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In an effort to prepare and study structures of the conjugated ene-allene type, 1,1-dibromo-4-methylenespiro[2.5]octane (1) was synthesized by dibromocarbene addition to 1,2-dimethylenecyclohexane^{1,2,3,4} and reacted with methyl lithium. It was anticipated that cyclopropylidene 2 would be formed and lead to ene-allene 3^{5,6,7,8}. Instead, however, bicyclo[4.3.0]nona-1(6),7(8)-diene (4) was formed as the exclusive product in high yield. Identification was based on spectral data $\sqrt{\text{NMR}}$ 6.13 δ (multiplet, 2H), 2.71 δ (multiplet, 2H), 2.27 δ (multiplet, 4H), 1.66 δ (multiplet, 4H); IR 3060 cm^{-1} , 1630 cm^{-1} , 1530 cm^{-1} , 1380 cm^{-1} , 910 cm^{-1} , 863 cm^{-1} , 842 cm^{-1} , 685 cm^{-1} ; UV $\lambda_{\text{max}}=255.5 \text{ nm}$ and $\epsilon_{\text{max}}=2,740$ and a suitable elemental analysis. Reports indicate that such a reaction sequence is not uncommon as Skattebol⁷ and Blakesley⁹ have reacted numerous gem-dibromovinylcyclopropanes with methyl lithium and have obtained both conjugated ene-allenes and cyclopentadienes. Therefore, the absence of ene-allene 3 and the presence of one cyclopentadiene 4 was regarded as significant. The lack of ene-allene from 2 may be determined by the stereoconfiguration of the double bond relative to the cyclopropylidene as a fixed s-cis isomer. Skattebol⁷ has investigated similar compounds, which can exist as both s-cis and s-trans conformers. Since we had obtained only a cyclopentadiene from a fixed s-cis isomer, it seemed that the product distribution might be influenced by the conformation of the precursor.

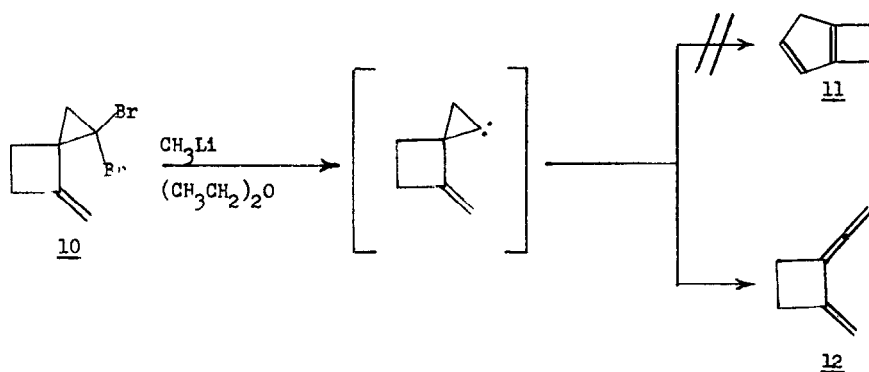


For comparative purposes, 7,7-dichloro-1-vinylbicyclo[4.1.0]heptane (5) was synthesized by dichlorocarbene addition to 1-ethynylcyclohexene followed by hydrogenation using Lindlar's catalyst. The dibromo analog of 5 was attempted, but hydrogenation proved unsuccessful. Identification of 5 was by spectral data $\sqrt{\text{NMR}}$ 5.93 δ (doublet of doublets, $J=18$ hz, $J=10$ hz, 1H), 5.11 δ (doublet of doublets, $J=18$ hz, $J=2$ hz, 1H), 5.11 δ (doublet of doublets, $J=10$ hz, $J=2$ hz, 1H), 2.10 δ -1.66 δ (multiplet, 4H), 1.65 δ -1.10 δ (multiplet, 5H); IR 3090 cm^{-1} , 1640 cm^{-1} , 913 cm^{-1} , 857 cm^{-1} , 813 cm^{-1} , 785 cm^{-1} ; mass spectrum with a parent peak at 190 $\bar{7}$ and a suitable elemental analysis. It is noteworthy that 5 can interconvert as *s-trans* and *s-cis* conformers. The reaction of 5 with methyl lithium proceeded slowly with only 10% converted in three days at room temperature. A single product was obtained, cyclopentadiene 4, an end product inconsistent with all pathways proposed by Skattebol⁷. Isomers 6 and/or 7 which were predicted by the mechanisms of Skattebol⁷ evidently were unstable in the presence of the excess methyl lithium and formed cyclopentadienide anion 8 which, on protonation by water, led to 4. It is interesting too that 4 has been reported as the sole product from a thermolysis of 9 indicating that it is the most stable of the three possible cyclopentadienes¹⁰ 4, 6, and 7.

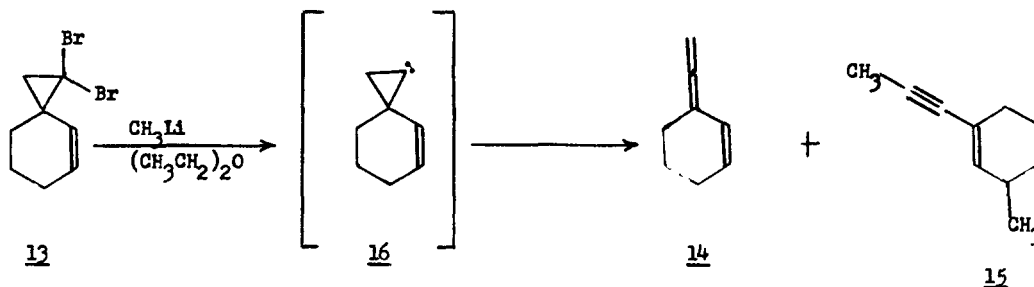


Since it has been shown that cyclopropylidenes can interact with double bonds and produce cyclopentadienes^{7,9}, 1,1-dibromo-4-methylenespiro[2.3]hexane (10), a fixed *s-cis* homolog of

1, was generated by dibromocarbene addition to 1,2-dimethylenecyclobutane³. The reaction of 10 with methyl lithium was investigated to ascertain if the cyclopentadiene 11 would be formed although it would be highly strained. It was thought that the production of 11 would be disfavored, and possibly ene-allene 12 would be obtained. Indeed, 12 was the only adduct and identification was based on spectral data [$\sqrt{\text{NMR}}$ 5.10 δ -4.80 δ (multiplet, 4H), 2.90 δ -2.45 δ (multiplet, 4H); IR 3100 cm^{-1} , 1950 cm^{-1} (strong), 1730 cm^{-1} , 1675 cm^{-1} , 1650 cm^{-1} , 868 cm^{-1} (strong); mass spectrum with parent peak at 92] and a suitable elemental analysis. Evidently, the generation of 12 is preferred over the bicyclic cyclopentadiene 11.



The synthesis of 13, a fixed *s-trans* homolog of 1, was performed via dibromocarbene addition to 3-methylenecyclohexene^{11,12}, in the expectation that its reaction with methyl lithium would yield ene-allene 14. In addition to 14, an alkylation product 15 was observed. Identification of 14 was based on spectral data [$\sqrt{\text{NMR}}$ 5.97 δ (doublet, $J=10$ hz, 1H), 5.80 δ -5.45 δ (multiplet, 1H), 4.85 δ -4.64 δ (multiplet, 2H), 2.50 δ -1.45 δ (multiplet, 6H); IR 3080 cm^{-1} , 1960 cm^{-1} (strong), 850 cm^{-1} (strong), 741 cm^{-1} (strong); mass spectrum with a parent peak at 106; UV with a $\lambda_{\text{max}}=227$ nm, $\epsilon_{\text{max}}=7,350$] and a suitable elemental analysis. Compound 15 was similarly confirmed by spectral data [$\sqrt{\text{NMR}}$ 5.97 δ (multiplet, 1H), 2.71 δ (singlet, 1H), 2.40 δ -1.80 δ (multiplet, 4H), 1.80 δ -1.53 δ (multiplet, 3H), 0.95 δ (doublet, $J=6$ hz, 3H); IR 3333 cm^{-1} (strong), 3060 cm^{-1} , 2205 cm^{-1} , 1380 cm^{-1} ; mass spectrum with a parent peak at 120; UV with $\lambda_{\text{max}}=230$ nm and $\epsilon_{\text{max}}=11,400$] and a suitable elemental analysis. From the fixed *s-trans* cyclopropylidene 16, an ene-allene 14 was obtained. Had the vinyl group been in the *s-cis* geometry in relation to the cyclopropylidene as in 2, rearrangement would likely have occurred and have led to cyclopentadiene formation. It can be seen that the fixed *s-trans* nature of 16 negates interaction of the cyclopropylidene with the double bond and subsequent cyclopentadiene formation.



In conclusion, both the strain inherent in ring size and the geometry of the double bond in relation to the gem-dibromocyclopropane affect methyl lithium product distribution.

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