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1,2-CYCLOOCTADIENE, A PRODUCT OBSERVED FROM THE REACTION OF 8,8-DIBROMOBICYCLO[5.1.0] OCTANE WITH METHYLLITHIUM*

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It is well established that the reaction between gem-dibromocyclopropanes and methyllithium generally affords allenes (1,2,3) and evidence has been presented which suggests that a carbene or carbenoid complex is an intermediate in the process (4,5,6). The reaction of strained methylenedibromocyclopropanes presently under investigation has been observed to give a product bearing a new methyl group. This observation prompted a study of the similar reaction of 8,8-dibromobicyclo[5.1.0]octane (I), a system which would appear capable of giving the highly strained and as yet unknown 1,2-cyclooctadiene (II) for inclusion in this study.

The addition of I to ethereal methyllithium at 0° was observed to give five products, four of which were isolated by preparative gas-liquid chromatography (III, IV, V and VI). 1,2-Cyclooctadiene (II) could be detected only immediately after quenching the reaction mixture with water and was found to be present to the extent of about 8%.

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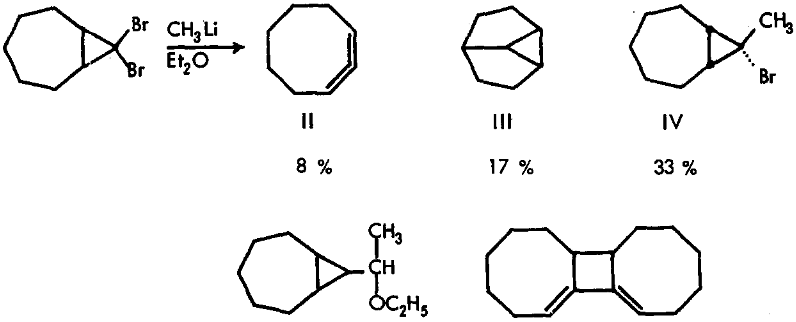
An infrared spectrum of the reaction mixture obtained immediately after quenching exhibits a medium-intensity band at 5.1 μ, a characteristic absorption for allenes. Concentration of the cold reaction mixture resulted in the disappearance of the 5.1 μ band while absorption at 6.05 μ, typical of conjugated dienes, grew in. Catalytic hydrogenation of a freshly prepared reaction mixture afforded 7-8 % of cyclooctane which was isolated and identified by comparisons with an authentic sample. Similar treatment of a reaction mixture which had been aged for 12 hours and freed of solvent did not give cyclooctane but only III, IV, V and the tetrahydro derivative of VI. Addition of dry HCl in the presence of PCl_5 to a freshly prepared reaction mixture containing II gave 3-chlorocyclooctene, the product expected by analogy with the known addition of HCl to 1,2-cyclononadiene (7). These data establish that the allene component II is the only one capable of giving rise to cyclooctane on reduction.



II 8 %

III 17 %

IV 33 %

V 10 %

VI 32 %

The structure of III was assigned on the basis of spectral and hydrogenation data as tricyclo[5.1.0.$0^{4,8}$]octane (8,10,11,12). Its infrared spectrum exhibits bands at 3030, 3050 and 1011 cm^{-1}. Hydrogenation (Pt, EtOH, HOAc) afforded a single product which was shown to be bicyclo[3.2.1]octane (11).

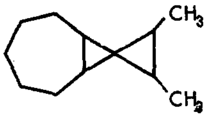
8-Bromo-*trans*-8-methylbicyclo[5.1.0]octane (IV) (MW 202 and 204, mass spectrometry) shows an NMR signal (sharp) for the methyl group at τ 8.25, typical of this type structure. Reduction with zinc acetic acid afforded only *trans*-8-methylbicyclo-[5.1.0]octane (8). Reduction of IV by sodium in methanol gave a mixture of *cis*- and *trans*-8-methylbicyclo[5.1.0]octane (27:73). The methyl group of the *trans* isomer gives rise to an NMR doublet centered at τ 9.0 (J = 5 c.p.s.) while that of the cis isomer inexplicably appears as a broadened singlet at τ 9.1. This relationship has also been observed between *cis*- and *trans*-7-methylbicyclo[4.1.0]heptane. A more compelling argument for the stereochemistry assigned to IV is the observation that it reacted completely with aqueous silver nitrate at 30° during 24 hours to give cyclooctene-3-ol. The *cis*-8-methyl isomer of IV would not be expected to react at all under these conditions (9).

Compound V, which is analogous to a previously described ether-insertion product (5) was characterized by use of mass spectrometry and NMR data, all of which are consistent. All physical properties of the head-to-head dimer of 1,2-cyclooctadiene (VI) are essentially identical with those described for this substance (12). It was further characterized by hydrogenation to the known (12) tetrahydro derivative, m.p. 57-58°.

It was found possible to intercept the carbenoid derived from I by generating it in the presence of a large excess of *cis*-2-butene. The principal product was the spiro compound (VII) (MW 164, mass spectrometry). Its NMR spectrum exhibits two methyl singlets at τ 8.98 and τ 9.09.

$$\mathrm{I} \xrightarrow[\mathrm{Et_2O}]{\mathrm{CH_3Li}} \mathrm{II} + \mathrm{III} + \mathrm{IV} + \mathrm{V} + \mathrm{VI} +$$

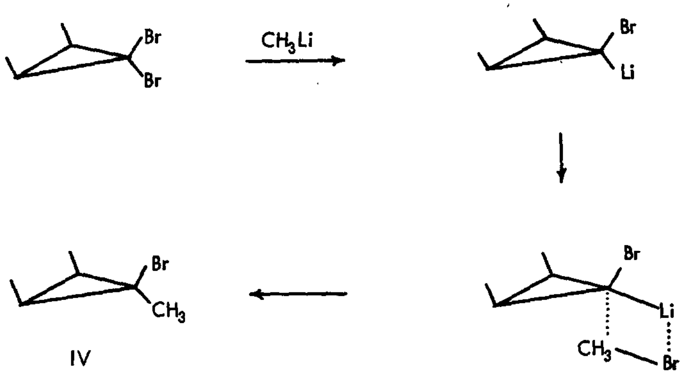
2-butene 3% 8% 13% 3% 15%



VII

58 %

It is noteworthy that the principal product from the reaction of I with methyllithium at 0° is IV, a type of product not previously observed in this kind of reaction (2,5). The analogous compound derived from 7,7-dibromobicyclo[4.1.0]heptane is also the principal product in that reaction, and it has stereochemistry identical with that of IV. In both cases the yield of bromo methyl compound diminishes as the temperature is lowered and this suggests that its origin is through reaction of methyl bromide (produced in the initial step) with an intermediate of the type shown. Good evidence has been presented in other systems for such an organometallic species (15). The most obvious mechanism for the formation of IV is insertion of a carbenoid species on methyl bromide but this is almost certainly incorrect as such a process should give a mixture of <u>cis</u> and <u>trans</u> isomers. A more plausible mechanism is that involving a four-center (or its equivalent) reaction between the organometallic and methyl bromide. It would appear that at low temperatures,



reaction is sufficiently slow to allow methyl bromide to diffuse away from the reaction sphere and the organometallic then either inserts as a carbenoid (giving III and V) or expands to the allene (II). At higher temperatures (0°) the reactivity of the organometallic is such as to capture methyl bromide before it can leave the reaction site.

Although the extreme reactivity of 1,2-cyclooctadiene has thwarted attempts to complete its characterization, efforts to this end are continuing.

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