

1,4-ADDITION OF DICHLOROCARBENE TO 1,2-BISMETHYLENOCYCLOHEPTANE

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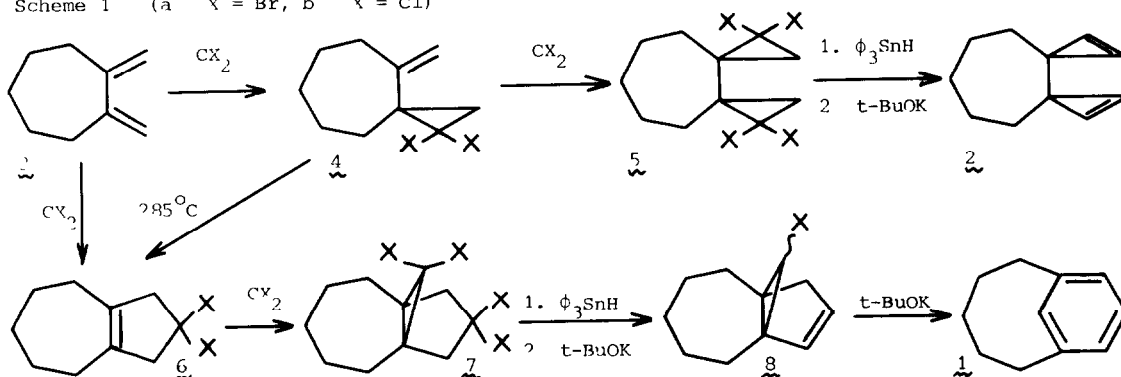
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Abstract The reaction of dichlorocarbene with 1,2-bismethylenecycloheptane (**3**) yields, besides the 1,2-addition product **4b**, the 1,4-addition product **6b** in a ratio 99:1.

Normally, carbenes add to 1,3-dienes - as to alkenes - in a 1,2-fashion. Numerous attempts have been made to achieve 1,4-addition reactions of carbenes. Most of these have either failed, are inconclusive or may be the result of rearrangement reactions subsequent to the initial 1,2-addition¹. Unambiguous one step additions seem to be involved in three special cases only: the addition of triplet dicyanocarbene to cyclooctatetraene², the intramolecular 1,4-addition in the formation of benzvalene³, and the homo-1,4-additions to the norbornadiene system⁴. We here report what we believe to be the first case of an intermolecular 1,4-addition of a singlet carbene to a 1,3-diene.

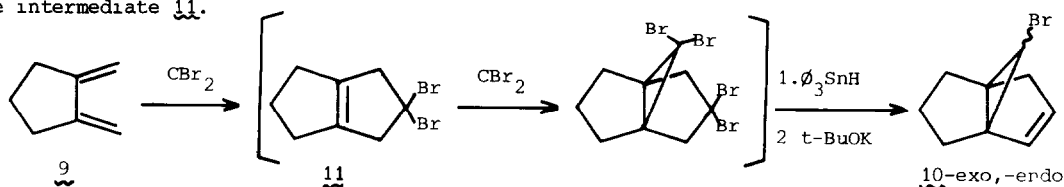
In a previous communication⁵, the formation of [5]metacyclophane (**1**) as a minor side product in the synthesis of 3,3'-pentamethylenebicyclopropenyl (**2**) was rationalized by invoking the occurrence of such a reaction (Scheme 1). While the expected normal 1,2-addition of dibromocarbene to 1,2-bismethylenecycloheptane (**3**) furnishes **4a** (and via **5a**, ultimately **2**), 1,4-addition was assumed to yield **6a**. By the indicated sequence of steps, **6a** would be converted to **8a**; the latter was detected in the reaction mixture and shown to yield **1**. This rationalization remained somewhat speculative as the crucial intermediates such as **6a** had not been isolated, therefore alternative mechanisms could not be fully excluded.

Scheme 1 (a X = Br, b X = Cl)



For the development of a new preparative approach to **1**⁶ we needed larger quantities of **4** which was to be converted to **6** by flow pyrolysis. In the synthesis of **2**, **4** was obtained only as a byproduct of **5** by the method of Makosza⁷ (using an excess of $CHCl_3$ (or $CHBr_3$) and aqueous $NaOH$

with cetyltrimethylammonium bromide as a phase transfer catalyst). When we performed the dichloro carbene addition according to Skattebøl⁸, adding 1.2 equiv. of CHCl_3 to 1.2 equiv t-BuOK suspended in a solution of 3 in pentane, 4b was obtained in 60% yield. No diadducts (5b) were formed. Besides 4b, the only other product was the isomer 6b which was identical with the product obtained from the flow pyrolysis of 4b. The ratio of 4b and 6b was 99:1. 6b must be a primary product of the carbene addition because 4b which had been completely purified from 6b by preparative GLC was unchanged under the conditions of the Skattebøl reaction in the absence of CHCl_3 , and because the thermal rearrangement of vinyl dichlorocyclopropanes is not observed below 200°C ⁹. The direct formation of 6b by dichlorocarbene addition to 3 is hereby unambiguously established. The postulated pathway for the formation of 1 in Scheme 1 thus becomes even more plausible. An analogous reaction has been described by Landheer¹⁰, who explained the formation of 10 from 9 via the intermediate 11.



Reflecting on the reasons why 1,4-additions occur in very selected cases only, the more or less rigid geometry comes to mind as a common, important factor. One step additions of singlet carbenes such as dichlorocarbene^{1b} to 1,3-dienes are symmetry-allowed, but only possible in cisoid conformations. Such conformations are enforced by geometry in cyclopentadiene³, norbornadiene⁴, 1,2-bismethylenecyclopentane¹⁰ and - to a lesser, but apparently sufficient degree - in 3. If one considers that in the relatively favorable case of 3, 1,4-addition occurs for ca. 1% only, it is not surprising that open chain 1,3-dienes with a predominantly transoid conformation¹¹ give normally no detectable amounts of 1,4-addition product. In this light the reported formation of a 1,4-adduct from dichlorocarbene and isoprene, based on admittedly inconclusive mass spectroscopic evidence¹², must be considered to be unlikely.

References and Notes

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