

4,6-DIOXA-5-PHENYL-2,8-DEHYDROCYCLOOCTYLIDENE: AN INDIVERTIBLE CARBENE

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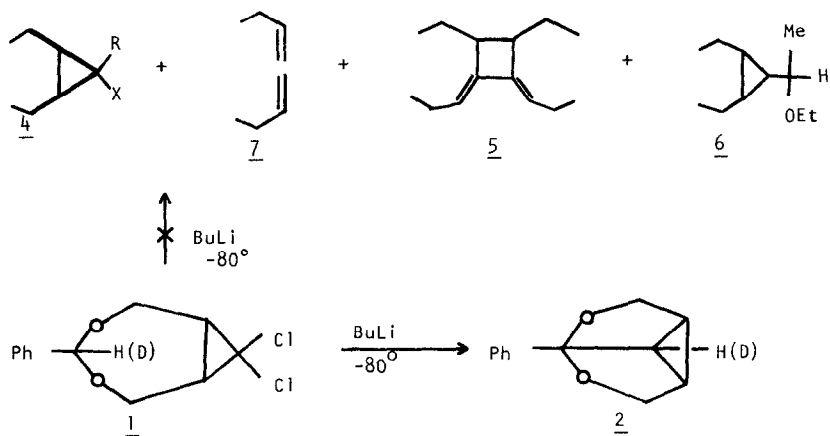
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Alkyl carbenes irrespective of their mode of formation show a proclivity for intramolecular insertion into  $\beta$ -carbon-hydrogen bonds to give olefins (1). However in cyclopropylidenes (carbenacyclopropanes) these 1,2-hydrogen shifts are considerably suppressed, and the target for insertion is now the  $\gamma$ - and to a very much lesser extent, the  $\delta$ -carbon-hydrogen bonds (2). An additional point of dissimilarity between both species, is the remarkable preference of alkyl carbenes to seek intramolecular stabilization, whereas with cyclopropylidenes, intermolecular reactions such as insertion into the solvent (2a,3) or coupling with another cyclopropylidene (2b,2c) have been found to occur to appreciable extents. These differences indicate a capability of cyclopropylidenes for discrimination, and this is further exemplified by the fact that in the presence of added olefins, their primary mode of reaction leads to spiro-pentane derivatives (2,3). These observations are in accordance with expectation, for olefins, being more nucleophilic than carbon-hydrogen bonds, should be victorious in competition for the electrophilic carbene (4). This communication deals with the unusual case of a cyclopropylidene for which intramolecular insertion into an  $\epsilon$ -carbon-hydrogen bond represents a more attractive reaction pathway than intermolecular addition to an external olefin.

Treatment of 8,8-dichloro-4-phenyl-3,5-dioxabicyclo[5.1.0.]octane (1) with n-butyl lithium in ether at  $-80^{\circ}\text{C}$  afforded a 45% yield of the novel caged compound 4-phenyl-3,5-dioxatricyclo[5.1.0.0<sup>4,8</sup>]octane, 2. (5). The reaction of a carbocyclic equivalent of 1, namely 8,8-dibromobicyclo[5.1.0.]octane, 3, with methyl lithium has been studied (3). If, as might have been expected, compound 1 followed a reaction pathway similar to that reported for 3, the reaction products would have been 4>5>2>6>7. Compound 2 proved to be only crystalline material obtained from the reaction and it was produced in three times greater quantity than was its carbocyclic analogue from 3 (3). Infrared examination of the total reaction product immediately after work-up failed to reveal any evidence for the allene 7, its dimer 5 (6), or any conjugated diene to which it might have tautomerised (3). The absence of the halide 4 (R = Bu or H; X = Cl) was apparent from a negative Lassaing test. This stands in marked contrast not only to the results from 3 (where R = Me; X = Br) but also with a recently reported

study (where R = H; X = Cl) (7) in which the chlorocyclopropane comprised 42% of the reaction product. Compound 6 was also not produced as judged by the absence of the requisite resonances in the nmr spectrum of the crude reaction product.

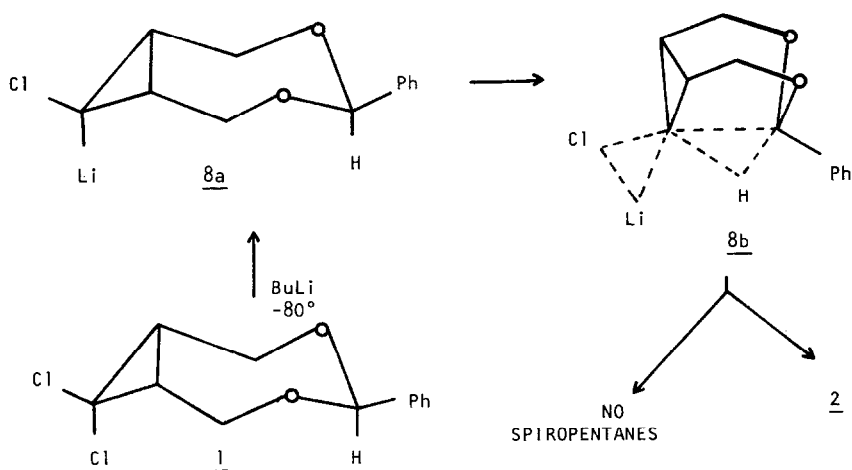


In some instances (2) cyclopropylidene dimers and bicyclobutyl derivatives have been isolated in good yield from reactions involving cyclopropyl carbenes. Corresponding compounds derived from 1 would possess a benzylidene methine proton, but the nmr spectrum of the reaction product was completely devoid of any resonances in the appropriate region (8). The latter information provides independent evidence for the absence of 4,5,6,7.

Since the typical products from reported reaction of cyclopropylidenes were not being formed in the reaction of 1, it was necessary to show that the formation of 2 proceeded in a straightforward manner. Accordingly the 4-deuterio analogue of 1, prepared using benzaldehyde-d (9) for the reported synthesis (5), was reacted with butyl lithium in the usual way (5). The resulting product was judged (nmr and mass spectrometry) to consist of 2 84% deuterated at the 8-position. Hence formation of 2 from 1 results from simple insertion into the methine proton of the benzylidene moiety. In order to demonstrate the intermediacy of the cyclopropylidene (or its carbenoid equivalent (10)), compound 1 was decomposed with butyl lithium in ether at

-80°C in the presence of a ten-fold excess of cyclohexene, tetramethylethylene, and 1,3-dioxo-2-phenyl-5-cycloheptene(5). In all three cases the crude reaction products on examination by mass spectrometry gave no evidence for parent ions or fragmentation patterns attributable to the expected spiropentanes. Furthermore, the nmr and mass spectra, buttressed by tlc evidence could be interpreted simply as arising from 2 and the added olefin.

Precedents compel that an organolithium chloride be considered as the initial product of reaction of 1 with butyl lithium. On the basis of results from the analogous reaction of dichloronorcarane, the exo-chloro isomer 8 is expected to predominate. Being formally an eight membered ring the preferred conformation should be the crown 8a (11); however, adoption of the boat conformation 8b brings the incipient carbene into steric contiguity with the carbon-4-hydrogen bond which, because of the two flanking oxygen atoms and its benzylic



nature is exceptionally nucleophilic. Insertion into the methine proton probably via the transition state depicted in 8b (12) is therefore facilitated.

The insertion is an example of a remarkably smooth transannular reaction in a medium sized ring. The results from 8,8-dibromobicyclo[5.1.0]octane, 3, (3) and methyl 4,6-O-benzylidene- $\alpha$ -D-erythro-hex-2-enopyranoside (13) indicate respectively, that neither steric nor, electronic forces acting separately can account for the exclusiveness with which 2 is produced from 1. However, both types of forces acting together produce a resultant so substantial that even an exceptionally nucleophilic olefin such as tetramethyl-ethylene is unable to capture

any of the intermediate carbene (carbenoid). The formal divalent carbon intermediate from 1, 4,6-dioxa-5-phenyl-2,8-dehydro cyclooctylidene, therefore provides an unusual example of a cyclopropylidene, totally indinvertible by external olefins.

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14. B. Fraser-Reid and B. Radutus, unpublished results.