Generation of Dimethylallene-carbene from 1,1-Dichloro-2,2-dimethylcyclopropane

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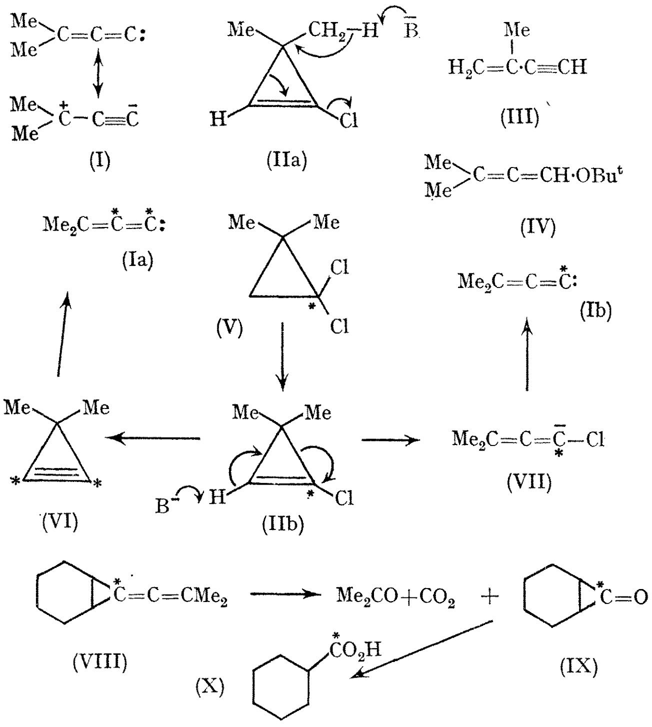
Summary Treatment of 1,1-dichloro-2,2-dimethylcyclopropane with butoxide ion in hexamethylphosphoramide generates dimethylallene-carbene formed *via* an unsymmetrical intermediate and not *via* dimethylcyclopropyne, together with 3-methylbutenyne.

THE zwitterionic allene-carbene C_5H_6(I, probably complexed) which has ambident reactivity,[1] is isomeric with dimethylcyclopropyne (VI) and it appeared of interest to investigate whether reactions formally capable of generating (VI) might in fact lead to (I). 1,1-Dichloro-2,2-dimethylcyclopropane[2] (0·2 mol.) in hexamethylphosphoramide[3] (20 ml.) was added to potassium t-butoxide (0·5 mol.) in hexamethylphosphoramide (60 ml.) and cyclohexene (20 mol.; carbene trap) held at reflux under nitrogen. Work-up gave 3-methylbutenyne (III) (22%)‡ together with 1-(2-methylpropenylidene)bicyclo[4,1,0]heptane (VIII) (6%), the trapped product from (I). Replacement of hexamethylphosphoramide by dimethyl sulphoxide gave yields of < 1% of (VIII). Omission of the cyclohexene in the hexamethylphosphoramide experiment gave 3-methylbutenyne (22%) and, after acid work-up, 3-methylcrotonaldehyde (10%). This latter may arise from the vinyl ether (IV), formed by trapping of (I) by t-butoxide ion.[4] Formation of 3-methylbutenyne involves proton abstraction from one methyl group of chlorodimethylcyclopropene (IIa) (*cf*. ref. 5).

In order to distinguish between the intervention and collapse of dimethylcyclopropyne, and an alternative elimination mechanism for the formation of (I), 1-[^{14}C]-1,1-dichloro-2,2-dimethylcyclopropane was made using dichlorocarbene generated from $^{14}CHCl_3$. The cyclopropane (V) was treated with potassium t-butoxide as above, and the trapped [^{14}C]carbene was isolated as (VIII) by preparative g.l.c. (30% Apiezon L on Chromosorb P/120°/glass column).



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‡ All products were isolated and compared spectrally with authentic specimens.

Degradation of (VIII) using the OsO_4-catalysed periodate system[6] gave acetone, carbon dioxide, and the presumed Favorski-type[7] cyclopropanone (IX) isolated as cyclohexane carboxylic acid. The carbon dioxide carried 2·0 ± 0·2% and the cyclohexane carboxylic acid 98·5 ± 2·0% of the original radioactivity (four experiments). Degradation with alkaline permanganate led to similar conclusions. This result shows that a symmetrical intermediate (VI) is not involved, or else constitutes a very minor pathway, in the formation of (I) from (V). It is likely that base-catalysed elimination leads to the chlorocyclopropene which undergoes a second elimination (*cf.* IIb) probably *via* (VII), the conjugate base of a chloroallene. The latter intermediate has been postulated in the base-catalysed reaction of 1-chloro-3,3-dimethylallene which gives (I).[8]

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