Cyclopropylidene Insertion. Evidence for Bicyclo[1.1.0]butan-2-olate Formation

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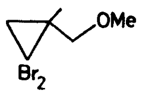
Summary *gem*-Dibromocyclopropylmethanols (**3**) react with methyl-lithium to give products derived from intermediate bicyclo[1.1.0]butan-2-olates (**4**) in addition to the allenyl alcohols (**5**).

Intramolecular insertion into C–H bonds is regarded as evidence for a cyclopropylidene intermediate in reactions of *gem*-dihalogenocyclopropanes and alkyl-lithiums.[1,2] Bicyclo[1.1.0]butanes have resulted from such reactions.

However, the ether (**1**) and methyl-lithium did not produce any bicyclobutane by insertion but formed the bicyclic compound (**2**);[3] structurally related ethers gave similar results.[3,4] We now report that analogous reactions of the alcohols (**3**) give products derived from the corresponding bicyclo[1.1.0]butan-2-olate (**4**) in addition to the allenyl alcohols (**5**). Such reactions have been previously reported to give only allenyl alcohols.[5]



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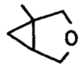

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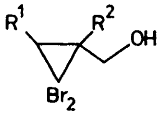

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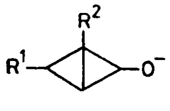

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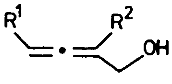

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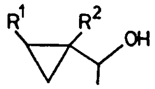

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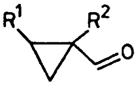

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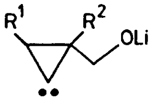

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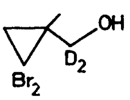

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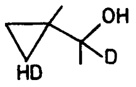

(11)

a; $R^1 = R^2 = H$
b; $R^1 = H$, $R^2 = Me$
c; $R^1 = R^2 = Me$
d; $R^1 = H$ $R^2 = Ph$

The parent compound (**3a**) was prepared by reduction of 2,2-dibromocyclopropanecarbaldehyde with sodium borohydride. Other starting materials were prepared from the respective ethyl 2,2-dibromocyclopropanecarboxylates by reduction with lithium aluminium hydride. Reaction of (**3a**) with an excess of methyl-lithium (molar ratio 1:2·2) in ether at -55 to -78 °C followed by addition of H_2O gave the allene (**5a**) (30%) and the cyclopropyl alcohol (**6a**) (15%) Similar treatment of (**3b**) resulted in about equal amounts of (**5b**) and (**6b**) (40% total yield). In the case of (**3c**) the reaction product consisted of three compounds, (**5c**) (45%), (**6c**) (10%), and the aldehyde (**7c**) (5%). The reaction of (**3d**) with methyl-lithium also afforded aldehydes; the isomers (**7d**) (15%) and (**8**) (25%) were isolated besides the allenyl alcohol (**5d**).

The allenes (**5**) are the expected products of these reactions.[6] The other products can be accounted for by the following mechanistic scheme: intramolecular insertion of the carbene (**9**) into the C–H bond adjacent to the oxygen function leads to the bicyclo[1.1.0]butanolate (**4**). Ring opening of (**4**) could yield two isomeric aldehydes as observed in the reaction of (**3d**); the relative amounts would probably reflect the stability of the intermediate carbanion. Attempts to trap (**4**) as the corresponding ether or by reaction with benzenethiol[7] were unsuccessful.

Labelling experiments provided conclusive evidence for this scheme. Treatment of the deuteriated alcohol (**10**) with methyl-lithium afforded the expected allene and the alcohol (**11**) with labelling in complete agreement with the insertion mechanism. It further remained to clarify the fate of the cyclopropyl anion formed by ring-opening of (**4**). Quenching of the reaction mixture from (**3b**) with D_2O caused no incorporation of deuterium in the ring which suggests that the anion abstracts a proton from the solvent. Clearly, the cyclopropyl alcohols (**6**) derive from the corresponding aldehydes and methyl-lithium.

Our results provide evidence for the existence of bicyclo[1.1.0]butan-2-ol and derivatives. Considering the marked tendency of cyclopropanol to undergo ring-opening under acidic or basic conditions,[8] it is not surprising that bicyclobutanol escapes isolation and even trapping under our conditions.

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