

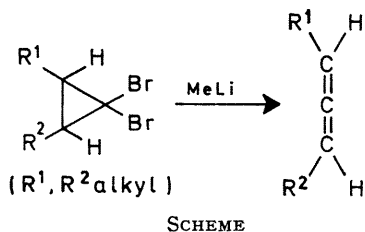
Preparation of 3-Oxabicyclo[3,1,0]hexanes; a Useful Carbenoid Insertion Reaction

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Summary Insertion of a "carbenacyclopropane" into C—H bonds adjacent to oxygen provides a simple and potentially general preparation of alkyl substituted 3-oxabicyclo[3,1,0]hexanes.

THE reaction of alkyl substituted *gem*-dibromocyclopropanes with methyl-lithium has provided a high-yield synthesis of allenes (Scheme).¹



Skattebøl reported that the ether (I) underwent an analogous reaction to give (II) as the only volatile product when treated with methyl-lithium at -30 to -40° .¹

When (I) was treated with methyl-lithium[†] in ether at -30° to -32° , one major volatile product was indeed obtained (61%), together with one minor volatile product (*ca.* 5%). However, the major product was not the allene (II), but instead was characterised as 1,4-dimethyl-3-oxabicyclo[3,1,0]hexane (III)[‡] [n.m.r. spectrum: τ 6.00 dq, J 3 and 6 Hz, further broadened, 1H), 6.37 (d, J 8 Hz, A part of AB system, 1H), 6.60 (d, J 8 Hz, B part of AB system, slightly broadened, 1H) 8.83 (s, 3H), 8.89 (d, J 6 Hz, 3H), *ca.* 8.9 (m, under signal at 8.89, 1H), § 9.44 (complex 1H), 9.74 (complex, 1H)].[¶]

Compound (III) can be thought of as resulting from the insertion of an intermediate carbenoid species related to (IV; $R^1 = \text{Me}$, $R^2 = \text{H}$) (a carbenacyclopropane) into the

[†] Obtained from Alfa Inorganics.

[‡] New compounds were characterised by elemental analysis or high-resolution mass measurements on the molecular ion, together with the usual spectroscopic techniques.

§ On running the n.m.r. spectrum in C_6D_6 solution, this signal was moved above the methyl signals and was observed as a complex multiplet.

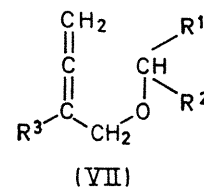
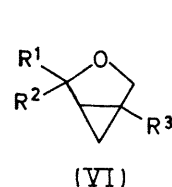
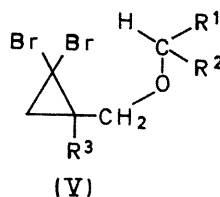
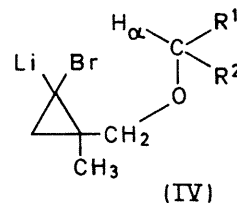
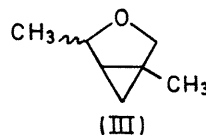
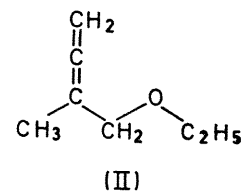
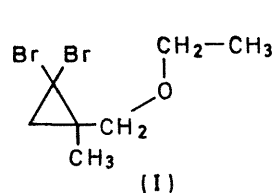
¶ From the n.m.r. spectrum this was a pure isomer; however, it was not possible to decide clearly the orientation at C-4 from the coupling constant J_{45} , since this is generally less than 2 Hz for both *cis*- and *trans*-couplings in this ring system. [This observation comes from the spectra of (VIa—d) as well as that recorded for VIe⁵]. Further work is under way to prove the orientation at C-4.

C-H_α bond adjacent to oxygen. Carbenacyclopropanes are known to undergo intramolecular insertion into the C-H bonds of certain hydrocarbons when the reaction shown in the Scheme is suppressed by joining R¹ and R² in a small or medium-sized ring.² The formation of (III) in the present case possibly occurs due to the effect of an adjacent oxygen atom in activating C-H bonds to insertion by carbenes, e.g. dihalogenocarbenes,³ though a change in the structure and reactivity of the carbenoid intermediate due to intramolecular complexing with oxygen may also be responsible.⁴

When (I) was treated with methyl-lithium in ether at 25–35°, (III) was again obtained as the major volatile product (48%), but the yield of the minor product was much higher (32%).** The latter was in fact characterised as the allene (II) [n.m.r. spectrum: τ 5.43 (m, 2H), 6.17 (br. t, J 2 Hz, 2H), 6.63 (q, J 7.5 Hz, 2H), 8.32 (t, J 3 Hz, 3H), 8.75 (t, J 7.5 Hz, 3H); i.r. spectrum: strong band at 1965 cm⁻¹].

We have found that carbenoids related to structures of type (IV) will insert into primary (R¹ = R² = H) and tertiary (R¹ = R² = Me) as well as secondary C-H_α bonds. Thus, when (Va) was treated with methyl-lithium in ether at -35°, (VIa) (63%) was obtained, together with a trace of (VIIa); when the reaction was carried out at 25–35°, a 1:1 mixture of (VIa) and (VIIa) was obtained (82% combined yield). When (Vb) was treated with methyl-lithium at -27 to -30°, (VIb) (53%) was obtained, together with a trace of (VIIb); at 25–35° a 4:5 mixture of (VIb) and (VIIb) was obtained (60% combined yield). Compounds (Vc) and (Vd) gave (VIc) (61%) and (VID) (80%), respectively, as the only major volatile products when treated with methyl-lithium at 25–35°, while (Ve) gave the parent system (VIe) (18%)⁵ as the major volatile product, together with a number of unidentified minor products.

Thus the reactions of (I) and (Va–e) with methyl-lithium all produce the corresponding 3-oxabicyclo[3,1,0]-



- (a) R¹ = R² = R³ = Me
 (b) R¹ = R² = H, R³ = Me
 (c) R¹ = R² = Me, R³ = H
 (d) R² = R³ = H, R¹ = -CH = CH₂
 (e) R¹ = R² = R³ = H

hexanes, in some cases together with the corresponding allene, and the amount of allene can be reduced by carrying out the reaction at lower temperatures.

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** All the reactions of (I) or (Va–e) with methyl-lithium produced less volatile products as well as those described above. The proportion of less-volatile products increased as the reaction temperature was reduced; their nature will be discussed in a future publication (cf. ref. 4).

¹ L. Skattebøl, *Acta Chem. Scand.*, 1963, **17**, 1683.

² W. R. Moore and H. R. Ward, *J. Org. Chem.*, 1960, **25**, 2073; W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, 1961, **83**, 2019; W. R. Moore and H. R. Ward, *J. Org. Chem.*, 1962, **27**, 4179; E. T. Marquis and P. D. Gardner, *Chem. Comm.*, 1966, 726; *Tetrahedron Letters*, 1966, 2793; C. G. Cardenas, B. A. Shoulders, and P. D. Gardner, *J. Org. Chem.*, 1967, **32**, 1220.

³ J. C. Anderson and C. B. Reese, *Chem. and Ind.*, 1963, 575.

⁴ K. G. Taylor, W. E. Hobbs, and M. Saquet, *J. Org. Chem.*, 1971, **36**, 369.

⁵ T. Shono, A. Oku, T. Morikawa, M. Kimura, and R. Oda, *Bull. Chem. Soc. Japan*, 1965, **38**, 940.