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

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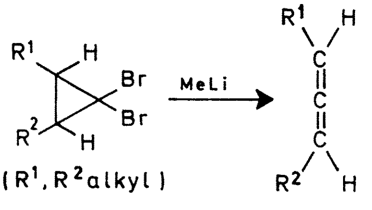
Summary Insertion of a "carbenacyclopropane" into C–H bonds adjacent to oxygen provides a simple and potentially general preparation of alkyl substituted 3-oxabicyclo-[3,1,0]hexanes.

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



SCHEME

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; $R^1 = Me$, $R^2 = H$) (a carbenacyclopropane) into the

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† 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.

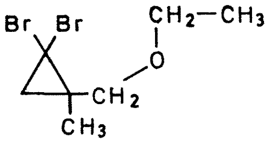
¶ From the n.m.r. spectrum this was a pure isomer; however, it was not possible to decide clearly the orientation at C-4 from the coupling constant J_{45}, since this is generally less than 2 Hz for both *cis*- and *trans*-couplings in this ring system. [This observation comes from the spectra of (VIa—d) as well as that recorded for VIe[5]]. 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 R^1 and R^2 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]

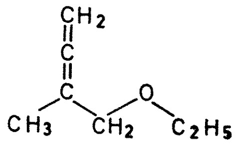
When (I) was treated with methyl-lithium in ether at 25—35°, (III) was again obtained as the major volatile product (48%), but the yield of the minor product was much higher (32%).** The latter was in fact characterised as the allene (II) [n.m.r. spectrum: τ 5·43 (m, 2H), 6·17 (br. t., J 2 Hz, 2H), 6·63 (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 ($R^1 = R^2 = H$) and tertiary ($R^1 = R^2 = Me$) 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.

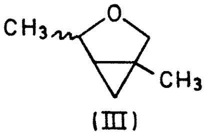
Thus the reactions of (I) and (Va—e) with methyl-lithium all produce the corresponding 3-oxabicyclo[3,1,0]-hexanes, in some cases together with the corresponding allene, and the amount of allene can be reduced by carrying out the reaction at lower temperatures.



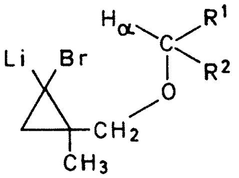
(I)



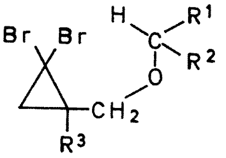
(II)



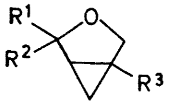
(III)



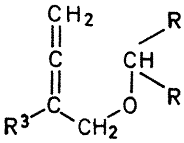
(IV)



(V)



(VI)



(VII)

(a) $R^1 = R^2 = R^3 = Me$
(b) $R^1 = R^2 = H$, $R^3 = Me$
(c) $R^1 = R^2 = Me$, $R^3 = H$
(d) $R^2 = R^3 = H$, $R^1 = -CH = CH_2$
(e) $R^1 = R^2 = R^3 = H$

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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.