A Carbenoid Route to the 6-Oxatricyclo[3,2,1,0^{2,7}]octane Ring System

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Summary The reaction of dibromides (III) with methyl-lithium leads to the tricyclic ethers (IV) and (V).

In some cases the reaction of *gem*-dibromocyclopropanes with alkyl-lithium reagents gives carbenoids which may ring open to allenes or undergo inter- or intra-molecular insertion and addition reactions, depending on the exact molecular structure;[1] molecular rearrangements which may involve such species have also been reported.[2] In other cases an intermediate lithio-bromocyclopropane is stabilised by intramolecular interaction with the oxygen of an ether, and aqueous work up produces a monobromocyclopropane.[3] We now report a reaction involving intramolecular interaction with an alcohol oxygen which does not appear to fit in either category.

Ketone (I) was obtained from (II) by reaction with dibromocarbene[†] followed by hydrolysis. Reduction of (I) with $LiAlH_4$ in ether gave a single alcohol characterised as the *cis*-isomer (IIIa); similarly reaction with methyl magnesium bromide in ether gave (IIIb). Treatment of (IIIb) with methyl-lithium (2·3M; Ventron) in ether followed by quenching with H_2O after 10 min gave two volatile components, (IVb) (37%) and (Vb) (33%).[‡] Compound (Vb) [τ 7·7—8·9 (complex, 8H), 8·76 (s, 3H)] was cleanly reduced by Na–liq. NH_3 to give (IVb) [τ 6·17 (dd, *J* 4·3, 5·4 Hz, 1H), 7·8—9·0 (complex, 7H), 8·9 (s, 3H), 9·40 (m, 1H)].[§] Reaction of (IIIa) with methyl-lithium in ether gave analogous products (IVa) and (Va); (Va) showed a broad multiplet at τ 5·8 (1H), together with a complex set of signals from τ 7·7 to 8·9, while (IVa) showed in addition a

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[†] Generated by phase-transfer catalysis[4] or from $KOBu^t$–$CHBr_3$ in petrol.

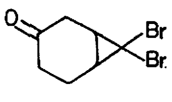
[‡] Less volatile products containing -OH groups were also observed, but none were simple intramolecular insertion products of the carbenoid. (VI, X = Me) is also reported to give no simple insertion products on reaction with MeLi.[5]

[§] Irradiation of the signal at τ 9·40 caused that at τ 6·17 to collapse to a doublet, *J* 4·3 Hz.

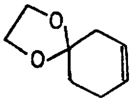
second proton at τ 6·0 and a single (cyclopropane) proton multiplet at τ 9·4. As expected, all four products showed no -OH bands in the i.r. spectrum.

Treatment of (Va) with excess methyl-lithium in ether for 20 min at 25° followed by H_2O quenching caused *ca.* 75% reaction to produce (IVa), suggesting that such a process might have been responsible for the formation of (IVa) from (IIIa) in the reaction above. However, while treatment of (Va) with MeLi followed by D_2O quenching gave (VII), reaction of (IIIa) with MeLi followed by D_2O gave (IVa) with no appreciable deuterium incorporation. Indeed, when (VI, X = D) was treated with MeLi followed by H_2O, (VII) was isolated showing *ca.* 70% incorporation of deuterium. Thus (IV) is produced principally by an intramolecular carbenoid insertion into the O-H(D) bond. (VIII) undergoes an analogous reaction with Bu^{n}Li giving 3-isopropyl-5-methyl-2-oxabicyclo[3,1,0]hexane as one product. No product analogous to (V) is reported.[6]

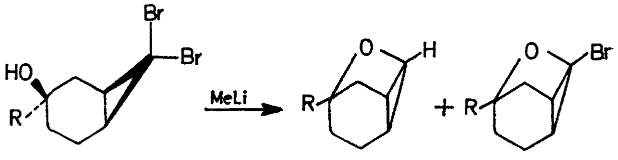
The origin of (V) is at present less clear, and the most obvious mechanism, intramolecular displacement of bromide by alkoxide does not fit the normal pattern of cyclopropane reactivity. However, the reactions described provide a ready route to the tricyclic ring system and further reactions of (IV) and the strained cyclopropanone bromoacetals (V) are under investigation.



(I)

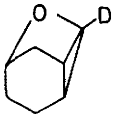


(II)

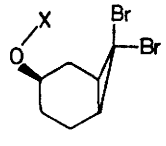


(III) (IV) (V)

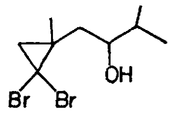
(a) R = H, (b) R = Me



(VII)



(VI)



(VIII)

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[1] See W. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic Press, London, 1974.

[2] L. Skattebøl, *Tetrahedron*, 1967, **23**, 1107; M. S. Baird and C. B. Reese, *J.C.S. Chem. Comm.*, 1972, 523.

[3] K. G. Taylor, W. E. Hobbs, and M. Saquet, *J. Org. Chem.*, 1971, **36**, 369; see also G. Köbrich and H. Büttner, *Tetrahedron*, 1969, **25**, 2223; G. Köbrich and W. Goyert, *ibid.*, 1968, **24**, 4327; D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, 1965, **87**, 4147.

[4] For a review see E. V. Dehmlow, *Angew. Chem. Internat. Edn.*, 1974, **13**, 170.

[5] L. A. Paquette, G. Zon, and R. T. Taylor, *J. Org. Chem.*, 1974, **39**, 2677.

[6] B. Ragonnet, M. Santelli, and M. Bertrand, *Bull. Soc. chim. France*, 1973, 3119.