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THE ADDITIONS OF CARBENE TO ENDOMETHYLENE CYCLIC COMPOUNDS

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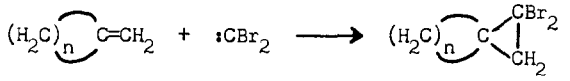
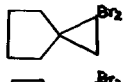
IT has been shown by Doering[1] and others that carbenes add to double bonds to give cyclopropane derivatives. However, spiro-compounds involving the cyclopropane ring normally were prepared by ring closure through 1:3-elimination.[2,3,4]

We have observed that dibromocarbene adds readily to methylenecyclohexane, methylenecyclopentane and methylenecyclobutane.



When an excess of the endomethylene cyclic compound was treated with dibromocarbene at -5~0°C, we obtained spiro-derivatives, 1,1-dibromospiro [2.3]hexane I, 1,1-dibromospiro[2.4]heptane II and 1,1-dibromospiro[2.5] octane III, in 60~75 per cent yield.

		b.p.	n_D^{20}	Yield (%)	I.R. bands (cm^{-1})
I		60-61/5.5 mm	1.5411	60	1428s 1062s 1037s 1007*s
II		75-76/6 mm	1.5437	61	1447s 1065s 1042s 1018*s 965m 939m
III		76/3 mm	1.5462	74	1453s 1042s 1023*s 954

* Cyclopropane ring

These compounds have no characteristic I.R. bands for the CH_3 group but do have spectra characteristic of the cyclopropane ring as shown. The compound III was easily reduced to hydrocarbon by lithium aluminium hydride and gave spiro[2.5]octane which showed a similar infra-red spectrum to that of the compound reported by Buckley.[5] These results show that carbene easily adds to the exomethylene group of cyclic molecules and gives spiro-compounds which must have fairly high strain energy.

The method which we have found opens a new route for the preparation of spiro-derivatives.

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[1] Doering and Hofmann, J. Amer. Chem. Soc. 76, 6162 (1954).

[2] Applequist, Fanta and Henrikson, J. Org. Chem. 23, 1715 (1958).

[3] Slobodin and Blinova, J. Allgem. Chem. 24, 621 (1954).

[4] Shortridge, Craig, Greenlee, Derfer and Boord, J. Amer. Chem. Soc. 70, 946 (1948).

[5] Bridson-Jones, Buckley, Cross and Driver, J. Chem. Soc. 2999 (1951).