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HIGHLY FUNCTIONALISED CARBENES AND CYCLOPROPENES FROM TETRAHALOCYCYLOPROPANES

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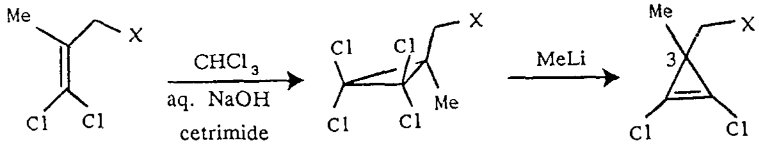
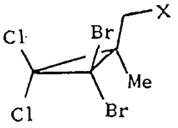
1,2-Dehalogenation of tetrachlorocyclopropanes (2, X = Cl, OMe, NPr^i_2, Ph) and (4, X = OMe) by methyl lithium leads to dichlorocyclopropenes (3, X = Cl, OMe, NPr^i_2, Ph) and the carbene (6) respectively; in contrast, the dibromocyclopropane (4, X = Cl) is converted to the cyclobutene (11) by a 1,3-dehalogenation.

There have been a number of recent reports of synthetic applications of halogenated cyclopropenes;[1] we now describe a simple route to such systems having additional functionality at C-3. Dihalocyclopropanation of (1, X = Cl, OMe, NPr^i_2, Ph)[2] occurs readily under phase transfer conditions with either $CHCl_3$ or $CHBr_3$, aq.NaOH and cetrimide to give (2, X = Cl, OMe, NPr^i_2, Ph) and (4, X = Cl, OMe) respectively. Reaction of (2, X = Cl) with 1.1 mol.equiv. of methyl lithium in ether at 0 °C for 20 m,[3] leads to (3, X = Cl) (82%).[4] In the same way, (2, X = OMe, NPr^i_2, Ph) are converted to the corresponding cyclopropenes (3, X = OMe, NPr^i_2, Ph).

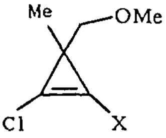


(1) (2) (3)

Compound (3, X = Cl) can be stored for several days at 0 °C in ether solution; (3, X = NPr^i_2) decomposes rapidly at 0 - 20 °C, but is stable for several hours at -40 °C. Compounds (3, X = OMe, Ph) are of intermediate stability, but can readily be handled at 0 - 20 °C.[5] For example, further reaction of (3, X = OMe) with methyl lithium for 1h at 20 °C, leads to (5, X = Me), presumably by an addition - elimination reaction of methyl lithium at the double bond facilitated by co-ordination of the lithium to the ether substituent.



(4)



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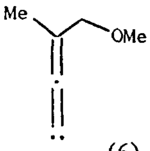
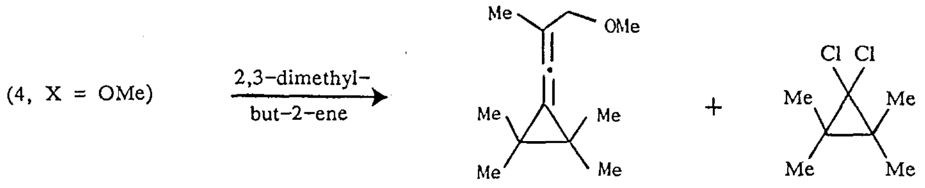


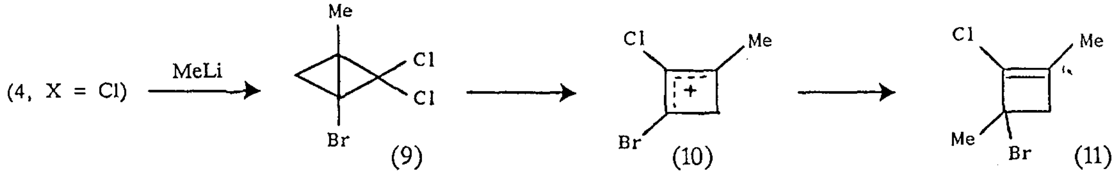
(6)

Treatment of (4, X = OMe) with two mol.equiv. of methyl lithium at -78 to 20 °C in the presence of 2,3-dimethylbut-2-ene leads to the cyclopropane (7) (48%). This reaction apparently proceeds by lithium-bromine exchange and loss of lithium chloride to produce (5, X = Br) which reacts with the excess of methyl lithium to produce the allenic isoprenoid carbene (6), which adds to the alkene.[6] A minor product (8) (ca. 10%), is apparently derived by addition of dichlorocarbene to the alkene. The source of this carbene in this reaction is not yet clear.



(7) (8)

In contrast, reaction of (4, X = Cl) with 2.2 mol.equiv. of methyl lithium at −78 °C in the presence of 2,3-dimethylbut-2-ene and quenching at that temperature leads to no carbene trapping products, and the cyclobutene (11)[7] is isolated (59%). This is again most reasonably explained in terms of an initial lithium-bromine exchange; 1,3-elimination of lithium chloride would then lead to a bicyclobutane, (9).[8] Ready loss of chloride ion to produce (10),[9] and regioselective trapping by excess methyl lithium could then lead to the cyclobutene. Thus there appears to be a dramatic difference in the reactions of (2, X = Cl) and (4, X = Cl) with methyl lithium; since the 1,3-elimination would seem to require a syn-geometry of an intermediate organolithium bond with the chloromethyl group, the reactions may be controlled by the relative rates of lithium-halogen exchange, interconversion of geometrical isomers,[10] and elimination.



(9) (10) (11)

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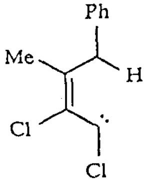
1. See eg., B. Halton and M.G. Banwell, *Cyclopropenes*, in *The Chemistry of Functional Groups, Cyclopropanes,* Vol.2, Ed. Z. Rappoport, Wiley, 1988.
2. Chloretone is converted to (1, X = Cl) by treatment with thionyl chloride and potassium iodide (a modification of the procedure described by D.G.Kundiger, H.Pledger and L.E.Ott, *J.Amer.Chem.Soc.*, 1955, *77*, 6659). Reaction with alkoxides, amines or phenyl magnesium bromide produces (1, X = OMe, NPr$^i_2$, Ph) respectively.
3. M.S. Baird, S.R. Buxton and J.S. Whitley, *Tetrahedron Letters,* 1984, 1509.
4. Which shows δ_H 3.6 (2H, s), 1.4 (3H, s); δ_C 118.4s, 51.6t, 41.9s, 19.4q.
5. At 20 °C, (3, X = Ph) rearranges in ca. 36h to Z,E-1,2-dichloro-3-methyl-4-phenylbuta-1,3-diene; this apparently involves ring-opening to the carbene (12) which undergoes a formal 1,4-hydrogen shift. Similarly, (3, X = OMe) forms a dimer apparently derived by reaction of the corresponding diene with unreacted cyclopropene.



(12)

6. M.S.Baird, *Tetrahedron Letters,* 1984, 4829.
7. Compound (11) showed δ_H 3.02 (1H, d, J 10.6 Hz), 2.71 (1H, d, J 10.6 Hz), 1.87 (3H, s), 1.76 (3H, br.s); δ_C 138s, 129s, 62s, 50t, 28q, 13q. Preparative g.l.c. caused elimination of HBr to give 2-chloro-3-methylene-1-methylcyclobutene (δ_H 4.68 (1H, br.s), 4.45 (1H, br.s), 2.78 (2H, br.s), 1.92 (3H, s)).
8. N.O.Nilsen, L.Skattebol, M.S.Baird, S.R.Buxton and P.D.Slowey, *Tetrahedron Letters,* 1984, 2887.
9. B.M.Trost and R.C.Atkins, *J.Chem.Soc.Chem.Comm.,* 1971, 1254; E.V.Dehmlow, *Tetrahedron Letters*, 1975, 203.
10. See eg., D.Seyferth and R.L.Lambert, *J.Organometal.Chem.*, 1973, *55*, C53.

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