

CYCLOPROPENE-CARBENE REARRANGEMENTS AT LOW TEMPERATURES.

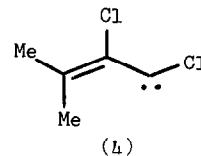
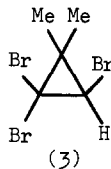
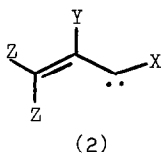
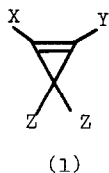
GENERATION AND TRAPPING OF 1,2-DICHLORO-3-METHYLBUT-2-EN-1-YLIDENE

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Summary Reaction of (5, X = H, Cl, Br) with methyl lithium in ether in the presence of alkenes leads to cyclopropanes, e.g. (6), apparently derived by trapping of an intermediate carbene (4); in the case of (5, X = Br), the precursor of the carbene, a cyclopropene (1, X = Y = Cl, Z = Me), may be trapped by addition of bromine at -90°C .

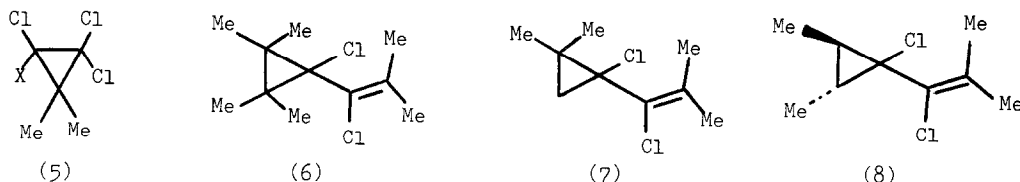
Cyclopropenes (1) are known to undergo thermal or photochemical ring opening to produce unsaturated carbenes (2).¹ The thermal reaction usually requires relatively high temperatures unless the cyclopropene is fused to a second five or six-membered ring; for example, the tetrachloride (1, X = Y = Z = Cl) rearranges to (2, X = Y = Z = Cl) at 180°C .² In some cases, however, the cyclopropene-carbene rearrangement occurs even at or below ambient temperature; thus (1, X = SOEt, Y = H, Z = Me) ring opens at -25°C , and the resulting carbene (2, X = SOEt, Y = H, Z = Me) is readily trapped by alkenes.³



We recently reported that several 1,1,2-trihalocyclopropanes undergo ready 1,2-dehydrohalogenation on reaction with RLi to produce relatively stable 1-halocyclopropenes, but that treatment of (3) with MeLi led to 3-bromo-3-methylbut-1-yne apparently by rearrangement of an intermediate (1, X = Br, Y = H, Z = Me) at temperatures above ca. -80°C .⁴ We now report the generation of (1, X = Y = Cl, Z = Me) and its rearrangement to (4).⁵

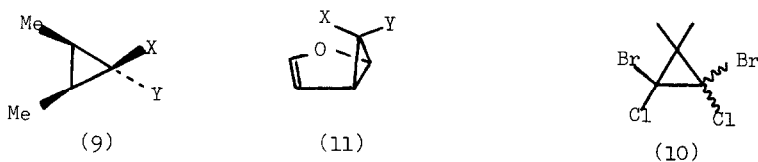
The trichloride (5, X = H) and tetrahalides (5, X = Br, Cl) were readily prepared by reaction of dichlorocarbene, generated under phase transfer conditions from chloroform - aq. NaOH -cetrinide, with the corresponding halo-alkenes.⁶ Treatment of (5, X = H) with methyl lithium-ether for 15 min at 20°C in the presence of 2,3-dimethyl-but-2-ene caused complete reaction of the starting material and the formation of a single product (6) [δ_{H} 1.11 (s, 3 H), 1.17 (s, 3 H), 1.19 (s, 3 H), 1.24 (s, 3 H), 1.82 (s, 3 H), 1.84 (s, 3 H)]⁷ (56%). Compound (6) is apparently

derived by 1,2-dehydrochlorination of (5, X = H) to produce (1, X = Y = Cl, Z = Me), followed by ring-opening to (4) and trapping by the alkene. In the same way, reaction of (5, X = Cl) or (5, X = Br) with MeLi-Et₂O for 30 min at 20°C or 1 min at -40°C* respectively in the presence of the alkene led to an identical product (75, 60%). In these cases an apparent 1,2-dehalogenation has occurred, the bromide reacting at lower temperature because of the known greater rate of lithium-bromine rather than lithium-chlorine exchange.⁸



When the above reactions were repeated using 2-methylprop-1-ene or trans-but-2-ene in place of 2,3-dimethyl-but-2-ene, a single product, (7) or (8) respectively, was again obtained from each of the polyhalides (5, X = H, Cl, Br).⁹ When the reactions were carried out in the presence of cis-but-2-ene two products (9a,b) were obtained in ratio ca. 8:1; these were not separated but the major isomer was characterised as exo-alkenyl form (9a) by analogy with the addition of (2, X = Y = Z = Cl) to the alkene.²

A more detailed examination of the reaction of (5, X = Br) with MeLi-ether in the presence of 2,3-dimethylbut-2-ene indicated that although the tetrahalide reacted rapidly even at -70°C, the product (6) did not appear until the temperature was allowed to reach 0°C for ca. 5 min; indeed, when the temperature was allowed to reach -20°C for 5 min and a second alkene, 2-methylprop-1-ene, was then added, work-up at ambient temperature gave a mixture of both (6) and (7). This is consistent with the formation of an intermediate cyclopropene (1, X = Y = Cl, Z = Me) at -70°C, which ring opens to (4) only at ca. 0°C. Confirmation of the presence of (1, X = Y = Cl, Z = Me) was obtained by treating (5, X = Br) with MeLi-Et₂O at -90°C to 95°C for 5 min and then adding excess Br₂-CCl₄ at that temperature, when a new tetrahalide (10) was isolated (78% as a ca. 3:2 mixture of cis- and trans-forms).¹⁰



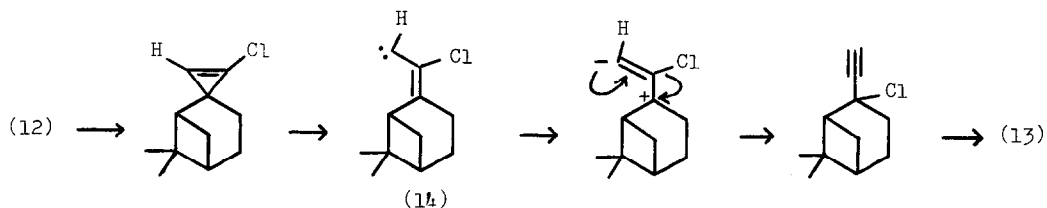
- (a) X = Cl, Y = C(Cl) = CMe₂
 (b) X = C(Cl) = CMe₂, Y = Cl

When (5, X = H) was treated with MeLi-Et₂O in the presence of furan the product (11), obtained as a ca. 5:1 mixture of *exo*- and *endo*-isomers, was again derived by 1,2-addition of carbene (4) to the diene. Apparently ring-opening of the intermediate cyclopropane (1, X = Y = Cl, Z = Me) proceeds faster than does its [4+2]-cycloaddition to furan; this is in sharp contrast to the reaction of (1, Z = Me; X = H, Y = CO₂Me; X = H, Y = CN; X = Y = Me) with furan, all of which lead to [4+2]-cycloadducts.¹¹

The ready ring-opening of (1, X = Z = Cl, Y = Me) is also in contrast to the apparent stability of (1, X = Cl, Y = alkyl, Z = Me) at ambient temperature.^{11h} However, it is mirrored in the reported ring-opening of (1, X = Br, Y = H, Z = Me) at low temperature^h and in the isolation of ring-opened products from the dehydrochlorination of 2,2-dichloro-1,1-dimethylcyclopropane.¹² Moreover, the same effect can be seen in the dehydrochlorination of other 1,1-dialkyl-2,2-dichlorocyclopropanes. Thus reaction of the β -pinene adduct (12) with KOBu^t-DMSO at 20°C leads to a single major product (13) (41%) [δ_{H} : 6.3-5.8 (m, 2 H), 4.8 (s, 2 H), 2.8-0.9 (m, 10 H, including 1.35 (s, 3 H) and 0.9 (s, 3 H)); ν_{max} . 1940 cm⁻¹].¹³



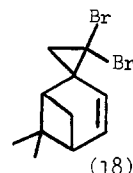
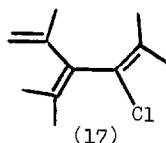
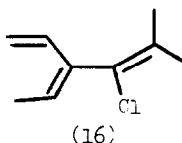
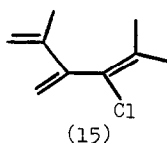
The mechanism of this reaction is at present uncertain but by analogy with the formation of 3-bromo-3-methylbut-1-yne from 1-bromo-3,3-dimethylcyclopropane, a route involving ring-opening of an intermediate chlorocyclopropane to give the vinylcarbene (14) may be operating:



The mechanisms of these reactions are being further examined by labelling studies and synthetic applications of carbene (4), particularly in terpene synthesis, are being studied. We wish to thank SERC and Bush Boake Allen Ltd. for the award of a studentship to SRB.

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2. W. Weber and A. de Meijere, Angew.Chem.Int.Edn., **19**, (1980) 138.
3. M. Franck-Neumann and J.J. Lohmann, Angew.Chem.Int.Edn., **16**, (1977) 323.
4. M.S. Baird and W. Nethercott, Tetrahedron Letters, 1983, 605.
5. Vinylchlorocarbene has been generated by 1,1-elimination of lithium chloride from 1,1-dichloro-1-lithioprop-2-ene, and can be trapped by alkenes in moderate yield (R.A.Moss and R.C.Munjal, Synthesis, 1979, 425).
6. There was no evidence of any rearrangement in these reactions equivalent to that observed in the addition of dibromocarbene to 1,2-dichloroethene (M.E. Hendrick and M. Jones, Tetrahedron Letters, 1978, 4249).
7. The signals did not change even at 70°C, suggesting a high barrier to rotation about the cyclopropane.²
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9. Attempts to purify (7) or (8) by preparative g.l.c. at 180°C using a metal inlet system at 200°C led to dehydrochlorination in each case, to give (15) and (16) respectively. In the same way (6) led to (17).



10. The mixture was apparently homogeneous by t.l.c. or g.l.c.. However, ¹H n.m.r. showed two equal area singlets at δ 1.57 and 1.51 due to the cis- isomer, and one singlet at δ 1.53 due to the trans-isomer. The ¹³C spectrum showed signals at δ_{CCl₄} 21.0q, 24.5q, 27.9q, 38.5s, 62.7s and 62.8s. The signal at 38.5 is at almost exactly the same chemical shift as CMe₂ in (5, X = Cl), and presumably arises by accidental overlap of the corresponding carbons in cis- and trans- (12). The signals at 62.7 and 62.8 are very similar chemical shifts to the carbons bearing chlorine and bromine in (5, X = Br) (61.8) and 3-chloro-1,1-dimethyl-2,2,3-tribromocyclopropane (61.8). Addition of bromine to cyclopropene itself is reported to occur in a trans-manner (K.B. Wiberg and W.J. Bentley, J.Amer.Chem.Soc., **82**, (1960) 6375).
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12. L. Crombie, P.J. Griffiths and B.J. Walker, J.Chem.Soc.,Chem.Commun., 1969, 1206.
13. This was identical to the product obtained (51%) by cyclopropylidene-allene rearrangement on treatment of the mono-dibromocarbene adduct (18) of verbenene with MeLi-Et₂O at 20° - 30°C.
14. T.C. Shields, B.A. Loving and P.D. Gardner, J.Chem.Soc.,Chem.Commun., 1967, 556.

*The products were quenched by addition of water at the given temperature and allowed to reach ambient temperature for work-up.

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