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The Stereochemistry of Ring-opening of 3-Alkyl-1,1-dihalocyclopropenes to Vinylcarbenes at Ambient Temperature

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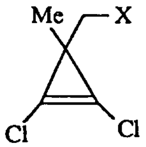
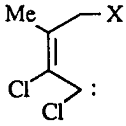
Reaction of 3-alkyl-1,2-dibromocyclopropenes with electron-rich or electron-poor alkenes in solution at 0 - 20 °C leads to cyclopropanes apparently derived by stereoselective trapping of a single isomer of a vinylcarbene; in the absence of an alkene, the cyclopropenes rearrange to alkynes.

We have shown that 3,3-dialkyl-1,2-dihalocyclopropenes rearrange to vinylcarbenes at 0 to 20 °C and that in the case of cyclopropenes (1) there is a considerable degree of stereocontrol in the ring-opening, the carbenes (2, X = Cl, OMe, Ph) being trapped by an added alkene rather than the isomeric species, (3).[1]



(1)



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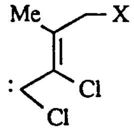
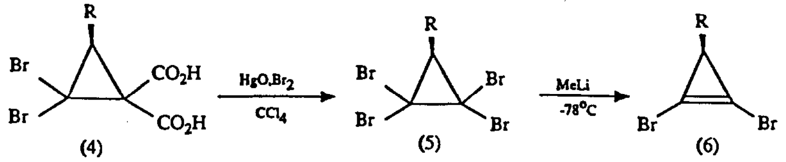


(3)

These reactions occurred at a much lower temperature than is typical for ring-opening of other cyclopropenes which have been reported to involve rearrangement to a vinylcarbene; for example, tetramethyl- and tetrachlorocyclopropenes and 3,3-dimethylcyclopropene require temperatures of 150 - 180 °C.[2,3,4] It was not clear what factors caused the ease of reaction and controlled the stereochemistry, and, in particular, whether both alkyl-groups on C-3 were necessary; for example, 1,3-diethylcyclopropene only ring-opens at about 180 °C.[5] Moreover 1-halo- and 1,2-dihalocyclopropenes having no substituent at C-3 ring-open in the gas phase to produce haloallenes;[6] the mechanism of this reaction remains to be determined. We now describe the ring-opening of 3-monoalkyl-1,2-dihalocyclopropenes in solution at ambient temperature, and intramolecular trapping of the derived carbenes.

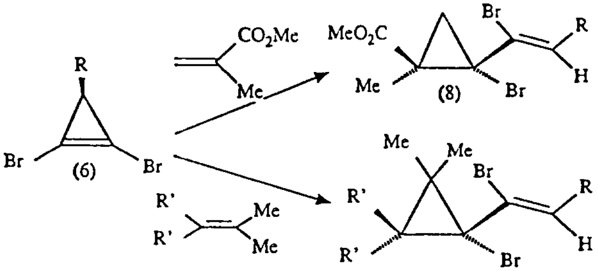
The tetrabromide (5a) was prepared (68 %) by refluxing the diacid (4a)[7] with mercuric oxide in carbon tetrachloride and then adding bromine.[8] Treatment of (5a) with one mol.equiv. of methyl lithium at -78 °C led to the dibromocyclopropene (6a) (70 %).[9]



a, R = $CH(CH_3)_2$; b, R = CH_3; c, R = C_5H_{11}

On standing for 16 h at 20 °C in $CDCl_3$ the cyclopropene (6a) rearranged to the alkyne (7a) as the only major product by ^1H n.m.r.[10] Similar rearrangements have been reported for 1-halo-3,3-dimethylcyclopropenes and have been explained in terms of a rearrangement of an intermediate carbene, although this could not be trapped by an added alkene.[11] Moreover, in a closely related case, rearrangement of 1-bromo-2-t-butylcyclopropene to 1-bromo-4,4-dimethylpent-2-yne has been found to proceed more rapidly in the presence of lithium bromide, suggesting that an intermolecular reaction is involved.[12]

In the present case, however, addition of an excess of methyl methacrylate to (6a) in ether led to the formation of a single major cyclopropane, (8a) (60 %).[13] The stereochemistry of this product was proved by conversion to the corresponding acid (9) (70 %) by reaction with trimethylsilyliodide in the dark at 80 °C;[14] the structure of (9) was established by X-ray crystallography.[15]



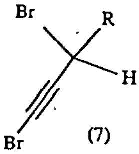
a, R = $CH(CH_3)_2$; b, R = CH_3; c, R = C_5H_{11}

R' = Me (10)

R' = H (11)

The formation of (8a) suggests that (6a) rearranges to the carbene (12a) with the Z-stereochemistry about the alkene, an apparent contrast to the ring-opening of (2, X = Cl, OMe, Ph).[1] However, as in the case of the latter carbenes, addition to methyl methacrylate is highly stereocontrolled, leading to the cyclopropane with vinyl and ester groups *cis*- to each other. The ^1H spectrum of the crude product contained additional signals corresponding to ca. 10 % of those for (8a), including a methoxy signal at δ_H 3.8. For reasons given below, this minor product is thought to be (13a), isomeric with (8a) about the cyclopropane rather than the alkene.

Reaction of (5b,c)$^+$ with 1.1 mol.equiv. of methyl lithium in ether as above led to the corresponding cyclopropenes (6b,c). Treatment of the ethereal solutions after aqueous work-up with methyl methacrylate gave the cyclopropanes (8b,c) (71, 68 %). The stereochemistry of these was assigned by analogy with (8a). The n.m.r. spectra in each case included signals for the methoxy-group, the alkene hydrogen and the cyclopropane hydrogens at very similar chemical shifts to those for (8a); in each case, a minor product was obtained (ca. 10 %) which showed a methoxy-signal at the same chemical shift as that for the minor product in the reaction of (6a). If the crude products from the reaction of (5b) with methyl lithium were allowed to stand for 18 h before the addition of water, the cyclopropene rearranged to the alkyne (7b) (55 %).[**]



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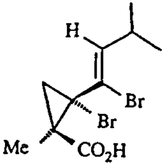
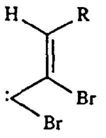


(9)



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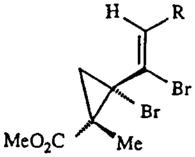

(13)

a, R = $CH(CH_3)_2$;
b, R = CH_3;
c, R = C_5H_{11}

In the same way, reaction of (6a-c) with 2,3-dimethylbut-2-ene led to the corresponding cyclopropanes (10a-c) (68, 75, 70 %) while reaction of (6a) with 2-methylprop-1-ene led to (11a) (59 %), the stereochemistries being assigned in each case by analogy with (8). When measured at 25 °C, the 250 MHz ^1H and 62.5 MHz ^{13}C n.m.r. spectra for (10a-c) each included signals which were very broad because rotation about the bond between the ring and the alkene is not fast on the n.m.r. timescale.[16] However, at -10 to -40 °C, the lines became sharp; the resulting spectra of the crude products showed no evidence for the formation of more than one isomer, indicating that in this case only one stereoisomer of the carbene is trapped. Because of this observation, the minor products of carbene trapping by methyl methacrylate are characterised as being isomeric about the cyclopropane rather than the alkene.

The stereochemistry of ring-opening of cyclopropenes (6) is therefore the reverse of that observed for (1), ie. the carbene which is trapped has the larger 3-substituent of the cyclopropene E-to the carbene centre. This effect is being studied by means of semi-empirical calculations.[17]

We thank SERC for the award of a studentship to H.L.F.

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7. The acid (4a) was prepared by reaction of diethyl isobutylidenemalonate with bromoform and conc. aqueous sodium hydroxide in the presence of TEBA for 72 h at 60 °C; at shorter reaction times this led to the corresponding diethyl ester (M.S.Baird and M.E.Gerrard, **Tetrahedron Letts.**, 1985, 6353). The acids (4b,c) were prepared in the same way from the corresponding diethyl alkylidenemalonate, except that the esters were isolated, and then converted to the acids by hydrolysis with aqueous-ethanolic sodium hydroxide.
8. A similar bis(bromodecarboxylation) of cyclopropanedicarboxylic acid itself has been reported to occur in low yield (C.Blankenship and L.A.Paquette, **Syn.Commun.**, 1984, **14**, 983).
9. This showed δ_H 2.49 (1H, d, J 4.2 Hz), 1.85 (1H, d sep, J 4.2, 6.8 Hz), 0.89 (6H, d, J 6.8 Hz).
10. Compound (7a) showed ν_{max} 2210 cm^{-1}; δ_H 4.46 (1H, d, J 4.6 Hz), 2.05 (1H, m), 1.11 (3H, d, J 6.6 Hz), 1.09 (3H, d, J 6.6 Hz); δ_C 77.33s, 48.11s, 45.46d, 35.76d, 19.66q, 19.22q. The ^1H n.m.r. spectrum of the crude product included three additional sets of signals at δ 6.6, 3.2, and 2.8 corresponding to ca. 10 % of the product; these were not present after flash distillation.
11. M.S.Baird and W.Nethercott, **Tetrahedron Letts.**, 1983, 605; M.S.Baird, S.R.Buxton and H.H.Hussain, **J.Chem.Res.**, 1986, S310.
12. J.R.Al Dulayymi and M.S.Baird, unpublished results.
13. Compound (8a) showed δ_H 5.88 (1H, d, J 8.9 Hz), 3.66 (3H, s), 2.62 (1H, m), 2.33 (1H, d, J 6.5 Hz), 1.62 (3H, s), 1.44 (1H, d, J 6.5 Hz), 0.99 (6H, d, J 6.7 Hz). This spectrum, and also that of (10 a-c) showed considerable changes with temperature; these will be analysed in a full paper.
14. A minor product was characterised as 4-methylpent-1-yn-1-yl 3-iodo-2-methylpropenoate of unknown stereochemistry. If the reaction was carried out at 40 °C, t.l.c. showed that this alkyne and (9) were formed at ca. equal rates and a 1:1 mixture was obtained on work up.
15. We thank Dr.W.Clegg (Department of Chemistry, Univ. of Newcastle) for carrying out this structure determination, a detailed account of which will appear in a full paper.
16. Thus compound (10b) showed δ_H(250 MHz, 298 K) 6.0 (1H, q, J 6.5 Hz), 1.8 (3H, d, J 6.5 Hz), 1.17 (6H, br.s), 1.07 (6H, br.s); (233 K) 6.0 (1H, q, J 6.5 Hz), 1.8 (3H, d, J 6.5 Hz), and 1.33, 1.21, 1.19, 1.10 (each 3H, s); δ_C(62.5 MHz, 298 K) 130.4, 61.4, 23.6 (br), 21.8 (br), 20.7 (br), 19.17 (br), 17.4; (233 K) 130.5, 129.8, 61.5, 30.5, 28.5, 23.6, 21.7, 20.75, 18.95, 17.6.
17. J.R.Al Dulayymi, M.S.Baird, H.Rzepa and V.Thoss, paper in preparation.

\+ Prepared in the same way from (4b,c). Compound (5b) showed δ_H 2.02 (1H, q, J 6.2 Hz), 1.36 (3H, d, J 6.2 Hz); δ_C 42.27, 40.8, 16.01.

** A minor product (ca. 10 %) which showed δ_H 5.3 (q, J 7 Hz) and no other signals apart from any hidden by those of the major isomer could be the allene, 1,1-dibromobuta-1,2-diene; the structure of this compound remains to be proved.

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