LABELLING STUDIES OF THE

RING OPENING OF 1-BROMO-2-CHLORO-3,3-DIMETHYLCYCLOPROPENE

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1-Bromo-2-chloro-3,3-dimethylcyclopropene reacts with methyl lithium in the
presence of 2,3-dimethylbut-2-ene at above -70°C to give (4); ^{12}C labelling
shows that C-2 of the cyclopropane becomes the centre carbon of the allene.

We have shown [1] that 1,2-dichloro-3,3-dimethylcyclopropene rearranges at
below ambient temperature to the carbene (1, X= Y= Cl), which may be trapped
by a variety of alkenes. It seems likely that 1-bromo- and 1-chloro-
3,3-dialkyl-cyclopropenes also undergo ring opening to carbenes at below
ambient temperature [2], though 1,3,3-trimethylcyclopropene [3] and 2-chloro-
1,3,3-trialkylcyclopropenes [4] appear to be much more thermally stable. We are
presently examining the effect of substituents on the ring opening , and now
report some reactions of 1-bromo-2-chloro-3,3-dimethylcyclopropene.

(1)   (2)   (3)   (4)   (5)
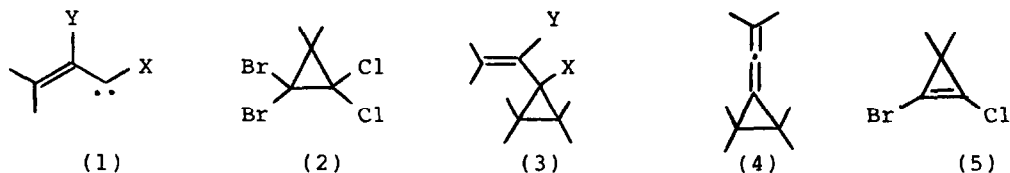
Treatment of (2)[5] with methyl lithium in ether for 2min at -90° C in the
presence of 2,3-dimethylbut-2-ene , followed by quenching with water at that
temperature and warming to ambient temperature for 30min led to a solid which
was a mixture of two $C_{11}H_{18}BrCl$ isomers (47%). The ^{1}H n.m.r. of the product [6]
was very similar to that observed for (3, X=Y=Cl) [1], except that twice as many
signals were present, and could be interpreted in terms of an ca. 1:1 mixture
of the bromochlorides (3,X=Cl, Y=Br) and (3,X=Br, Y=Cl). The ^{13}C spectrum [6]

was consistent with this assignment, showing four signals in the alkene region and two typical of the 1-carbon of a 1-halo-1-vinylcyclopropane. Treatment of the mixture with MeLi in ether for 15min at 20-30° C followed by quenching with water caused one of the dihalides to be converted to the allene (4) by a 1,2-dehalogenation. However, the second isomer remained unchanged and was characterised as (3, X=Cl, Y=Br)[7]. Subtraction of the signals for this compound from the ^{1}H and ^{13}C n.m.r. spectra of the mixture left signals which were in complete agreement with structure (3, X=Br, Y=Cl). The formation of the two bromochlorides can be explained in terms of initial 1,2-dehalogenation of (2) to produce (5) followed by ring opening on warming to produce the isomeric carbenes (1, X=Br, Y=Cl) and (1, X=Cl, Y=Br) and trapping of these by the alkene. The presence of the cyclopropene (5) at low temperature was confirmed by treatment of (2) with methyl lithium at -90° C, followed by quenching with water at that temperature and then addition of bromine in ether at -80° C, when (6) was obtained (60%).[8] In addition, (2) was treated with MeLi at -90° in the presence of 2,3-dimethyl-but-2-ene, excess base was destroyed by addition of water at that temperature, and most of the solvent was removed from the organic layer at -50°C and 1mmHg. N.m.r. of the remaining liquid at -40°C showed only one major signal (a singlet at δ_H 1.26) which could not be assigned to 2,3-dimethyl- but-2-ene or residual ether. On warming to 10°C this signal disappeared and was replaced by those due to (3,X=Cl, Y=Br) and (3, X=Br, Y=Cl); the half-life of this process was about 20min.
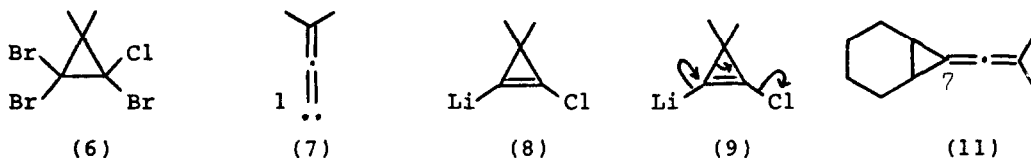
When (2) was treated with excess methyl lithium at -90° C in the presence of 2,3-dimethylbut-2-ene and then either stirred for 5min at -65 to -70°C and quenched with water at that temperature or allowed to reach 20°C before quenching, the reaction took a different course and the allene (4) was isolated (59%) as the only major product. At first sight this may be explained in terms of initial formation of the mixture of bromochlorides (3) followed by

dehalogenation; however, this may be ruled out by the formation of (4) even at -70°C and because only one of the isomers reacts with methyl lithium even at 20°, as described above. Since (5) is known to be present in the reaction solution and to be relatively thermally stable below 0°C, it seems likely that (4) is derived by reaction of (5) with excess MeLi. One route to the allene would involve trapping of (7) by 2,3-dimethylbut-2-ene. The carbene may in principle be derived by dehalogenation of the cyclopropene by excess MeLi , either directly or through an organolithium intermediate. In either case, the first step would presumably be attack on bromine, eg. to give (8), rather than attack on chlorine. The lithio-species (8) might then eliminate LiCl to produce a cyclopropyne and thence (7), or eliminate concurrently with rearrangement to (7); in the latter case either C-1 or C-2 may formally become C-1 of (7). In order examine the reaction further, the ^{12}C labelled cyclopropane (10)[9,10] was treated with excess methyl lithium at -90° C in the presence of 2,3-dimethylbut-2-ene and the solution was allowed to reach 20° C before quenching with water. This led to allene (4´) which was shown by ^{13}C n.m.r. to be labelled only at the centre carbon of the allene [11].This rules out the intermediacy of the symmetrical 3,3-dimethylcyclopropyne, but is in agreement with a rearrangement of (8) in the sense shown in (9), ie. the carbon bearing the chlorine becomes the central carbon of the allenic carbene. Although such an explanation fits the experimental results, it is not the only possibility. For example, one intriguing alternative is that (8) rearranges to the α-lithiocarbene (1,X=Li ,Y=Cl), which is trapped by the alkene and then eliminates LiCl.
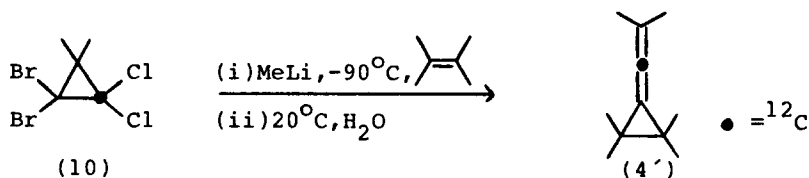
The cyclopropyne has also been ruled out as an intermediate in the formation of (11) from 2,2-dichloro-1,1-dimethylcyclopropane and potassium t-butoxide in DMSO in the presence of cyclohexene, but in this case C-2 of the cyclopropane becomes exclusively C-7 of the allene (11).[12]

1. M.S.Baird, S.R.Buxton and J.S.Whitley, Tetrahedron Letters, 1984,1509.

2. M.S.Baird and W.Nethercott, Tetrahedron Letters, 1983,605.

3. eg., G.L.Closs and L.E.Closs, J.Amer.Chem.Soc., 1963, 85, 99.

4. eg., T.C.Shields , B.A.Loving and P.D.Gardner, J.Chem.Soc.Chem.Commun., 1967, 556; M.S.Baird and H.Hussain, unpublished results.

5. M.S.Baird, W.Nethercott and P.D.Slowey, submitted for publication.

6. The broad band decoupled spectrum showed peaks at δ_C 139.6, 136.1, 131.0, 122.4, 62.9, 59.4, 31.4, 30.8, 28.0, 27.4, 25.1, 22.5, 22.4, 22.0, 20.8, 20.3, 19.95, 19.7, 19.4 and 19.2.The signals at 62.9 and 59.4 are assigned to the cycylopropyl-carbons bonded to halogen; the carbon at lower field is assigned to the one adjacent to chlorine, ie. that in (3,X=Cl, Y=Br).

7. Compound (3,X=Cl, Y=Br) showed signals at δ_C 139.6, 122.4, 62.9, 31.4, 28.0, 25.1, 22.4, 20.8, 19.95, and 19.7; δ_H 1.87(3H, s), 1.81(3H, s), 1.25(3H, s), 1.16(3H, s), 1.08(3H, s).

8. Identical to an authentic sample prepared from 1-bromo-1-chloro-2-methyl-prop-1-ene , bromoform and base in the presence of TEBA.[5]

9. Prepared from 1,1-dibromo-2-methylprop-1-ene, [12]$CDCl_3$ and aqueous sodium hydroxide in the presence of TEBA under phase transfer conditions.

10. Treatment of (10) with methyl lithium in ether at -90°C in the presence of 2,3-dimethylbut-2-ene, quenching with water at that temperature and warming to 20°C gave a mixture of bromochlorides (3,X=Cl, Y=Br) and (3,X=Br ,Y=Cl) "labelled" with ^{12}C at the carbons adjacent to chlorine. The ^{13}C spectrum was identical to that of the unlabelled mixture, apart from the absence of the signals at 131.0 and 62.9. This confirms the assingnment of structure (3,X=Cl, Y=Br) to the isomer which does not react with methyl lithium.[7]

11. The allene (4) shows signals at δ_C 21.4, 21.6, 27.2, 96.1, 97.0 and 183.3 .The signal at 183.3 was absent in the spectrum of the ^{12}C labelled compound (4´).

12. L.Crombie, P.J.Griffiths and B.J.Walker, J.Chem.Soc. Chem.Commun. ,1969, 1206.