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A SIMPLE ROUTE TO 1-BROMOBICYCLO[1.1.0]BUTANES BY INTRAMOLECULAR TRAPPING OF 1-BROMO-1-LITHIOCYCLOPROPANES

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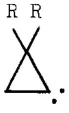
Summary: Reaction of the dibromides (5) and (10) with methyl lithium in ether leads to products derived by 1,3-dehalogenation, (6) and (11), whereas (15) and (16) undergo 1,1-dehalogenation and rearrangement to allenes, (17) and (18).

The reaction of 1,1-dibromocyclopropanes with methyl lithium generally leads to cyclopropylidenes (1) which rearrange to allenes[1] or undergo a variety of carbenic reactions such as addition to double bonds, insertion into single bonds or ylid-formation with heteroatoms[2]. The initial process has been shown to be a lithium-halogen exchange to produce (2). Such lithiobromides have been trapped at low temperatures in a variety of intermolecular processes, for example with carbon dioxide, carbonyl compounds or halo-alkanes[3]. By contrast, their intra-molecular reactions have been studied very little. The reaction of (3) with MeLi leading to (4) does however involve a double intramolecular trapping of lithiobromocyclopropanes by esters[4].



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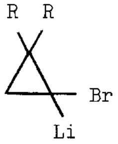

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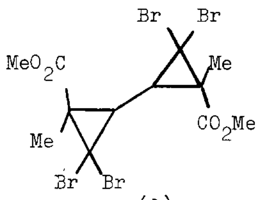

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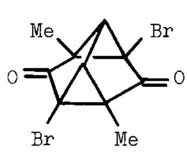
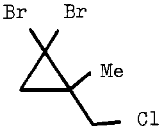


(4)

Moreover, treatment of a range of 1,1,2-trihalocyclopropanes with MeLi leads to 1,2-dehalogenation, formally by trapping of a 1-lithio-1-halocyclopropane by a C_2-halogen bond[5]. We now report the trapping of (2) by a C_3-halogen bond.

Reaction of (5) with methyl lithium in ether at -40° leads to a single major product (6), b.p. 20° at 1mm Hg (50%) (δ_H: 1.31 (2H,s), 1.60 (3H,s), 1.80 (2H,s); δ_C: 11.23s, 12.48q, 20.00s, 41.23t)[7]. Minor products (ca. 5%) included 3-chloro-2-methylbuta-1,3-diene and *trans*-1-bromo-3-methylbuta-1,3-diene (7)[8]. The bicyclobutane (6) is apparently derived by intramolecular displacement of chloride ion from the intermediate (8, R_1 = H, R_2 = Me, X = Li, Y = Br). It seems likely that the syn-relationship of carbon-lithium bond and leaving group is necessary for the displacement to occur, and therefore either that the lithium halogen exchange leads selectively to the syn-lithio form or that (8, R_1 = H, R_2 = Me, X = Li, Y = Br) and (8, R_1 = H, R_2 = Me, X = Br, Y = Li) are both formed and are interconvertible under the reaction conditions, possibly via halogen exchange with unreacted dibromide[3].



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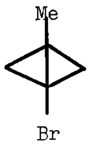

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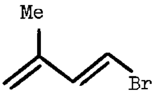

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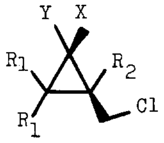

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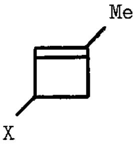
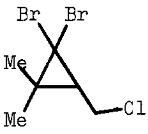


(9)

Compound (6) rearranges over several days in ether at 20° to the cyclobutene (9, X = Br) (δ_H: 1.77 (3H, tt, J 1.65, 1.25 Hz), 2.77 (1H, d. sextet, J 13.5, 1.25 Hz), 3.09 (1H, dddq, J 0. 5, 3.75, 13.5, 1.25 Hz), 4.9 (1H, dddq, J 0.75, 1.25 3.75, 1.65 Hz), 5.81 (1H, dddq, J 0.5, 0.75, 1.25, 1.65 Hz); δ_C: 16.5q, 43.3d, 45.8t, 132.0d, 148s)[9]; the rearrangement is catalysed by palladium chloride but under these conditions ca. 20% rearrangement to the diene (7) is also observed. Compound (9, X = Br) provides a convenient source of other cyclobutenes; thus reaction with sodium t-butylthiolate in methanol leads to the thioether (9, X = SBu-t) with no apparent attack at the carbon bearing the methyl group.

Treatment of the trihalide (10) with MeLi-ether at -40° leads to two products in ratio 3:1. The major product is the bicyclobutane (11) (δ_H: 0.9 (3H, s), 1.24 (3H, s), 1.53 (1H, dd, J3.5, 1.5 Hz), 1.71 (1H, d, J 1.5 Hz), 2.16 (1H, dd, J 3.5, 1.5 Hz)), derived by a similar intramolecular trapping of (8; R_1 = Me, R_2 = H, X = Li, Y = Br). The minor product is (12) (δ_H: 1.96 (3H, s, $W1/_2$ = 1.5 Hz), 2.02 (3H, s, $W1/_2$ = 1.5 Hz), 5.2 (1H, d, J = 10 Hz), 5.6 (1H, d, J = 16 Hz), 6.7 (1H, dd, J = 16, 10 Hz). The origin of this compound is not clear; however it does not appear to be derived by rearrangement of (11)[10] since an examination of the crude reaction mixture shows the presence of both (11) and (12) at -40° but on warming compound (11) rearranges to (13) rather than to (12). This rearrangement requires several hours to reach completion at 20°, but is catalysed by the addition of a trace of acetic acid[10]. It is possible that (12) is derived by a one step fragmentation of a lithiobromide as in (14); the mechanism of this reaction and the stereochemistry of the lithiobromides leading to (6) and (11) are the subject of further investigation.



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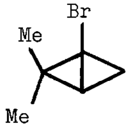

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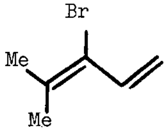

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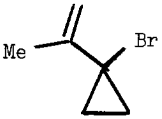

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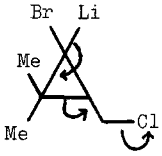
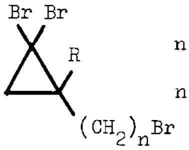


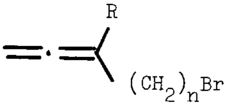
(14)

Intramolecular trapping of the 1-lithio-1-bromocyclopropane by a carbon-halogen bond is not observed when the latter is at position 4- or 5-. Thus treatment of (15, R = H and Me) or (16, R = H) with methyl lithium in ether at 20° leads to the allenes (17, R = H and Me) (57, 60%) and (18, R = H) (75%) respectively. However, formation of (6) and (11) does provide a convenient route to 1-bromobicyclobutanes, which have previously been obtained from the corresponding bicyclobutane by lithiation at the 1-position followed by halogenation.[11]



n = 2, (15)

n = 3, (16)



n = 2, (17)

n = 3, (18)

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1. H. Hopf, in "The Chemistry of Ketenes, Allenes and Related Compounds", Ed. S. Patai, Part 2, Wiley, New York, 1980, Chapter 20; see also, e.g., L. Skatteb⌀l, Acta Chem. Scand., 1963, **17**, 1683.
2. See e.g., M.S. Baird, J.C.S.Perkin Trans.I, 1979, 1020; M.S. Baird and A.R. Allan, J.Chem.Res., S, 1982, 290; M.S. Baird, ibid., 1981, 352; and references therein.
3. D. Seyferth, R.L. Lambert, and M. Massol, J.Organometallic Chem., 1975, **88**, 255.
4. K. Kratzat, F.W. Nader and T. Schwarz, Angew.Chem.Int.Edn., 1981, **20**, 589.
5. M.S. Baird and W. Nethercott, Tetrahedron Letters, 1983, 605.
6. Reaction of 1-bromo-2-chloromethyl- or 1-bromo-2-ethoxymethyl-cyclopropanes with magnesium in tetrahydrofuran is reported to lead to bicyclo[1.1.0]butane, buta-1,3-diene and cyclobutene. The stereochemistry about the cyclopropane was not discussed; however the 1-bromides were obtained by zinc-methanol reduction of the corresponding dibromides

(N.M. Abramova and S.V. Zatova, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 697). Reduction of 1,1-dibromo-2-chloromethylcyclopropane with zinc-hydrochloric acid is reported to lead to a 55:45 mixture of E- and Z- 1-bromo-2-chloromethylcyclopropanes; reaction of the mixture with sodium-dioxan leads to bicyclo[1.1.0]butane (65%) (D. Seebach, R. Hassig and J. Gabriel, Helv.Chim.Acta, 1983, 66, 308).

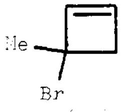
7. Compound (6) reacted with thiophenol in ether at 0° to give an ca. 1:1 mixture of 3-bromo-3-(thiophenyl)-1-methylcyclobutane and 3-bromo-1-(thiophenyl)-1-methylcyclobutane.

8. Identical to a sample obtained from 1,1,1-tribromo-3-methylbut-3-ene by reaction with n-butyl lithium-THF-ether pentane and then water at -115° to produce 1,1-dibromo-3-methyl-but-3-ene and then dehydrobromination with DBU (S.R. Buxton, unpublished results).

9. The 60 MHz p.m.r. spectrum of (9, X = Br) was identical to that published for the product of addition of HBr to methylenecyclcbutene (E.F. Kiefer and J.D. Roberts, J.Amer. Chem.Soc., 1962, 84, 784), and assigned the (unexpected) structure (19). It seems likely that the two products are identical; the ^{13}C n.m.r. and detailed analysis of the 360 MHz p.m.r. confirm our structural assignment.

10. See e.g., L. Skattebøl, Tetrahedron Letters, 1970, 2360; W.R. Moore, K.G. Taylor, P. Muller, S.S. Hall and Z.L.F. Gaibel, ibid., 1970, 2365. For a similar ring opening of 2,2-dimethyl-1-trimethylsilylbicyclo[1.1.0]butane, see M.S. Baird, S.R. Buxton and M. Mitra, Tetrahedron Letters, 1982, 2701.

11. G. Szeimies, J. Harnisch and O. Baumgartel, J.Amer.Chem.Soc., 1977, 99, 5183.



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