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INTRAMOLECULAR TRAPPING OF α-ALKYL-α-TRIMETHYLSILYL-CARBENES (CARBENOIDS) BY ADDITION TO CARBON-CARBON DOUBLE BONDS

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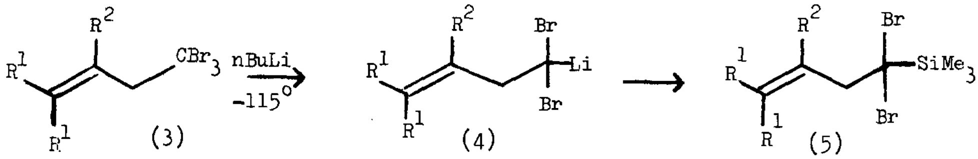
1,1-Dibromo-1-trimethylsilylbut-3-enes (5) react with MeLi at 25-35° to produce 1-trimethylsilylbicyclo[1.1.0]butanes (6), apparently by intramolecular addition of an intermediate carbene (carbenoid) (8) to the 3,4-related alkene.

Reports of α-(trialkylsilyl)-carbenes generally concern rearrangement or intermolecular trapping of α-phenyl-α-trimethysilylcarbene (1, R = Ph)[1] and trimethylsilylcarbene itself (1, R = H).[2] These species have usually been generated from the corresponding diazo-compound,[1,2] although pyrolysis of $(Me_3Si)_2CR.OH$ at 500° is reported to produce (1).[3] Thermal decomposition has also been used to generate (1, R = Cl) from $(Me_3Si.CCl_2)_2Hg$, and the carbene has been trapped by alkenes.[4] However, one attractive route to α-silylcarbenes, α-elimination from 1-halo-1-trimethylsilylalkanes, is not widely successful. Reaction of $Me_3Si.CH_2Cl$ with lithium tetramethylpiperidide does lead to (1, R = H) which is trapped by alkenes in modest yield,[5] and treatment of $Me_3Si.CHCl_2$ with sodium or potassium vapour is reported to produce the same carbene.[6] However, lithiation of $Me_3Si.CH(Cl)R$ with s-BuLi leads to (2; R = H, Me) which are comparatively stable even at -40°,[7] and a range of α-halo-α-trimethylsilyl-anions decompose thermally by pathways which apparently do not include alkylcarbene formation.[8]

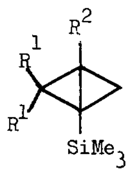
$$R-\ddot{C}-SiMe_3 \quad (1) \qquad\qquad Me_3Si-\underset{Li}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}-R \quad (2)$$

Treatment of the tribromides (3; $R^1 = R^2 = H$, $R^1 = Me$, $R^2 = H$ and $R^1 = H$, $R^2 = Me$)[9] with n-BuLi in THF-ether-pentane at -115° leads to the lithiodibromides (4), which may be trapped by a variety of electrophiles.[10] In particular, reaction with chlorotrimethylsilane leads to the dibromosilanes (5) (69, 76, 50% respectively).

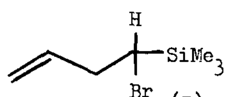


(3) (4) (5)

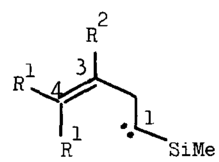
Reaction of (5, $R^1 = R^2 = H$) with MeLi-ether at 20-35° gives a single major volatile product, which shows n.m.r. and i.r. data identical to those reported for (6, $R^1 = R^2 = H$)[11] (47%), together with less volatile products including (7) (22%) and a trace of 1-bromo-1-trimethylsilylbuta-1,3-diene.* In the same way (5, R^1 = Me, R^2 = H) and (5, R^1 = H, R^2 = Me) give the bicyclobutanes (6, R^1 = Me, R^2 = H)[12] (53%) and (6, R^1 = H, R^2 = Me)[13] (48%) respectively. These bicyclic products (6) are apparently derived by lithium-halogen exchange in (5) and loss of lithium bromide to produce the carbenes (8), or related carbenoids, which undergo efficient addition to the 3,4-related alkene bond.



(6)



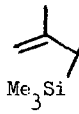
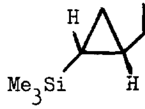
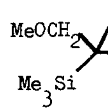
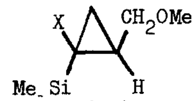
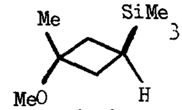
(7)



(8)

Such a process has also been reported to occur in the case of CH_2=CH-CH_2-CH:, although the major product of this reaction was buta-1,3-diene, produced by a 1,2-hydrogen shift;[14] alkylated derivatives of this carbene also lead to bicyclo[1.1.0]butanes.[15] The fact that the products of 1,2-hydrogen shifts are not observed in the reactions of compounds (5) with MeLi suggests that this process is relatively slow in (8), allowing other carbene reactions to compete effectively.

Bicyclo[1.1.0]butanes are known to be extremely sensitive to heat and to a range of acids and metallic derivatives, often undergoing extensive rearrangement.[15,16] In view of the known propensity of silicon for stabilizing a positive charge at the β-position, but not at the α-position[17] it was of interest to examine the reactions of compounds (6). On treatment with silver perchlorate in benzene for 18 hr at 20°, (6, R^1 = Me, R^2 = H) gave 1-isopropenyl-1-trimethylsilylcyclopropane (9); this is exactly analogous to the isomerisation of 1,2,2-trimethylbicyclo[1.1.0]butane to 1-isopropenyl-1-methylcyclopropane.[18] However, on treatment of (6, R^1 = Me, R^2 = H) with a catalytic amount of p-toluene sulphonic acid in benzene for 30 min at 20°, an alternative bond-cleavage occurred, leading to (10) (45%). In contrast, the parent trimethylsilylbicyclo[1.1.0]butane (6, $R^1 = R^2 = H$)

 (9)  (10)  (11)  (12)  (13)

proved to be remarkably resistent to rearrangement on treatment with either p-TsOH or $AgClO_4$ in benzene at 20°.[11] However, reaction with a catalytic amount of $AgClO_4$ in methanol for 5 min leads to a <u>ca.</u> 1:1 mixture of (11) and (12; X = H).[+] The n.m.r. spectrum of (12, X = H) shows a single proton signal at δ −0.3 assigned to the cyclopropane proton adjacent to silicon.[19†] This shows couplings of 10, 6.5 and 7.5 Hz, consistent with one <u>cis</u>- and two <u>trans</u>-coupling constants across the cyclopropane;[19] on this basis (12) is assigned the <u>trans</u>-stereochemistry, suggesting that the 1,3-bond has broken with retention of stereochemistry as reported in simple bicyclo[1.1.0]butanes.[16] Compound (6, $R^1 = H$, $R^2 = Me$) rearranges slowly with $AgClO_4$-benzene but the results are difficult to reproduce. However, on reaction with $AgClO_4$-MeOH a single product, (13), is isolated [δ 3.19 (s, 3H), 2.19 (m, 2H), 1.77 (m, 2H), 1.66 (m, 1H, including two couplings of 9.5 and two of 10.5 Hz), 1.19 (s, 3H), − 0.5 (s, 9H)].[20] Although bicyclo[1.1.0]butanes are known to undergo <u>cis</u>-addition across the 1,3-bond, the formation of (13) is in marked contrast to the ring opening of 1,3-dimethylbicyclo[1.1.0]butane to 1,3-dimethylbutadiene.[21]

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1. W. Ando, A. Sekiguchi, T. Hagiwara and T. Migita, <u>J.C.S.Chem.Comm.</u>, 1974, 372; W. Ando, A. Sekiguchi, J. Ogiwara and T. Migita, <u>ibid.</u>, 1975, 145; G.R. Chambers and M. Jones, <u>Tetrahedron Letters</u>, 1978, 5193.

2. R.N. Haszeldine, D.L. Scott and A.E. Tipping, <u>J.C.S.Perkin I</u>, 1974, 1440; D. Seyferth, A.W. Dow, H. Menzal and T.C. Flood, <u>J.Amer.Chem.Soc.</u>, <u>90</u>, 1980 (1968); R.L. Kreeger and H. Shechter, <u>Tetrahedron Letters</u>, 1975, 2061; O.L. Chapman, C.-C. Chang, J. Kolc, M.E. Jung and J.A. Lowe, <u>J.Amer.Chem.Soc.</u>, <u>98</u>, 7844 (1976); M.R. Chedekel, M. Skoglund, R.L. Kreeger and H. Shechter, <u>ibid.</u>, 7846.

3. A. Sekiguchi and W. Ando, <u>Tetrahedron Letters</u>, 1979, 4077; <u>J.Org.Chem.</u>, <u>45</u>, 5286 (1980).

4. D. Seyferth and E.M. Hanson, <u>J.Organometal.Chem.</u>, <u>27</u>, 19 (1971); <u>J.Amer.Chem.Soc.</u>, <u>90</u>, 2438 (1968).

5. R.A. Olofson, D.H. Hoskin and K.D. Lotts, Tetrahedron Letters, 1978, 1677.‡
6. P.S. Skell and E.J. Goldstein, J.Amer.Chem.Soc., 86, 1442 (1964).
7. F. Cooke and P. Magnus, J.C.S.Chem.Comm., 1977, 513; C. Burford, F. Cooke, E. Ehlinger, and P. Magnus, J.Amer.Chem.Soc., 99, 4536 (1977); see also T.J. Barton and S.K. Hoekman, ibid., 102, 1584 (1980).
8. D. Seyferth, E.M. Hanson, and F.M. Armbrecht, J.Organometal.Chem., 23, 361 (1970); D. Seyferth, R.L. Lambert, and E.M. Hanson, ibid., 24, 647 (1970); the corresponding dichloride (2, R = Cl) has also been described, but decomposition to a carbene at higher temperature is not reported. (D. Seyferth, F.M. Armbrecht and E.M. Hanson, ibid., 10, P27 (1967)).
9. M.S. Baird, A.G.W. Baxter, B.R.J. Devlin and R.J.G. Searle, J.C.S.Chem.Comm., 1979, 210.
10. M.S. Baird, S.R. Buxton and M. Mitra, unpublished results. For similar reactions with other tribromides see J. Villieras, M. Rembaud, R. Tarhoun and B. Kirschleger, Synthesis, 1981, 68.
11. H.M. Cohen, J.Organometal.Chem., 9, 357 (1967).
12. ^{1}H n.m.r. : δ 0.0 (s, 9H), 0.96 (s, 3H), 1.2 (s, 3H), 1.16 – 1.46 (m, 2H), 1.65 (d, J = 2 Hz, 1H); $\nu_{max.}$ 840, 1252 cm^{-1}.
13. ^{1}H n.m.r. : δ 0.05 (s, 9H), 0.3 (s, 2H), 1.15 (s, 2H), 1.58 (s, 3H).
14. D.M. Lemal, F. Menger and G.W. Clark, J.Amer.Chem.Soc., 85, 2529 (1963).
15. G.L. Closs and P.E. Pfeffer, ibid., 90, 2452 (1968).
16. See e.g. L.A. Paquette, R.P. Henzel, S.E. Wilson, J.Amer.Chem.Soc., 94, 7780 (1972); L.A. Paquette, 'Metal Catalysed Reactions in Strained Ring Compounds', MTP International Review of Science, Organic Chemistry, Vol. 5, Alicyclic Compounds, Ed. W. Parker Butterworths, 1973.
17. See e.g. E. Colvin, Silicon in Organic Synthesis, Butterworths, 1981.
18. W.R. Moore, K.G. Taylor, P. Müller, S.S. Hall, and Z.L.F. Gaibel, Tetrahedron Letters, 1970, 2365.
19. K.A. Williamson, C.A. Lanford and C.R. Nicholson, J.Amer.Chem.Soc., 86, 762 (1964).
20. Both cis- and trans-1,2-couplings in cyclobutanes are often of this order. See D.H. Williams and I. Fleming, Tetrahedron, 23, 2747 (1967).
21. M. Sakai, H.H. Westberg, H. Yamaguchi and S. Masamume, J.Amer.Chem.Soc., 93, 4611 (1971).

*The latter is also obtained by treatment of (5, $R^1 = R^2 = H$) with diazabicyclononene

+360 MHz ^{1}H n.m.r. revealed a small unidentified impurity in (12), although this was homogeneous by g.l.c..

†This assignment was confirmed by treating (6, $R^1 = R^2 = H$) with CH_3OD-$AgClO_4$. The ^{1}H n.m.r. spectrum of isolated (12, X = D) showed essentially complete loss of the signal at δ –0.3, and no evidence of deuteriation at other positions.

‡See also J.W. Connolly and P.F. Fryer, J.Organometal.Chem., 30, 315 (1971).

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