Substituent Effects in the Insertion of Cyclopropylidenes into 3,4-Related C–H-Bonds

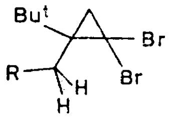
By Mark S. Baird

(*Department of Organic Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne* NE1 7RU)

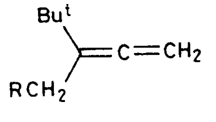
Summary The carbenes (**4**, R = aryl) (or related carbenoids) undergo competitive rearrangement to allenes (**2**) and insertion into a C–H bond 3,4-related to the carbene centre to produce (**3**); the product ratio can be correlated with substituent σ-constants, leading to a ρ-value of −0·50 ± 0·01 for the insertion.

The insertion of carbenes into C–H bonds is normally facilitated by the presence of an α-oxygen, both in inter-[1] and intra-molecular[2] processes. However, whereas (**1**, R = H) reacts with MeLi to give both (**2**, R = H) and (**3**, R = H) *via* (**4**) or a related carbenoid,[3] (**1**, R = OPh) leads only to (**2**, R = OPh) at 25—35 °C.[4]† Furthermore the carbene (**5**) inserts into the C(3)–H rather than the C(2)–H bond; this has been explained in terms of an early transition state for the latter process when C–H bond nucleophilicity will dominate in controlling the reaction rate.[5] However, the lack of insertion into the tertiary isopropyl C–H bond in (**6**) has been ascribed to steric crowding in a product-like transition state,[6] and unusual substituent effects are reported for reactions of arylcyclopropylidenes.[7]

The reactivities of carbenes in intermolecular processes, and particularly in cycloadditions, have been analysed by competition experiments, leading, for example, to the dual parameter equation of Moss *et al.*[8] We now report the use of intramolecular competition studies in analysing cyclopropylidene insertion into 3,4-related C–H bonds.



(**1**)



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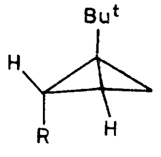
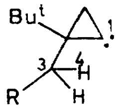
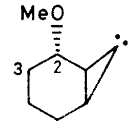


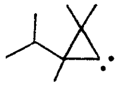
(**3**)



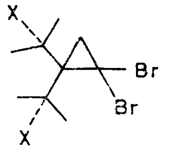
(**4**)



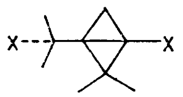
(**5**)



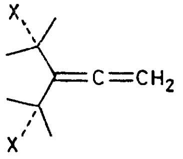
(**6**)



(**7**)



(**8**)



(**9**)

The dibromide (**1**, R = Ph)‡ reacts with methyllithium in ether§ at 25—35 °C to produce a 1:2·77 mixture of (**2**, R = Ph) and (**3**, R = Ph) as the only major products.¶ The latter is characterised as the *endo*-isomer on

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† In related systems addition to the aromatic ring is also observed. (L. Skattebøl, personal communication). Insertion into a 3,4-related C–H bond has been reported in the reaction of substituted (2,2-dibromocyclopropyl)methanols with MeLi (N. O. Nilsen, L. K. Sydnes, and L. Skattebøl, *J.C.S. Chem. Comm.*, 1978, 128).

‡ Prepared by reaction of the corresponding alkene (E. B. Sokolova, M. P. Shevanova, T. T. Ta'ng, and E. A. Troyanovskaya, *Zhur. obshch. Khim.*, 1964, **34**, 3085) with $CHBr_3$–aq. NaOH–cetrimide.

§ Prepared from Li and MeBr in Et_2O.

¶ The product ratio was determined by capillary g.l.c. on a 30 ft OV1 column, standardizing with artificially prepared mixtures of the two components.

the basis of its n.m.r. spectrum which includes a single-proton singlet at τ 9·15 for *endo*-H-4 and a single-proton triplet (J 3·4 Hz) at τ 6·65 for the benzylic *exo*-hydrogen.[9] The dibromides (**1**, R = 4-MeC_6H_4, 4-ClC_6H_4, and 4-$CF_3.C_6H_4$)‡ react similarly to give the corresponding allenes (**2**) and bicyclobutanes (**3**) in ratios of 1 : 3·25, 1 : 2·03, and 1 : 1·46, respectively. To a first approximation, the rate of opening of the cyclopropylidene (**4**, R = 4-XC_6H_4) to allene will not be affected by the nature of X. Changes in the (**2**) : (**3**) ratio can therefore be attributed to alterations in the rate of the insertion reaction brought about by interaction of X with the benzylic C–H bonds. A Hammett plot of log[ratio (**3**)/(**2**)] against σ for the substituent[10] leads to a good straight line, $\rho = -0{\cdot}50 \pm 0{\cdot}01$; this corresponds to an insertion involving little build-up of charge at carbon in the transition state and is similar to the value obtained for insertion of $:CCl_2$ into $XC_6H_4.SiMe_2H$[11a] but rather smaller than those for methylene insertion into Si–H bonds[11a] and $:CCl_2$ insertion into the benzylic C–H bond of 2-phenylbutane.[11b]

The dibromide (**7**, X = H), prepared by reaction of 1,1-di-isopropylethylene with $CHBr_3$–aq. NaOH–cetrimide, reacts with MeLi at 25—35 °C to give the bicyclobutane (**8**, X = H)[6] and allene (**9**, X = H). Comparison of the product ratio with that for the reaction of (**7**, X = ^2H) with MeLi to produce (**8**, X = ^2H) and (**9**, X = ^2H) leads to an H/^2H isotope effect of 1·7 for the insertion.** The absolute values of the ratios of (**8**) to (**9**) increase by *ca.* 20% when the reactions are carried out at −43 to −47 °C but the isotope effect remains constant. The value is rather larger than that for insertion into a 3,4-related CH-bond by alkylcarbenes[12] but very close to that in a related carbenoid reaction.[13]

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** This calculation was carried out by assuming the rate of allene formation to be independent of ^2H-substitution.

[1] J. C. Anderson and C. B. Reese, *Chem. and Ind.*, 1963, 575; for other examples see W. Kirmse, 'Carbene Chemistry,' 2nd Edn., Academic Press, London, 1971.

[2] See for example M. S. Baird, *Chem. Comm.*, 1971, 1145.

[3] D. W. Brown, M. E. Hendrick, and M. Jones, *Tetrahedron Letters*, 1973, 3951.

[4] M. S. Baird and D. Jackson, unpublished results.

[5] L. A. Paquette, G. Zon, and R. T. Taylor, *J. Org. Chem.*, 1974, **39**, 2677.

[6] D. P. G. Hamon and V. C. Trenerry, *Tetrahedron Letters*, 1974, 1371.

[7] T. Shono, I. Nishiguchi, T. Komamura, and K. Fujita, *Tetrahedron Letters*, 1977, 4327.

[8] See R. A. Moss, M. A. Joyce, and J. K. Huselton, *Tetrahedron Letters*, 1975, 4621.

[9] W. Kirmse and H. Lechte, *Annalen*, 1970, **739**, 231; W. R. Moore and J. B. Hill, *Tetrahedron Letters*, 1970, 4553; J. B. Sieja, *J. Amer. Chem. Soc.*, 1971, **93**, 130 and references therein.

[10] L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1970.

[11] (a) D. Seyferth, R. Damrauer, R. M. Turkel, and L. J. Todd, *J. Organometallic Chem.*, 1969, **17**, 367; J. Nishimura, J. Furukawa, and N. Kawabata, *ibid.*, 1971, **29**, 237; D. Seyferth, R. Damrauer, J. Y-P. Mui, and T. F. Jula, *J. Amer. Chem. Soc.*, 1968, **90**, 2944; (b) D. Seyferth and Y. M. Cheng, *ibid.*, 1973, 6763.

[12] W. Kirmse, H. D. von Scholz, and H. Arnold, *Annalen*, 1968, **711**, 22.

[13] M. J. Goldstein and S. J. Baum, *J. Amer. Chem. Soc.*, 1963, **85**, 1885.