A Novel Route to 3-Derivatives of 1,2-Dihydrobenzocyclobutene ('Benzocyclobutene')

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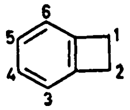
Summary Lithiation of 1,2-dihydrobenzocyclobutene can be used as a route to 3-trimethyl-silyl- and -stannyl-derivatives, which can then be converted into other 3-derivatives.

Because electrophilic substitution of 1,2-dihydrobenzocyclobutene ('benzocyclobutene') (I) gives 4-derivatives, often along with much ring-opening, 3-derivatives are rare.[1] In fact only the 3-carboxy-derivative has been made from (I) itself (and that only in 6% yield by metallation with n-pentylsodium followed by carbonation[2]), but the 3-chloro- (made by forming the ring system with the chlorine atom already attached to the appropriate carbon atom[3]), and the 3-trimethylsilyl-compound (made from the 3-chloro-compound[3]) are also known. We have now found that the 3-trimethylsilyl- and 3-trimethylstannyl-derivatives can be obtained in 19 and 30% yield, respectively (after separation by fractional distillation from other derivatives), by metallation of (I) with n-butyl-lithium–tetramethylethylenediamine in refluxing ether for 4—10 h followed by treatment with the appropriate Me_3MCl compound. Cleavage of the aryl–MR_3 bonds can then be used to introduce functional groups into the 3-position. Thus treatment of the 3-trimethylstannyl-compound with bromine or with iodine monochloride in carbon tetrachloride gives the 3-bromo- (b.p. 40° at *ca.* 0·2 mmHg) or 3-iodo-derivative (b.p. 73—75) at *ca.* 0·9 mmHg) in over 90% yield. The 3-trimethylsilyl-compound gives the same derivatives in over 70% yield, and also gives the 3-acetoxymercuri-derivative, m.p. 77—78°, in 82% yield on treatment with mercury(II) acetate in glacial acetic acid. Conversion of the 3-bromo-derivative into the Grignard reagent, followed by carbonation gives the known[2] 3-carboxy-compound, m.p. 190—192°, in 90% yield. Useful points of entry to 3-derivatives are thus made available; in particular, cleavage of the aryl–MR_3 bonds[4] can be expected to lead directly to the introduction of a range of functional groups, such as NO, NO_2, or SO_3H into the 3-position.



(I)

Satisfactory elemental analyses and n.m.r. spectra were obtained for all the 3-derivatives.

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[1] I. L. Klundt, *Chem. Rev.*, 1970, **70**, 471.

[2] R. A. Finnegan, *J. Org. Chem.*, 1965, **30**, 1333.

[3] A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.* (*B*), 1969, 12.

[4] See, *e.g.* C. Eaborn and R. W. Bott, 'Organometallic Compounds of the Group IV Elements', ed. A. G. MacDiarmid, vol. 1, part 1, 1968, pp. 407—431; E. H. Bartlett, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.* (*C*), 1970, 1717.