Dimetallation of Phenylacetylene. Selective *ortho*-Substitution

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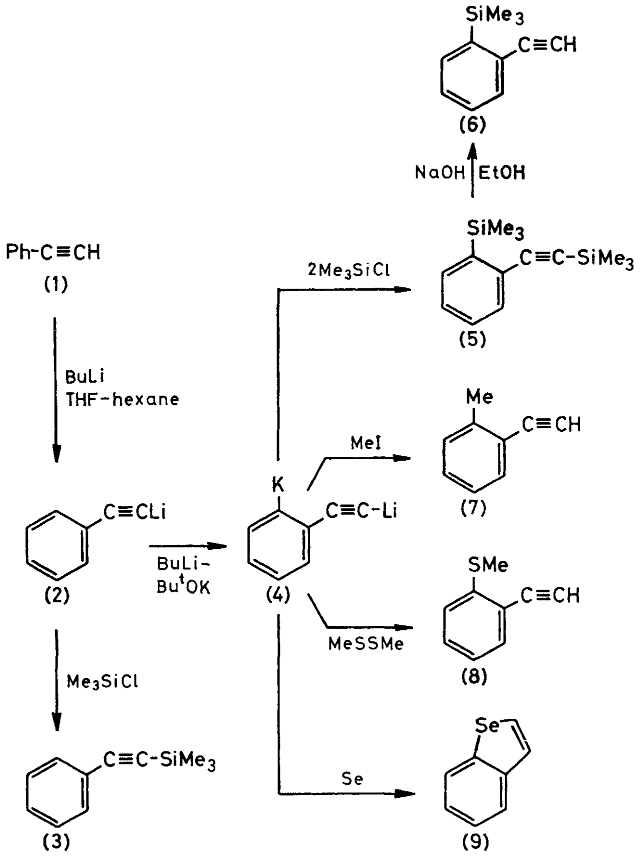
Summary Reaction of lithium phenylacetylide with the complex BuLi–Bu^{t}OK in a mixture of tetrahydrofuran and hexane leads to the *ortho*-metallated phenylacetylide; subsequent addition of methyl iodide, dimethyl disulphide, trimethylchlorosilane, and selenium gives the corresponding *ortho*-substituted phenylacetylenes and benzoselenophen.

IN the course of our studies on dimetallation of acetylenes[1,2] we have investigated the possibility of removing an aromatic proton from lithium phenylacetylide (**2**). Interaction at room temperature between phenylacetylene (**1**) and 2 equiv. of butyl-lithium in a mixture of tetrahydrofuran (THF) and hexane did not result in the desired ring metallation as was concluded from the exclusive isolation of (**3**) after addition of an excess of trimethylchlorosilane. When, however, a mixture, of (**1**), butyl-lithium, and potassium t-butoxide (*cf*. ref. 3,4) (0·1, 0·22, and 0·11 mol, respectively) in THF and hexane (about 200 and 150 ml, respectively) was allowed to stand at −20 °C for 1·5—2 h, subsequent addition of Me_3SiCl (0·30 mol) gave trimethylsilyl(2-trimethylsilylphenyl)acetylene (**5**) in about 90% yield. After reaction with only 1 equiv. of Me_3SiCl a mixture of comparable amounts of the starting compound (**1**), the disilylated acetylene (**5**) and the mono-trimethylsilyl derivatives (**3**) and (**6**) was obtained.



In contrast with the reaction with 1 equiv. of Me_3SiCl, the reactions with methyl iodide and dimethyl disulphide (0·1 mol) at -50 to -60 °C were completely regiospecific and afforded (**7**) and (**8**) in 88 and 78% yield, respectively. The structure of the isolated products was confirmed by ^1H and ^{13}C n.m.r., i.r., and mass spectra. Additional evidence for the *ortho*-metallation was obtained by the reaction with powdered selenium. Reaction of the solution of (**4**) with selenium (0·11 mol) at -20 to -5 °C in the presence of hexamethylphosphoric triamide (50 ml), followed by addition of Bu^tOH (0·10 mol) at 20 to 30 °C gave benzo[*b*]selenophen (**9**) in 75% yield. The exclusive metallation of (**2**) in the *ortho*-position has its analogues in the *ortho*-metallation of hetero-substituted benzenes such as anisole[5] and dimethylaminobenzene.[6] The *ortho*-metallation of (**2**) provides an excellent synthetic method for *ortho*-substituted phenylacetylenes, which are not easily accessible in other ways.

In regiospecific functionalizations of dilithiated acetylenes Li–C≡C–CH(Li)R to HC≡C-CH(E)R with a number of electrophilic reagents (E)[1,2,7,8] the differences in basicity or polarisability between sp- and sp^3-centres has been invoked to explain the selectivity. Examples of a discrimination between an sp- and sp^2-centre, as shown by MeI, MeSSMe and Se have, to our knowledge, not been described earlier. Although the reaction of (**4**) with 1 equiv. of Me_3SiCl is not regiospecific, the desired compound (**6**) can be obtained in 87% overall yield by treating the reaction mixture obtained by addition of an excess of Me_3SiCl to (**4**) with sodium hydroxide in ethanol.

We are currently studying dimetallation of HC≡C–CH=CH_2, HC≡C–C(Me)=CH_2, and related systems.

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[1] L. Brandsma and E. Mugge, *Recl. Trav. Chim. Pays-Bas*, 1973, **92**, 628.
[2] H. Hommes, H. D. Verkruijsse, and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, 1980, **99**, 113.
[3] M. Schlosser, 'Polare Organometalle,' Springer–Verlag, 1974, p. 143.
[4] M. Schlosser, *J. Organomet. Chem.*, 1967, **8**, 9.
[5] R. A. Finnegan and J. W. Altschuld, *J. Organomet. Chem.*, 1967, **9**, 193.
[6] F. N. Jones, M. F. Zinn, and C. R. Hauser, *J. Org. Chem.*, 1963, **28**, 663.
[7] S. Bhanu and F. Scheinmann, *J. Chem. Soc., Chem. Commun.*, 1975, 817; A. J. G. Sagar and F. Scheinmann, *Synthesis*, 1976, 321.
[8] W. Priester and R. West, *J. Am. Chem. Soc.*, 1976, **98**, 8421.