

Dimetallation of Phenylacetylene. Selective *ortho*-Substitution

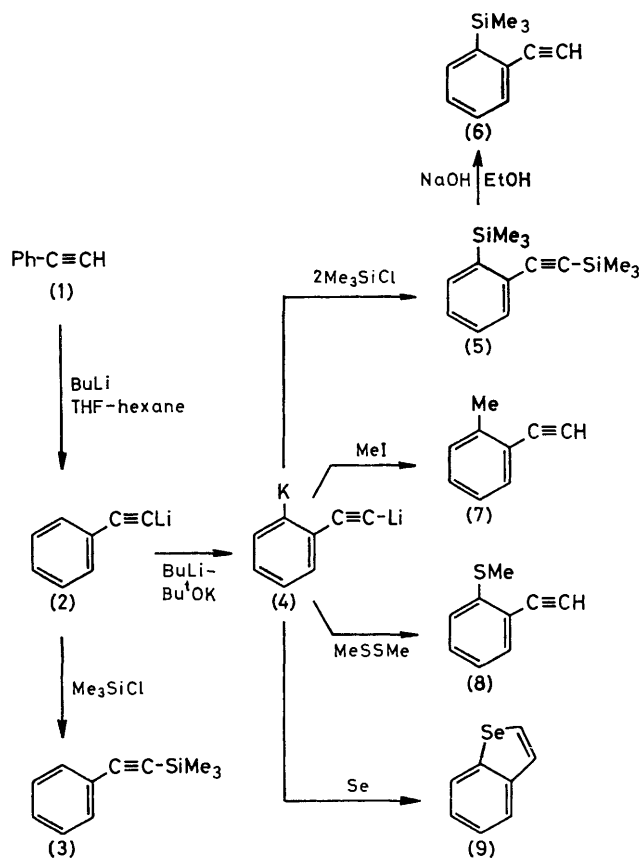
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Summary Reaction of lithium phenylacetylide with the complex $\text{BuLi-Bu}^t\text{OK}$ in a mixture of tetrahydrofuran and hexane leads to the *ortho*-metallated phenylacetylide; subsequent addition of methyl iodide, dimethyl disulphide, trimethylchlorosilane, 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 tetrahydro-

furan (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 Me₃SiCl, the reactions with methyl iodide and dimethyl disulphide (0.1 mol) at -50 to -60 °C were completely regioselective and afforded (7) and (8) in 88 and 78% yield, respectively. The structure of the isolated products was confirmed by ¹H and ¹³C 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 anisole⁵ 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 regioselective 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 sp³-centres has been invoked to explain the selectivity. Examples of a discrimination between an sp- and sp²-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 Me₃SiCl is not regioselective, the desired compound (6) can be obtained in 87% overall yield by treating the reaction mixture obtained by addition of an excess of Me₃SiCl to (4) with sodium hydroxide in ethanol.

We are currently studying dimetallation of HC≡C-CH=CH₂, HC≡C-C(Me)=CH₂, 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.