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# SYNTHESIS OF ARYLACETYLENES FROM ARYLCOPPER COMPOUNDS

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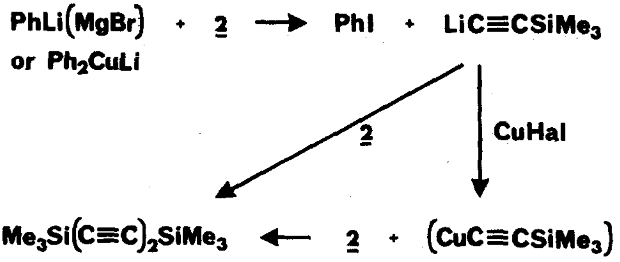
Whilst novel and efficient routes to arylacetylenes, $ArC\equiv CH$, based upon the construction of triple bonds within existing carbon-containing side chains,[1] continue to supplement older methods of synthesis, the development of protecting groups, a fairly recent innovation in acetylene chemistry,[2] has generated new approaches to the problem. To date, the latter have uniformly relied upon the Stephens Castro coupling[3] between an aryl iodide and a suitably protected cuprous acetylide, $CuC\equiv CR$ ($R = CH_2OTHP$,[4] $CH(OEt)_2$,[4] $CMe_2OCH(Me)OEt$[5]) for introduction of the acetylene moiety and may suffer from the disadvantage that elevated temperatures (e.g. refluxing pyridine) are necessary for reaction, furthermore removal of the protecting groups requires several steps.

In a conceptually simple procedure, complementary to the Stephens Castro method, we find that a wide range of arylcopper reagents (**1**) couple below room temperature with iodoethynyl(trimethyl)-silane (**2**) (readily available in high yield from ClI and $Me_3SiC\equiv CSiMe_3$[6]) to give arylethynyl(trimethyl)-silanes (**3**) in good yield. The protective $Me_3Si$- group can then be quantitatively removed by treatment with alkali[7] to give the desired arylacetylene (eq. 1)

$$\underset{\mathbf{1}}{ArCu} + \underset{\mathbf{2}}{IC\equiv CSiMe_3} \longrightarrow \underset{\mathbf{3}}{ArC\equiv CSiMe_3} \longrightarrow ArC\equiv CH \qquad (1)$$

Best results are obtained by adding an ethereal or THF solution of Grignard or aryllithium reagent (1 mole) to a vigorously stirred suspension of freshly prepared CuBr (1·1 mole) in ether[8] followed by (**2**) (0·8 mole) in THF. In order to complete coupling, the mixture is maintained initially at 0° for 3 hr, then at 20° for 6 hr. Isolation of (3) is unnecessary. After removal of solvent under reduced pressure, the residual concentrate is taken up in methanol and treated with dilute aqueous alkali at room temperature thus liberating the arylacetylene within a few minutes. By-product $Me_3Si(C\equiv C)_2SiMe_3$[9] and unreacted (2) are also conveniently desilylated by this procedure and the resulting butadiyne and iodoacetylene can then be easily removed under reduced pressure. Experiments with phenylcopper reveal the coupling conditions described to be superior to those involving prior isolation and purification of the organocopper reagent.[10] Use of a catalytic quantity of Cu(I) salt or addition of the Grignard or organolithium reagent to a mixture of Cu(I) salt and (2) yield much iodobenzene together with $Me_3Si(C\equiv C)_2SiMe_3$, presumably as a result of halogen-metal exchange. Use of the cuprate complex, $Ph_2CuLi$,[11] in ether or THF gives the same result (eq. 2) whilst soluble phosphine complexes such as $[PhCu(n\text{-}Bu_3P)]_4$[12] yield only 20-30% of $PhC\equiv CSiMe_3$.



(2)

The accompanying table lists compounds (3) prepared according to eq. 1. Yields (based upon 2) not necessarily optimum, are quoted for pure products.[14] The preparations of 2-, and 3-substituted arylacetylenes are noteworthy in that the ketone or aldehyde precursors most often required for conventional syntheses are not readily accessible.

The method is timely in view of the detailed reports now available for the preparation of individual arylcopper reagents.[15]

TABLE

$ArC\equiv CSiMe_3$ (3) compounds prepared from ArCu reagents and $IC\equiv CSiMe_3$ (2).

| Ar | Yield(%) | Ar | Yield(%) |
|---|---|---|---|
| $C_6H_5$* | 64 | 3-$FC_6H_4$ | 29 |
| 2-$MeC_6H_4$ | 48 | 4-$Me_2NC_6H_4$ | 52 |
| 3-$MeC_6H_4$ | 80 | 2-$Me_2NCH_2C_6H_4$ | 38 |
| 2-$MeOC_6H_4$ | 45 | 2-$Me_2N$-4-$MeC_6H_3$ | 20 |
| 3-$MeOC_6H_4$ | 33 | 2-Naphthyl | 47 |
| 3-$CF_3C_6H_4$ | 30 | 2-Furyl* | 47 |
| 2-$CF_3C_6H_4$ | 51 | 2-(5-Me)furyl* | 61 |
| 4-$CF_3C_6H_4$ | 38 | 2-Thienyl** | 32 |

* ArCu reagent prepared and initial coupling conducted between -20 and -30°.

** Ether:pyridine solvent. The yield of 2-thienyl$C\equiv CSiMe_3$ was 90% when the compound $BrC\equiv CSiMe_3$[13] was used in place of (2). Increased yields with the bromo reagent were not observed in couplings with other ArCu compounds.

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