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# REACTION OF COPPER ACETYLIDES WITH HALOGENO-ACETYLENES

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A recent publication (1) pointed out the synthetic utility of the reaction between copper acetylides and halogeno-olefins in pyridine solution. The process was compared with that occurring with analogous iodoaromatic compounds and it was stated that this displacement will only take place when the halogen atom is attached to an $sp^2$ hybridised carbon atom.

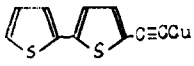
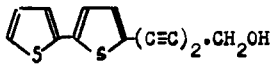
However, in view of very recent evidence (2) that a halogen atom attached to an $sp^3$ hybridised carbon atom will undergo displacement under similar conditions, it should be emphasised that halogen atoms attached to sp hybridised carbon atoms can also be easily displaced.

Thus, the cuprous acetylides listed in Table I undergo immediate exothermic reaction with the halogeno-acetylenes listed, in pyridine solution at room temperature, to give the corresponding diynes.

This reaction can be regarded as a special case of the well-known Cadiot-Chodkiewicz coupling (3) and it has already been suggested (4) that it may be an essential step in this reaction.

There are frequently cases in which the use of a cuprous acetylide rather than a free acetylene is preferred for coupling reactions and some of these will be discussed in our full publication.

TABLE I

| Acetylide | Halogeno-acetylene | Product | Yield % |
|---|---|---|---|
| $MeC{\equiv}CCu$ | $BrC{\equiv}C.CH_2OH$ | $Me.(C{\equiv}C)_2.CH_2OH$ | 60 |
| $Me(C{\equiv}C)_2Cu$ | $BrC{\equiv}C.CH_2OH$ | $Me.(C{\equiv}C)_2.CH_2OH$ | 66 |
| $PhC{\equiv}CCu$ | $BrC{\equiv}C.CH_2OH$ | $Ph.(C{\equiv}C)_2.CH_2OH$ | 65 |
| $PhC{\equiv}CCu$ | $IC{\equiv}C.Ph$ | $Ph.(C{\equiv}C)_2.Ph$ | 96 |
|  | $BrC{\equiv}C.CH_2OH$ |  | 71* |

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*m.p. 92 - 93°. All other compounds had m.p.s. identical with literature values.