

Reactions of Organocopper Compounds with Halogeno-olefins

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ORGANOCOPPER COMPOUNDS react with iodo-aromatic and heterocyclic compounds,^{1,2} but of their reactions with halogeno-olefins, other than with cuprous salts, such as cuprous cyanide,³ little is known.

We have found that copper acetylides suspended in dimethylformamide or pyridine react readily with halogeno-olefins between 40—100° to give

the corresponding ethynyl-olefins in good yields (see Table 1), *e.g.*,



The reactions are rapid and multiple substitution occurs with suitable olefins. During the reactions the copper derivatives (prepared by the standard method),⁴ which are initially insoluble, slowly

TABLE 1

Reaction of copper acetylides with halogeno-olefins

Olefin	Acetylide	Product	Yield %
CHI=CHCl	PhC≡CCu	PhC≡C-CH=CHCl	90
CHI=CHCl	PhOCH ₂ ·C≡CCu	PhOCH ₂ ·C≡C-CH=CHCl	70
CHI=CHI	PhC≡CCu	PhC≡C-CH=CH·C≡CPh	90
CHI=CHI	PhOCH ₂ ·C≡CCu	(PhOCH ₂ ·C≡C-CH=) ₂	40
Cl ₂ =Cl ₂	PhC≡CCu	(PhC≡C) ₂ C=C(C≡CPh) ₂	40
PhCH=CHBr	PhC≡CCu	PhCH=CH-C≡CPh	75

TABLE 2

Reaction of perfluoroalkyl iodides with halogeno-olefins

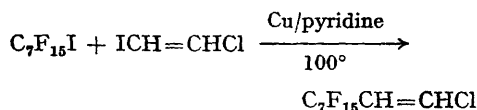
Olefin	Perfluoroalkyl iodide	Product	Yield %
ICH=CHCl	I[CF ₂] ₃ I	[CF ₂] ₃ (CH=CHCl) ₂	96
ICH=CHCl	C ₇ F ₁₅ I	C ₇ F ₁₅ ·CH=CHCl	65
ICH=CHI	C ₇ F ₁₅ I	(C ₇ F ₁₅ ·CH=) ₂	50
PhCH=CHBr	C ₇ F ₁₅ I	C ₇ F ₁₅ ·CH=CHPh	95
PhCH=CHBr	C ₃ F ₇ I	C ₃ F ₇ ·CH=CHPh	82
PhCH=CHBr	I[CF ₂] ₃ I	[CF ₂] ₃ (CH=CHPh) ₂	95
PhCH=CHBr	CF ₃ ·CH ₂ I	PhCH=CH·CH ₂ ·CF ₃	18

The compounds described above all had satisfactory analyses and molecular weight.

dissolve to give a red solution which turns brown with precipitation of copper halide when the reaction is complete, usually in 1—12 hr.

The ease of replacement of halogen is I > Br > Cl with no replacement of fluorine; this agrees with results in the aromatic area,⁵ and the reaction will only take place when the displaced halogen is attached to an *sp*² hybridised carbon atom. We have so far been unable to replace halogen on a saturated carbon atom.

A related aspect concerns the coupling of perfluoro-alkyl iodides with halogeno-olefins, which can be carried out by heating a mixture of the olefin, the iodide, and copper bronze in pyridine or dimethylformamide, *e.g.*,



Excellent yields of the coupling products are obtained (see Table 2) and the order of ease of replacement of halogen is again I > Br > Cl with

no displacement on *sp*³ carbon. A closely related reaction, the coupling of perfluoroalkyl iodides with aryl iodides or bromides in the presence of copper, has previously been reported by other workers.⁶

The coupling reactions of perfluoroalkyl iodides probably take place *via* perfluoro-alkyl copper compounds since treatment of C₇F₁₅I with copper bronze in pyridine gives a homogenous solution which undergoes the coupling reaction with halogeno-olefins and which shows a ¹⁹F n.m.r. spectrum different from C₇F₁₅I and not inconsistent with the proposed C₇F₁₅Cu. The other perfluoro-alkyl iodides employed did not give detectably soluble copper derivatives. If perfluoroalkyl copper compounds are indeed intermediates, this again reflects the greater stability of perfluoro-alkyl transition-metal compounds over their hydrocarbon analogues;⁷ alkyl iodides do not undergo the above coupling reaction and alkyl copper compounds are known to be unstable.

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