

Reactions of Organocopper Compounds. Part I

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Perfluoroheptylcopper(I), perfluoropropylcopper(I), and hexafluorotrimethylenedicopper(I) react with halogeno-olefins to yield the corresponding polyfluoroalkyl-substituted derivatives. Similar reactions with phenylethynylcopper(I) and phenylthiocopper(I) are reported. The role of copper and its co-ordination to organic species are illustrated by the reactions of butyl chloride and benzyl chloride with butylthiocopper(I) and copper(I) cyanide in the absence and presence of ligands which readily bind copper. A rationalisation of the reactions of halogen on an sp^2 carbon atom is advanced.

RECENTLY there has been considerable interest in reactions initiated by organocopper(I) derivatives¹ and in dialkylcopper(II) complexes.² In a preliminary communication³ we reported the reactions of polyfluoroalkylcopper(I) derivatives and ethynylcopper(I) derivatives with halogeno-olefins; these and other results are now described in more detail.

The present investigation followed from two observations: (i) that polyfluoroalkyl iodides reacted directly with metallic copper to form⁴ polyfluoroalkylcopper derivatives, which with iodoaromatic compounds gave polyfluoroalkylarenes; and (ii) that the Ullmann process, which works well with perfluoroaryl iodides, could be extended⁵ to the synthesis of styrene deriv-

atives by reaction of copper with an aryl iodide and an iodo-halogenoethylene. The reaction of perfluoroheptyl iodide with copper in dimethylformamide, pyridine, or dimethyl sulphoxide gave air-sensitive solutions of perfluoroheptylcopper. Treatment of the solutions with *trans*-1-chloro-2-iodoethylene afforded *trans*-1-chloro-2-perfluoroheptylethylene. The same result was obtained simply by heating a mixture of perfluoroiodoheptane, 1-chloro-2-iodoethylene, and copper in dimethylformamide or pyridine. Under similar conditions the copper compound reacted with *trans*-di-iodoethylene and β -bromostyrene to yield 1,2-bis-(perfluoroheptyl)ethylene and β -perfluoroheptylstyrene respectively.

³ J. Burdon, P. L. Coe, C. R. Marsh, and J. C. Tatlow, *Chem. Comm.*, 1967, 1259.

⁴ J. Thrower and V. C. R. McLoughlin, *Tetrahedron*, 1969, 25, 5921.

⁵ G. Camaggi, S. F. Campbell, D. R. A. Perry, R. Stephens, and J. C. Tatlow, *Tetrahedron*, 1966, 22, 1755.

¹ (a) R. D. Stephens and C. E. Castro, *J. Org. Chem.*, 1963, 28, 3133; (b) R. E. Atkinson, R. F. Curtis, D. M. Jones, and J. A. Taylor, *J. Chem. Soc. (C)*, 1969, 2173.

² E. J. Corey and J. A. Katzenellenbogen, *J. Amer. Chem. Soc.*, 1969, 91, 1851.

90–100° the yellow solid rapidly dissolved to give a red solution which after 2 h had turned black. This solution was poured on to ice-concentrated hydrochloric acid (1:1) and the solids were filtered off and washed with water. The filtrate and washings were extracted with ether (3 × 50 ml); the extracts were dried (MgSO₄) and evaporated to leave a brown solid which on recrystallisation from light petroleum (b.p. 60–80°) gave 1,6-diphenylhex-trans-3-ene-1,5-diyne (2.2 g), m.p. 113–114° (Found: C, 94.5; H, 5.3. C₁₈H₁₂ requires C, 94.7; H, 5.3%), λ_{max.} (EtOH) 223, 310, 322, and 333 nm (ε 15,850, 36,000, 48,200, and 38,700).

1,6-Diphenyl-3,4-bis(phenylethynyl)hex-3-ene-1,5-diyne.— Phenylethynylcopper(I) (3.4 g, 0.02 mol) was added to a

ethylene (5.6 g, 0.02 mol) and phenylthiocopper(I) (6.9 g, 0.02 mol) were stirred and heated under reflux in dimethylformamide (50 ml) for 14 h under nitrogen and the mixture was then cooled and filtered. Addition of water to the filtrate gave a white solid which on crystallisation from ethanol gave *trans*-1,2-bis(phenylthio)ethylene (3.4 g), m.p. 63° (lit.,⁶ 63–64°), identical with an authentic sample.

Reaction of *n*-Butyl Chloride with *n*-Butylthiocopper(I).— (a) *Alone*. *n*-Butyl chloride (1.8 g) and *n*-butylthiocopper(I) (3 g) were stirred and heated together in dimethylformamide (25 ml) under nitrogen at 120° for 2 h and then cooled. Extraction with ether and distillation gave *n*-butyl chloride (1.2 g).

Physical data for some fluoro-olefins

Fluoroalkyl iodide	Halogeno-olefin	Product	B.p. (°C/mmHg)	Yield (%)	Found (%)			Required (%)		
					C	H	Cl	C	H	Cl
I[CF ₂] ₃ I	PhCH:CHBr	PhCH:CH·[CF ₂] ₃ ·CH:CHPh	158–160/3	95	64.0	3.6		64.0	3.9	
C ₃ F ₇ I	PhCH:CHBr	PhCH:CH·C ₃ F ₇	182	82	48.9	2.7		48.5	2.6	
C ₇ F ₁₅ I	PhCH:CHBr	PhCH:CH·C ₇ F ₁₅	114–116/20	95	38.3	1.6		38.1	1.5	
CF ₃ ·CH ₂ I	PhCH:CHBr	PhCH:CH·CH ₂ ·CF ₃	88–90/20	18	64.3	5.0		64.5	4.9	
C ₇ F ₁₅ I	ICH:CHCl	C ₇ F ₁₅ ·CH:CHCl	128	65	24.9	0.35	8.2	25.1	0.5	8.2
C ₇ F ₁₁ I	ICH:CHI	C ₇ F ₁₅ ·CH:CH·C ₇ H ₁₅	160*	50	25.0	0.3		25.1	0.3	

* M.p. 27 °C

solution of tetraiodoethylene (2.7 g, 5 mmol) in dry pyridine (50 ml). The mixture was stirred and slowly heated; at 40° a red-brown solution was formed. The temperature was raised to 80° and the heating continued for 2 h. Work-up as before gave 1,6-diphenyl-3,4-bis(phenylethynyl)hex-3-ene-1,5-diyne (1.1 g), m.p. 84° (Found: C, 95.4; H, 4.7. C₃₄H₂₀ requires C, 95.3; H, 4.7%), λ_{max.} (EtOH) 221, 231, 255, 276, 286, 298, 318, and 325 nm (ε 41,700, 38,000, 42,000, 19,500, 20,000, 33,800, 26,300, 18,400, and 50,500).

1-Chloro-4-phenylbut-1-en-3-yne.— Phenylethynylcopper(I) (5.4 g, 0.03 mol) was added to *trans*-1-chloro-2-iodoethylene (5.7 g, 0.03 mol) in dry pyridine (50 ml). The mixture was heated under nitrogen at 100° for 2 h; work-up as before yielded 1-chloro-4-phenylbut-1-en-3-yne (4.5 g), b.p. 76–78° at 0.4 mmHg (Found: C, 73.7; H, 4.3; Cl, 21.7. C₁₀H₇Cl requires C, 73.8; H, 4.3; Cl, 21.8%).

1-Chloro-5-phenoxy*pent*-*trans*-1-en-3-yne.— 1-Chloro-2-iodoethylene (5 g) and 3-phenoxyprop-1-ynylcopper(I) (5.2 g) were heated at 100° under nitrogen in dry pyridine (50 ml). After 1 h the mixture was worked-up as before to yield 1-chloro-5-phenoxy*pent*-*trans*-1-en-3-yne (4 g), b.p. 110° at 0.3 mmHg (Found: C, 68.9; H, 4.8; Cl, 18.2. C₁₁H₉ClO requires C, 68.6; H, 4.7; Cl, 18.4%).

trans-1,2-Bis(phenylthio)ethylene.— *trans*-1,2-Di-iodo-

(b) *In the presence of thiourea*. In a similar experiment to (a), *n*-butyl chloride (4.1 g), *n*-butylthiocopper(I) (7.6 g), and thiourea (15 g) gave di-*n*-butyl sulphide (3.4 g), b.p. 178–180°, identical with an authentic sample.

Reaction of Copper(I) Cyanide with *n*-Butyl Chloride.— (a) *Alone*. *n*-Butyl chloride (1.8 g) and copper(I) cyanide (1.8 g) were heated together in dimethylformamide (25 ml) at 150° with stirring for 24 h. Work-up as before gave unchanged *n*-butyl chloride (1.2 g).

(b) *In quinoline*. Repetition of the foregoing reaction but in quinoline (25 ml) afforded valeronitrile (1.05 g), b.p. 140°, identical with an authentic sample.

Reaction of Benzyl Chloride with Copper(I) Cyanide.— (a) *Alone*. Benzyl chloride (1.26 g) and copper(I) cyanide (0.9 g) were heated together at 150° in dimethylformamide (25 ml) for 14 h; work-up as before gave unchanged benzyl chloride (1 g).

(b) *In quinoline*. A similar reaction to (a) but in quinoline (20 ml) gave benzyl cyanide (0.6 g), identical with an authentic sample.

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