Reactions of Organocopper Compounds. Part I

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Perfluoroheptylcopper(I), perfluoropropylcopper(I), and hexafluorotrimethylenedicopper(I) react with halog 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 sp² 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 extended ⁵ 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 transdi-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.

Perfluoro-n-propylcopper reacted similarly with β -bromostyrene to yield β -perfluoropropylstyrene while 1,1,1-trifluoroiodoethane reacted with the styrene to give, in poor yield, 4,4,4-trifluoro-1-phenylbut-1-ene. It has been shown ⁴ that a dicopper derivative can be prepared from hexafluoro-1,3-di-iodopropane; this derivative reacted with 1-chloro-2-iodoethylene and β -bromostyrene to yield the corresponding compounds 1,7-dichloro-3,3,4,4,5,5-hexafluorohepta-*trans*-1,*trans*-6diene and 3,3,4,4,5,5-hexafluoro-1,7-diphenylhepta-1,6diene.

Since the reactions of polyfluoroalkylcopper derivatives with halogeno-olefins resemble closely their reactions with aryl iodides, analogous reactions of olefins with other types of copper derivatives were investigated.

There have recently been reports 1a of the reactions of ethynylcopper(I) derivatives with iodo-arenes, and it seemed likely that such reactions might occur with halogeno-olefins. Accordingly, phenylethynylcopper(I) was treated with *trans*-di-iodoethylene, tetraiodoethylene, and *trans*-1-chloro-2-iodoethylene to give the corresponding acetylene-substituted ethylenes in high yield. Similarly 3-phenoxyprop-1-ynylcopper(I) reacted in the expected manner with *trans*-1-chloro-2-iodoethylene to yield *trans*-1-chloro-5-phenoxypent-1-en-3yne. The yields of all the above reactions were in the range 60—90%.

Although these reactions indicate clearly the ease of reaction of copper derivatives with halogen on sp^2 carbon atoms, it was possible that there was a unique feature of the C-Cu bonds influencing the reaction. It has previously ⁶ been shown that under slightly different conditions phenylthiocopper(I) reacts with a mixture of *cis*- and *trans*-1,2-dibromoethylene. We repeated the reaction under our conditions with *trans*-1,2-di-iodoethylene and obtained 1,2-bis(phenylthio)-ethylene in good yield.

The reactions so far described all occur at sp^2 carbon atoms; in view of recent work with copper(II) complexes² it was desirable to investigate reactions at sp^3 carbon atoms. When n-butyl chloride was treated with copper(I) cyanide or n-butyl thiocopper(I) in dimethylformamide, or benzyl chloride was similarly treated with copper(I) cyanide, only starting material was recovered in each case. Under the same conditions, halogenoaromatic compounds reacted readily to give the expected derivatives. If, however, the reactions were repeated in the presence of thiourea or quinoline, both of which are known to bind strongly to copper, the products valeronitrile, di-n-butyl sulphide, and phenylacetonitrile, respectively, were obtained in high yield. These results suggest that the ability to coordinate readily to copper is important in effecting the reactions, rather than ionisation of the copper derivative. Thus, in the cases of halogeno-aromatic and -olefinic compounds, a strong co-ordination to copper

exists, enhanced by $d-\pi$ interaction, and this brings the substrate sufficiently close to the copper derivatives for ligand exchange (see later) to occur. In the cases of saturated species, little or no co-ordination takes place; hence there is no reaction. Reaction can occur if the copper salt is treated with strong ligands, *e.g.* thiourea or quinoline effectively bond to copper as $(CuL_4)^+$, leaving the counterion (*e.g.* BuⁿS⁻ from BuⁿSCu) available for normal nucleophilic attack.

We envisage a mechanism for the reaction of halogenoolefins which is similar to that previously proposed ⁷ (see Scheme). The ligand exchange $(I) \longrightarrow (II)$ is

$$RCuL_{3} + -C = C - Hal \longrightarrow [RCuL_{2}HalC = C -] + L$$

$$L = solvent$$

$$V$$

$$Products + Cu(Hal)L_{3} \leftarrow [RC = Cu(Hal)L_{2}]$$

$$(II)$$

probably best explained in terms of a four-centre reaction. An essential feature is that a solvent ligand can be replaced by the attacking halogeno-compound, and we consider that this only occurs when the halogen is attached to an sp^{-8} or sp^2 -hybridised carbon atom. In the course of this work we have found that perfluoro-alkylcopper compounds will not react with polyhalogeno-olefins containing more than two reactive halogen atoms.

A possible alternative mechanism could involve addition of RCu to the double bond followed by elimination of CuX, but this seems less likely.

We have established a simple method for direct displacement of a vinylic halogen atom by any group which can be converted into a copper derivative. This process could be of considerable synthetic utility.

EXPERIMENTAL

1,7-Dichloro-3,3,4,4,5,5-hexafluorohepta-trans-1,trans-6-

diene.—Hexafluoro-1,3-di-iodopropane (4 g, 0.01 mol) was heated and stirred at 120° under nitrogen with trans-1-chloro-2-iodoethylene (3.6 g, 0.02 mol) and activated copper bronze (3 g) in dimethylformamide (25 ml). The mixture was heated for 12 h, after which time there was a copious white precipitate of copper iodide, and was then poured into water and extracted with ether (3 \times 50 ml). The extracts were dried (MgSO₄) and distilled to leave an oily residue, which on distillation *in vacuo* afforded 1,7-*di*-*chloro*-3,3,4,4,5,5-*hexafluorohepta*-trans-1,trans-6-*diene* (2.6 g), b.p. 42° at 20 mmHg (Found: C, 30.8; H, 2.0; Cl, 25.9. C₇H₄Cl₂F₆ requires C, 30.8; H, 1.6; Cl, 26.0%). By the same procedure the compounds shown in the Table were prepared.

1,6-Diphenylhex-trans-3-ene-1,5-diyne.— Phenylethynyl copper(1) $(3\cdot 4 \text{ g}, 0\cdot 02 \text{ mol})$ and trans-1,2-di-iodoethylene $(2\cdot 6 \text{ g}, 0\cdot 01 \text{ mol})$ were stirred together in dry pyridine (50 ml) under nitrogen. The mixture was heated, and at

⁷ R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1964, 1097.

⁸ P. L. Coe and N. E. Milner, unpublished work.

⁶ R. Adams and A. Ferretti, J. Amer. Chem. Soc., 1959, 81, 4927.

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(1) (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	Halogeno-		B.p. (°C/	Yield	Found (%)			Required (%)		
iodide	olefin	Product	mmHg)	(%)	С	\mathbf{H}	Cl	С	н	Cl
$I[CF_2]_3I$	PhCH:CHBr	PhCH:CH·[CF2]5·CH:CHPh	158 - 160/3	95	64.0	$3 \cdot 6$		64.0	$3 \cdot 9$	
C_3F_7I	PhCH:CHBr	PhCH:CH·C ₃ F ₇	182	82	48.9	2.7		48.5	$2 \cdot 6$	
$C_{7}F_{15}I$	PhCH:CHBr	PhCH: $CH \cdot C_7 F_{15}$	114 - 116/20	95	38.3	$1 \cdot 6$		38.1	1.5	
CF3 CH2I	PhCH:CHBr	PhCH:CH·CH ₂ ·CF ₃	8890/20	18	64.3	$5 \cdot 0$		64.5	$4 \cdot 9$	
C ₇ F ₁₅ I	ICH:CHCl	C ₇ F ₁₅ ·CH:CHCl	128	65	$24 \cdot 9$	0.32	8·2	25.1	0.5	$8 \cdot 2$
$C_7F_{11}I$	ICH:CHI	C ₇ F ₁₅ ·CH:CH·C ₇ H ₁₅	160 ª	50	25.0	0.3		$25 \cdot 1$	0.3	
е М.р. 27 °С										

solution of tetraiodoethylene (2.7 g, 5 mmol) in dry pyridine (50 mol). 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. Workup 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(1) (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. $C_{10}H_7Cl$ requires C, 73·8; H, 4·3; Cl, 21·8%).

1-Chloro-5-phenoxypent-trans-1-en-3-yne. 1-Chloro-2iodoethylene (5 g) and 3-phenoxyprop-1-ynylcopper(1) (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-phenoxypent-trans-1-en-3-yne (4 g), b.p. 110° at 0·3 mmHg (Found: C, 68·9; H, 4·8; Cl, 18·2. $C_{11}H_{g}ClO$ 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 $(4\cdot 1 \text{ g})$, n-butylthiocopper(I) $(7\cdot 6 \text{ g})$, and thiourea (15 g) gave di-n-butyl sulphide $(3\cdot 4 \text{ g})$, b.p. $178-180^{\circ}$, 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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