Journal of Organometallic Chemistry, 70 (1974) 147—152
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PERFLUOROALKYLCOPPER(I) COMPOUNDS

IV*. REACTIONS OF PERFLUOROALKYLCOPPER(I) COMPOUNDS WITH ACETYLENES AND HALOGENOACETYLENES

P.L. COE and N.E. MILNER
Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham B15 2TT (Great Britain)

(Received September 29th, 1973)

Summary

Perfluoro-n-heptylcopper(I) has been treated with 1-hexyne and 1-decyne to give 1-perfluoro-n-heptyl-1-hexene and-1-decene respectively. Reaction of the copper derivative with propargyl bromide and 3-hydroxy-3-methyl-1-butyne yielded 1-perfluoro-n-heptyl-1,2-propadiene and 1-perfluoroheptyl-3-methyl-1,2-butadiene respectively. Reactions of perfluoroalkylcopper (I) compounds $CF_3(CF_2)_nCu$(n = 4—8) with 1-iodo-2-phenylacetylene gave the corresponding perfluoroalkyl phenyl acetylenes. Perfluoro-n-heptylcopper(I) and 3-hydroxy-1-iodo-3-methyl-1-butyne gave the expected acetylene.

In previous papers in this series we have described the reaction of perfluoroalkylcopper(I) derivatives with olefins [2], halogenoolefins [3] and aromatic compounds [1]. We now report similar reactions with acetylenes and halogenoacetylenes.

There are many examples of reactions of copper acetylides with halogeno compounds [4] but fewer cases of the reverse process, the coupling of copper compounds with halogenoacetylenes. Important results in this area were first described by Chodkiewicz [5] who reported the reactions of bromoalkynes with copper acetylides. More recently other workers have described the reaction of copper acetylides [6] and arylcopper(I) derivatives [7] with iodoalkynes. Whereas in most of this previous work the copper derivative was an acetylide, there are few, if any, reports of the reaction of pure copper alkyls with iodoalkynes. It is this latter type of process we now describe.

Our earlier work [1—3] and that of Thrower et al. [8] showed that perfluoroalkylcopper(I) compounds react either by coordination to halogen on unsaturated carbon [3,8] or by "free radical" type processes [1,2].

---

* For Part III see ref. 1.

Thus, treatment of 1-hexyne with perfluoro-n-heptylcopper(I) in DMSO afforded a high boiling oil, shown by GLC to be a single component. Elemental analysis and mass spectrometry indicated the compound to be a 1/1 adduct of the copper compound and the acetylene. ^{19}F and ^{1}H NMR spectroscopy confirmed the product to be 1-(perfluoro-n-heptyl)-1-hexene identical to the product previously obtained from dehydro-iodination of the adduct of perfluoro-n-heptyl iodide and 1-hexene [1]. No other compounds could be detected. In a similar way 1-decyne gave 1-(perfluoroheptyl)-1-decene.

In an attempt to introduce a functional group into compounds of the above type, the reaction of perfluoroheptylcopper with propargyl bromide was investigated. A very vigorous reaction occurred to yield, after extensive purification, a clear oil. Mass spectrometry and elemental analysis indicated the product to be free of bromine and were consistent with an empirical formula $C_{10}H_3F_{15}$. ^{1}H NMR spectroscopy indicated the presence of olefinic rather than acetylenic protons and no CH_2Br group. Infrared spectroscopy revealed strong bands at 1955 and 1995 cm^{-1}; absorptions in this region are characteristic of allenes [9] and we assign the structure of the adduct as 1-(perfluoro-n-heptyl)-1,2-propadiene. The formation of allenes from propargyl derivatives is fairly well documented and this is a further example. A similar reaction of perfluoro-n-heptylcopper(I) with 3-hydroxy-3-methyl-1-butyne yielded 1-perfluoro-n-heptyl-3-methyl-1,2-butadiene, and the characteristic allenic absorption at 1990 cm^{-1} is again present in the IR spectrum.

Having established that alkynes will react with perfluoroalkylcopper(I) compounds under "free radical" conditions, we investigated the reactions of a number of perfluorocoppers with iodoalkynes. In particular we used 1-iodo-2-phenylacetylene but in the case of perfluoro-n-heptylcopper(I) we also studied 1-iodo-3-hydroxy-3-methyl-1-butyne. Thus, perfluoro-n-amyl-, -hexyl-, -heptyl-, -octyl-, and -nonyl-copper(I) derivatives and 1-iodo-2-phenylacetylene yielded the corresponding perfluoroalkylphenylacetylene. The reaction was complicated by the formation of 1,4-diphenylbutadiyne. This side reaction was quite rapid at 100° but could be almost completely supressed by working at 5° when the DMSO solution of the perfluoroalkylcopper(I) derivative was beginning to solidify.

A similar reaction between perfluoro-n-heptylcopper(I) and 1-iodo-3-hydroxy-3-methyl-1-butyne yielded 1-perfluoro-n-heptyl-3-hydroxyl-3-methyl-1-butyne and a trace of 2,7 dihydroxy-2,7-dimethyl-3,5-octadiyne.

Thus, we have shown that acetylenes and halogenoacetylenes react with perfluoroalkylcopper(I) compounds in a similar manner to the reactions of these derivatives with olefins and halogenoolefins. We envisage the "free radical" reactions to proceed as suggested previously for olefins [1], i.e.

$$R_fCu \rightarrow R_f^{\cdot} + Cu$$

$$R_f^{\cdot} + CH{\equiv}CR \rightarrow R_fCH{=}\dot{C}R$$

$$R_fCH{=}\dot{C}R + XH \rightarrow R_fCH{=}CHR + X\cdot$$

However, in the olefin case two products were found because elimination of H· from $R_f{-}CH_2{-}\dot{C}H{-}CH_2R$ to give $RCH_2{-}CH{=}CH{-}R$ is a relatively straightforward process, and indeed occurred to ca. 60% of the product; in the acetylene case only one compound was isolated presumably because elimination of H· to give the allene is less favoured. However, if the neighbouring carbon atom holds a better leaving group than H, (e.g. Br or OH, as in propargyl bromide or 3-hydroxy-3-methyl-1-butyne) elimination to the allene appears more favourable, and the only isolated products in these cases were allenes. The latter is paralleled by the reaction of $C_7F_{15}Cu$ with allyl bromide [2].

We envisage the reaction with halogenoacetylenes involves coordination of the halogen to copper followed by ligand exchange within the reaction sphere of the copper atom as previously postulated [3] for reactions of halogeno olefins and aryl halides [8].

The results further demonstrate the usefulness of perfluoroalkylcopper(I) derivatives in the preparation of some novel fluorohydrocarbons.

Experimental

Reaction of perfluoroheptylcopper with 1-hexyne

A mixture of perfluoro-n-heptyl iodide (5.0 g), activated copper bronze (1.5 g, an excess) and DMSO (5 ml) was heated and stirred at 110° under an atmosphere of nitrogen for 45 min.

1-Hexyne (1.0 g, a slight excess) was added, a green precipitate formed immediately, probably due to formation of the cuprous acetylide. The mixture was heated and stirred at 110° for 15 h, copper was not deposited. The mixture was extracted with ether and the combined extracts filtered, washed, dried ($MgSO_4$) and the ether distilled off. The 1-hexyne solution was distilled in vacuo to give an oil (1.0 g). Analytical GPC revealed that although the oil contained only one major component, purification by GPC would be very difficult and wasteful of product due to small amounts of impurity with almost identical retention times to the major component.

The experiment was, therefore, repeated under identical conditions except that an excess (10 ml) of 1-hexyne was used. After extraction and distillation in vacuo as before, crude product (1.4 g) was obtained. Further purification by GPC (SE 30/Celite 1/4, 150° FR 5 l/h) afforded 1-(perfluoroheptyl)-1-hexene (0.85 g) b.p. 201—202°. (Found: C, 34.6; H, 2.6; F, 63.5. $C_{13}H_{11}F_{15}$ calcd.: C, 34.5; H, 2.4; F, 63.1%.)

Reaction of perfluoroheptylcopper with 1-decyne

A mixture of perfluoro-n-heptyl iodide (5.0 g), activated copper bronze (1.5 g, an excess) and DMSO (5 ml) was heated and stirred at 110° under an atmosphere of nitrogen for 45 min.

1-Decyne (10 ml, an excess) was added and the mixture heated and stirred at 110° for 15 h. The mixture was extracted with ether and the combined extracts filtered, washed, dried ($MgSO_4$) and the ether distilled off. The 1-decyne solution was distilled in vacuo to give crude product (1.0 g). Further purification by GPC (SE 30/Celite 1/4, 200°, FR 5 l/h) afforded 1-(perfluoro-n-heptyl)-1-decene (0.35 g), b.p. 258°. (Found: C, 40.5; H, 3.5; F, 56.2. $C_{17}H_{19}F_{15}$ calcd.: C, 40.2; H, 3.74; F, 56.1%.)

Reaction of perfluoroheptylcopper with propargyl bromide

A mixture of perfluoro-n-heptyl iodide (5.0 g), activated copper bronze (1.5 g, an excess) and DMSO (5 ml) was heated and stirred at 110° under an atmosphere of nitrogen for 45 min.

Propargyl bromide (10 ml, an excess) was added and an extremely violent exothermic reaction occurred. The mixture was stirred for 5 min at room temperature and extracted with ether. The combined extracts were filtered, washed, dried ($MgSO_4$) and the ether distilled off. The black propargyl bromide solution was distilled (with great difficulty due to a minor explosion in the flask) to give a crude black oil (1.0 g) which fumed in moist air. Further purification by GPC (SE 30/Celite 1/4, 125°, F.R. 5 l/h) afforded 1-(perfluoro-n-heptyl)-1,2-propadiene (0.4 g), b.p. 152°. (Found: C, 29.1; H, 0.7; F, 70.0. $C_{10}H_3F_{15}$ calcd.: C, 29.4; H, 0.73; F, 69.9%.)

Reaction of perfluoro-n-amylcopper with 1-iodo-2-phenylacetylene

A mixture of perfluoroamyl iodide (4.0 g), activated copper bronze (1.3 g) and DMSO (5 ml) was heated and stirred at 110° under an atmosphere of nitrogen for 45 min. The mixture was cooled, by means of an ice bath, until it just began to solidify. 1-Iodo-2-phenylacetylene (2.3 g) was added dropwise such that the reaction exotherm just prevented the mixture from solidifying. After the addition the mixture was allowed to warm to room temperature and was stirred for 30 min.

The mixture was extracted with ether and the combined extracts filtered, washed, dried ($MgSO_4$) and the ether distilled off to give crude product (1.4 g) and 1,4-diphenylbutadiyne (0.4 g) identified by infra-red spectroscopy. TLC on the crude products showed only one major product and slight amounts of 1,4-diphenylbutadiyne and 1-iodo-2-phenylacetylene. Further purification by column chromatography, using a 30 × 2.5 cm. column packed with silica (chromatography grade) and eluting with 40—60° boiling range petrol, afforded product (0.9 g). Final purification by GPC (SE 30/Celite 1/4, 200° FR 5 l/h) yielded 1-(perfluoro-n-amyl)-2-phenylacetylene (0.6 g), b.p. 217°. (Found: C, 41.6; H, 1.4; F, 56.2. $C_{13}H_5F_{11}$ calcd.: C, 42.1; H, 1.35; F, 56.5%.)

Reaction of perfluoro-n-hexylcopper with 1-iodo-2-phenylacetylene

A mixture of perfluorohexyl iodide (4.5 g), activated copper bronze (1.3 g) and DMSO (5 ml) was heated and stirred at 110° under an atmosphere of nitrogen for 45 min. 1-Iodo-2-phenylacetylene (2.3 g) was slowly added using the same cooling technique as before. The mixture was allowed to warm to room temperature and stirred for ca. 30 min.

The mixture was extracted with ether and the combined extracts filtered, washed, dried ($MgSO_4$) and the ether distilled off to give crude product (2.0 g) and 1,4-diphenylbutadiyne (0.3 g) identified by infra-red spectroscopy. Further purification, as before, by column chromatography afforded product (1.0 g). Final purification by GPC (SE 30/Celite 1/4, 200°, FR 5 l/h) yielded 1-perfluorohexyl-2-phenylacetylene (0.7 g) b.p. 227°. IR, PMR, ^{19}F NMR and mass spectra were all consistent with the proposed structure.

Reaction of perfluoro-n-heptylcopper with 1-iodo-2-phenylacetylene

A mixture of perfluoroheptyl iodide (5.0 g), activated copper bronze (1.3 g) and DMSO (5 ml) was heated and stirred at 110° under an atmosphere of nitrogen for 45 min. 1-Iodo-2-phenylacetylene (2.3 g) was slowly added using the same cooling technique as before. The mixture was allowed to warm to room temperature and stirred for 30 min.

The mixture was extracted with ether and the combined extracts filtered, washed, dried ($MgSO_4$) and the ether distilled off to give crude product (2.9 g) and 1,4-diphenylbutadiyne (0.3 g) identified by infra-red spectroscopy. Further purification, as before, by column chromatography afforded product (1.9 g). Final purification by GPC (SE 30/Celite 1/4, 200°, FR 5 l/h) yielded 1-(perfluoro-n-heptyl)-2-phenylacetylene (1.1 g), b.p. 240—242°. (Found: C, 38.6; H, 1.2. $C_{15}H_5F_{15}$ calcd.: C, 38.3; H, 1.06%.)

Reaction of perfluoro-n-octylcopper with 1-iodo-2-phenylacetylene

A mixture of perfluorooctyl iodide (5.5 g), activated copper bronze (1.3 g) and DMSO (5 ml) was heated and stirred at 110° under an atmosphere of nitrogen for 1 h when all the metallic copper had disappeared from the mixture. 1-Iodo-2-phenylacetylene was slowly added using the same cooling technique as before. The mixture was allowed to warm to room temperature and stirred for 30 min.

The mixture was extracted with ether and the combined extracts filtered, washed, dried ($MgSO_4$) and the ether distilled off to give crude product (3.4 g) and 1,4-diphenylbutadiyne (0.3 g) identified by infra-red spectroscopy. Further purification, as before, by column chromatography afforded product (2.4 g). Final purification by GPC (SE 30/Celite 1/4, 220°, FR 5 l/h) yielded 1-(perfluoro-n-octyl)-2-phenylacetylene (0.7 g), b.p. 252°. (Found: C, 37.3; H, 1.15 ; F. 62.0. $C_{16}H_5F_{17}$ calcd.: C, 36.9; H, 0.96; F, 62.1%.)

Reaction of perfluoro-n-nonylcopper with 1-iodo-2-phenylacetylene

A mixture of perfluoro-n-nonyl iodide (6.0 g), activated copper bronze (1.3 g) and DMSO (5 ml) was heated and stirred at 110° under an atmosphere of nitrogen for 90 min when all the metallic copper had disappeared from the mixture. 1-Iodo-2-phenylacetylene (2.3 g) was slowly added using the same cooling technique as before. The mixture was allowed to warm to room temperature and stirred for 30 min.

The mixture was extracted with ether and the combined extracts filtered, washed, dried ($MgSO_4$) and the ether distilled off to give crude product (4.3 g) and 1,4-diphenylbutadiyne (0.4 g) identified by IR spectroscopy. Further purification, as before, by column chromatography afforded product (2.9 g). Final purification by GPC (SE 30/Celite 1/4, 230°, FR 5 l/h) yielded 1-(perfluoro-n-nonyl)2-phenylacetylene (0.9 g), b.p. 260°. (Found: C, 35.1; H, 0.9; F, 62.9. $C_{17}H_5F_{19}$ calcd.: C, 35.8; H, 0.9; F, 63.2%.)

Reaction of perfluoro-n-heptylcopper with 1-iodo-3-hydroxy-3-methyl-1-butyne

A mixture of perfluoro-n-heptyl iodide (5.0 g), activated copper bronze (1.3 g) and DMSO (5 ml) was heated and stirred at 110° under an atmosphere of nitrogen for 45 min. 1-Iodo-3-hydroxy-3-methyl-1-butyne (2.1 g) was slowly added using the same cooling technique as before. The mixture was allowed to warm to room temperature and stirred for 30 min.

The mixture was extracted with ether and the combined extracts filtered, washed, dried ($MgSO_4$) and the ether distilled off to give crude product (1.5 g) and a white solid (0.6 g). Further purification of the solid by crystallisation from aqueous ethanol afforded, 2,7-dihydroxy-2,7-dimethyl-3,5-octadiyne (0.4 g), subsequently identified by IR spectroscopy. Further purification of the oil by distillation in vacuo afforded 1-(perfluoroheptyl)-3-hydroxy-3-methyl-1-butyne (0.9 g), b.p. 200°. (Found: C, 31.5; H, 1.6; F, 62.8. $C_{12}H_7F_{15}O$ calcd.: C, 31.9; H, 1.55; F, 63.0%.)

Reaction of 1-iodo-3-hydroxy-3-methyl-1-butyne with copper

A mixture of 1-iodo-3-hydroxy-3-methyl-1-butyne (1.6 g), activated copper bronze (1.5 g, an excess) and DMSO (10 ml) was heated and stirred at 110° under an atmosphere of nitrogen for 48 h.

The mixture was extracted with ether and the combined extracts filtered, washed, dried ($MgSO_4$) and the ether distilled off to give crude solid product (0.4 g). Further purification by sublimation in vacuo yielded product (0.25 g). Crystallisation from 60—100° boiling range petrol afforded 2,7-dihydroxy-2,7-dimethyl-3,5-octadiyne (0.2 g) m.p. 134°. IR, PMR and mass spectroscopic data were consistent with the proposed structure.

Reaction of perfluoro-n-heptylcopper with 3-hydroxy-3-methyl-1-butyne

A mixture of perfluoro-n-heptyl iodide (0.5 g), activated copper bronze (1.5 g, an excess) and DMSO (5 ml) was heated and stirred at 110° under an atmosphere of nitrogen for 45 min.

3-Hydroxy-3-methyl-1-butyne (0.84 g) was added when a red colouration was instantly produced (probably due to acetylide formation). The mixture was heated and stirred at 110° for 15 h. The mixture was extracted with ether and the combined extracts filtered, washed, dried ($MgSO_4$) and the ether distilled off. The oil was distilled to give crude product (0.6 g) which was further purified by GPC (SE 30/Celite 1/4, 175°, FR 5 l/h) yielding 1-(perfluoro-n-heptyl)-3-methyl-1,2-butadiene (0.3 g). (Found: C, 33.2; H, 1.5; F, 65.6. $C_{12}H_7F_{15}$ calcd.: C, 33.0; H, 1.6; F, 65.4%.)

References

1 P.L. Coe and N.E. Milner, J. Fluorine Chem., 2 (1972/73) 167.
2 P.L. Coe and N.E. Milner, J. Organometal. Chem., 39 (1972) 395.
3 J. Burdon, P.L. Coe, C.R. Marsh and J.C. Tatlow, J. Chem. Soc., Perkin Trans. I, (1972) 639.
4 R.D. Stephens and C.E. Castro, J. Org. Chem., 28 (1963) 3313.
5 P. Chodkiewicz, Ann. Chim. (Paris), 2 (1967) 819.
6 R.F. Curtis and J.A. Taylor, Tetrahedron Lett., (1968) 2919.
7 R. Oliver and D.R.M. Walton, Tetrahedron Lett., (1972) 5209.
8 V.C.R. McLoughlin and J Thrower, Tetrahedron, 25 (1969) 5921.
9 L.J. Bellamy, Infra Red Spectra of Complex Molecules, Methuen, London, 1954, p. 57.