

PERFLUOROALKYLCOPPER(I) COMPOUNDS

II*. REACTIONS OF PERFLUOROALKYLCOPPER(I) COMPOUNDS AND PERFLUOROALKYL IODIDE/COPPER MIXTURES WITH OLEFINS

P. L. COE and N. E. MILNER

Chemistry Department, University of Birmingham (Great Britain)

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SUMMARY

Perfluoroheptylcopper(I) with 1-heptene and 1-dodecene gives mixtures of 1-(perfluoroheptyl)heptane and 1-(perfluoroheptyl)-2-heptene and of 1-(perfluoroheptyl)dodecane and 1-(perfluoroheptyl)-2-dodecene, respectively. In similar reactions cyclohexene and cycloheptene yield only the (perfluoroalkyl)cycloalkane whereas cyclopentene yields only the olefin. Reaction with allyl bromide proceeds with double bond migration and loss of bromine. A mild copper-catalysed addition of perfluoroalkyl iodides to olefins has also been discovered.

INTRODUCTION

Following the original observation that perfluoroalkylcopper(I) compounds react with halogeno aromatics², to give (perfluoroalkyl)benzenes (recently published²) we reported some reactions of these copper species with halogeno olefins³. The present paper describes further extensions of the synthetic utility of these novel organometallics—reactions with simple olefins.

RESULTS AND DISCUSSION

When an excess of 1-heptene was treated with perfluoroheptylcopper(I)^{2,3} in DMSO a mixture of two components in the ratio of 1/2 was obtained. IR and NMR spectroscopy indicated that the mixture consisted of a saturated and an unsaturated compound, and on the basis of integration of peak areas on the ¹H NMR spectrum the olefin was the major component. Hydrogenation of the mixture gave a single compound, in good yield, which was identical to the product from reductive dehalogenation of 1-perfluoroheptyl-2-iodoheptane (see later), and had the same NMR spectrum as the saturated component of the original mixture. These data showed that the mixture was 1-(perfluoroheptyl)heptane (I) and a perfluoroheptyl-

* For Part I see ref. 1.

heptene (II). The position of the double bond was established from the structure of the adduct with allyl bromide (see below). When 1-dodecene was used as the starting olefin, 1-(perfluoroheptyl)dodecane (III) and a perfluoroheptyl dodecene (IV) were obtained.

Reaction of perfluoroheptylcopper(I) with allyl bromide yielded a single bromine-free product, ^1H NMR spectroscopy showed two groups of peaks at 3.9–5 τ and 7.2 τ in the ratio of 3/2. The 3.9–5 τ group appears to be two overlapping signals, one a complex multiplet and the other essentially a sharp signal at 4.6 τ thus the low field signals are clearly olefinic, leaving the high field signal, a triplet of doublets due to a CH_2 group. The splittings suggest coupling to a CF_2 and a CH group. These observations are consistent with the product being 3-(perfluoroheptyl)-1-propene (V). This was confirmed by oxidation of (V) to perfluoroheptylacetic acid (VI). The ^1H NMR results from this experiment were significant in determining the position of the double bond in the olefins derived from 1-heptene and 1-dodecene. Each contained a band at 7.2–7.5 τ which was a triplet of doublets. This band was also present in the bromination product of the 1-heptene derivative and arises from a $\text{CF}_2\text{-CH}_2\text{-CH}$ system. This indicates that the two olefins (I) and (IV) were 1-(perfluoroheptyl)-2-heptene and 1-(perfluoroheptyl)-2-dodecene. Further, dehydroiodination of 1-perfluoroheptyl-2-iodoheptane (see later) yields a different olefin, 1-(perfluoroheptyl)-1-heptene, in which the 7.2 τ band was absent.

Similar reactions were carried out with cyclohexene and cycloheptene, only the saturated compounds (perfluoroheptyl)cyclohexane (VII) and -cycloheptane (VIII) were obtained. Each of these compounds gave the expected elemental analysis ^1H and ^{19}F NMR spectra and had the parent ion in their mass spectra. A different result was obtained when cyclopentene was the olefin, only a perfluoroheptyl olefin was obtained. On the basis of ^1H NMR spectroscopy, which showed four peaks in the ratio 2/1/2/2 at 3.7–4.5, 6.6, 7.6 and 7.9 τ , mass spectrometry and analysis, the product is suggested to be 1-(perfluoroheptyl)-2-cyclopentene (IX). The only other possible structure is the 3-cyclopentene which is symmetrical, and thus each CH_2 group is identical, whereas in our compound the CH_2 groups show distinctly as peaks at 7.6 and 7.9 τ .

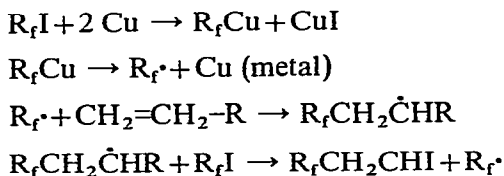
Reactions carried out with allyl alcohol norbornadiene, 2,3-dihydropyran and methyl acrylate resulted either in polymerisation or complex mixtures of products.

These reactions seem best to be rationalised in terms of a free radical mechanism. However, the precise time at which the radicals are formed cannot clearly be defined. Of the several possibilities which exist, two seem to be more likely; first, an addition of R_fCu across the double bond to form a species of the type $\text{R}_f\text{CH}_2\text{CH}(\text{Cu})\text{R}$, which now being effectively a hydrocarbon copper(I) compound will be less stable than R_fCu . This now breaks down to a radical $\text{R}_f\text{CH}_2\dot{\text{C}}\text{HR}$ and copper, the radical can then either abstract a hydrogen atom or lose a hydrogen atom to give the observed products. Secondly, dissociation of the R_fCu to $\text{R}_f\cdot$ and copper, the fluoroalkyl radical then adds to the olefin to give $\text{R}_f\text{CH}_2\dot{\text{C}}\text{HR}$ which by abstraction or elimination again gives the observed products. The ready polymerisation of some olefins and the formation of R_fH in other reactions of R_fCu^4 leads us to favour the latter mechanism to be the one most likely to operate in these reactions.

The addition of fluoroalkyl iodides to olefins has been achieved either thermally⁵ at relatively high temperatures or photochemically⁶ or by radical initiation⁷. In

the course of our work with olefins we have shown that copper can catalyse these additions under quite mild conditions. Thus, treatment of 1-heptene, 1-dodecene and cyclohexene with fluoroalkyl iodides in the presence of either molar or trace amounts of copper afforded the corresponding adducts in good yield. The products were characterised by NMR spectroscopy, elemental analysis, mass spectrometry, by reductive dehalogenation with zinc and ammonium chloride and by dehydroiodination to the corresponding olefin (see above) with base.

The following scheme which parallels the thermal process seems to rationalise the mechanism of this reaction:



i.e. a radical chain process.

EXPERIMENTAL

Preparative GPC was carried out on a 9m × 9mm column packed with 14% SE. 30 on Chromosorb P at the temperatures stated using N₂ as carrier gas.

Reaction of perfluoroheptylcopper with 1-heptene

A mixture of perfluoroheptyl 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-Heptene (15 ml, an excess) was added and the mixture heated and stirred at 110° for 4 h when copper was deposited. The mixture was extracted with ether and the combined extracts filtered, washed, dried (MgSO₄) and the ether distilled off. The 1-heptene solution was distilled *in vacuo* to give crude product (1.6 g). Further purification by GPC (200°C, 5 l/h) afforded a mixture (1.0 g) which could not be further resolved by GPC. PMR and ¹⁹F NMR showed the mixture to consist of 1-(perfluoroheptyl)heptane and 1-(perfluoroheptyl)-2-heptene in the ratio 1/2 respectively. Further characterisation was carried out on this mixture. (Found: C, 36.0; H, 3.0; F, 60.8. C₁₄H₁₅F₁₅ calcd.: C, 35.9; H, 3.2; F, 61.0. C₁₄H₁₃F₁₅ calcd.: C, 36.1; H, 2.8; F, 61.1 %.)

Catalytic hydrogenation of the mixture of 1-(perfluoroheptyl)heptane and 1-(perfluoroheptyl)-2-heptene

A mixture of 1-(perfluoroheptyl)heptane and 1-(perfluoroheptyl)-2-heptene (1.0 g), palladium on charcoal catalyst (ca. 0.2 g) and ethanol (10 ml) was shaken in an atmosphere of hydrogen at room temperature for 72 h when hydrogen was absorbed (ca. 70 ml).

The palladium catalyst was filtered off and washed with ether (ca. 30 ml). The combined ether and ethanol solutions were washed with water (3 × 100 ml), dried (MgSO₄) and the ether distilled off to give crude product (0.65 g). Further purification

by GPC (180°, 4 l/h) afforded 1-(perfluoroheptyl)heptane (0.45 g) b.p. 220° as the sole isolatable product. Identification was by comparison of PMR, ¹⁹F NMR, infrared and mass spectra with those of the authentic compound (see later).

Bromination of the mixture of 1-(perfluoroheptyl)heptane and 1-(perfluoroheptyl)-2-heptene

To a stirred mixture of 1-(perfluoroheptyl)heptane and 1-(perfluoroheptyl)-2-heptene (1.0 g) dissolved in carbon tetrachloride (10 ml), bromine (0.4 g) dissolved in carbon tetrachloride (1 ml) was added over a period of 15 min. The mixture was stirred at room temperature for 2 h and the solvent evaporated *in vacuo* to give crude product (1.0 g). Further purification by GPC proved impossible due to decomposition of the product. The crude material was therefore purified by repeated fractional distillation *in vacuo* to give two products:

(i). Virtually pure 1-(perfluoroheptyl)heptane (0.1 g), identified by GPC and infrared spectroscopy.

(ii). Pure 2,3-dibromo-1-(perfluoroheptyl)heptane (0.4 g) which decomposed above 200°. (Found: C, 27.3; H, 2.3; F, 45.2. C₁₄H₁₃Br₂F₁₅ calcd.: C, 26.8; H, 2.1; F, 44.5%.)

Reductive dehalogenation of 1-(perfluoroheptyl)-2-iodoheptane

To a stirred mixture of 1-(perfluoroheptyl)-2-iodoheptane (3.5 g), ammonium chloride (0.4 g) and 75% aqueous ethanol (50 ml) at 0°, powdered zinc (1.3 g) was added over a period of 30 min. The mixture was stirred at 0° for 90 min, filtered and the residue washed with ether (30 ml). The combined ethanol and ether solutions were washed with water (3 × 100 ml), dried (MgSO₄) and the ether distilled off to give crude product (2.6 g). Distillation *in vacuo* gave product (2.2 g). Further purification by GPC (180°, 4 l/h) afforded 1-(perfluoroheptyl)heptane (0.9 g) b.p. 221°. (Found: C, 36.0; H, 3.4; F, 60.9. C₁₄H₁₅F₁₅ calcd.: C, 35.9; H, 3.2; F, 61.0%.)

Dehydrohalogenation of 1-(perfluoroheptyl)-2-iodoheptane

To stirred ethanol (10 ml) at 0°, sodium (0.3 g) was added over a period of 10 min. When the solution had warmed to room temperature, 1-(perfluoroheptyl)-2-iodoheptane (3.5 g) was added and the mixture heated at reflux for 3 h when the mixture went black.

The mixture was poured into water (250 ml) and extracted with ether (3 × 20 ml). The combined extracts were washed with water (3 × 100 ml), dried (MgSO₄) and the ether distilled off to give a crude product (2.6 g). Distillation *in vacuo* gave product (2.3 g). Further purification by GPC (4 l/h) afforded 1-(perfluoroheptyl)-1-heptene (1.6 g) b.p. 219°–220°. (Found: C, 36.5; H, 2.7; F, 61.2. C₁₄H₁₃F₁₅ calcd.: C, 36.1; H, 2.8; F, 61.1%.)

Reaction of perfluoroheptyl copper with 1-dodecene

A mixture of perfluoroheptyl 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-Dodecene (1.7 g) was added and the mixture heated and stirred at 110° for 15 h, copper was not deposited. The mixture was extracted with ether and the com-

bined extracts filtered, washed, dried (MgSO_4) and the ether distilled off. The 1-dodecene solution was distilled *in vacuo* to give crude product (1.4 g). Further purification by GPC (5 l/h) afforded a mixture (0.9 g) b.p. 289° which could not be further resolved by GPC, PMR and ^{19}F NMR (also by analogy with the mixture obtained from reaction of perfluoroheptyl copper and 1-heptene) showed the mixture to consist of 1-(perfluoroheptyl)dodecane and 1-(perfluoroheptyl)-2-dodecene in the ratio 1/2 respectively.

Reaction of perfluoroheptylcopper with allyl bromide

A mixture of perfluoroheptyl 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.

Allyl bromide (10 ml, an excess) was added with extreme caution (violent reaction). The mixture was stirred for 10 min at room temperature and extracted with ether. The combined extracts were filtered, washed, dried (MgSO_4) and the ether distilled off. The allyl bromide solution was distilled to give a reddish brown crude product (1.5 g) which decolourised immediately on addition of silver powder. Further purification by GPC (150° , 5 l/h) afforded 1-(perfluoroheptyl)-2-propene (0.8 g) b.p. 145° . (Found: C, 29.1; H, 1.3; F, 69.2. $\text{C}_{10}\text{H}_5\text{F}_{15}$ calcd.: C, 29.3; H, 1.22; F, 69.5%.)

The olefin (1.0 g) was oxidised by potassium permanganate (2 g) in acetone (10 ml) to yield (perfluoroheptyl) acetic acid (0.5 g) characterised as its *S*-benzylisothiuronium salt, m.p. 154° (Found: C, 34.6; H, 2.5; N, 5.0. $\text{C}_{17}\text{H}_{13}\text{F}_{15}\text{N}_2\text{O}_2\text{S}$ calcd.: C, 34.4; H, 2.2; N, 4.7%.)

Reaction of perfluoroheptylcopper with cycloheptene

A mixture of perfluoroheptyl 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.

The apparatus was allowed to cool while being flushed with a slow stream of nitrogen (ca. 1 l/h). Cycloheptene (15 ml, an excess) was added and the apparatus sealed by means of a mercury valve (to allow for expansion of the contents during heating). The mixture was heated and stirred at 110° for 15 h, metallic copper being deposited.

The mixture was extracted with ether and the combined extracts filtered, washed, dried (MgSO_4) and the ether distilled off. The cycloheptene solution was distilled *in vacuo* to give crude product (1.8 g). Further purification by GPC (180° , 5 l/h) afforded (perfluoroheptyl)cycloheptane (0.9 g) b.p. $233\text{--}234^\circ$. (Found: C, 36.2; H, 2.9; F, 61.0. $\text{C}_{14}\text{H}_{13}\text{F}_{15}$ calcd.: C, 36.1; H, 2.8; F, 61.1%.)

Reaction of perfluoroheptylcopper with cyclohexene

A mixture of perfluoroheptyl 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.

Cyclohexene (15 ml, an excess) was added and the mixture stirred at 115° for 15 h when copper was deposited. The mixture was extracted with ether and the combined extracts filtered, washed, dried (MgSO_4) and the ether distilled off. The cyclohexene solution was distilled *in vacuo* to give crude product (1.4 g) which was further

purified by GPC (200°, 5 l/h) to give (perfluoroheptyl)cyclohexane (1.0 g) b.p. 210°. (Found: C, 34.75; H, 2.4; F, 63.6. C₁₃H₁₁F₁₅ calcd.: C, 34.6; H, 2.22; F, 63.2%)

Reaction of perfluoroheptylcopper with cyclopentene

A mixture of perfluoroheptyl 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.

Cyclopentene (7 ml, an excess) was added and the mixture heated and stirred at 110° for 72 h when copper was deposited. The mixture was extracted with ether and the combined extracts filtered, washed, dried (MgSO₄) and the ether distilled off. The cyclopentene solution was distilled *in vacuo* to yield crude product (1.5 g). Further purification by GPC (150°, 5 l/h) afforded 1-(perfluoroheptyl)-2-cyclopentene (0.7 g) b.p. 192°. (Found: C, 33.5; H, 1.5; F, 64.9. C₁₂H₇F₁₅ calcd.: C, 33.0; H, 1.6; F, 65.4%)

Reaction of perfluoroheptyl iodide with 1-heptene

A mixture of perfluoroheptyl iodide (5 g) copper bronze (1.5 g, an excess), DMSO (5 ml) and 1-heptene (15 ml, an excess) was heated and stirred at 110° under an atmosphere of nitrogen for 15 h when the reaction mixture appeared unchanged.

The mixture was extracted with ether and the combined extracts filtered, washed, dried (MgSO₄) and the ether distilled off. Distillation of the 1-heptene solution *in vacuo* gave crude product (4.0 g). Analytical GPC revealed that this contained only one major component and a trace amount of the perfluoroheptylcopper addition product. Purification of the crude product by GPC (column 200°, 5 l/h) afforded 1-(perfluoroheptyl)-2-iodoheptane (2.4 g) b.p. 260°. (Found: C, 28.3; H, 2.7; F, 48.0. C₁₄H₁₄F₁₅I calcd.: C, 28.3; H, 2.36; F, 48.0%)

Reaction of perfluoroheptyl iodide with 1-dodecene

A mixture of perfluoroheptyl iodide (5.0 g), activated copper bronze (1.5 g, an excess), 1-dodecene (15 ml, an excess) and DMSO (5 ml) was heated and stirred at 110° under an atmosphere of nitrogen for 15 h when the reaction mixture appeared unchanged.

The mixture was extracted with ether and the combined extracts filtered, washed, dried (MgSO₄) and the ether distilled off. Distillation of the 1-dodecene solution *in vacuo* gave crude product (4.3 g). Analytical GPC revealed that this contained a small quantity of the perfluoroheptyl copper addition product, the main product, however, was so high boiling that it was not recorded. The product was, therefore, purified by distillation *in vacuo* to give 1-(perfluoroheptyl)-2-iodododecane (1.0 g). This was characterised by PMR, ¹⁹F NMR, infrared and mass spectroscopy (also by analogy with the previous experiment).

Reaction of perfluoroheptyl iodide with 1-heptene in the presence of a catalytic amount of copper

A mixture of perfluoroheptyl iodide (5.0 g), activated copper bronze (0.4 g, 1/3 calculated amount), DMSO (5 ml) and 1-heptene (10 ml, an excess) was heated and stirred at 110° under an atmosphere of nitrogen for 15 h.

The mixture was extracted with ether and the combined extracts filtered, washed, dried (MgSO₄) and the ether distilled off. The 1-heptene solution was distilled

in vacuo to give crude product (4.6 g). Analytical GPC showed that this contained only one major component and a trace amount of the perfluoroheptylcopper addition product. Further purification of the crude product by GPC (200°, 5 l/h) afforded 1-(perfluoroheptyl)-2-iodoheptane (2.7 g). (Identified by infrared spectroscopy.)

Reaction of perfluoroethyl iodide with cyclohexene

A mixture of perfluoroethyl iodide (2.5 g), activated copper bronze (1.5 g, an excess), DMSO (5 ml) and cyclohexene (15 ml, an excess) was sealed in a carius tube under an atmosphere of nitrogen. The tube was shaken and heated at 100° for 15 h when the contents of the tube appeared unchanged.

The mixture was extracted with ether and the combined extracts filtered, washed, dried (MgSO₄) and the ether distilled off. The cyclohexene solution was distilled *in vacuo* to give crude product (2.0 g). Analytical GPC showed two major components with very similar retention times and in the ratio of 1/2 with respect to retention time. Purification by GPC (200°, 5 l/h) afforded two products:

(i). 1-(Perfluoroethyl)-2-iodocyclohexane (0.25 g) b.p. 194°, identified as the *trans* isomer by PMR and ¹⁹F NMR spectroscopy.

(ii). 1-(Perfluoroethyl)-2-iodocyclohexane (0.5 g) b.p. 213°, identified as the *cis* isomer by PMR and ¹⁹F NMR spectroscopy.

Elemental analysis was carried out on a 1/1 mixture of these two compounds. (Found: C, 29.0; H, 3.2; F, 28.8. C₈H₁₀F₅I calcd.: C, 29.2; H, 3.05; F, 29.0%.)

Reaction of perfluoroheptyl iodide with cyclohexene

A mixture of perfluoroheptyl iodide (5.0 g), activated copper bronze (1.5 g, an excess), DMSO (5 ml) and cyclohexene (15 ml, an excess) was heated and stirred at 110° under an atmosphere of nitrogen for 15 h when the reaction mixture appeared unchanged.

The mixture was extracted with ether and the combined extracts filtered, washed, dried (MgSO₄) and the ether distilled off. Distillation of the cyclohexene solution *in vacuo* gave crude product (3.5 g). Analytical GPC showed this to contain a small quantity of the perfluoroheptylcopper addition product and two long-retained major components of similar retention time in the ratio 2/3 with respect to retention time. Further purification by GPC (200°, 5 l/h) afforded two products:

(i). *Trans*-1-(perfluoroheptyl)-2-iodocyclohexane (0.6 g);

(ii). *Cis*-1-(perfluoroheptyl)-2-iodocyclohexane (0.9 g).

Only semi-pure samples of these two compounds could be obtained due to their lack of thermal stability. The identification was by infrared PMR, ¹⁹F NMR and mass spectroscopy (also by analogy with the previous experiment).

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