Journal of Fluorine Chemistry
Elsevier Sequoia S.A., Lausanne — Printed in Switzerland

(PERFLUOROALKYL)COPPER(I) COMPOUNDS
III.* REACTION OF (PERFLUOROALKYL)COPPER(I) COMPOUNDS WITH AROMATIC HYDROCARBONS

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(Received January 21, 1972)

SUMMARY

(Perfluoroheptyl)copper reacts with aromatic compounds to give the corresponding perfluoroheptyl arenes. Thus benzene and *p*-xylene yield (perfluoroheptyl)benzene and 1-perfluoroheptyl-2,5-dimethylbenzene respectively. Toluene and nitrobenzene afford mixtures of *o*- and *p*-substituted compounds. Chlorobenzene yields products derived from halogen displacement as well as the expected *o*/*p* mixture.

INTRODUCTION

In previous papers, reactions of (perfluoroalkyl)copper compounds with iodoarenes[2] halogeno-olefins[3] and olefins[1] have been described. We now report the reaction of aromatic hydrocarbons with these reagents.

There are a number of reports of perfluoroalkylation[4,5] of aromatic compounds, usually under vigorous conditions. We have found that our alkylations take place under relatively mild conditions using (perfluoroalkyl)copper compounds.

RESULTS AND DISCUSSION

Treatment of a solution of (perfluoroheptyl)copper in DMSO[4] with excess benzene under reflux afforded a volatile compound, shown to be 1*H*-pentadecafluoroheptane, and a high boiling liquid, shown by comparison with an authentic sample prepared by the method of Thrower and Mcloughlin[2], to be (perfluoro-

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* For Part II, see ref. 1.

heptyl)benzene. A similar reaction with (perfluoropropyl)copper yielded the corresponding arene.

In a similar reaction using *p*-xylene,1-perfluoroheptyl-2,5-dimethylbenzene was obtained. The product was characterised by ^1H and ^{19}F NMR, mass spectrometry and elemental analysis. There clearly was no problem of orientation as only one mono-substituted isomer can be formed. In this and subsequent experiments, 1*H*-pentadecafluoroheptane was also formed but was not quantitatively isolated.

The reaction with toluene afforded two products, shown by ^1H and ^{19}F NMR spectroscopy to be a mixture, which could just be resolved by GLC, of two isomers of (perfluoroheptyl)methylbenzene in the ratio 1:2. The ^1H NMR spectrum showed two methyl signals at 7.58 τ and 7.52 τ respectively, the 7.58 τ signal was a singlet and the 7.52 τ signal a triplet. The singlet was at the same field position as that of the methyl group in an authentic sample of 1-perfluoroheptyl-4-methylbenzene. Enrichment of the mixture (no separation could be achieved by GLC) with this latter isomer showed it to be the major component. On the basis of the triplet splitting of the methyl group found in the minor component, it is assigned as the *ortho* isomer.

In a similar experiment with nitrobenzene, a low yield of a mixture of two compounds in the ratio of 1 : 1 was isolated. Separation by column chromatography afforded 1-perfluoroheptyl-2-nitrobenzene and 1-perfluoroheptyl-4-nitrobenzene, identical to authentic samples prepared by the method of Thrower and Mcloughlin.

Reaction with chlorobenzene gave a mixture of three components which were separated by GLC. ^1H and ^{19}F NMR spectroscopy, mass spectrometry, IR spectroscopy and elemental analysis indicated the components to be 1-chloro-2-(perfluoroheptyl)benzene, 1-chloro-4-(perfluoroheptyl)benzene and (perfluoroheptyl)benzene. In the former two compounds, the ^1H NMR spectrum showed a pattern for the aromatic protons very similar to that for the corresponding isomers of the substituted nitro compounds whilst the (perfluoroheptyl)benzene was identical to an authentic sample.

In each of these reactions metallic copper was precipitated and 1*H*-pentadecafluoroheptane was produced. In view of this and earlier work with olefins, it is suggested that the reaction probably proceeds *via* a free-radical mechanism as shown below:

$$\begin{aligned}
&C_7F_{15}Cu \rightarrow C_7F_{15}\bullet + Cu\ (\text{metal})\\
&C_7F_{15}\bullet + ArH \rightarrow C_7F_{15}ArH\bullet\\
&C_7F_{15}ArH\bullet \rightarrow C_7F_{15}Ar + H\bullet\\
&C_7F_{15}\bullet + RH \rightarrow C_7F_{15}H + R\bullet\\
&2R\bullet \rightarrow R_2\\
&2H\bullet \rightarrow H_2
\end{aligned}$$

The orientation observed in these reactions is of interest since it does not follow the pattern generally found in free-radical reactions of aromatic substrates[6], in which mostly the *ortho* isomer is formed with appreciable amounts of the *meta* and *para* isomers. It should be noted, however, that in earlier work[5] on the reactions of perfluoroalkyl radicals with aromatics, unusual orientations of products were reported, *e.g.* toluene and $C_3F_7\bullet$ yielded two isomers in the ratio 1:3 although the isomers were not identified, and in a similar reaction (perfluoropropyl)benzene gave only one bis-(perfluoropropyl)benzene, the orientation of which was not established. These and our own results suggest an "electrophilic"-type radical, which may be capable of some orientation. The manner in which the radicals are formed is open to question, either "free" radicals or some sort of electron redistribution within the co-ordination sphere of the copper will satisfactorily fit the results obtained.

The possibility that the reactions proceeded by a copper-catalysed addition of $C_7F_{15}I$, or by a simple thermal cleavage of $C_7F_{15}I$ needs to be excluded. It was shown that the treatment of benzene with $C_7F_{15}I$ in DMSO gave no reaction under the conditions where $C_7F_{15}Cu$ reacted. Further, treatment of benzene with $C_7F_{15}I$ and copper, without pre-forming $C_7F_{15}Cu$, gave only a small conversion to $C_7F_{15}C_6H_5$ under the same conditions as those when $C_7F_{15}Cu$ completely reacted.

It seems that the relative ease of decomposition of $C_7F_{15}Cu$ increases with decreasing solvation power of the solvent. Thus, in DMSO the copper species is relatively stable, in ether slow decomposition to $C_7F_{15}H$ occurs and in hydrocarbon solvents rapid decomposition and/or reaction occurs.

Under our reaction conditions no tractable products could be obtained from hexa- or penta-fluorobenzene.

EXPERIMENTAL

Reaction of (perfluoroheptyl)copper with benzene

Perfluoroheptyl iodide (5.0 g), copper bronze (1.5 g) and DMSO (5 ml) were heated and stirred at 110° under a nitrogen atmosphere for 45 min. Benzene (15 ml) was added and the mixture stirred and heated at 110° for 15 h; metallic copper was deposited. The mixture was extracted with ether (3 × 20 ml), the combined extracts were washed with water (3 × 100 ml), dried ($MgSO_4$) and the ether evaporated. The resulting benzene solution was distilled to leave an oil which was distilled *in vacuo* to yield (perfluoroheptyl)benzene (1.3 g) b.p. 206°. (Found: C, 35.4; H, 1.2; F, 63.7%. Calc. for $C_{13}H_5F_{15}$: C, 35.0; H, 1.1; F, 63.2%.)

In a similar experiment, a liquid air trap was connected to the outlet of the reflux condenser and 1*H*-pentadecafluoroheptane (2.0 g), identical with an authentic sample, was obtained.

Reaction of (perfluoropropyl)copper with benzene

A similar experiment to that described above using perfluoropropyl iodide (3.0 g) yielded (perfluoropropyl)benzene (0.3 g) b.p. 134°. (Found: C, 43.8; H, 1.9; F, 53.9%. Calc. for $C_9H_5F_7$: C, 43.9; H, 2.0; F, 54.1%.)

Reaction of (perfluoroheptyl)copper with p-*xylene*

p-Xylene (15 ml) was added to a solution of (perfluoroheptyl)copper (from $C_7F_{15}I$ 5 g) in DMSO (5 ml). The mixture was refluxed for 15 h at 110° when copper was deposited. The resulting mixture was extracted with ether (3 × 20 ml) and the combined extracts washed, dried ($MgSO_4$) and filtered. Evaporation of the ether and distillation of the excess *p*-xylene afforded 1-perfluoroheptyl-2,5-dimethylbenzene (nc) (1.7 g) b.p. 234°. (Found: C, 38.1; H, 2.1; F, 60.4%. Calc. for $C_{15}H_9F_{15}$: C, 38.0; H, 1.9; F, 60.1%.)

Reaction of (perfluoroheptyl)copper with toluene

Toluene (10 ml) was added to (perfluoroheptyl) copper (from $C_7F_{15}I$ 5 g) in DMSO (5 ml). The mixture was refluxed 15 h at 110°, cooled, extracted with ether (3 × 20 ml). The combined extracts were filtered, washed, dried ($MgSO_4$) and the ether distilled to yield, after distillation of the toluene, a mixture of 1-perfluoroheptyl-2-methylbenzene and 1-perfluoroheptyl-4-methylbenzene in the ratio of 1:2 (1.5 g) b.p. 225°. (Found: C, 36.5; H, 1.7; F, 62.2%. Calc. for $C_{14}H_7F_{15}$: C, 36.5; H, 1.5; F, 62.0%.) ^1H NMR spectroscopy indicated the presence of a multiplet at 2.67 τ, a triplet at 7.52 τ and a singlet at 7.58 τ. Enrichment of the mixture with 1-perfluoroheptyl-4-methylbenzene (see below) increased the GLC peak size of the major component. No preparative separation could be achieved on the GLC equipment available.

Preparation of 1-perfluoroheptyl-4-methylbenzene

A mixture of perfluoroheptyl iodide (5.0 g), activated copper bronze (1.9 g), DMF (10 ml) and *p*-iodotoluene was heated and stirred at 120° under a nitrogen atmosphere for 15 h. The mixture was extracted with ether (3×20 ml), the combined extracts filtered, washed and dried ($MgSO_4$). Evaporation of the ether, followed by distillation of the resulting oil yielded 1-perfluoroheptyl-4-methylbenzene (nc) (3.4 g) b.p. 225–226°. (Found: C, 36.6; H, 1.8; F, 61.8%. Calc. for $C_{14}H_7F_{15}$: C, 36.5; H, 1.5; F, 62.0%.) ^1H NMR spectroscopy indicated an A_2B_2 spectrum at 2.65 τ and a singlet at 7.58 τ.

Reaction of (perfluoroheptyl)copper with nitrobenzene

Nitrobenzene (20 ml) was added to a solution of (perfluoroheptyl)copper (from $C_7F_{15}I$ 10 g) in DMSO (10 ml). The mixture was heated at 110° for 15 h, extracted with ether (3×20 ml) and the combined extracts filtered, washed and dried ($MgSO_4$). Evaporation of the ether and distillation of the nitrobenzene gave a tarry residue (1.5 g). TLC revealed three components, one of which was slow moving. Separation of the mixture by column chromatography yielded two components which were purified by sublimation *in vacuo* to yield (i) 1-perfluoroheptyl-4-nitrobenzene (0.25 g) m.p. 68–69° and (ii) 1-perfluoroheptyl-2-nitrobenzene (0.25 g) m.p. 58–59°, identical to authentic samples (see below).

Preparation of the isomeric (perfluoroheptyl)nitrobenzenes

(a) 1-Perfluoroheptyl-2-nitrobenzene

1-Iodo-2-nitrobenzene (2.5 g) in DMSO (5 ml) was added to (perfluoroheptyl)copper (from $C_7F_{15}I$ 5 g) in DMSO (5 ml). The mixture was heated and stirred at 110° for 15 h, and then extracted with ether (3 × 20 ml). The combined ether extracts were filtered, washed and dried ($MgSO_4$). Evaporation of the ether gave a solid (3.1 g) which on purification by recrystallisation from aqueous ethanol gave 1-perfluoroheptyl-2-nitrobenzene (nc) (2.5 g) m.p. 59°. (Found: C, 31.7; H, 1.2; F, 58.5; N, 2.8%. Calc. for $C_{13}H_4F_{15}NO_2$: C, 31.8; H, 0.8; F, 58.0; N, 2.85%.)

(b) 1-Perfluoroheptyl-3-nitrobenzene

In a similar experiment using 1-iodo-3-nitrobenzene (2.5 g), 1-perfluoroheptyl-3-nitrobenzene (nc) (2.1 g) m.p. 39° was obtained. (Found: C, 31.7; H, 1.2; F, 38.2%. Calc. for $C_{13}H_4F_{15}NO_2$: C, 31.8; H, 0.8; F, 58%.)

(c) 1-Perfluoroheptyl-4-nitrobenzene

Similarly, 1-perfluoroheptyl-4-nitrobenzene (nc) (3.0 g) m.p. 69–70°, (Found: C, 31.7; H, 1.2; F, 58.1; N, 2.6%. Calc. for $C_{13}H_4F_{15}NO_2$: C, 31.8; H, 0.8; F, 58.0; N, 2.8%), was obtained.

Reaction of (perfluoroheptyl)copper with chlorobenzene

Chlorobenzene (15 ml) was added to (perfluoroheptyl)copper (from $C_7F_{15}I$ 5 g) in DMSO (5 ml). The mixture was heated at 110° for 15 h with stirring, cooled and extracted with ether (3 × 20 ml). The ether layer was washed, dried ($MgSO_4$) and the ether evaporated to leave an oil. Distillation of this latter to remove the chlorobenzene gave a mixture of three components (1.7 g) which were separated by GLC to yield (i) (perfluoroheptyl)benzene (0.2 g), (ii) 1-chloro-4-(perfluoroheptyl)benzene (nc) (0.7 g) b.p. 234° and (iii) 1-chloro-2-(perfluoroheptyl)benzene (nc) (0.2 g). A mixture of (ii) and (iii) gave on elemental analysis: (Found: C, 32.2; H, 0.9; F, 59.1%. Calc. for $C_{13}H_4ClF_{15}$: C, 32.5; H, 0.8; F, 59.4%). The ^1H NMR spectra of (ii) and (iii) were shown to be very similar in the aromatic region to the correspondingly substituted nitrobenzenes.

Reaction of perfluoroheptyl iodide with benzene

(a) In DMSO, no copper present

A mixture of perfluoroheptyl iodide (2.5 g), DMSO (2.5 ml) and benzene were heated at 100° for 15 h. Examination of the ether extract of the mixture revealed only benzene and the iodide present.

(b) Copper present, no DMSO

A mixture of perfluoroheptyl iodide (5 g), copper bronze (1.5 g) and benzene was heated at 100° for 15 h. Working up of the mixture as above afforded the iodide (1.6 g) and (perfluoroheptyl)benzene (0.4 g) identified by IR spectroscopic comparison.

ACKNOWLEDGEMENTS

The authors wish to thank the Procurement Executive, Ministry of Defence, for support of this work (N.E.M.) and to Mr. J. Thrower and Dr. V. C. R. Mcloughlin for helpful discussion, and Professor J. C. Tatlow for his encouragement.

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