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THE SYNTHESIS OF POLYFLUORO-β-DIKETONES AND THEIR COPPER DERIVATIVES

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SUMMARY

The synthesis of 3*H*,3*H*-octadecafluoroundeca-2,4-dione, 9*H*,9*H*-triacontafluoroheptadeca-8,10-dione and their copper chelates is described.

INTRODUCTION

We wished to synthesise some long-chain highly fluorinated β-diketones and their copper derivatives.

A large number of β-diketones, $RCOCH_2COR'$ have been prepared, in which R is perfluoroalkyl and R′ aryl or alkyl, by the Claisen condensation of the ester of a perfluoroalkanoic acid with a methyl alkyl ketone, and β-diketones containing $-CF_3$[1], $-C_2F_5$[2], $-C_3F_7$[3] and $-C_4F_7$[4] groups have been reported. In addition, diketones with both R– and R′– perfluoroalkyl have been synthesised, including[5,6] compounds in which $R = CF_3-$; $R' = CF_3-$, C_2F_5-, C_3F_7- or undecafluoronorbornyl, and $R = C_2F_5-$; $R' = C_2F_5-$ or C_3F_7-.

RESULTS

We now describe two new β-diketones and their copper derivatives in which $R = C_7F_{15}-$ and $R' = CF_3-$ or $C_7F_{15}-$. The first of these, $C_7F_{15}COCH_2COCF_3$, was prepared by the Claisen condensation of the ethyl ester of pentadecafluoro-n-octanoic acid with 1,1,1-trifluoroacetone using sodium ethoxide as base. The β-diketone so formed was converted *in situ* to the copper chelate, which formed a dihydrate in moist air. The free diketone was obtained by treatment of the copper compound with H_2S. The same copper chelate and diketone were obtained by the alternative route employing the condensation of ethyl trifluoroacetate with methyl pentadecafluoro-n-heptyl ketone. This ketone was itself synthesised by the reaction between methyl magnesium iodide and lithium pentadecafluoro-n-octanoate, and was characterised by spectroscopy and formation of a 2,4-dinitrophenylhydrazine in the usual way.

Similarly, using sodium ethoxide as condensing agent, 9*H*,9*H*-tricontafluoroheptadeca-8,10-dione was obtained from ethyl pentadecafluoro-n-octanoate and methylpentadecafluoro-n-heptylketone *via* the copper derivative. It proved impossible to obtain a satisfactory sample of the copper compound, the purification procedures always yielding a pasty mixture of solid and liquid. The yield of CuS obtained on liberating the ketone with H_2S suggested that the product was mixture of the 1:1 and 1:2 adducts.

Attempts were made to condense the ester and ketone using NaH, better yields having been claimed[7] with this reagent. In addition, sodium ethoxide has been reported to decompose ethyl pentadecafluoro-n-octanoate[8]. However, the products isolated from condensation with NaH were unchanged ester and ketone, together with a liquid, b.p. 200–202°, not fully identified, but with properties suggesting that it arose from an aldol condensation of the ketone.

Attempts were made, without success, to prepare lead chelates of 9*H*, 9*H*-tricontafluoroheptadeca-8,10-dione from lead chloride and powdered lead itself. This failure is in accord with previous experience[6] that lead chelates of fluorine-containing ketones are prepared with increasing difficulty as the size of the ligand increases.

EXPERIMENTAL

NMR spectra were measured on a Perkin–Elmer R10 spectrometer, the ^1H spectra at 60 MHz with tetramethylsilane (TMS) as internal standard. Chemical shifts are given in τ values ($0\tau = 10$ ppm downfield from TMS). Fluorine NMR spectra were measured at 56.4 MHz using CCl_3F as internal standard with chemical shifts in ppm upfield of CCl_3F (φ^* values).

Methylpentadecafluoro-n-heptyl ketone

Pentadecafluoro-n-octanoic acid (11.2 g) was added to lithium carbonate (1.0 g) in water (20 ml). The solution was evaporated and the precipitated salt dried at 120° to give lithium pentadecafluoro-n-octanoate, m.p. 192°. The lithium salt (10.35 g) in ether (25 ml) was cooled in ice and to the vigorously stirred mixture was added drop-wise methyl magnesium iodide (6.2 g) in ether. After stirring for 3 h at room temperature the mixture was cooled to 0°, 20% H_2SO_4 (50 ml) added, and the ether layer separated. The aqueous layer was extracted with ether (4×20 ml) and the ether layers combined. These were then washed with sodium metabisulphite solution and water, dried ($MgSO_4$), and evaporated. The residue was distilled to give methylpentadecafluoro-n-heptyl ketone (nc) (6.25 g), b.p. 157° (Found C, 26.1; H, 0.95. $C_9H_3F_{15}O$ requires C, 26.2; H, 0.7%). The IR spectrum contained a strong absorption at 1770 cm^{-1} ($>$C=O). The proton NMR spectrum consisted of one signal at τ 7.59, (triplet, $J = 1.5$ Hz), due to the methyl group. The ^{19}F NMR spectrum consisted of signals at φ^* 81.7 (CF_3–), 124.7 (–CF_2–) and a series of signals from φ^* 119–122 (–CF_2–). The intensity ratios of these signals were 3:2:10 respectively. The ketone and 2,4-dinitrophenylhydrazine were dissolved in ethanol and refluxed with a few drops of conc. HCl. The precipitate was recrystallised from petroleum ether to give methylpentadecafluoro-n-heptyl-2,4-dinitrophenylhydrazone, (nc) m.p. 113.5° (Found C, 30.6; H, 1.2; F, 48.1; N, 9.7. $C_{15}H_7F_{15}N_4O_4$ requires C, 30.4; H, 1.2; F, 48.2; N, 9.5%).

*Copper derivative of 3*H*,3*H*-octadecafluoroundeca-2,4-dione*

(a) Using ethylpentadecafluoro-n-octanoate

Sodium ethoxide (3.5 g), prepared by dissolving sodium in ethanol (distilled from magnesium ethoxide), evaporation of the solution and drying the residue at 100°/0.02 mmHg for 3 h, was suspended in dry ether (40 ml). Ethyl pentadecafluoro-n-octanoate[9] (22.0 g) was added and the mixture cooled to 0°. 1,1,1-Trifluoroacetone (5.6 g) was then added and the mixture stirred for 60 h at 5–10°, when the mixture was neutralised by the addition of aq. $NaHSO_4$. An aqueous solution of cupric acetate was added, and the ether distilled from the mixture. The aqueous residue was ether extracted, the extracts dried ($MgSO_4$) and evaporated to give a green residue (8.5 g) which was recrystallised three times from ethanol and vacuum sublimed to give a light blue solid. This rapidly turned green in the atmosphere, the compound so obtained being identified as the dihydrated copper derivative of 3*H*,3*H*-octadecafluoroundeca-2,4-dione (nc) (6.0 g), m.p. 102–5° (Found C, 23.9; H, 1.0; F, 61.8. $C_{22}H_6F_{36}O_6Cu$ requires C, 23.6; H, 0.6; F, 61.2%).

(b) Using ethyltrifluoroacetate

The title compound (7.1 g) was added to sodium ethoxide (3.5 g) suspended in ether (40 ml). Methyl pentadecafluoro-n-heptyl ketone (20.6 g) was then added and the solution stirred for 45 h at 25°. The mixture was then treated as in (a) to give the dihydrated copper derivative of 3*H*,3*H*-octadecafluoroundeca-2,4-pione (4.5 g), identical with the sample prepared by the alternative route.

*Preparation of 3*H*,3*H*-octadecafluoroundeca-2,4-dione*

The copper derivative of the ketone (3.09 g) was dissolved in ether and H_2S bubbled through the solution for 1 h. The precipitated CuS (0.252 g) was filtered off and the ethereal solution evaporated. The residue was distilled under reduced pressure to give 3*H*,3*H*-octadecafluoroundeca-2,4-dione (nc) (1.6 g), b.p. 74–6°/15 mmHg (Found C, 26.0; H, 0.4; F, 67.0. $C_{11}H_2F_{18}O_2$ requires C, 26.0; H, 0.4; F, 67.5%). The UV spectrum (ethanol) gave $\lambda_{max.}$ 308 nm (ε 16700). The IR spectrum showed two moderately strong absorption maxima at 1625 and 1680 cm^{-1} (typical for a β-diketone), a weak absorption at 3130 cm^{-1}

(=C–H) and a broad band from 2800–3600 (–OH). The ^{1}H NMR spectrum consisted of two signals, one at 12.98 ppm downfield from TMS, (singlet), the other at τ 3.60. These signals were in the intensity ratio 1:1, and were assigned to –OH and =C–H respectively. The ^{19}F NMR spectrum consisted of signals with intensity ratios 3:3:2:10 at φ* 77.1 ($-CO-\underline{CF_3}$), 81.5 ($-CF_2-\underline{CF_3}$), 126.5 ($-CF_2-$) and 120.9–122.4 ($-CF_2-$). These spectra are in agreement with the proposed structure.

Preparation of 9H,9H-*tricontafluoroheptadeca-8,10-dione*

Ethyl pentadecafluoro-n-octanoate (20.0 g) was added to sodium ethoxide (3.5 g) suspended in dry ether (40 ml). When complete solution had occurred, methyl pentadecafluoro-n-heptyl ketone (18.0 g) was added and the mixture stirred for 50 h at 25°. The solution was then neutralised with aq. $NaHSO_4$ and aq. cupric acetate added. The ether was distilled off and the aqueous residue extracted with ether. The ethereal extracts were dried ($MgSO_4$) and evaporated to give a green residue (20 g), b.p. 115°/0.01 mmHg. Attempts to obtain a pure sample of the copper derivative by fractional distillation and sublimation, crystallisation from various solvents, and column chromatography were unsuccessful. The impure copper derivative (7.5 g) was dissolved in ether and H_2S passed into the solution for 1 h. The cupric sulphide (0.6 g) was filtered off and the ether evaporated. The residue was distilled under reduced pressure and recrystallised from chloroform to give 9*H*,9*H*-tricontafluoroheptadeca-8,10-dione (nc) (3.0 g), b.p. 92–5°/ 15 mmHg, m.p. 51.5° (Found C, 25,2; H, 0.3; F, 70.6. $C_{17}H_2F_{30}O_2$ requires C, 25.2; H, 0.3; F, 70.5%). The UV spectrum in ether gave $\lambda_{max.}$ 276 nm (ε 7370); in ethanol $\lambda_{max.}$ 311 nm. The IR spectrum showed absorption maxima at 1605, 1675 and 1773 cm^{-1} with a broad diffuse band from 2400–3600 cm^{-1}. The ^{1}H NMR spectrum consisted of two signals at τ 0.45 (singlet) and 3.52 in the intensity ratio 1:1, which were assigned to –OH and =C–H respectively. The ^{19}F NMR spectrum consisted of signals with intensity ratios 3:2:10 at φ* 81.4, 126.4 and 119.9–121.0. These spectra are consistent with the proposed structure.

Attempted condensation using sodium hydride

Ethyl pentadecafluoro-n-octanoate (6.6 g), sodium hydride (0.36 g) and ether (40 ml) were stirred together and methyl pentadecafluoro-n-heptyl ketone (6.2 g) in dry ether (10 ml) slowly added. The mixture was refluxed for 20 h and filtered to give a solid (3.4 g). The filtrate was evaporated, and the residue (8.2 g) shown to be a mixture of ester and ketone starting material (8:2) by GLC and IR spectra. The solid was shaken with dil. H_2SO_4 and the mixture extracted with ether. The ethereal solution was dried ($MgSO_4$) and evaporated to leave a liquid residue (2.1 g), b.p. 200–202°. From the IR, UV and mass spectra the compound was tentatively identified as the aldol condensation product of methyl pentadecafluoro-n-heptyl ketone.

Attempted preparation of lead derivatives of 9H,9H-*tricontafluoro-heptadeca-8,10-dione*

(a) The dione (0.4 g), distilled in vacuum from P_2O_5 was dissolved in dry $CHCl_3$ and refluxed with dry $PbCl_2$ for 5 h. UV spectroscopy showed that no chelate had formed.

(b) Lead tartrate (0.4 g) was heated to decomposition in a stream of N_2. The residue was cooled to 25° under N_2, 9*H*,9*H*-tricontafluoroheptadeca-8,10-dione (0.4 g) in $CHCl_3$ added, and the mixture refluxed for 4 h. No chelate was formed.

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