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1,4-Dilithiooctafluorobutane[*]

Perfluoro-n-propyllithium[1], perfluoroisopropyllithium[2], and perfluoro-n-heptyllithium[3] are useful intermediates despite some restrictions arising from their instability. The first dilithioperfluoroalkane, 1,4-dilithiooctafluorobutane, has now been prepared by metal–halogen exchange in ether at −80°, and characterised by its reaction with acetaldehyde to give 2,7-dihydroxy-3,3,4,4,5,5,6,6-octafluorooctane in at least 18 % yield. This diol, which readily yielded a bis(*p*-nitrobenzoate) derivative, was also obtained from diethyl octafluoroadipate and a mixture of methylmagnesium iodide and isopropylmagnesium bromide (a reaction reported[4] for monofunctional esters). One pure crystalline form of the diol, and two of the bis(*p*-nitrobenzoate), were isolated by fractional crystallisation.

Although the stability of 1,4-dilithiooctafluorobutane is limited even at −80°, dilithioperfluoroalkanes should prove, using simultaneous or alternating addition techniques, as useful intermediates as the perfluoroalkyllithiums.

Experimental

2,7-Dihydroxy-3,3,4,4,5,5,6,6-octafluorooctane from diethyl octafluoroadipate. To a stirred solution of the mixed Grignard reagents[4] from magnesium (8.4 g, 0.35 g-atom), methyl iodide (18.0 g, 0.13 mole), and isopropylmagnesium bromide (23.0 g, 0.19 mole) in ether (175 ml), diethyl octafluoroadipate (20.0 g, 0.058 mole) in ether (10 ml) was added under nitrogen at 5–10° during 1 h. After being allowed to stand overnight, the mixture was refluxed for 1 h, and then hydrolysed with 6 *N* hydrochloric acid (100 ml). The ethereal layer, and two 50 ml ether extracts, were dried ($MgSO_4$). Removal of solvent afforded a very viscous liquid fraction (6.9 g), b.p. 152°/50 mm,

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which crystallised with difficulty from benzene to give a colourless solid (4.9 g), m.p. 45–65°. Two recrystallisations from benzene and three recrystallisations from benzene/cyclohexane gave 2,7-dihydroxy-3,3,4,4,5,5,6,6-octafluorooctane (I), (0.8 g), m.p. 88.5–90.5°. (Found: C, 32.8; H, 3.6; F, 52.7. $C_8H_{10}F_8O_2$ calcd.: C, 33.1; H, 3.5; F, 52.4%.) ν_{max} (KBr) twin maxima 3400 and 3330 (bonded hydroxyl), and ν_{max} (2% w/v in benzene) 3575 cm^{-1} (free hydroxyl). The mass spectrum showed a low intensity parent peak at *m/e* 290 (< 1% intensity of base peak at *m/e* 45). A second diol fraction (3.2 g), m.p. 45–60°, with mass spectrum identical to that of (I), was obtained by concentration of the mother liquors.

When 0.2 g of (I) was gently refluxed with *p*-nitrobenzoyl chloride (0.4 g) in pyridine (5 g), and the mixture poured on to conc. hydrochloric acid and ice, a cream solid (0.42 g) was obtained; this, recrystallised twice from ethanol, gave the bis(*p*-nitrobenzoate) (0.28 g), m.p. 134–136°. (Found: C, 45.1; H, 3.4; F, 25.5; N, 5.1. $C_{22}H_{16}F_8N_2O_8$ calcd.: C, 44.9; H, 2.7; F, 25.8; N, 4.8%.) Similarly, 0.5 g of the diol fraction, m.p. 45–60°, gave solid (0.86 g) which, recrystallised four times from absolute ethanol, gave a second form of the bis(*p*-nitrobenzoate) (0.19 g), m.p. 147.5–149.5°. (Found: C, 44.8; H, 2.9; F, 26.7; N, 4.4. $C_{22}H_{16}F_8N_2O_8$ calcd.: C, 44.9; H, 2.7; F, 25.8; N, 4.8%.)

2,7-Dihydroxy-3,3,4,4,5,5,6,6-octafluorooctane from 1,4-dilithiooctafluorobutane. n-Butyllithium (22.5 ml, of 1.92 *M* ethereal solution, 0.043 mole) and acetaldehyde (1.9 g, 0.043 mole) in ether (22.5 ml) were added alternately (1.5 ml aliquots of n-butyllithium at 5 min intervals, each followed by an equal volume of the aldehyde solution) to a stirred solution of 1,4-diiodooctafluorobutane (9.8 g, 0.022 mole) in ether (150 ml) under nitrogen at —80 to —85°. The mixture was kept at that temperature for 20 min, allowed to warm to room temperature, then hydrolysed with 2 *N* sulphuric acid (50 ml), and finally refluxed for 30 minutes. The cold-trap condensate yielded perfluorobutadiene (0.2 g). The ethereal layer and two 25 ml ether extracts were dried ($MgSO_4$), and the solvent removed to leave a residue, which was shown by gas chromatography to contain butyl iodide (6.6 g, 83%). The residue gave a fraction (1.8 g) at 220° (bath)/50–152 mm, which on standing deposited pale brown crystals (1.1 g), m.p. 40–60°. Recrystallisation three times from benzene/cyclohexane afforded diol (0.14 g), m.p. 87–89°, which had infrared and mass spectra identical to those of (I). The mother liquors yielded a fraction (0.38 g), m.p. 54–77°, with mass spectrum identical to that of (I).

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