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Short Communication

Heptafluorobenzyl bromide

R. H. MOBBS *

Research Department, Imperial Smelting Corporation Ltd., Avonmouth, Bristol (Great Britain)
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Perfluoroalkyl bromides have sometimes been used in free-radical telomerisation reactions with olefins and fluoro-olefins[1,2,3] although the iodides are usually preferred because of the easier fission of the C–I bond. We were interested in preparing pentafluorophenyl compounds having an attached polyfluoroalkyl chain. Available methods for the synthesis of such compounds are few, the most widely applicable probably being the reaction of a pentafluorophenyl Grignard with a perfluoroalkyl acid chloride[4] or aldehyde[5]. Fluorination of the resultant ketone (formed after oxidation in the case of the aldehyde product) with sulphur tetrafluoride yields the desired compound. We decided to synthesise perfluorobenzyl bromide because it seemed possible that it might undergo telomerisation reactions with fluoro-olefins, or if it proved too unreactive it might be converted to the iodide by lithiation and reaction with iodine.

Heptafluorobenzyl bromide was prepared by thermal bromination of difluoromethylpentafluorobenzene at temperatures in the range 380–590°. At 450° the product was obtained in 45% yield although optimum conditions were not determined. The starting difluoromethylpentafluorobenzene was initially prepared by the action of sulphur tetrafluoride upon pentafluorobenzaldehyde. Later, the better and more convenient fluorination of dichloromethylpentafluorobenzene was disclosed to us[6]. Other bromination procedures including bromine in carbon tetrachloride with UV irradiation, bromine and oleum, bromine and aluminium, and *N*-bromosuccinimide with or without UV irradiation, were tried but failed to give any bromide, with good recoveries of starting material being obtained in each case. In contrast, *N*-bromosuccinimide and UV irradiation have been used to convert 1,4-bis-(difluoromethyl)benzene to 1,4-bis-(bromodifluoromethyl)-benzene[7]. However the conditions for our bromination of difluoromethylpentafluorobenzene were similar to those used for 1,1,1-trifluoroethane[8] and 1,1-difluoroethane[9] where 50% and 75% yields of 1-bromo-2,2,2-trifluoroethane and 1-bromo-2,2-difluoroethane respectively were obtained.

Although the fairly vigorous bromination conditions might suggest that the C–H bond in difluoromethylpentafluorobenzene has some polar character, since

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* Present address: Chemistry Department, The University, Manchester (Great Britain).

radical attack occurs more easily as bond polarity decreases, attempts to metalate it with methyl-lithium were unsuccessful. Substitution of the *p*-fluorine atom by a methyl group occurred and only 4-difluoromethyl-2,3,5,6-tetrafluorotoluene was isolated in 54% yield, together with starting material. The I π-effect, which has been used to explain the feeble acidity of the methyl group hydrogen atoms in 4-methylpentafluoropyridine[10], would also be expected to operate here, and reduce the acidity of the hydrogen in the difluoromethyl group.

Heptafluorobenzyl bromide when heated with copper bronze in a sealed ampoule at 284° for 48 h coupled to give perfluorodibenzyl, thus providing additional confirmation of the structure.

Two preliminary unsuccessful reactions have been carried out with the new bromide. In the first, the bromide and tetrafluoroethylene were heated together in a sealed tube at 190° for 72 h in the presence of azo-bis-isobutyronitrile. Little if any telomerisation occurred, and 97% of the product consisted of the starting bromide together with a little unidentified higher boiling material. In the second reaction, an attempt was made to prepare heptafluorophenylacetic acid by treating heptafluorobenzyl bromide in diethyl ether solution at −90° with n-butyl-lithium in hexane and carbonating the reaction mixture. No acidic product was isolated, and it seemed from the products detected that both metalation and nucleophilic attack by the butyl anion had occurred.

Experimental

Infrared spectra were measured on a Perkin–Elmer 337 spectrophotometer. Sulphur tetrafluoride (du Pont de Nemours & Co.) was used without further purification. Melting points are uncorrected.

Difluoromethylpentafluorobenzene

Pentafluorobenzaldehyde (80 g, 0.41 mole) and sulphur tetrafluoride (93 g, 0.88 mole) were shaken and heated together in an 800 ml capacity stainless-steel autoclave at 140–150° for 8 h and at 160–170° for 3 h. The reaction mixture was poured into a stirred suspension of sodium fluoride (5 g) in dry pentane (100 ml), the mixture filtered, and the filtrate evaporated to leave a residue (74.5 g) which was distilled (15 cm column packed with 3 mm Pyrex helices) giving difluoromethylpentafluorobenzene (45.5 g, 51% yield), b.p. 124–127°, 98.6% by GLC (2 m × 6 mm o.d. propylene glycol LB550X–Chromosorb P (15:85) at 150° and He carrier gas). A mid-cut b.p. 124–125° was 99+% material. (Found: C, 38.6; H, 0.6; F, 60.9. Calc. for C_7HF_7: C, 38.5; H, 0.5; F, 61.0%.)

Heptafluorobenzyl bromide (nc)

Liquid bromine (155 g, 0.97 mole) and difluoromethylpentafluorobenzene (60 g, 0.28 mole) were added simultaneously over 10 h to the top of a vertically-mounted column (45 × 1.5 cm) packed with Pyrex helices (5 × 3 mm) and heated throughout its length at 450°. When addition was complete, a nitrogen stream was used to sweep through residual material, the whole product being collected in two cooled receivers. The crude product was washed with sodium bisulphite solution then with water and dried. Distillation of this material (53.7 g) gave impure heptafluorobenzyl bromide (40.3 g, 45% yield) 93% by GLC, and a higher boiling residue (8.8 g). Negligible amounts of difluoromethylpentafluorobenzene were recovered.

Preparative GLC (6 m × 1 cm polypropylene glycol LB 550X–Chromosorb W (20:80) at 150° and He carrier gas) of a portion of impure heptafluorobenzyl bromide gave 99+% pure material. (Found: C, 28.3; Br, 26.6; F, 44.9. C_7BrF_7 requires C, 28.3; Br, 26.9; F, 44.8%.) The IR spectrum $\nu_{max.}$ (liq. film) 1520 cm^{-1} (fluorinated aromatic ring) showed no C–H absorption.

Using the same mole ratio of bromine to difluoromethylpentafluorobenzene, several preparations were carried out in the same apparatus at temperatures from 380° to 590°. At the lowest temperature, much starting material (39%) was recovered while at the highest temperature high-boiling by-products (26%) were formed and recovery of organic material was poor.

Perfluorodibenzyl (nc)

Heptafluorobenzyl bromide (3 g, 93% by GLC, 0.009 mole) and copper bronze (3 g, 0.047 g atom Cu) were heated together in a sealed Pyrex ampoule at 284° for 48 h. The brown product was extracted with diethyl ether and the combined extracts were evaporated leaving a tarry residue from which pale green crystals (0.5 g) were obtained by sublimation (80°/0.05 mmHg). Recrystallisation (ethanol) gave white crystals (0.35 g) m.p. 123–124° of perfluorodibenzyl. (Found: C, 38.9; F, 61.6. $C_{14}F_{14}$ requires C, 38.7; F, 61.3%.) The IR spectrum was in accord with the proposed structure.

Attempted preparation of perfluorobenzyl iodide

Difluoromethylpentafluorobenzene (21.8 g, 0.1 mole) in dry diethyl ether (200 ml) was stirred at −70° while a solution of methyl-lithium in diethyl ether (112 ml, 0.1 mole) was added over 0.5 h. Little rise in temperature occurred, and only *ca.* 5% of the theoretical yield of methane was evolved. The mixture was stirred at −55° for 4 h, a solution of iodine (25.4 g, 0.2 mole) in diethyl ether (200 ml) was added and the mixture was stirred a further hour. Water (200 ml) was added, the diethyl ether phase separated, washed with sodium metabisulphite solution and dried. Fractional distillation of the crude product (20.4 g) gave 4-difluoromethyl-2,3,5,6-tetrafluorotoluene (nc) (11.5 g, 54% yield) b.p. 68–70°/32 mmHg, 98.8% by GLC (2 m × 6 mm o.d. silicone stopcock grease–Chromosorb W (25:75) at 150° and He carrier gas). (Found: C, 44.8; H, 2.1; F, 53.4. $C_8H_4F_6$ requires C, 44.9; H, 1.9; F, 53.3%.) The IR spectrum was in agreement with the proposed structure, $\nu_{max.}$ (liq. film) 2950 cm^{-1} (C–H), 1505 cm^{-1} (fluorinated aromatic ring).

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