

THE FLUORINATION OF POLYFLUOROBIPHENYLS CONTAINING BROMINE

M. E. HARLEY AND A. E. PEDLER

*Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT
(Great Britain)*

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SUMMARY

2-Bromononafluorobiphenyl, 2,2'-, 3,3'- and 4,4'-dibromo-octafluorobiphenyl have been fluorinated using CoF_3 at 100–140°. The first two of these compounds lost bromine and gave eicosafuoro-1-cyclohexylcyclohexene and perfluorobicyclohexyl in addition to 2-bromoheptadecafluorobicyclohex-1,1'-enyl. From the latter two biphenyls the corresponding dibromo-eicosafuorobicyclohexyl derivatives were obtained in good yield. 3,3'-Dibromo-octafluorobiphenyl was obtained by the bromination of 2,3,4,6,2',3',4',6'-octafluorobiphenyl which was itself prepared by a coupling reaction of 1-bromo-2,3,4,6-tetrafluorobenzene using copper bronze.

INTRODUCTION

The low-temperature (100–150°) fluorination¹ of polyfluoroaromatic compounds over CoF_3 results in the formation of polyfluorocyclic olefins and dienes, in addition to saturated compounds. At higher temperatures (300–350°), the only products found are saturated². We have investigated the low-temperature fluorination of four bromopolyfluorobiphenyl compounds in order to synthesize the corresponding bromopolyfluorobicyclohexyl derivative following the observation¹ that bromopentafluorobenzene could be fluorinated over CoF_3 at 100° to give undecafluorocyclohexyl bromide.

RESULTS AND DISCUSSION

The compounds selected for fluorination were 2-bromononafluorobiphenyl, 2,2'-, 4,4'- and 3,3'-dibromo-octafluorobiphenyl, the first three of which were synthesized as previously described³. Repeated attempts to synthesize 3,3'-

dibromo-octafluorobiphenyl from 1,3-dibromotetrafluorobenzene using *n*-butyllithium and TiCl_4 were unsuccessful, only starting material being recovered in 50% yield. Likewise, attempts to obtain the biphenyl by the Ullman self-coupling reaction of 1,3-dibromotetrafluorobenzene were also unsuccessful, only starting material and an intractable residue (presumably polyphenyls of high molecular weight) being obtained. 3,3'-Dibromo-octafluorobiphenyl was finally synthesized by the bromination of 2,3,4,6,2',3',4',6'-octafluorobiphenyl using bromine in oleum. The 2,3,4,6,2',3',4',6'-octafluorobiphenyl was itself prepared in good yield by the reaction of 1-bromo-2,3,4,6-tetrafluorobenzene with copper bronze.

2-Bromononafluorobiphenyl was fluorinated at 140° over CoF_3 to give a complex mixture of products with a considerable loss of bromine. From the mixture was isolated the known compounds perfluorobicyclohexyl, octadecafluorobicyclo-1,1'-enyl and eicosafluoro-1-cyclohexylcyclohexene, together with a new compound identified as 2-bromoheptadecafluorobicyclohex-1,1'-enyl by chemical analysis, mass spectrometry and IR and UV spectra. The ^{19}F NMR spectra were of no assistance in assigning a structure to the compound due to the complicated coupling present. Mass spectrometry suggested that 2-bromoheneicosfluorobicyclohexyl was present as only a minor product of the fluorination.

2,2'-Dibromo-octafluorobiphenyl was likewise fluorinated at 250° , the sole product being perfluorobicyclohexyl. At low temperatures (140°), a complex mixture of products was obtained, which was not separable by preparative-scale gas-liquid chromatography into pure components. Measurement of the mass spectrum of mixtures obtained by a partial separation of the reaction product showed that much bromine had been lost on fluorination, and that the bromine remaining was incorporated into unsaturated compounds.

The fluorination of 3,3'-dibromo-octafluorobiphenyl at 100° gave a product consisting mainly of one compound identified as 3,3'-dibromo-eicosafluorobicyclohexyl. Fluorination of the biphenyl at temperatures appreciably above 100° resulted in the loss of bromine, although a better weight recovery of organic material could be obtained. 4,4'-Dibromo-octafluorobiphenyl was fluorinated at 140° to give, in good yield, 4,4'-dibromo-eicosafluorobicyclohexyl.

The loss or retention of bromine after fluorination clearly depends on the position of the bromine atoms in the biphenyl substrate. Bromine atoms in the 4,4' and 3,3' positions were little affected by the fluorination process, although an appreciably lower temperature was required for the fluorination of 3,3'-dibromo-octafluorobiphenyl before the corresponding bicyclohexyl emerged as the major product. Fluorination of biphenyls containing bromine in the 2 and 2' positions resulted in almost complete loss of bromine even at temperatures as low as 100° , and there was little evidence to suggest the formation of a bromine-containing bicyclohexyl in these cases.

These results become explicable when the steric interactions in the various molecules are considered. UV spectroscopy shows that bromine atoms in the 2

and 2' positions of biphenyls are subject to strong steric interference⁵. It may therefore be expected that they will be relatively readily replaced by fluorine. These steric effects are absent for substituents in the 3 or 4 positions, and the formation of the corresponding dibromo-eicosafuorobicyclohexyl becomes more likely.

It is of interest to note that the unsaturated compounds formed have the double bonds adjacent to the ring junction, suggesting that these are the most difficult to fluorinate. This may be due to steric interaction associated with the introduction of fluorine into the 1 position.

EXPERIMENTAL

NMR spectroscopy

Spectra were recorded on a Perkin-Elmer R10 spectrometer, ¹H spectra at 60 MHz and ¹⁹F spectra at 56.4 MHz, in deuterio-acetone as a solvent. The internal standard for ¹⁹F spectra was CCl₃F, chemical shifts being quoted in ppm high field, the standard for ¹H spectra being TMS, the chemical shift being given in τ values.

Gas-phase chromatography

The following columns were used for gas-phase chromatography: column 1, 180 cm \times 4 mm i.d., silicone gum: Celite = 1:6; column 2, 488 cm \times 3.5 mm i.d., silicone gum: Celite = 1:7; column 3, 456 cm \times 6 mm i.d., silicone gum: Celite = 1:6; column 4, stainless-steel capillary column 100 m \times 0.25 mm i.d., coated with Ucon oil LB 550X.

Fluorination

Samples were fluorinated over CoF₃ (150 g) at various temperatures using the apparatus and technique previously described^{6,7}. The compound was vaporized into a stream of nitrogen (5 l h⁻¹) flowing through the reactor and collected in a trap cooled in liquid air, the flow of N₂ being continued for 4 h after the admittance of the sample was completed. The contents of the trap were then washed with sodium metabisulphite solution, water and weighed.

3,3'-Dibromo-octafluorobiphenyl

(a) Butyl-lithium and TiCl₄

1,3-Dibromotetrafluorobenzene (9.6 g) was dissolved in dry ether (120 ml) and stirred at -78° under N₂, when n-butyl-lithium in n-hexane (16 ml; 0.130 g ml⁻¹) was added slowly. The mixture was stirred for 15 min, TiCl₄ (10 ml) added and the solution stirred for a further 4 h at -78° . The solution was then allowed to stand at 25 $^\circ$ for 24 h when water (120 ml) was added and the organic layer separated. The ethereal solution was washed with water (3 \times 100 ml), dried

(MgSO₄) and evaporated. The residue was distilled to give 1,3-dibromotetrafluorobenzene (4.8 g) only, identified by IR spectroscopy and GLC.

(b) *Copper bronze*

1,3-Dibromotetrafluorobenzene (4.0 g), activated copper bronze (3.0 g) and dry DMF (30 ml) were heated at 125° for 5 h with stirring. The mixture was poured into water and the solid filtered off and dissolved in ether. The aqueous residue was ether-extracted and the ether fractions combined, dried (MgSO₄) and evaporated to leave an unidentifiable residue (2.1 g).

(c) *2,3,4,6,2',3',4',6'-Octafluorobiphenyl*

1-Bromo-2,3,4,6-tetrafluorobenzene⁸ (7.0 g), activated copper bronze (5.0 g) and dry DMF (60 ml) were heated at 130° for 16 h under N₂ with stirring. The mixture was poured into water, filtered and the filtrate extracted with ether. The solid filtered off was extracted with ether and the two ethereal solutions combined, dried (MgSO₄) and evaporated. The residue (5.8 g) was separated by column chromatography (silica gel, petroleum ether, boiling range 40–60°) to give 2,3,4,6,2',3',4',6'-octafluorobiphenyl (nc) (2.9 g), m.p. 66°. (Found: C, 48.3; H, 1.0%. C₁₂H₂F₈ requires C, 48.3; H, 0.7%.) The mass spectrum showed a top mass peak at 298 (required) and the IR spectrum an absorption at 3085 cm⁻¹ (aryl C–H). The ¹⁹F NMR spectrum consisted of four signals at 113.5, 129.5, 131.0 and 164.5 ppm, of relative intensities 1:1:1:1, in agreement with the assigned structure. The ¹H NMR spectrum consisted of one signal (a multiplet) at 7.0 τ.

A mixture of the octafluorobiphenyl (1.9 g), bromine (3.0 g), aluminium tribromide (0.1 g) and fuming H₂SO₄ (9 ml; 20% SO₃) was stirred at 60° for 3 h, and then poured on to ice. The aqueous solution was extracted with ether, the ethereal extract separated, dried (MgSO₄) and evaporated to leave a residue (2.9 g). Purification of the residue by column chromatography (silica gel, petroleum ether, boiling range 40–60°) afforded 3,3'-dibromo-octafluorobiphenyl (nc) (1.9 g), m.p. 29–30°. (Found: C, 31.3; H, 0.0; F, 33.3%. C₁₂Br₂F₈ requires C, 31.4; H, 0.0; F, 33.2%.) The mass spectrum showed a top mass peak at 458 with two Br atoms (required 458). The ¹⁹F NMR spectrum consisted of four signals at 107.9, 121.9, 131.6 and 161.1 ppm, with relative intensities 1:1:1:1, consistent with the proposed structure.

Fluorination of 2-bromononafluorobiphenyl

The biphenyl (8.5 g) prepared as previously described³ was fluorinated at 140° and a liquid product (8.3 g) obtained. Analytical GLC (column 1, 100°) showed a multi-component mixture. The product (6.7 g) was separated by preparative-scale gas-liquid chromatography (column 2, 100°) into (a) fraction 1, a three-component mixture (4.0 g), (b) fraction 2 (0.32 g) and (c) a mixture of compounds (0.35 g). The mass spectrum of the mixture showed a peak at 624 (C₁₂BrF₂₁), although peaks of higher mass were observed.

Fraction 1 (1 g) was further separated (column 3, 100°) into (i) octadecafluorobicyclohex-1,1'-enyl (0.26 g), identified by a comparison of the IR spectrum with that of an authentic sample⁹, (ii) perfluorobicyclohexyl (0.11 g), identified by the IR spectrum⁶ and (iii) eicosafuoro-1-cyclohexylcyclohexene (0.40 g), b.p. 175° (cited¹⁰ 172°). (Found: C, 27.3; H, 0.0%. $C_{12}F_{20}$ requires C, 27.5; H, 0.0%.) Mass spectrometry gave a top mass peak 523 ($C_{12}F_{20}^+$ requires 524). The IR spectrum showed absorptions at 1680 and 1665 cm^{-1} (cited¹⁰ 1686 and 1672 cm^{-1}).

Fraction 2, a single component, was identified as 2-bromoheptadecafluorobicyclohex-1,1'-enyl (nc) (0.32 g), b.p. 180°. (Found: C, 26.2; H, 0.1%. $C_{12}BrF_{17}$ requires C, 26.4; H, 0.0%.) Mass spectrometry gave a top mass peak 546, with only one bromine atom present ($C_{12}BrF_{17}^+$ requires 548). The UV spectrum showed a strong absorbance at 224 nm ($\epsilon = 5400$) and the IR spectrum showed absorption bands at 1700 cm^{-1} and 1630 cm^{-1} ($>C=C<$).

Fluorination of 2,2'-dibromo-octafluorobiphenyl

The compound (2.0 g) was fluorinated in the usual way at 250° to give a product (1.7 g), m.p. 73–74°, identified by IR spectrometry as perfluorobicyclohexyl⁶ (cited m.p. 74–75°).

Fluorination of the biphenyl (2.0 g) at 140° gave a liquid product (1.4 g) which was shown by GLC (column 4, 50°) to be a complex mixture of products. The mixture was separated (column 2, 85°) into fraction (a), (0.5 g), shown by mass spectrometry to contain no bromine and fraction (b), (0.2 g), which gave a mass spectrum with peaks at 610 containing two bromine atoms ($C_{12}Br_2F_{16}^+$) and 586 containing one bromine atom ($C_{12}BrF_{19}^+$).

Fluorination of 3,3'-dibromo-octafluorobiphenyl

The biphenyl (4.6 g) was fluorinated in the usual way at 100° to give a product (2.2 g) which was shown by GLC to contain one major component. Separation by preparative-scale GLC (column 3, 125°) afforded 3,3'-dibromo-eicosafuorobicyclohexyl (nc) b.p. 172° (0.45 g). (Found: C, 21.4; H, 0.1; F, 55.8%. $C_{12}Br_2F_{20}$ requires C, 21.1; H, 0.0; F, 55.6%.) Mass spectrometry gave a top mass peak of 686 with two bromine atoms present ($C_{12}Br_2F_{20}^+$ requires 686).

Fluorination of 4,4'-dibromo-octafluorobiphenyl

The biphenyl (4.0 g) was fluorinated at 140° to give a solid product (3.6 g) which was shown by analytical GLC (column 1, 120°) to consist of one component. The solid was sublimed at 80°/10 mmHg and recrystallized from ethanol to give 4,4'-dibromo-eicosafuorobicyclohexyl (nc) (1.7 g), m.p. 88–89°. (Found: C, 21.3; H, 0.0; F, 55.3%. $C_{12}Br_2F_{20}$ requires C, 21.1; H, 0.0; F, 55.6%.) Mass spectrometry gave a top mass peak of 686 with two bromine atoms ($C_{12}Br_2F_{20}^+$).

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