Journal of Fluorine Chemistry, 3 (1973/74) 35–39

HOMOLYTIC REACTIONS OF POLYFLUOROAROMATIC COMPOUNDS
V. THE REACTION OF PENTAFLUOROPHENYL RADICALS WITH FLUOROBENZENE

J. P. B. SANDALL, R. BOLTON AND G. H. WILLIAMS

Bedford College, (University of London), Regent's Park, London NW1 4NS (Gt. Britain)

(Received October 18, 1972)

SUMMARY

The arylation of fluorobenzene with pentafluorophenyl radicals obtained by the reaction of the corresponding aniline with pentyl nitrite is described. The reaction involves attack at the 2′-, 3′- and 4′- positions. The composition of the mixture and the nature of its components were determined by ^{19}F NMR spectroscopy and were confirmed by gas–liquid chromatography.

INTRODUCTION

The reaction of pentafluoroaniline with pentyl nitrite in aromatic solvents at about 80° has been shown[1] to result in the formation of pentafluorophenyl radicals. Using toluene, and chloro-, bromo- and nitro-benzene as solvents, the previous workers determined the relative proportions of the isomeric biaryls obtained, and thus found evidence for the postulate[2] that pentafluorophenyl radicals display a large measure of electrophilic character. In order to extend these investigations and throw light on the electronic behaviour of the fluorine atom in fluorobenzene under these conditions of free-radical substitution, the reaction between fluorobenzene and pentafluoroaniline with pentyl nitrite was examined. Other sources of $C_6F_5\bullet$ had allowed halogen to be displaced from the heavier halogenobenzenes[3] but as yet the displacement of fluorine from fluorobenzene has not been reported.

RESULTS AND DISCUSSION

The biaryl fraction (A), isolated by steam-distillation in 37% yield, gave a ^{19}F NMR spectrum (Table 1) which consisted of seven main groups of lines in the general region of absorption by fluoroaromatic compounds (100–170 ppm upfield of $CFCl_3$). The peaks in this spectrum were assigned by comparison with the spectra of authentic samples of 2,2′,3,4,5,6- and 2,3,4,4′,5,6-hexafluorobiphenyl, as were the peaks of the spectrum of the compound isolated from the biaryl fraction by repeated crystallisation (B). The spectra of 4,4′-difluoro- and 2,3,4,5,6-pentafluoro-biphenyl were also obtained for comparison.

The spectrum of (B) is identical in all respects to that of 2,3,4,4′,5,6-hexafluorobiphenyl, an identification confirmed by m.p. and mixed m.p.. It is not unexpected that the 4′-isomer is the least soluble, and so the product most readily obtained by repeated recrystallisation. The peak at 111.7 ppm is due to a *p*-substituted fluorine atom, and shows the same splitting pattern due to coupling with the aromatic protons as that of 4,4′-difluorobiphenyl, despite the different chemical shift (115.8 ppm). The coupling constants, *J*(F,H), are 8.0 and 5.3 Hz in (B), and 8.3 and 5.2 Hz in the difluorobiphenyl.

TABLE 1

^{19}F NMR CHEMICAL SHIFTS*

Compound	Chemical shifts[a]						
(A)	111.5	112.2	112.9	140.9	143.6	156.1	163.1
(B)	111.7				143.6	156.1	163.1
2,2′,3,4,5,6-hexafluorobiphenyl			112.8	140.9		156.1	163.1
			(1)	(2)		(1)	(2)
2,3,4,4′,5,6-hexafluorobiphenyl[b]	111.7				143.6	156.1	163.1
	(1)				(2)	(1)	(2)
2,3,4,5,6-pentafluorobiphenyl[c]					143.9	156.8	163.2
					(2)	(1)	(2)
4,4′-difluorobiphenyl	115.8						

* Upfield of $CFCl_3$; ppm.

[a] Figures in parenthesis give ratio of the integrals for the corresponding peaks.

[b] 111.2, 144.0, 156.3, and 163.2 ppm reported for 2,3,4,4′,5,6-hexafluorobiphenyl; also 111.9, 143.5, 155.6, and 162.8 ppm for the 2,3,3′,4,5,6-isomer (ref. 4).

[c] 144.1, 156.7, and 163.0 ppm reported (ref. 5).

The biaryl mixture (A) appears to consist of the isomeric 2,3,4,5,6,*x*′-hexafluorobiphenyls. The peaks at 111.5, 112.2 and 112.9 ppm may be assigned to the 4′-, 3′- and 2′-fluorine atoms respectively; the four peaks at 140.9, 143.6, 156.1 and 163.1 ppm are due to the pentafluorophenyl ring. Examination of the peaks centred at 156.1 ppm in the two authentic hexafluorobiphenyls shows the usual "triplet of triplets" splitting typical of a fluorine atom in the 4- position of a pentafluorophenyl compound[6]; this assignment is confirmed by the integration. The peaks at 140.9 and 143.6 ppm in these two compounds are assigned to the 2- and 6-fluorine atoms, and those at 163.1 ppm to the 3- and 5-fluorine atoms. These values are in line with the figures reported[5] for 65 pentafluorophenyl compounds. It is interesting that the peak due to the 2- and 6-fluorine atoms in

2,2′,3,4,5,6-hexafluorobiphenyl is shifted nearly 2 ppm to lower field compared with that in both pentafluorobiphenyl and 2,3,4,4′,5,6-hexafluorobiphenyl, showing the marked effect of a 2′-, compared with a 4′-, fluorine atom upon the 2- and 6-fluorine atoms in the pentafluorophenyl fragment.

The complex structure of the peak at 140.9 ppm in 2,2′,3,4,5,6-hexafluorobiphenyl is due to spin–spin coupling with J(F,F) of the order of 0.5 Hz occurring between the 2′- and the 2- and 6-fluorine atoms. Corresponding coupling is found in the complex structure at 112.8 ppm. The identification of the peak at 112.9 ppm in (A) as being due to this isomer is strengthened by the observation of exactly similar phenomena in this peak and in the peak at 140.9 ppm. No coupling is observed between the 4′- and the 2- and 6-fluorine atoms in 2,3,4,4′,5,6-hexafluorobiphenyl, nor between protons and the 2- and 6-fluorine atoms in 2,3,4,5,6-pentafluorobiphenyl.

The peak at 143.6 ppm must be due to the approximate superposition of signals arising from the 2- and 6-fluorine atoms of the other two isomers, while the peaks at 156.1 and 163.1 ppm consist of peaks from all three isomers. The fine structures of all of these peaks confirm this interpretation.

The three separate peaks due to the 2′-, 3′- and 4′-fluorine atoms in the three isomers enables the isomer ratio in the mixed product to be measured. The occurrence of the peak due to the 2- and 6-fluorine atoms in 2,2′,3,4,5,6-hexafluorobiphenyl at some distance from the corresponding peak for the other isomers enables an independent measurement of the ratio 2′:(3′+4′) to be made. The integrals of these two groups of peaks which are 30 ppm apart cannot be compared directly, as they were obtained under different spectrometer conditions. The results are given in Table 2.

TABLE 2

F atom	Peak (ppm)	Integral	2′:(3′+4′)	(2′+4′)/3′
4′	111.5	125		
3′	112.2	142	0.734	2.26
2′	112.9	196		
	140.9	95	0.748	
	143.6	127		

Both early and late fractions of the steam-distillate were used in analysis as (A); no differences were found. Integrals were based upon several repeated integrations. The agreement between the two sets of figures for the ratio 2′:(3′+4′) is probably within the experimental error, and puts a maximum value of 1.0% for the 2,3,4,5,6-pentafluorobiphenyl content of the biaryl mixture. These results (Table 2) give the analysis of the biaryl fraction as 42.5% 2′-isomer, 30.7% 3′-isomer and 26.9% 4′-isomer.

Gas–liquid chromatography did not permit complete separation of the three isomers under conditions which gave easily measured peaks. The identification of the components of the biaryl fraction was only possible by adding known amounts of authentic products to the reaction product. This showed that the response of the detector was approximately equal for all three isomers, and that slight differences in the flow rate during the elution of earlier components could alter the retention time of a species sufficiently for its identity to be mistaken. The order of elution (*o, m, p*) and the overlapping between the peaks made integration difficult. Consistent results were obtained, however, and the analysis of three different mixtures gave the composition as 42 ± 2% 2′-isomer, 26 ± 2% 3′-isomer and 32 ± 2% 4′-isomer quoting mean deviations from the mean.

The differences between GLC and NMR analyses are almost entirely in the two later components, where overlapping and resulting difficulty of integration made accurate measurement impossible. Under conditions in which better separation could be achieved, the apparent amount of 3′-isomer increased at the expense of the 4′-isomer. It seems that, had complete separation been achieved, a closer agreement between GLC and NMR results could have been found.

The experimental results confirm the general trends already found[7] in the attack of $C_6F_5\bullet$ upon other halogenobenzenes.

EXPERIMENTAL

Reaction of pentafluoroaniline and pentyl nitrite with fluorobenzene

Pentafluoroaniline (6 g) in fluorobenzene (19 ml) was treated with pentyl nitrite (4.4 ml) dropwise over 30 min. After refluxing for 1.5 h, the excess of solvent was removed by distillation. Steam-distillation of the residue gave a mixed product (A), m.p. 80–95° (3.2 g). (Found: C, 55.0; H, 1.66; F, 43.4%. $C_{12}H_4F_6$ requires C, 55.0; H, 1.53; F, 43.5%.) The ^1H NMR spectrum of (A) showed only the presence of hydrogen bonded to aromatic carbon. The gas chromatogram, using a Perkin–Elmer F21 instrument with Apiezon L upon Chromosorb as stationary phase, showed only the presence of three, probably isomeric, components.

Five recrystallisations of (A) from ethanol gave a product (B) as white needles, m.p. 115–116° (70 mg) (2,3,4,4′,5,6-hexafluorobiphenyl has m.p. 118–119°)[4].

2,3,4,4′,5,6-Hexafluorobiphenyl

p-Fluorobenzoyl chloride (8 g; from *p*-fluorobenzoic acid) and an aqueous solution of sodium hydroxide (15%; 18 ml) were added slowly over 30 min to aqueous hydrogen peroxide (10%; 25 ml) at 0–5°. After the addition the mixture was stirred and allowed to reach room temperature overnight, when the precipitated peroxide was filtered off and was dried *in vacuo* after copious washing with water.

This material (5.5 g) was added to hexafluorobenzene (20 ml) and maintained at 80° for 3 days in a sealed Carius tube. On removal of the solvent from the reaction mixture, steam-distillation of the residue gave a crystalline solid in the distillate. This was washed with dilute aqueous sodium hydroxide and with water, and was subsequently recrystallised from ethanol, m.p. 116°–117°.

Specimens of 2,3,4,5,6-pentafluorobiphenyl and 2,2',3,4,5,6-hexafluorobiphenyl were kindly donated by Dr. M. W. Coleman, and a specimen of 4,4'-difluorobiphenyl by Dr. D. M. Hall.

^{19}F NMR spectra were taken on a Varian HA–60 instrument operated at 56.4 MHz. Solutions in fluorotrichloromethane of strength approximately 10 mole % were used. Shifts are given in ppm upfield of $CFCl_3$ (internal standard). In the case of the mixed product (A), the spectral signal-to-noise ratio was improved by the use of a digital signal averager (E. G. and G. Nuclear Ltd., model 546V) in order to obtain an adequate spectrum for the study of the fine structure.

ACKNOWLEDGEMENTS

We thank Imperial Smelting Corporation Ltd. for gifts of fluorocarbons and Mr. G. Howell for help in obtaining NMR spectra.

REFERENCES

1 P. H. Oldham, G. H. Williams and B. A. Wilson, *J. Chem. Soc. (C)*, (1971) 1094.
2 G. H. Williams, *Intra-Sci. Chem. Reports*, *3* (1969) 229.
3 W. R. Foster and G. H. Williams, *J. Chem. Soc.*, (1962) 2682; G. B. Gill and G. H. Williams, *J. Chem. Soc.*, (1965) 995, 2127; P. Lewis and G. H. Williams, *J. Chem. Soc. (B)*, (1966) 880.
4 W. A. Sheppard, *J. Amer. Chem. Soc.*, *92* (1970) 5419.
5 L. W. Pushkima, A. P. Stepanov, V. S. Zhulov and A. D. Haumov, *J. Org. Chem. U.S.S.R.*, *8* (1972) 586.
6 I. J. Lawrenson, *J. Chem. Soc.*, (1965) 1117.
7 G. H. Williams, *Essays on Free Radical Chemistry, Special Publication No. 24*, Chemical Society, London, p. 25.