

F-NMR-spectroscopy for the identification of photo products generated from aromatic iodo compounds*—IV†

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Abstract—The investigation demonstrates the analytical power of F-NMR spectroscopy for the identification of isomeric substituted fluorobiphenyls. The biphenyls are formed by u.v. irradiation of iodobenzenes in aromatic solvents. A special procedure for the identification is outlined and tendencies of the results—chemical shifts and relative rates for the production of isomers—are discussed in consideration of electronic and steric substituent effects.

INTRODUCTION

Aromatic iodo compounds have some importance in the field of arylation of aromatic compounds [1, 2]. On account of the relatively low bond strength they lose their iodine atom when they are irradiated by u.v. light, even under mild conditions. In this process aryl radicals are formed which react with aromatic molecules present as solvent molecules by formation of arylation products, with yields up to 100% in favourable cases.

In the course of an examination of the photochemical behaviour of aromatic nitro compounds we used the arylation products of iodo compounds for comparison [3-5]. Figure 1 represents the overall reaction mechanism. The reaction shows the formation of isomeric biphenyls. For one single experiment R is fixed whereas the substituent X can occupy the *ortho*, *meta* or *para* position. The relative yields of the isomers have a definite ratio characteristic of a substitution by radicals.

As fluorine was chosen either for R or X F-NMR spectroscopy could be used for the

identification of the arylation products. The main aim of this investigation was to demonstrate the analytical capacity of NMR for a series of substituted fluorobiphenyls (OH, OCH₃, CH₃, F, Cl, COOCH₃, NO₂); NMR spectral data of such compounds have not been published yet. The results can be explained in terms of electronic and sterical substituent effects.

EXPERIMENTAL

The iodo substrates were commercially available (Riedel de Haën, Eastman Organic Chemicals, ICN/K&K) except the benzoic acid methyl esters which were synthesized from the acids (Riedel de Haën). Most solvents (Merck, Riedel de Haën, Fluka) were of the 'reagent grade' quality or better; otherwise they were purified by suitable methods.

The irradiation apparatus consisted of a hollow cylindrical vessel, a magnetic excentric stirrer and a u.v. lamp (Q81, Original Hanau). The experiments were performed without filter devices. The concentrations of the iodo compounds lay in the range of 10⁻¹ mol l⁻¹. Photolyses were generally carried out for 20 h. The average temperature of the reaction chamber was 30°C, except for the irradiations in phenol, where a temperature of about 45°C was maintained by a thermostat because of the higher melting point of the solvent.

After irradiation the solution volume (about 50 ml) was reduced to about 3 ml by evaporation which mainly removed the solvent—fluorobenzene had to be removed completely—but losses of the iodo substrates and reaction products were also observed, especially in the higher boiling solvents. The remainder was diluted by about 2 ml of hexadeuteroacetone and the solution filtered into a 12 mm NMR tube.

The F-NMR spectra were recorded using a Varian XL-100-15 spectrometer with a fluorine resonance frequency of about 94 MHz. The chemical shifts were taken from singlet spectra which were obtained by decoupling the corresponding protons. The peak positions are reported in ppm from fluorobenzene chosen as internal reference, positive values to lower field.*

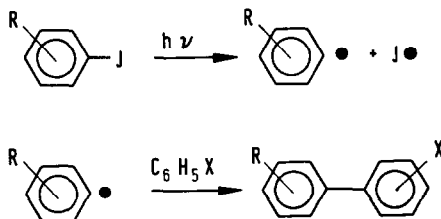


Fig. 1. Reaction mechanism for the u.v. irradiation of iodo compounds in aromatic solvents.

*Partial results of the examination were presented as a discussion paper at the meeting of the GDCh-group 'Magnetische Resonanzspektroskopie' in Steinhagen/Germany, October 1979.

†For parts I, II, III see references [3], [4] and [5].

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*Conversion equation for the reference trichloro-fluoromethane conventionally used:

$$\delta_{\text{trichloro-fluoromethane}} = -113.6 + \delta_{\text{fluorobenzene}}$$

RESULTS AND DISCUSSION

Figure 2 representatively shows decoupled F-NMR spectra of substituted biphenyls formed by irradiation in fluorobenzene and anisole. The results are listed in Tables 1, 2 and 3. The isomeric biphenyls could be identified successfully mainly

Table 1. Chemical shifts δ_F (ppm) of biphenyls $C_6H_4R-C_6H_4F$ formed by u.v. irradiation of iodo compounds in fluorobenzene and (in brackets) C_6H_5R

R	2-R, 2'-F	2-R, 3'-F	2-R, 4'-F
OH	-0,66 (-1,04)	-1,04 (-0,22)	-3,25 (-2,93)
OCH ₃	-0,80 (-0,89)	-1,12 (-1,17)	-3,09 (-3,14)
CH ₃	-1,73 (-1,76)	-0,36 (-0,37)	-2,97 (-2,97)
H	-4,92	0,14	-2,72
F	-1,50	-0,04	-1,50
Cl	-0,91 (-0,96)	-0,24 (-0,31)	-1,55 (-1,59)
COOCH ₃	-3,46 (-3,62)	-0,73 (-0,85)	-2,58 (-2,65)
NO ₂	-3,15 (-3,24)	0,33 (0,36)	-0,86 (-0,81)
	3-R, 2'-F	3-R, 3'-F	3-R, 4'-F
OH	-4,40 (-4,76)	0,00 (0,06)	-2,77 (-2,63)
OCH ₃	-4,50 (-4,59)	0,05 (0,00)	-2,55 (-2,61)
CH ₃	-4,69 (-4,77)	-0,03 (-0,04)	-2,91 (-2,91)
H	-4,92	0,14	-2,72
F	-4,77	0,38	-1,67
Cl	-4,72 (-4,76)	0,47 (0,40)	-1,60 (-1,63)
COOCH ₃	-4,99 (-5,09)	0,50 (0,36)	-1,83 (-1,98)
NO ₂	-4,94 (-5,06)	0,86 (0,83)	-0,70 (-0,67)
	4-R, 2'-F	4-R, 3'-F	4-R, 4'-F
OH	-4,98 (-5,27)	-0,15 (-0,13)	-4,12 (-3,95)
OCH ₃	-5,00 (-5,13)	-0,05 (-0,14)	-3,72 (-3,79)
CH ₃	-4,87 (-4,91)	-0,04 (-0,04)	-3,21 (-3,21)
H	-4,92	0,14	-2,72
F	-5,13	0,21	-2,66
Cl	-4,77 (-4,83)	0,37 (0,30)	-2,05 (-2,09)
COOCH ₃	-4,39 (-4,50)	0,54 (0,41)	-1,16 (-1,29)
NO ₂	-4,22 (-4,30)	0,91 (0,86)	0,09 (0,03)

Table 2. Relative yields (%) of isomeric biphenyls $C_6H_4R-C_6H_4F$ formed by u.v. irradiation of iodo compounds in fluorobenzene

R	2-R			3-R			4-R		
	2'-F	3'-F	4'-F	2'-F	3'-F	4'-F	2'-F	3'-F	4'-F
OH	54	34	12	52	33	15	54	37	9
OCH ₃	46	39	15	55	34	11	55	35	10
CH ₃	47	37	16	53	33	14	54	35	11
H	51	38	11	51	38	11	51	38	11
F	41	37	22	55	33	12	54	33	13
Cl	46	38	16	53	33	14	57	32	11
COOCH ₃	36	47	17	52	36	12	58	32	10
NO ₂	24	54	22	53	32	15	55	34	11

Table 3. Relative yields (%) of isomeric biphenyls $C_6H_4F-C_6H_4R$ formed by u.v. irradiation of iodo compounds in C_6H_5R

R	2-F			3-F			4-F		
	2'-R	3'-R	4'-R	2'-R	3'-R	4'-R	2'-R	3'-R	4'-R
OH	69	15	16	64	16	20	61	23	16
OCH ₃	61	13	26	72	13	15	72	11	17
CH ₃	49	29	22	59	*	*	59	25	16
F	41	37	22	55	33	12	54	33	13
Cl	31	37	32	55	26	19	58	24	18
COOCH ₃	33	29	38	52	16	32	57	17	26
NO ₂	31	27	42	49	16	35	51	20	29

*The yields could not be calculated on account of peak overlapping.

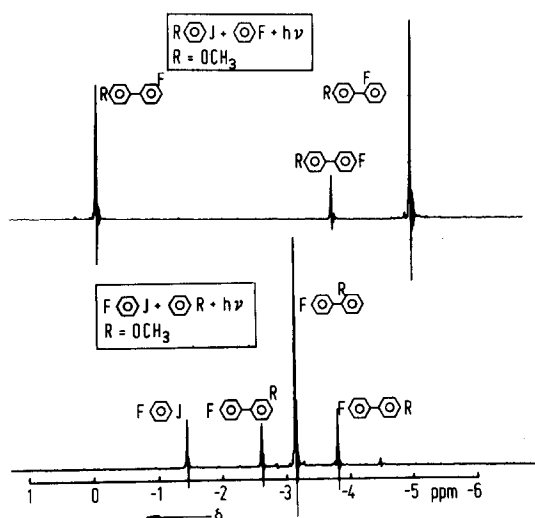


Fig. 2. Decoupled F-NMR spectra of substituted biphenyls formed by irradiation of iodo compounds.

by using the distinct connections between the two following sets of experiments:

irradiation of RC_6H_4I in fluorobenzene (Fig. 3a);
irradiation of FC_6H_4I in C_6H_5R (Fig. 3b).

Each set led to the production of all isomers possible, i.e. nine compounds for R unequal F, but apparently with a different sequence of products. Additionally the chemical shifts of the unsubstituted fluorobiphenyls and the spectral pattern of the undecoupled spectra were used for comparison as well as isomers' distributions in radical aryl-ation processes.

Table 1 contains the chemical shifts of both

irradiation series. The differences in the data are due to solvent effects as the measurements were not—as already mentioned—carried out with pure solutions of the isomers. But on the whole the deviations are relatively small except for the OH-group where differences up to 0.8 ppm can be recognized.

Substitution of a benzene molecule influences the *ortho*, *meta* and *para* positions to the substituent in different ways: the *ortho* position is influenced by a combination of inductive, resonance and sterical effects, the *meta* position mainly by inductive effects and the *para* position

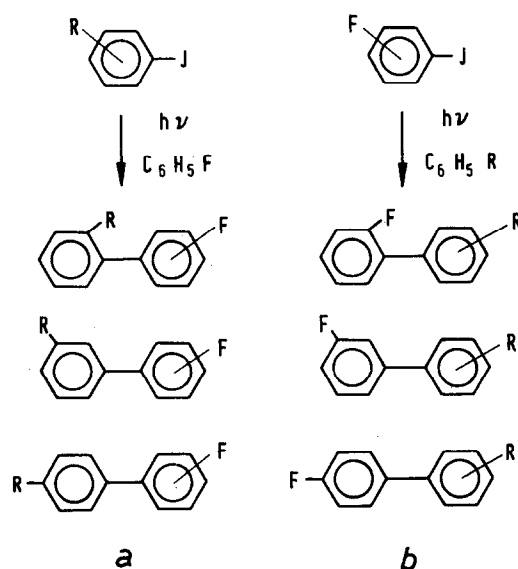


Fig. 3. Schemes for the formation of substituted fluoro-biphenyls.

mainly by resonance effects. Some workers tried to gain information about the electron distribution in aromatic systems by examining the F-NMR spectra of fluorobenzene derivatives. A correlation of chemical shifts and Hammett substituent constants σ lead to more or less satisfactory results [7]. In the biphenyls the substituent R influences both aromatic rings. The fluorine resonances are still remarkably sensitive to changes in the neighbouring aromatic ring, of course to a lower extent than for the substituted fluorobenzenes. Variations of the chemical shifts with respect to σ -constants or more recent data describing charge distributions in monosubstituted benzenes [8] can be recognized in the biphenyls as well. A better approach would be, however, to compare the chemical shifts with electron densities for the substituted biphenyls under study.

Table 2 contains the relative yields for the production of the isomeric compounds formed by irradiation in fluorobenzene. It becomes obvious that the product distribution is determined pre-vaillingly by the substituent of the solvent. The biphenyls with R in the meta or para position show relatively similar isomer percentages. Roughly all yields correspond to the values of the phenylation of fluorobenzene ($o : m : p = 51 : 38 : 11$) in which only electronic effects of the substituent R are involved. The photolytic arylation may be compared with chemical arylations, the decomposition of benzoyl peroxide in fluorobenzene at 80°C (54 : 31 : 15 [9]) and of *N*-nitrosoacetanilide in fluorobenzene (53 : 36 : 10). The error width of the listed values seems to be too great as to allow an insight into the polarization of the radical introduced by the substituent R.

As expected the situation changes remarkably if R is in the ortho position, i.e., if steric effects come into play. Accordingly greater deviations are observed in the first column of Table 2. The yields of the 2-R,2'-F-compounds are reduced to a different extent, except for R=OH. For COOCH₃ and NO₂ the 'normal' distribution order ($o > m > p$) is even inverted.

Table 3 represents the relative yields for the arylation products formed by irradiation of fluoriodobenzenes in C₆H₅R. Opposite to the first experiments' set the values show distinct differences, but for a definite substituent the yields of the 3-F,R- and 4-F,R-biphenyls resemble each other. They may be compared with chemical phenylation data neglecting polarization effects of the substituent F. The listed yields* were obtained

*Data from [6] unless otherwise stated.

by decomposition of benzoyl peroxide at 80°C in the following aromatic solvents (corresponding values of Table 3 in brackets):

Toluene:	67:19:14	(59:25:16)
Fluorobenzene: (see above)	54:31:15[9]	(54:33:13)
Chlorobenzene:	50:32:18 or 57:27:16[10]	(58:24:18)
Benzoic acid methyl ester:	58:17:25	(57:17:26)
Nitrobenzene:	62:10:28	(51:20:29)

The correspondence of the data can be considered satisfactory, at least the sequence of the yields is the same in each case. Two different values for the chemical phenylation of chlorobenzene are entered in order to indicate the spread of experimental errors.

In the case of R=OH and R=OCH₃ the formation of the F-,2'-R-compounds (e.g. 61%, 72% resp.) appears to be especially favoured. Different from the other substituents the production rates of the 2-F,2'-R-biphenyls (69%, 61% resp.) remain at a relatively high level, in spite of supposedly strong steric effects. This outstanding behaviour may be explained by the assumption of a preorientation process between the iodo compound and the solvent molecules compensating for losses by steric hindrance.

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