Tetrahedron. Vol. 24, pp. 6883 to 6887. Pergamon Press 1968. Printed in Great Britain

ANION RADICALS OF SOME FLUOROBIPHENYLS

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(*Received in USA* 8 *May* 1968; *Received in the UK for publication* 27 *June* 1968)

Abstract—Potassium 4,4′-difluorobiphenylide, 4-fluorobiphenylide and potassium 3,3′-difluorobiphenylide are stable at −80° in tetrahydrofuran. 4-Chlorobiphenyl, 4-bromobiphenyl and 4,4′-dibromobiphenyl apparently react with potassium at low temperatures to form radicals which decompose immediately by halide elimination. The ESR spectra of the 4,4′-difluorobiphenylide and 3,3′-difluorobiphenylide radicals and the polarographic behaviour, *p*-band positions, and results of LCAO–MO calculations for the parent, neutral compounds are reported.

THE previously reported aromatic, fluorine-substituted radicals, including tetrafluoro-*p*-benzosemiquinone[1] and various fluoro-substituted nitrobenzenes,[2–5] have contained other substituents which tended to decrease the spin density of fluorine. The neutral and stable tris(pentafluorophenyl)methyl radical has been reported.[6] The purpose of the present work was to investigate by electron spin resonance anion radicals containing only halogen substituents.

RESULTS

The electron spin resonance spectra of solutions of potassium 4,4′-difluorobiphenylide and 3,3′-difluorobiphenylide in tetrahydrofuran at −80° are presented in Figs 1 and 2. The hyperfine splitting constants are given in Table 1. Splitting by protons in the 2-positions of 4,4′-difluorobiphenylide is too small to be resolved; in other biphenylides[7] the splitting by the protons in the 2-position is always much more than in the 3-position. The assignment of the splitting constants in 3,3′-difluorobiphenylide is difficult, owing to the presence of five sets of two equivalent nuclei which produce five triplets for one isomer and to the possibility of both *cis* and *trans* isomers. The values in Table 1 were assigned on the basis of calculated McLachlan spin densities ($h = 3{\cdot}0$,[8] $k = 0{\cdot}7$,[8] $\delta = 0{\cdot}1$,[8] and $\lambda \doteq 1{\cdot}2$),[7] and the equation, $a_H = Q\rho_i$ ($Q = 28$ gauss).[9]

Calculations including wide ranges of values of h and k and the equations, $a_H = Q\rho_i$ and $a_F = Q^C_{CF}\rho_C + Q^F_{FC}AP_{CF}\rho_C$,[10] did not lead to consistent agreement between calculated and observed splitting constants. The latter equation involves a small difference between two large terms and is extremely sensitive to the estimated value of P_{CF}.

The green solutions containing the 4,4′-difluorobiphenylide and 4-fluorobiphenylide radicals upon being warmed to room temperature first became orange and showed no ESR absorption. Then the solutions became bluish and exhibited the ESR spectrum of unsubstituted biphenylide.

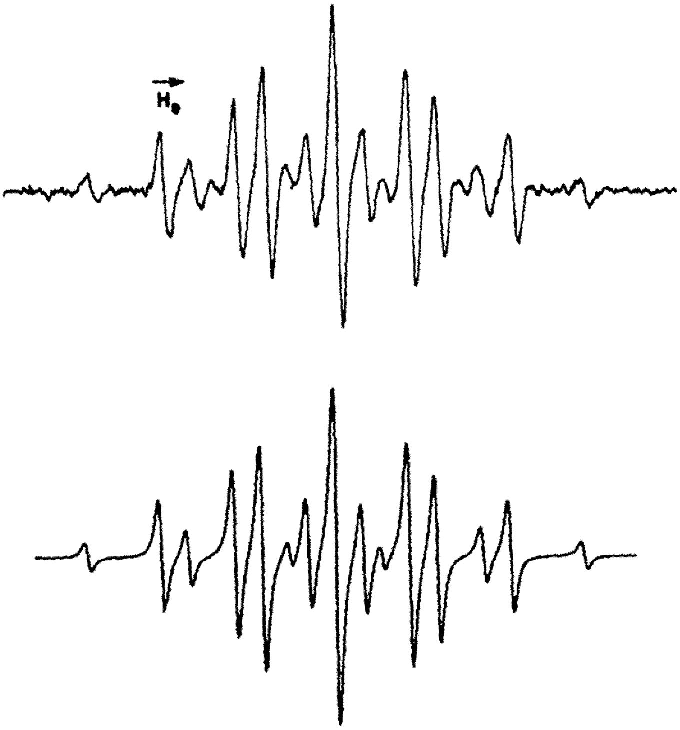


FIG. 1 Observed (top) and computed ESR spectra of potassium 4,4'-difluorobiphenylide in THF at −80°. The arrow corresponds in length to one gauss and also indicates the direction of increasing magnetic field.

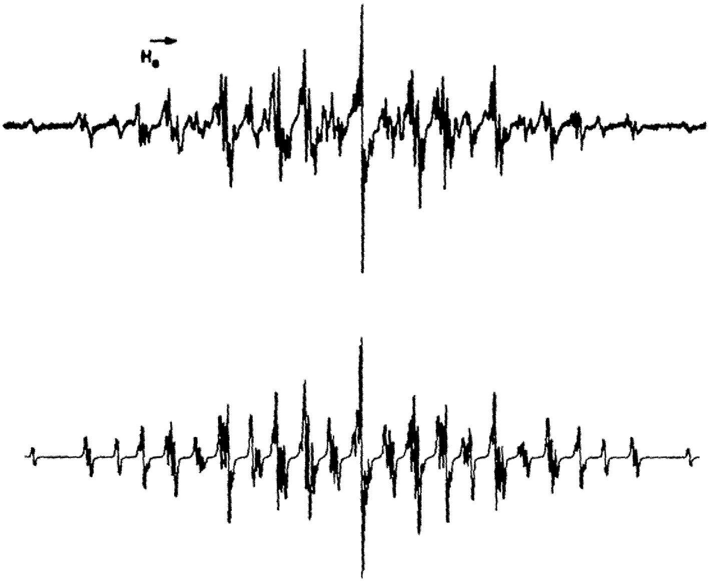
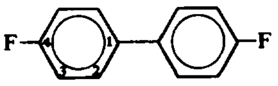
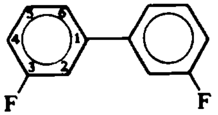


FIG. 2 Observed (top) and computed ESR spectra of potassium 3,3'-difluorobiphenylide in THF at −80°.

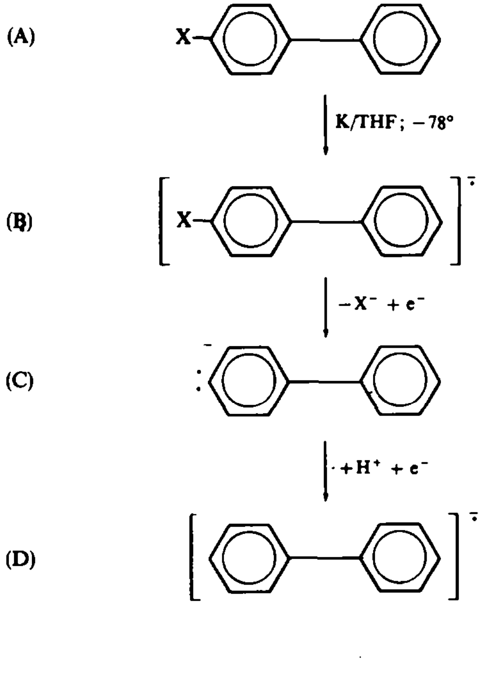
TABLE 1. HYPERFINE SPLITTING CONSTANTS AND SPIN DENSITIES

	Atom	a_i (gauss)	ρ_i		
			Experimental	Hückel	McLachlan
	1	—	—	0·122	0·129
	2	2·28	0·082	0·083	0·095
	3	—	—	0·026	−0·014
	4	—	—	0·155	0·203
	F	3·13	—	0·006	0·006
	1	—	—	0·117	0·120
	2	2·16	0·077	0·060	0·061
	3	—	—	0·030	−0·009
	4	5·13	0·183	0·169	0·229
	5	2·04 (or 0·05)	0·073 (or 0·002)	0·012	−0·040
	6	3·24	0·116	0·111	0·140
	F	0·05 (or 2·04)	—	0·001	−0·001

During exposure of 4-bromobiphenyl, 4-chloribiphenyl, or 4,4′-dibromobiphenyl to potassium at low temperatures, formation of the corresponding anion radicals was indicated by a transient yellow-green color. The solutions immediately became orange and finally bluish. The only observable ESR spectrum was that of biphenyl in the bluish solutions.

DISCUSSION

The halogen-substituted anion radicals appear to decompose by a common pathway but at greatly different rates:



(A) X = F, Cl, Br

(B) X = F, anion observed in ESR
X = Cl, Br no ESR spectrum

(C) X = F, Cl, Br orange; no ESR spectrum

(D) X = F, Cl, Br Biphenylide ESR spectrum

The intermediate C is consistent with the occurrence of the same orange color regardless of the halogen present and with the apparent diamagnetism. The intermediate C probably abstracts a proton from the solvent, and subsequently the biphenyl is reduced by the potassium in solution to give the anion radical. The reaction of lithium metal with chloronaphthalenes in ethyl ether is reported[11] to proceed through the formation of an ion pair which immediately decomposes to form naphthyllithium. Also comparable to the present results was the observation[11] by ESR of only one radical, lithium naphthalenide. The relative stability of the fluorobiphenyl radicals can be attributed to both the relatively high C—F bond energy and the transfer of the unpaired electron to the vacant *d* orbitals of chlorine and bromine, but not fluorine, resulting in the immediate formation of chloride or bromide ions.

2,2′-Difluorobiphenyl did not form an anion radical probably because of non-planarity and the consequently high energy of the lowest normally unoccupied molecular orbital. From electron diffraction measurements,[12] the interannular angle in 2,2′-difluorobiphenyl is 60° ± 5°.

Since a polarogram of 4,4′-difluorobiphenyl revealed only a wave due to solvent (dimethylformamide) reduction, −3·5 v. *vs* Ag/sat. $AgNO_3$, the lowest unoccupied molecular orbital of 4,4′-difluorobiphenyl is much higher in energy than that of biphenyl. The energy of the *p*-band, ($^1B_{2u}$ or ^1L_a), corresponding to the transition from the highest occupied to the lowest unoccupied molecular orbital, increased in the order: biphenyl (247·1 mμ) < 4,4′-difluorobiphenyl (244·0 mμ) < 2,2′-difluorobiphenyl (234·0 mμ). Again, non-planarity appears to be important in the neutral compound.

EXPERIMENTAL

Observed m.p's and sources of the biphenyls were: 4-fluorobiphenyl, m.p. 69°, Pierce Chemical Company; 4,4′-difluorobiphenyl, m.p. 89–90°; Pierce Chemical Company; 3,3′-difluorobiphenyl, City Chemical Company; 2,2′-difluorobiphenyl, m.p. 114–116°; City Chemical Company; 4-chlorobiphenyl, m.p. 72°, K and K Laboratories; 4-bromobiphenyl, m.p. 91°, Eastman Chemicals Company; and 4,4′-dibromobiphenyl, m.p. 164°, Eastman Chemicals Company. Tetrahydrofuran (Eastman Organic Chemicals) was distilled from lithium aluminium hydride, and dimethylformamide (Eastman Spectrograde) was dried over calcium hydride and distilled at 15 mm in glassware connected only by O-ring joints.

A polarographic scan of a solution containing 10^{-3}M, 4,4′-difluorobiphenyl and 0·1M tetra-*n*-butyl ammonium perchlorate in dimethylformamide was made with an instrument described elsewhere.[13, 14]

The UV spectra were obtained on a Cary 14 spectrometer using 1 cm quartz cells. The compounds were all approximately 2×10^{-5}M in spectra grade heptane (Spectroquality; Matheson, Coleman and Bell).

Reductions were carried out with clean potassium surfaces and at temperatures from −110° to −78° depending upon the cold bath.[15] ESR spectra were run with a Varian Associates, Inc., X-Band spectrometer operating with 100 kc/sec modulation and a 12 in electromagnet. The Fieldial was calibrated with the spectrum of potassium nitrosodisulfonate ($a_N = 13{\cdot}05$ gauss). Simulated spectra were obtained with a CDC 3400 computer and CALCOMP plotter.

4,4′-Difluorobiphenyl. The reduction with K proceeded at −78° in THF to give a green soln for which the ESR spectrum was recorded at −80°. When allowed to warm to room temp, the soln changed to an orange color which failed to give an ESR signal. After several hours at room temp the soln became an ill-defined blue-orange color and exhibited an ESR spectrum identical with that observed for the biphenyl anion radical. When the reduction was carried out at a lower temp (−95°) several attempts produced only yellow solns which gave no ESR signal.

4-Fluorobiphenyl. The sample gave a green soln when reduced with K in THF in a bath kept below −80°.

The ESR spectrum, recorded at −85°, was complex and was not interpreted. Warming the soln produced the same orange color and biphenyl radical anion behavior reported above.

2,2'-Difluorobiphenyl. A THF soln of the sample was exposed to a clean K mirror at −95°. A yellow soln formed slowly which failed to give an ESR signal. A comparable result was obtained at −78°. On warming, the solns changed to an orange color which remained at room temp.

3,3'-Difluorobiphenyl. When reduced with K in THF at −95°, this compound produced a purple soln for which the ESR spectrum was recorded at −80°. The soln changes upon warming to room temp but no well-defined colors were observed.

4-Bromobiphenyl, 4-chlorobiphenyl, or 4,4'-dibromobiphenyl. Reduction of these compounds by K in THF at temps varying from −110° to −78° produced in all cases an orange soln which gave no ESR signal. During some experiments it was possible to observe initially a yellow-green color, but this color quickly changed to orange. In all cases after a few days at room temp, the orange soln changed to an ill-defined orange-blue color and gave an ESR spectrum identical with that observed for the biphenyl anion radical.

Acknowledgements—This research was supported in part by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center. L.W.B. expresses appreciation for a predoctoral fellowship from the Division of General Medical Sciences, United States Public Health Service. We thank Doctors E. R. Brown, D. E. Smith and D. F. Shriver for valuable assistance.

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