[CONTRIBUTION FROM THE BATTELLE MEMORIAL INSTITUTE]

THE CHEMISTRY OF HYDRAZYL FREE RADICALS. II. SYNTHESIS AND DISSOCIATION OF TETRA-(4-FLUOROPHENYL)HYDRAZINE[1]

F. BENINGTON, ELEANOR V. SHOOP,[2] AND R. H. POIRIER

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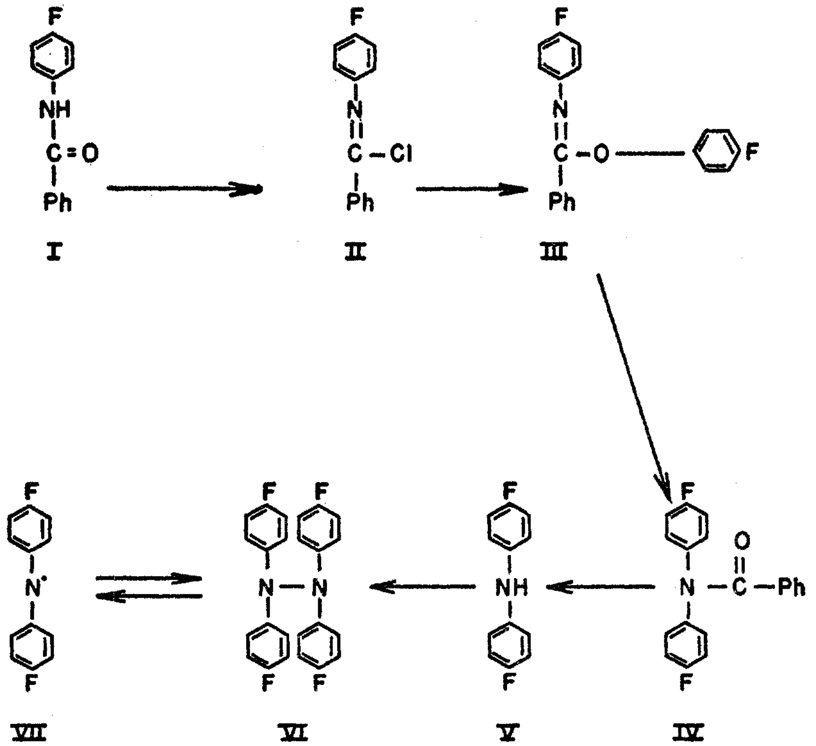
In the further investigation into the use of free radical reagents for detecting and identifying gaseous atoms and free radicals in combustion systems (1), we have prepared tetra-(4-fluorophenyl)hydrazine (VI) and have studied its dissociation. Initially, it was thought that the fluorine atoms in the hydrazine VI would sufficiently enhance its solubility in fluorocarbons so that the resulting solutions could be used in the detection of gaseous free radicals by means of the technique described by Benington (2). However, VI was found to be nearly insoluble in perfluorocarbons, which were considered suitable for combustion studies. This paper is largely concerned with the synthesis of VI and its dissociation into di-(4-fluorophenyl)amino radicals (VII).



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[2] Present location, The American Cyanamid Company, Stamford, Connecticut.

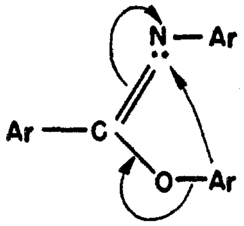
RESULTS

Tetra-(4-fluorophenyl)hydrazine was conveniently synthesized through a series of reactions which had previously been described for other tetraphenylhydrazines. Thus, 4-fluorobenzanilide was converted to the corresponding benzimino chloride (II) by heating with phosphorus pentachloride (3). Treatment of II with sodium 4-fluorophenoxide gave 4-fluorophenylbenzimino-4-fluorophenyl ether (III) (4, 5), which rearranged to N,N-di-(4-fluorophenyl)-benzamide (IV) on heating to 280°. Alkaline hydrolysis of IV led to di-(4-fluorophenyl)amine (V), which was finally oxidized with lead peroxide to tetra-(4-fluorophenyl)hydrazine (VI).

Dilute solutions of VI in benzene at 25° possessed a dark green color which is attributed to the presence of the corresponding diarylamino radical VII, for the color disappeared upon cooling the solution to 6°. Rough magnetic susceptibility measurements indicated that VI dissociated to VII to the extent of 5–8% in benzene at 20°.

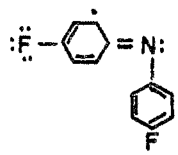
DISCUSSION

The rearrangement of 4-fluorophenylbenzimino-4-fluorophenyl ether (III) to N,N-di-(4-fluorophenyl)benzamide (IV) proceeds with more difficulty than does that of its bromo analog (4), which in turn, rearranges less readily than the unsubstituted phenylbenzimino ether (6). These iminoaryl ethers require respectively 18, 2, and 1 hours of heating at 280° for an 80–85% conversion to the benzamide. Chapman (6) has shown that the presence of electronegative groups on the phenoxy nucleus or electropositive groups on either the phenylimino or benzimido ring enhances the transformation. The transformation was first represented as a unimolecular change in which the oxygen-linked group migrates intramolecularly with the two covalency electrons to the nitrogen atom. Alternatively, he suggested (7) that the attraction of the phenoxy ring to the unshared electrons of the imino-nitrogen initiated the rearrangement. The retarding action of the strong electronegative fluorine atom when present on both the phenoxy and benzimino rings seems to be in agreement with the latter mechanism.



VIII

The enhanced dissociation of VI is explained by assuming that the fluorine atom inductively withdraws electrons from both halves of the molecule, thus causing mutual repulsion of the diphenylamino radicals. Stabilization of the free radical presumably occurs through structures IX and X, which are similar to those proposed in the case of methoxy and dimethylamino substituted diphenylamino radicals (8, 9). However, the nitro group stabilizes the undissociated tetraarylhydrazine by resonating with the hydrazine N atoms (XI) and thus suppress the scission of the N—N bond. Stabilizations of this kind cannot occur when the substituents are electron-releasing groups, since in this case a ten-electron valence shell would be created about the hydrazine nitrogen atom.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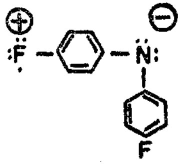
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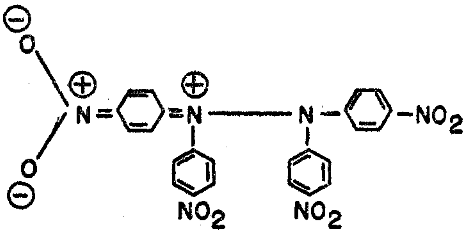
XI

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EXPERIMENTAL

4-Fluorophenol. 4-Ethoxy-1-fluorobenzene was prepared in 26.6% yield according to the procedure of Suter, *et al.* (10). A solution of 4-ethoxy-1-fluorobenzene (163 g.) in 181 cc. of acetic anhydride was refluxed with 326 cc. of 48% hydriodic acid until the evolution of ethyl iodide ceased. After making the reaction mixture nearly neutral with a 20% sodium hydroxide solution, the crude 4-fluorophenol was extracted with three 100-cc. portions of ether. The combined extracts were dried over magnesium sulfate and the solvent was then evaporated on a steam-bath. Vacuum distillation of the residue afforded 79.9 g. (60.5%) of pure 4-fluorophenol, b.p. 74–75°/10.5 mm.

4-Fluoroaniline. 1-Fluoro-4-nitrobenzene (125 g.) in an equal volume of 95% ethanol was selectively hydrogenated at 85° in the presence of 1.0 g. of Raney nickel and 1230 p.s.i. of hydrogen until 2.0 moles of hydrogen was absorbed for each mole of nitro compound. Upon filtering and distilling the hydrogenation mixture, 80 g. (72%) of 4-fluoroaniline, b.p. 186–187° was obtained.

4-Fluorobenzanilide (I). 4-Fluoroaniline, upon treatment with benzoyl chloride in the presence of an excess of 10% aqueous alkali, gave a nearly quantitative yield of 4-fluorobenzanilide (I), m.p. 181° after recrystallization from 95% ethanol.

N-4-Fluorophenylbenzimino-4-fluorophenyl ether (III). A mixture of 18.3 g. of I and 17.7 g. of phosphorus pentachloride was heated on a water-bath (3). After the mixture had completely liquefied and after hydrogen chloride was no longer evolved, the phosphorus oxychloride was stripped from the reaction mixture at reduced pressure. The residue of crude 4-fluorophenylbenzimino chloride (II), without further purification, was dissolved in absolute ether and was treated with an alcoholic suspension of sodium 4-fluorophenoxide. The suspension was prepared by reacting 28.6 g. of 4-fluorophenol with 4.9 g. of sodium chips in 150 cc. of absolute ethanol. The precipitate which separated on stirring this mixture for 24 hours was filtered off and was alternately washed with small portions of dilute hydrochloric acid and 5% aqueous caustic. Recrystallization of this product from absolute methanol gave 16.2 g. (62%) of N-4-fluorophenylbenzimino-4-fluorophenyl ether (III), m.p. 109–110°, as colorless hexagonal plates.

Anal. Calc'd for $C_{19}H_{13}F_2NO$: N, 4.5. Found: N, 4.5.

N,N-Di-(4-fluorophenyl)benzamide (IV). The benzimino ether (III) (19 g.) was sealed off in a Pyrex glass ampoule after evacuating to about 25 mm. The ampoule was then placed in a steel microbomb and heated at 280° for 18 hours (6). The product was recrystallized four times from 95% ethanol. Compound IV (15.2 g.)(80%) was obtained as shining white needles, m.p. 132°.

Di-(4-fluorophenyl)amine (V). A mixture of 30.8 g. of IV, 30.6 g. of potassium hydroxide pellets, and 306 cc. of 95% ethanol was refluxed for 0.5 hours. After cooling, the clear solution was poured into 450 cc. of water and the alcohol was removed by distillation. The residual aqueous solution was extracted several times with ether and the combined organic phases were dried over magnesium sulfate. After evaporating the solvent, the red, oily residue was solidified by cooling to −70° in a Dry Ice-acetone bath. Recrystallization of the crude material gave 19.6 g. of (V) (96%) as pink prisms, m.p. 39–40° (corrected).[3] Sublimation of V failed to alter the melting point, but yielded a colorless product.

Anal. Calc'd for $C_{12}H_9F_2N$: C, 70.2; H, 4.4; N, 6.8.
Found: C, 70.2; H, 4.5; N, 6.7.

Tetra-(4-fluorophenyl)hydrazine (VI). A solution of 18.19 g. of V in 490 cc. of dry benzene was treated with 19.9 g. of lead peroxide (PbO_2), and the mixture was stirred at room temperature for 63 hours. After filtration to remove the lead salts, the filtrate was evaporated to dryness below 30° under reduced pressure. The dark green residue was dissolved in the minimum volume of chloroform and five times this quantity of hot ethanol was added to precipitate the hydrazine (VI) (12). The precipitated material was carefully washed on a filter plate with a small volume of ice-cold chloroform. By twice repeating the precipitation from chloroform-ethanol, 2.51 g. of pure VI was obtained as snow-white prisms, m.p. 121° (dec.). This compound is photosensitive and becomes deep green upon exposure to active light.

Anal. Calc'd for $C_{24}H_{16}F_4N_2$: N, 6.8. Found: N, 6.7.

Dissociation of VI *into di-(4-fluorophenyl)amino* (VII). A 0.09 mol-% solution of VI in thiophene-free benzene at 25° exhibited the deep green color which is characteristic of the free diarylamino radical (VII). By cooling the solution to a temperature near the freezing point of the solvent, it became nearly colorless; this change is attributed to the decrease in the dissociation of VI with decreasing temperature.

Rough magnetic susceptibility measurements were made on a 0.09 mol-% solution of VI in benzene using a Gouy balance similar to the instrument described by Michaelis (13). Unfortunately, a relatively high instrument error in conjunction with a moderately rapid rate of disproportionation[4] of VI led to uncertain values for the extent of dissociation of VI at 20°. By correcting for these errors, it was estimated that VI is 5 to 8% dissociated under these conditions.

SUMMARY

1. The preparation of tetra-(4-fluorophenyl)hydrazine and several new fluorine-containing intermediates is reported.

2. An explanation for the relatively slow transformation rate of N-4-fluorophenylbenzimino-4-fluorophenyl ether in the Chapman rearrangement is presented.

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[3] A preparation of V by the Ullman method, in 9.6% yield has been reported by Leonard and Sutton (11); the reported m.p. is 37.5°.

[4] By analogy to similar hydrazines (8), the disproportionation products should be di-(4-fluorophenyl)amine and N,N′-bis-(4-fluorophenyl)-2,6-difluoro-9,10-dihydrophenazine.

3. The dissociation of tetra-(4-fluorophenyl)hydrazine to the di-(4-fluorophenyl)amino radical in benzene solution was shown to be 5 to 8% at room temperature.

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REFERENCES

(1) POIRIER, KAHLER, AND BENINGTON, *J. Org. Chem.*, **17**, 1437 (1952).
(2) BENINGTON, *Third Symposium on Combustion, Flame and Explosion Phenomena*, Williams and Wilkins Company, Baltimore, 1949, p. 448.
(3) WALLACH, *Ann.*, **184**, 77 (1877).
(4) CROUNSE AND RAIFORD, *J. Am. Chem. Soc.*, **67**, 875 (1945).
(5) HANTZSCH, *Ber.*, **26**, 927 (1893).
(6) CHAPMAN, *J. Chem. Soc.*, 1743 (1927).
(7) CHAPMAN, *Ann. Repts on Progr. Chem.* (*Chem. Soc. London*), **26**, 122 (1929).
(8) WIELAND AND LECHER, *Ann.*, **381**, 206 (1911).
(9) WIELAND, *Ber.*, **48**, 1078 (1915).
(10) SUTER, LAWSON, AND SMITH, *J. Am. Chem. Soc.*, **61**, 162 (1939).
(11) LEONARD AND SUTTON, *J. Am. Chem. Soc.*, **70**, 1564 (1948).
(12) CHATTAWAY AND INGLE, *J. Chem. Soc.*, 1090 (1895).
(13) MICHAELIS, *Physical Methods of Organic Chemistry*, Volume I, Interscience Publishers, Inc., New York, 1946, p. 1213.