withdrawing group the relative rate ratio $(C_6H_5X/C_6H_6)K$ is decreased.[3] This decrease in $(C_6H_5X/C_6H_6)K$ is explained by assuming that as the radical nucleus becomes more electron deficient it becomes more difficult for it to react with the already electron deficient substituted benzene. The reverse, of course, is true if one of the substituents either on the benzene or the phenyl radical is electron donating and the other electron withdrawing.[4]

However, an examination of the examples of this phenomena compiled by Augood and Williams[4] suggests that as the substituents on the phenyl radical become more electron withdrawing the $(C_6H_5X/C_6H_6)K$ ratio may approach unity as a limit, rather than decreasing indefinitely: the lowest $(C_6H_5X/C_6H_6)K$ value reported was 0.94 for the competition of nitrobenzene and benzene for *p*-nitrophenyl radicals. This rate ratio we feel is within error of unity. If the $(C_6H_5X/C_6H_6)K$ values are approaching unity (or a related number) as a limit an explanation quite different from the one offered above would be required.

We felt the problem could be resolved by determining the $(C_6H_5Cl/C_6H_6)K$ for 3,4-dichlorophenyl radicals. Since the competitive reaction of benzene and chlorobenzene for phenyl radicals[2] yields a $(C_6H_5Cl/C_6H_6)K$ of 1.4 and for *p*-chlorophenyl radicals[3] a value of 1.0, we expected 3,4-dichlorophenyl radicals to fall below unity, confirming the original explanation, or remain at unity, The results of our experiments are recorded in Fig. 1.

The competitive reaction with phenyl radicals was carried out to compare our method of analysis, principally vapor phase chromatography, with those of previous investigators. The $(C_6H_5Cl/C_6H_6)K$ value obtained agrees within error with those previously reported. Competition of benzene and chlorobenzene for 3,4-dichlorophenyl radicals yields a $(C_6H_5Cl/C_6H_6)K$ of 0.73 ± .03 thus confirming the original explanation.

We believe the $(C_6H_5Cl/C_6H_6)K$ of 0.73 represents the first unequivocal example of a substituted benzene reacting more slowly than benzene in a simple Gomberg reaction[5] as a result of electronic influences.[6]

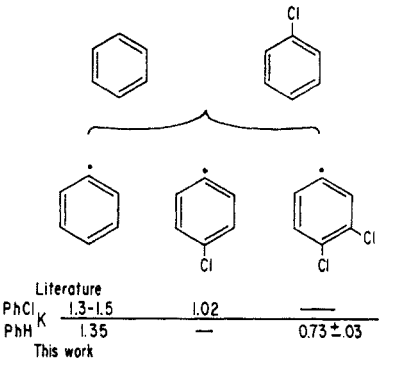

Fig. 1. Competition of benzene and chlorobenzene for various phenyl radicals

EXPERIMENTAL

Competitive reaction with phenyl radicals. Benzene diazonium chloride (0.1 mole) was prepared in the usual way[7] and the aqueous solution was then stirred vigorously with a mixture of 156 g. (2.0 moles) of benzene and 225 g. (2.0 moles) of chlorobenzene the temperature being maintained between 0° and 10°. To this mixture was rapidly added a solution of sodium acetate trihydrate, 50 g. dissolved in a minimum of water. The reaction mixture was allowed to come to room temperature and the reaction was followed by measuring the nitrogen evolved. Eighty per cent of the theoretical nitrogen was evolved in 12 hr. at room temperature. The temperature was gradually raised to 70° and kept there until nitrogen evolution ceased (total evolved nitrogen, 95%). The organic phase was washed with water, dried over magnesium sulfate and the mixed solvent removed through a 3 ft. Todd distilling apparatus. The biphenyl and chlorinated biphenyl mixture was then distilled from residue through a simple Claisen head, b.p. 115–125°/3 mm., yield 30% (based on analysis of product). The distillate was analyzed directly by vapor phase chromatography.[8] Analysis of the chromatograms indicated a $(C_6H_5Cl/C_6H_6)K$ of 1.35.

Competitive reaction with 3,4-dichlorophenyl radicals. 3,4-Dichlorobenzene diazonium chloride (0.1 mole) was treated exactly as described above. After removal of the mixed solvent the chlorinated biphenyl mixture was distilled from the residue, b.p. 130–170°/3 mm., yield 55% (based on analysis of product).

Analysis: Run No. 1, $(C_6H_5Cl/C_6H_6)K$ (from % C) 0.70, (from % Cl) 0.74, (from V.P.C.) 0.76; Run No. 2, $(C_6H_5Cl/C_6H_6)K$ (from V.P.C.) 0.75, Average equals 0.73±.03.

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(3) J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1425 (1955).

(4) D. R. Augood and G. H. Williams, *Chem. Revs.*, **57**, 170 (1957).

(5) M. J. S. Dewar and A. N. James have reported a very similar result during the decomposition of 3,5-dibromo-1,4-diazo oxide in aromatic solvents which they believe proceeds through a highly polar diradical. *J. Chem. Soc.*, 4265 (1958).

(6) Similar decreases in activity are recorded for particularly bulky substituents, *i.e. t*-butyl. J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 3352 (1954).

(7) D. F. DeTar and Abdul A. Kazimi, *J. Am. Chem. Soc.*, **77**, 3843 (1955).

(8) Vapor phase chromatograms were obtained with a Perkin Elmer model 154 Vapor Fractometer, using a 1.5 meter 10% silicone impregnated firebrick column at temperatures between 170° and 200°. Areas under the chromatographic peaks were measured with an Ott compensating planimeter.

Fluorinated Diuretic Agents

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Received December 17, 1959

The exceptional diuretic potency of 6-chloro-7-sulfamyl-1,2,4-benzothiadiazine-1,1-dioxide[2] and

of its 3,4-dihydro derivative[3] prompted us to synthesize the corresponding 6-fluoro compounds. Treatment of *m*-fluoroaniline with chlorosulfonic acid in the presence of sodium chloride gave the amorphous 1,3-bissulfonylchloride which on treatment with ammonia yielded crystalline 6-amino-4-fluorobenzene-1,3-disulfonamide (I). Cyclization with boiling formic acid[2] produced 6-fluoro-7-sulfamyl-1,2,4-benzothiadiazine-1,1-dioxide (II) reduced[3] by sodium borohydride to 6-fluoro-7-sulfamyl-3,4-dihydro-1,2,4-benzothiadiazine-1,1-dioxide (III). I, II, and III were potent diuretic agents in the saline-loaded female dog.[4]

EXPERIMENTAL[5]

6-Amino-4-fluorobenzene-1,3-disulfonamide (I). *m*-Fluoroaniline (28.2 g.) was added slowly to a cooled suspension of 0.5 g. sodium chloride in chlorosulfonic acid (50 g.) and the mixture then heated for 2.5 hr. by means of an oil bath held at 150–160°. The solution was cooled and poured with stirring into a mixture of ice and water. The gummy bissulfonyl chloride (9 g.) was collected by filtration, washed, dried, and added to 80 ml. of 30% ammonium hydroxide. The solution was heated for 1 hr. at 90°, concentrated at atmospheric pressure to a small volume and cooled yielding 4.65 g. of I. m.p. 220–223°. Recrystallization from water gave the analytical specimen, m.p. 233–235°, λ_{max} 261, 301 mμ, log ε 4.32, 3.53.

Anal. Calcd. for $C_6H_8FN_3O_4S_2$: C, 26.79; H, 2.99; F, 7.05; S, 23.78; N, 15.62. Found: C, 26.71; H, 2.88; F, 6.80; N, 15.16; S, 23.27.

6-Fluoro-7-sulfamyl-1,2,4-benzothiadiazine-1,1-dioxide (II). A mixture of I (4.47 g.) and 85% formic acid (100 ml.) was boiled for 2 hr. and then concentrated to dryness *in vacuo*. The residue was taken up in hot water and a small amount of insoluble material removed. Concentration of the solution and cooling yielded 3.23 g. of II, m.p. 285–290°. Further recrystallization from water raised the melting point to 309–310°, λ_{max} 271 mμ, log ε 4.08.

Anal. Calcd. for $C_7H_6FN_3O_4S_2$: C, 30.11; H, 2.16; F, 6.80; N, 15.05; S, 22.96. Found: C, 30.24; H, 2.30; F, 6.26; N, 14.83; S, 22.85.

6-Fluoro-7-sulfamyl-3,4-dihydro-1,2,4-benzothiadiazine-1,1-dioxide (III). A solution of 1.4 g. of II in 200 ml. of methanol was cooled to 0° and treated with a cold solution of sodium borohydride (3 g.) in 30 ml. of water. After standing for 1 hr. at 0° and for 14 hr. at 10° the solution was treated dropwise with acetic acid to destroy the excess hydride and then concentrated *in vacuo*. Extraction with ethyl acetate gave crude III which was crystallized from water yielding 0.67 g. of 3,4-dihydro compound, m.p. 218–220°. Pure III melted at 218–221°, λ_{max} 266, 305 mμ, log ε 4.35, 3.56.

Anal. Calcd. for $C_7H_8FN_3O_4S_2$: C, 29.89; H, 2.87; F, 6.75; N, 14.94; S, 22.80. Found: C, 30.03; H, 2.88; F, 6.32; N, 14.62; S, 22.39.

6-Propionylamino-4-fluorobenzene-1,3-dipropionylsulfonamide (IV). A solution of 0.81 g. of I in 100 ml. of propionic anhydride was boiled for 2 hr. The solvent was removed *in vacuo* and the residue crystallized from methanol yielding 0.58 g. of tripropionate (IV), m.p. 238–240°, λ_{max} 222, 268 mμ, log ε 4.21, 4.13.

Anal. Calcd. for $C_{15}H_{20}FN_3O_4S_2$: C, 41.18; H, 4.60; F, 4.34; N, 9.60; S, 14.66. Found: C, 41.58; H, 4.53; F, 4.10; N, 9.40; S, 14.39.

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(1) This material represents part of the professional thesis submitted by Srta. Carmen Pelayo to the Facultad de Química, Universidad Nacional Autónoma de México.

(2) F. C. Novello and J. M. Sprague, *J. Am. Chem. Soc.*, **79**, 2028 (1957).

(3) G. De Stevens, *Experientia*, **14**, 463 (1958).

(4) We wish to thank Mr. R. H. Tust of the Pharmacology Dept. of Eli Lilly for these assays.

(5) Melting points are uncorrected and ultraviolet absorption spectra were determined in 96% ethanol.

Preparation of Fluorocarbon α-Olefins

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Received December 21, 1959

Previous workers have shown that thermal decomposition of the alkali metal salts of perfluorocarboxylic acids produces high yields of olefins containing one less carbon atom.[1] When small

$$R_f CF_2—CF_2CO_2M \longrightarrow R_f—CF=CF_2 + MF + CO_2$$

amounts of the salt are used, α-olefin of high (≥ 90%) isomeric purity is obtained. As the bed depth of the salt is increased, the isomeric purity of the olefinic product decreases. The α-olefin of highest purity is produced early in the pyrolysis, and as the reaction progresses the product contains larger amounts of isomeric internal olefins. Since their boiling points generally differ by only a few degrees, the separation of the terminal and internal olefins is tedious.

Contrary to previous reports,[2] perfluorocarboxylic acids also undergo a similar general reaction to yield fluorocarbon olefins having one less carbon.

$$R_f—CF_2—CF_2—CO_2H \xrightarrow[\Delta]{} R_f—CF=CF_2 + CO_2 + HF$$

We have prepared olefins in good yield from linear and branched aliphatic perfluorocarboxylic acids, as well as linear ω-hydroperfluorocarboxylic acids.

The reaction is carried out by passing an anhydrous mixture of the acid and an inert gaseous diluent through a heated tube at temperatures of 400–650°. The flow rate of the inert gas is adjusted so that residence time of the acid in the hot zone of the tube is about five seconds. Decarboxylation appears to occur most readily when the acids are in vaporized form. Little or no isomerization of terminal to internal olefin is observed in the pyrolysis. This may be due to differences in catalytic activity of hydrogen fluoride and alkali metal fluorides, or to the low concentration of fluoride in the hot reaction zone, or both.

(1) J. D. LaZerte, U. S. Patent **2,601,536** issued June 24, 1952; L. J. Hals, T. S. Reid, and G. H. Smith, U. S. Patent **2,668,864**, issued Feb. 9, 1954; J. D. LaZerte, L. J. Hals, T. S. Reid, and G. H. Smith, *J. Am. Chem. Soc.* **75**, 4525 (1953).

(2) T. S. Reid, G. H. Smith, and W. H. Pearlson, U. S. Patent **2,746,997**, issued May 22, 1956.