

Anal. Calcd. for $C_{26}H_{23}O_5N_2I_4Na$: N, 2.55; I, 45.4. Found: N, 2.51; I, 45.2.

1,2,5,6-Dibenzanthranil-9-ureidothyroxine.—Treatment of the sodium salt of the 1,2,5,6-dibenzanthranil-9-ureidothyroxine with ethanolic acetic acid as above gave a 73% yield of the free acid, m.p. 177–180° (dec.). Formol titration of this material indicated negligible free amino group nitrogen.

Sodium Salt of 3,4-Benzpyrenyl-5-ureidothyroxine (IIIc).—One hundred milligrams (0.34 millimole) of 3,4-benzpyrenyl-5-isocyanate¹⁵ and 0.272 g. (0.34 millimole) of the sodium salt of thyroxine in 10 ml. of anhydrous pyridine were treated as described above. The product, weight 0.155 g., yield 42%, darkened at 160° and melted with decomposition at 171–172°.

Anal. Calcd. for $C_{36}H_{21}O_5N_2I_4Na$: N, 2.56; I, 46.4. Found: N, 2.51; I, 46.2.

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(15) H. J. Creech, *THIS JOURNAL*, **63**, 576 (1941).

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Replacement of the Primary Aromatic Amino Group by Hydrogen Using Diazonium Fluoroborates

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Many reagents have been used to replace the primary aromatic amino group by hydrogen; an excellent review of these methods has been given by Kornblum.^{1a} No one of these methods is universally applicable, and the yields vary considerably with both the method and the amine used; all of these deaminations are carried out using the diazotized amine. Usually the diazonium salt is not isolated; occasionally, however, stabilized dry diazonium salts have been used. Thus Hodgson and Marsden² stabilized diazotized amines with naphthalene-1,5-disulfonic acid or 2-naphthol-1-sulfonic acid and decomposed the resulting dry salt with ethanol in the presence of zinc or copper; they reported yields of the order of 90%. However, some workers have been unable to duplicate these results.³ Leslie and Turner⁴ obtained a 78% yield of 2-nitro-3'-bromobiphenyl from 4,4'-diamino-2-nitro-3'-bromobiphenyl by decomposing the bis-diazonium fluoroborate salt in absolute ethanol containing sulfuric acid. In this connection, it is of interest that Niemann, Benson and Mead⁵ report the incidental preparation of about 7% of ethyl 3-fluoro-4-methoxybenzoate simultaneously with the formation of ethyl 3,5-difluoro-4-methoxybenzoate in about 28% yield by the Schiemann reaction⁶ from 2-methoxy-3-fluoro-5-carbethoxybenzenediazonium fluoroborate, some deamination

occurring along with fluorine substitution. Some light may be thrown on the reason for this deamination by the observation of Schmelkes and Rubin⁷ who noted that if all the methanol used in washing the diazonium fluoroborate was not completely removed, some *p*-nitrotoluene was obtained in addition to the expected 2-fluoro-4-nitrotoluene in preparing the latter by the Schiemann reaction.

With the above facts in mind, it seemed desirable to see if more consistent yields in the deamination reaction could be obtained using the diazonium fluoroborates. These salts can be obtained in good yield and in excellent purity and, in addition, most of them are quite stable.⁸ This paper reports the results obtained by decomposing several different types of diazonium fluoroborates with ethanol in the presence of zinc; investigation of the reaction of diazonium fluoroborates with hypophosphorus acid and other deaminating reagents is underway. The yields obtained (based on the diazonium fluoroborate used) are reported in Table I; they are in most cases between 70–80%. The heterocyclic amines used gave quite low yields. Interestingly enough, the yield of benzene from benzenediazonium fluoroborate was rather poor (46.5%); in this case, a 1% yield of biphenyl was produced—the only instance in which a coupling reaction occurred. Another curious fact about this reaction was that appreciable amounts of diethyl acetal were formed; this compound was not observed in any of the other deaminations.

TABLE I

Amine	Yield, %	Diazonium fluoroborate Dec. point, °C.	Product obtained	Yield of product from diazonium fluoroborate, %
Aniline	91	104	Benzene	46.5 ^a
<i>o</i> -Toluidine	88	104	Toluene	82.2
<i>m</i> -Toluidine	84	104	Toluene	73.7
<i>p</i> -Toluidine	90	106	Toluene	84.8
<i>o</i> -Chloroaniline	91	166	Chlorobenzene	79.4
<i>m</i> -Chloroaniline	98	148	Chlorobenzene	82.6
<i>p</i> -Chloroaniline	89	153	Chlorobenzene	85.2
<i>p</i> -Phenetidine	80	103	Phenetole	71.0
Ethyl <i>p</i> -amino-benzoate	97	95	Ethyl benzoate	69.2
<i>p</i> -Nitroaniline	88	141	Nitrobenzene	80.0 ^b
Benzidine	90	142	Biphenyl	82.5
β -Naphthylamine	93 ^c	103	Naphthalene	64.1
<i>m</i> -Aminobenzo-trifluoride	87	148	Benzotrifluoride	74.3
2-Bromo-4-methyl-aniline	87	148	<i>m</i> -Bromotoluene	69.0
6-Aminoquinoline	95	85–93	Quinoline	34.0
3-Aminoquinoline	91	93	Quinoline	31.3
3-Aminopyridine	..	15	Pyridine	26.3 ^d

(1) The work reported in this paper is taken from the master's thesis submitted by Jack R. Graham to the Graduate School of the University of North Carolina, June, 1952.

(1a) N. Kornblum, in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 262.

(2) H. Hodgson and E. Marsden, *J. Chem. Soc.*, 207 (1949).

(3) Reference 1a, page 285.

(4) M. Leslie and E. Turner, *J. Chem. Soc.*, 1590 (1933).

(5) C. Niemann, A. Benson and J. Mead, *THIS JOURNAL*, **63**, 2204 (1941); also a private communication from Dr. Niemann.

(6) A. Roe, in "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 193.

^a A 1% yield of biphenyl was also obtained. ^b In this run, zinc was omitted; using zinc, the yield was only 58%. ^c Pure β -naphthylamine is necessary for preparation of stable diazonium fluoroborate. ^d A 12.2% yield of 3-ethoxy-pyridine was also obtained.

The use of zinc seems to catalyze the reaction and also to cut down the formation of ethyl ether, confirming the observation of Hodgson²; only in

(7) C. Schmelkes and M. Rubin, *THIS JOURNAL*, **66**, 1631 (1944).

the case of 3-aminopyridine was any ethoxy compound formed (12.3% yield). In the case of *p*-nitrobenzenediazonium fluoborate the presence of zinc reduced the yield of nitrobenzene to 58% and increased the amount of tarry residue; the yield without zinc was 80%.

The reaction was carried out by adding the pure diazonium fluoborate to a flask containing absolute ethanol and powdered zinc; the addition of the salt was carried out slowly enough so that the solution is refluxing gently. The solution was then filtered from the zinc, the alcohol distilled off, and the alcoholic distillate diluted with several times its volume of water or brine; the hydrocarbon separating out was then removed in a separatory funnel. The residue from the alcoholic distillate was made slightly alkaline and subjected to steam distillation; the organic material from the two distillations was purified in the usual manner.

Experimental

Preparation of Diazonium Fluoborates.—The diazonium fluoborates were prepared in the usual manner⁸; the yields are reported in Table I. It was found that better results were obtained with diazonium fluoborates prepared by diazotization in fluoboric acid than with those prepared by diazotization in hydrochloric acid followed by addition of sodium fluoborate. The yields of diazonium fluoborate were increased some if the solutions were further cooled by the addition of Dry Ice directly to the diazotized solution before filtration. All the diazonium fluoborates were washed as indicated in reference 6 to remove impurities, and were dried by spreading thinly on absorbent paper suspended on a wire rack. The preparation of the quinoline-diazonium fluoborates⁹ and 3-pyridinediazonium fluoborates⁹ required slightly different conditions as noted in the references given; 3-pyridinediazonium fluoborate decomposes at room temperature unless kept moist with petroleum ether. Of the other diazonium fluoborates reported, *o*-toluenediazonium fluoborate was fairly unstable, decomposing in a desiccator in 24 hours; *m*-toluenediazonium fluoborate decomposed within 48 hours.

Decomposition of Diazonium Fluoborates.—The diazonium salts were all decomposed in the same manner, as follows: One-tenth of a mole of the diazonium fluoborate was added slowly to 300 ml. of absolute ethanol and 15 g. of zinc dust contained in a one-necked 500-ml. round-bottomed flask fitted with an addition tube, to the top of which was attached a reflux condenser. The addition of the salt was slow enough to prevent violent reaction, but rapid enough to maintain a gentle reflux of the solution; a deep red color appeared as the salt was added. When all the salt had been added, the solution was refluxed gently for an hour, during which time the solution turned light straw in color. The solution was cooled, filtered from the zinc residue into a distillation flask, and the ethanol distilled off through an efficient fractionating column. The ethanol distillate was treated with six times its volume of saturated salt solution (except in experiments with the chloroanilines, when water was used); any organic product separating was removed in a separatory funnel. The residue from the distillation was made slightly alkaline and steam distilled. Any organic matter from the steam distillation was combined with that from the alcoholic distillation and purified by distillation or recrystallization. In every case, the residue in the distillation flask was then acidified and further distilled with steam; in no case did any organic matter distil from the acid solution. (The residue from the steam distillation was then extracted with ether to extract any organic material remaining; none was obtained in any case.)

In the case of benzenediazonium fluoborate, distillation of the organic fraction from the alcohol distillation gave in addition to benzene 9.1 g. of liquid, b.p. 102°, *n*_D²⁰ 1.3780; this proved to be diethyl acetal. From the basic steam distillation, 0.4 g. of biphenyl (m.p. 70°) was the only product isolated.

Variations in the decomposition procedure were tried, but found to be unsatisfactory. The addition of zinc dust to a suspension of the diazonium salt in alcohol produced greater amounts of tarry material and very low yields. Addition of an intimate mixture of zinc dust and the diazonium fluoborate to ethanol resulted in a more vigorous reaction; in the case of benzenediazonium fluoborate some fluorobenzene was isolated from the reaction mixture using this procedure.

The reaction products were in all cases known and were identified by melting point or boiling point and refractive index.

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Some α -Arylsulfonamido Acids and Amides

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This note will serve to record data on the preparation and properties of some previously undescribed benzene-, toluene- and *p*-ethylbenzenesulfonyl derivatives of alanine, sarcosine, α -aminoisobutyric acid and leucine. Techniques previously used^{1,2} were adapted to the preparation of the arylsulfonyl chloride; the acyl chloride from the arylsulfonamido acid and thionyl chloride; and the sulfonamido acid anides from the acid chlorides and ammonia. The reactions for the preparation of the leucine derivatives from *p*-ethylbenzenesulfonyl chloride are given in detail as typical. Properties

TABLE I

Compound	Yield, %	M.p. (°C., cor.)	Analyses ^a	
			Calcd.	Found
α -BENZENESULFONAMIDO-				
isocaproic acid	59	116–117 ^b	272.3 NE	272.1 NE
isobutyric acid	67.3	142–143 ^c	243.3 NE	241.4 NE
isocapramide	61.2	208–209	10.4 N	10.4 N
isobutyramide	55.4	195–196	11.6 N	11.6 N
propionamide	..	179	12.3 N	12.3 N
α -(<i>N</i> -Methylbenzenesulfonamido-)				
acetamide	..	174	12.3 N	12.3 N
α -Toluenesulfonamido-				
isocaproic acid	55	118–119 ^d	285.3 NE	286.5 NE
isobutyric acid	51.4	143–144 ^e	257.3 NE	256.3 NE
isocapramide	54.7	233–234	9.5 N	9.7 N
isobutyramide	69.5	221–222	10.9 N	10.6 N
α -(<i>p</i> -Ethylbenzenesulfonamido-)				
isocaproic acid	48	117–118	299.4 NE	299.9 NE
			4.7 N	4.8 N
isobutyric acid	60.5	131–132	271.3 NE	269.3 NE
			5.16 N	5.03 N
isocapramide	65.5	202–203	9.1 N	9.1 N
isobutyramide	66	198–199	10.4 N	10.2 N
acetic acid	..	128–129	5.45 N	5.53 N
acetamide	..	190–191	10.9 N	10.9 N

^a NE, neutral equivalent; N, nitrogen (Micro Tech Laboratory, Skokie, Illinois). ^b E. Fischer, *Ber.*, **33**, 2380 (1900). Reported m. p. 146°. We have no explanation for this discrepancy. ^c F. Fichter and M. Schmid, *Helv. Chim. Acta.*, **3**, 711 (1920). Reported m.p.s. 144° (benzene); 147° (toluene). ^d E. Fischer and N. Lipschitz, *Ber.*, **48**, 365 (1915). Reported m. p. 124°.

(1) R. H. Wiley and H. L. Davis, *THIS JOURNAL*, **73**, 494 (1951).

(2) R. H. Wiley, H. L. Davis, D. E. Gensheimer and N. R. Smith, *ibid.*, **74**, 936 (1952).

(8) A. Roe and F. H. Hawkins, *THIS JOURNAL*, **71**, 1785 (1949).

(9) A. Roe and F. H. Hawkins, *ibid.*, **69**, 2443 (1947).