

614. *Studies of Trifluoroacetic Acid. Part VIII.* Diazotisations of Aromatic Amines in Aqueous Trifluoroacetic Acid and Other Perhalogeno-carboxylic Acids.*

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Various aromatic amines, when diazotised in aqueous trifluoroacetic acid with sodium nitrite, give solid diazonium trifluoroacetates having the apparent formula $R \cdot N_2^+ - O_2C \cdot CF_3, CF_3 \cdot CO_2H$. Analogous salts are given by other acids, including heptafluorobutyric, trichloroacetic, and perfluoroadipic acids. Many of the acid salts may be kept for some time with little decomposition. They undergo the usual replacement and coupling reactions of diazonium salts in aqueous solution.

It was expected that diazotisation of aromatic amines would proceed normally in aqueous trifluoroacetic acid, since the latter is ionised to a considerable extent in dilute aqueous solution (Swarts, *Bull. Acad. roy. Belg.*, 1922, **8**, 343; Henne and Fox, *J. Amer. Chem. Soc.*, 1951, **73**, 2323). Normal reactions occurred with aniline, *p*-nitroaniline, and *p*-anisidine, the diazo-solution giving a good yield of the corresponding azo- β -naphthol coupling-product in each case. However, when *p*-toluidine, mesidine, 2:4-dimethyl-, *p*-chloro-, and *p*-bromo-aniline, in fairly concentrated trifluoroacetic acid solutions, were treated with aqueous sodium nitrite, colourless crystalline solids were deposited during the reactions. Addition of trifluoroacetic acid to aqueous toluene-*p*-diazonium chloride produced a lower layer from which a little of a similar solid crystallised. Solids were precipitated also, during diazotisations of aniline, *p*-toluidine, and *p*-chloroaniline in heptafluorobutyric acid,

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and of *p*-toluidine in trichloroacetic, perfluorohexanoic, tetrafluorosuccinic, and perfluoro-adipic acids. Investigation showed that these solid derivatives were double salts, each containing a free acid molecule as well as the diazonium carboxylate; analysis and equivalent weight determinations suggested the general formula $R \cdot N_2^+ \cdot O_2C \cdot R' \cdot R'' \cdot CO_2H$. Cryoscopic determinations on aqueous solutions (*ca.* 2%) of the acid trifluoroacetates of diazotised *p*-toluidine and mesidine revealed that about 3.8 g.-ions were present per g.-equiv. of the salts. Goldschmidt (*Ber.*, 1890, **23**, 3220) has shown, by depression of the freezing point of water, that diazonium salts of mineral acids are dissociated almost completely in dilute solutions.

After the isolation of each diazonium acid salt, β -naphthol in alkali was added to the combined aqueous mother-liquors and washings. The corresponding azo- β -naphthol coupling-derivatives were isolated in all cases, in yields which, in conjunction with those of the solid salts, showed that the diazotisations had been complete or nearly so.

In general, the solid diazonium salts were relatively soluble in water and in polar organic solvents such as ethyl alcohol, acetone, and dioxan, and almost insoluble in non-polar organic solvents such as benzene, ether, light petroleum, chloroform, etc. In the solid state the salts were stable in the cold, and most were but little affected by being stored for several weeks. None has detonated even on being struck, although obviously, until more is known of their properties, care should be exercised in handling them. Each salt has a definite melting point, which is usually low, and at that temperature decomposition, vigorous but not apparently explosive, occurs. The bonding of the free acids in the acid salts appears to be weak, although all the salts were dried for several hours at 15° *in vacuo* over phosphoric oxide with no obvious decomposition. Similar drying for a week over phosphoric oxide or sodium hydroxide caused only a small increase in the equivalent. When mesitylenediazonium acid trifluoroacetate was washed with wet ether a significant increase (*ca.* 20%) in the equivalent was observed.

In aqueous solution, the acid salts exhibited the usual reactions of diazonium salts, and a number of replacement and coupling reactions of the diazonium groups of the aryl components were carried out. These proceeded smoothly and the expected products were obtained in good yields.

Stable solid diazo-compounds are well known, the most common being stabilised as complex salts with metallic halides, etc., with complex anions (*e.g.*, fluoroborate), or as salts of arylsulphonic acids (Saunders, "The Aromatic Diazo-compounds and their Technical Applications," Arnold, London, 1947, p. 69). It appears, however, that few acid salts of the general type reported herein have been described. Water-soluble double salts of diazonium chlorides and hydrogen chloride are known (Hirsch, *Ber.*, 1897, **30**, 1148; Hantzsch, *ibid.*, p. 1153) but these usually are of the form $(ArN_2Cl)_3 \cdot HCl$, only a few having equimolar proportions of acid. Hydrated diazonium acid fluorides have been reported also (Hantzsch and Vock, *Ber.*, 1903, **36**, 2059). For these salts Hantzsch at first postulated a structure involving two triply-bound quinquevalent nitrogen atoms but later suggested that the acid was loosely attached (*Ber.*, 1930, **63**, 1786). Trifluoroacetic acid and other perfluoro-acids are known to form addition complexes, apparently of definite composition, with ethers and tertiary amines (Hauptschein and Grosse, *J. Amer. Chem. Soc.*, 1951, **73**, 5139). The double diazonium-perhalogeno-acid salts are virtually completely dissociated in solution and the binding forces are thus weak.

EXPERIMENTAL

Preparation of Diazonium Acid Salts.—To a mixture of the amine, a small volume of water, and the perhalogeno-acid (about 3 equiv. proportions) at 0–5° was added a concentrated aqueous solution (*ca.* 40%) of sodium nitrite until a very slight excess was present (starch-iodide test). In general, a precipitate appeared as the diazotisation proceeded; when the amine salt was not completely soluble, the precipitate usually changed its crystalline form during the reaction, conversion into the diazonium salt being complete. The precipitate was filtered off, washed with small quantities of ice-cold water, and dried, finally for several hours *in vacuo* at 15° over phosphoric oxide. Equivalents were determined by titration in aqueous solution against standard alkali.

The mother-liquors and washings were combined, and treated with β -naphthol in aqueous sodium hydroxide; the precipitated azo- β -naphthol derivative was filtered off, washed, dried, and recrystallised, usually from ethyl alcohol or from acetone.

Details of the *diazonium acid salts* prepared are given in the Table. It is probable that higher yields could be obtained in many cases by using more concentrated solutions and less wash-liquid.

Preparation of diazonium acid salts.

No.	Amine		Acid, R·CO ₂ H		H ₂ O (c.c.)	NaNO ₂ (g.)	Acid salt	
	Formula	g.	R	g.			g.	M. p. (decomp.)
I	<i>p</i> -C ₆ H ₄ Me·NH ₂	3·32	CF ₃	10·7	13·0	2·38	5·40	70—72°
II	<i>sym.</i> -Me ₂ C ₆ H ₃ ·NH ₂ ...	1·13	CF ₃	3·0	6·0	0·68	1·04	65
III	2 : 4 : 1-C ₆ H ₃ Me ₂ ·NH ₂	1·10	CF ₃	3·0	2·0	0·73	0·35	68
IV	<i>p</i> -C ₆ H ₄ Cl·NH ₂	2·50	CF ₃	8·9	2·0	1·55	2·53	71
V	<i>p</i> -C ₆ H ₄ Br·NH ₂	3·68	CF ₃	8·9	6·0	1·73	3·11	66
VI	<i>p</i> -C ₆ H ₄ Me·NH ₂	1·06	C ₃ F ₇	6·5	12·0	0·83	4·11	50—53
VII	NH ₂ Ph	0·49	C ₃ F ₇	3·4	1·5	0·43	1·45	31—34
VIII	<i>p</i> -C ₆ H ₄ Cl·NH ₂	0·67	C ₃ F ₇	3·8	2·0	0·46	2·27	75
IX	<i>p</i> -C ₆ H ₄ Me·NH ₂	2·64	CCl ₃	13·0	10·0	2·10	9·15	88

No.	Acid salt Formula	Required			Found			Azo- β -naphthol deriv.	
		C (%)	H (%)	Equiv.	C (%)	H (%)	Equiv.	g.	M. p.
I	C ₁₁ H ₈ O ₄ N ₂ F ₆ ^f ...	38·2	2·3	346	38·4	2·5	348	3·19	133—135° ^a
II	C ₁₃ H ₁₂ O ₄ N ₂ F ₆ ...	41·7	3·2	374	42·0	3·5	384	1·29	134—135° ^b
III	C ₁₂ H ₁₀ O ₄ N ₂ F ₆ ...	40·0	2·8	360	40·3	2·7	359	1·78	163° ^c
IV	C ₁₀ H ₈ O ₄ N ₂ ClF ₅ ^g	32·8	1·4	367	33·0	1·6	374	2·76	160—161° ^d
V	C ₁₀ H ₈ O ₄ N ₂ BrF ₅	29·2	1·2	411	29·3	1·1	419	3·92	169—171° ^e
VI	C ₁₅ H ₈ O ₄ N ₂ F ₁₄ ...	33·0	1·5	546	33·2	1·4	556	0·47	131—133° ^a
VII	C ₁₄ H ₈ O ₄ N ₂ F ₁₄ ...	31·6	1·1	—	31·6	1·3	—	0·43	132—133° ^a
VIII	C ₁₄ H ₈ O ₄ N ₂ ClF ₁₄ ...	29·7	0·9	567	29·9	0·7	568	0·25	161° ^d
IX	C ₁₁ H ₈ O ₄ N ₂ Cl ₆ ...	29·7	1·8	445	29·7	1·8	445	0·63	133° ^a

^a Also mixed m. p. ^b Found: C, 78·4; H, 6·3. Calc. for C₁₃H₁₈ON₂: C, 78·6; H, 6·2%. Bourne, Stacey, Tatlow, and Tedder (*J.*, 1952, 1695) gave m. p. 131—133°. ^c Norman (*J.*, 1919, **115**, 673, gave m. p. 166°. ^d Meldola and Streatfeild (*J.*, 1888, **53**, 664) gave m. p. 162·5°. ^e Bamberger (*Ber.*, 1895, **28**, 1218) gave m. p. 172—173°. ^f Found: F, 32·6. Required: F, 32·9%. ^g Found: F, 31·6. Required: F, 31·1%.

Toluene-p-diazonium Perfluoroadipate.—*p*-Toluidine (0·51 g.) with water (5·0 c.c.) containing perfluoroadipic acid (2·20 g.) (Tatlow and Worthington, *J.*, 1952, 1251) gave a precipitate. During diazotisation at 0—5° with sodium nitrite (0·44 g.) in water (1·0 c.c.) solid remained but changed in appearance. Filtration, washing, and drying afforded *toluene-p-diazonium perfluoroadipate* (1·00 g.), m. p. 100° (decomp.) (Found: C, 38·2; H, 1·6%; Equiv., 406. C₁₃H₈O₄N₂F₈ requires C, 38·2; H, 2·0%; Equiv., 408). The aqueous phase and washings gave, with alkaline β -naphthol, tolyl-*p*-azo- β -naphthol (0·42 g.), m. p. and mixed m. p. 132—133°.

Properties of Diazonium Acid Salts.—(a) *Toluene-p-diazonium acid trifluoroacetate.* At 15° this salt was moderately soluble in water, readily soluble in ethyl alcohol, acetone, and dioxan, and only very slightly soluble in benzene, ether, light petroleum, chloroform, and carbon tetrachloride.

Cryoscopic measurements on aqueous solutions (1—2%) gave f. p. depressions corresponding to a molecular weight of 90·5, *i.e.*, 3·8 g.-ions per g.-equiv. of the salt.

Addition of trifluoroacetic acid (3·0 c.c.) to a solution of toluene-*p*-diazonium chloride [prepared in the usual way from the amine (1·64 g.), concentrated hydrochloric acid (5·0 c.c.), water (2·0 c.c.), and sodium nitrite (1·18 g.) in water (5·0 c.c.)] produced a heavy lower layer. When cooled, this deposited colourless needles of the diazonium acid trifluoroacetate (0·089 g.).

An aqueous solution of the acid salt (3%) with β -naphthol in alkali gave tolyl-*p*-azo- β -naphthol (84%), m. p. and mixed m. p. 134—135°.

(b) *Mesitylenediazonium acid trifluoroacetate.* F. p. determinations of aqueous solutions (2—3%) of this salt indicated an apparent molecular weight of 98·5, corresponding to 3·8 g.-ions per g.-equiv. of salt. After the salt had been washed with undried ether the equivalent was 455 (cf. Hantzsch, *loc. cit.*, 1897, who found that almost all the free acid could be removed from the diazonium acid chlorides if they were washed with undried ether).

Replacement and Coupling Reactions of the Diazo-groups of Diazonium Trifluoroacetates.—The following are representative of conversions which can be effected by using standard techniques.

The amines (*ca.* 0.03 mol.) were diazotised at 0—5° by use of aqueous trifluoroacetic acid (approx. 0.09 mol., *ca.* 1.5N), concentrated aqueous sodium nitrite being added until a slight excess was present.

A solution of diazotised aniline, after 75 min. at 50° and 15 min. at 100°, afforded phenol (88%), m. p. 38—40°, b. p. 176—182°.

A solution of diazotised *p*-toluidine was treated with (*a*) an excess of aqueous potassium iodide (50%) to give *p*-iodotoluene (81%), m. p. 29—32°, b. p. 209—211°, and (*b*) cuprous cyanide, to give *p*-tolunitrile (70%), m. p. 26—28°, b. p. 213—215°.

Tetraozotised benzidine was treated with hypophosphorous acid (50%) at 15° for 4 hr., and at 100° for $\frac{1}{4}$ hr., to give diphenyl (63%), m. p. and mixed m. p. 69°.

The amines from which solid salts were prepared (see above) could be diazotised in dilute perhalogeno-acids, the salts remaining in solution, and the azo- β -naphthol coupling derivatives prepared in good yield.

o-Aminobenzotrifluoride (Jones, *J. Amer. Chem. Soc.*, 1947, **69**, 2346) was diazotised and coupled with β -naphthol (pH 8—10), to give 1-*o*-trifluoromethylphenylazo-2-naphthol (60%), m. p. 155° (Found: C, 64.5; H, 3.2. Calc. for C₁₇H₁₁ON₂F₃: C, 64.5; H, 3.5%), for which Cartwright and Tatlow (*J.*, 1953, 1994) gave m. p. 157—158°.

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