# The Chemistry of the Perfluoroaliphatic Acids and their Derivatives. VI. The Hofmann Reaction[1]

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A new method of preparation of monobromoperfluoroalkanes by the action of sodium hypobromite on a perfluoroamide having more than two carbon atoms is described. A possible reaction sequence is presented.[2]
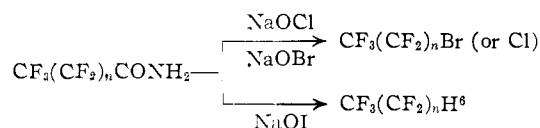
The treatment of a perfluorinated amide with an alkali hypohalite does not give the products predicted by the analogy of the Hofmann degradation[3,4]

$$C_nF_{2n+1}CONH_2 + NaOBr \longrightarrow$$
$$C_nF_{2n+1}NH_2 + CO_2 + NaX$$
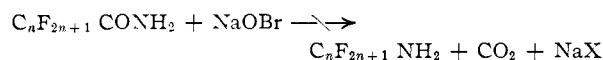
but gives instead different types of products. Furthermore, the reaction follows different patterns for trifluoroacetamide and for the perfluoroamides having three or more carbon atoms in the chain. Trifluoroacetamide was reported to yield not the expected and still unknown compound, CF_3NH_2, but instead hexafluoroethane[5] as the only isolable fluorinated compound.
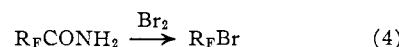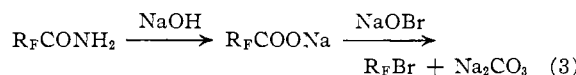
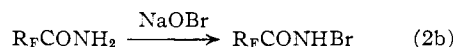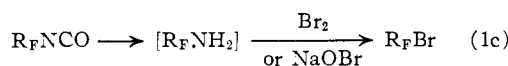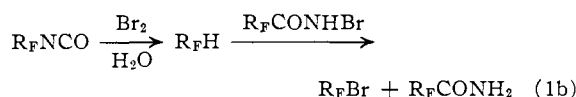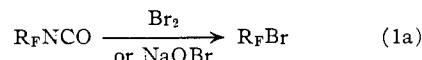$$2CF_3CONH_2 + NaOH + Br_2 \longrightarrow CF_3-CF_3$$

Contrary to both of the above equations, the reaction of alkali hypohalites with perfluorinated amides containing three or more carbon atoms yields the perfluoroalkyl chloride or bromide when sodium hypochlorite and sodium hypobromite are used and the hydride when sodium hypoiodite is used.

$$CF_3(CF_2)_nCONH_2 \begin{cases} \xrightarrow[NaOBr]{NaOCl} CF_3(CF_2)_nBr \text{ (or Cl)} \\ \xrightarrow[NaOI]{} CF_3(CF_2)_nH[6] \end{cases}$$

This reaction is important in the field of fluorine chemistry because it shows that the chemistry of the perfluoroamides is not uniform throughout the series, but breaks sharply between perfluoroacetamide and perfluoropropionamide, a change in kind and not in degree of reactivity. Furthermore, this reaction provides a convenient laboratory method for the preparation of monobromides and monochlorides of the perfluoro-substituted hydrocarbons. It avoids use of the exceedingly tricky and difficult reaction of anhydrous silver perfluorocarboxylate salts and the free halogen. These are inconvenient because of the rigorous anhydrous

conditions required[7-10] or the rarity of the perfluorinated solvents used.[10]

In trying to explain this reaction several possible reaction sequences were postulated

$$R_FCONH_2 \longrightarrow R_FCONHBr \longrightarrow R_FNCO \quad (1)$$

$$R_FNCO \xrightarrow[\text{or NaOBr}]{Br_2} R_FBr \quad (1a)$$

$$R_FNCO \xrightarrow[H_2O]{Br_2} R_FH \xrightarrow{R_FCONHBr}$$
$$R_FBr + R_FCONH_2 \quad (1b)$$

$$R_FNCO \longrightarrow [R_FNH_2] \xrightarrow[\text{or NaOBr}]{Br_2} R_FBr \quad (1c)$$

$$R_FCONH_2 \xrightarrow{NaOH} R_FCOONa \xrightarrow{\Delta} R_FH \quad (2a)$$

$$R_FCONH_2 \xrightarrow{NaOBr} R_FCONHBr \quad (2b)$$

$$R_FH + R_FCONHBr \longrightarrow R_FBr + R_FCONH_2[11] \quad (2c)$$

$$R_FCONH_2 \xrightarrow{NaOH} R_FCOONa \xrightarrow{NaOBr}$$
$$R_FBr + Na_2CO_3 \quad (3)$$

$$R_FCONH_2 \xrightarrow{Br_2} R_FBr \quad (4)$$

Reactions 1a, b and c were judged to be improbable because of the sensitivity of the perfluoroisocyanates to water[12] and because of the reaction of bromine and perfluoropropyl isocyanate (followed by water) did not produce the bromoperfluoroalkane, but instead n-hydroperfluoropropane, C_3F_7H.

Reaction 1c is also thought to be improbable for the reason that while the primary amine of formula $C_nF_{2n+1}NH_2$ is not known, the amines of formula $C_nF_{2n+1}CH_2NH_2$ are known[13-15] and the reaction of sodium hypobromite on 1,1-dihydroperfluorobutylamine, $C_3F_7CH_2NH_2$, did not produce the cor-

(1) The results of this research were reported as part of Paper No. 61, Abs. 29K, 122nd American Chemical Society Meeting, Atlantic City, N. J., September, 1952, and was referred to as reference 6 in Husted and Ahlbrecht, paper V, on Perfluoroacids, This Journal, 75, 1605 (1953).

(2) The original manuscript was submitted October 31, 1952. The work on the mechanism of the reaction was added later.

(3) E. S. Willis and J. F. Lane, "Organic Reactions," Editor-in-Chief, Roger Adams, Vol. III, Ch. 7, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 267.

(4) A. W. Hofmann, Ber., 14, 2725 (1881).

(5) E. Gryszkiewicz-Trochimowski, A. Sporzynski and A. Wnuk, Rec. trav. chim., 66, 426 (1947).

(6) Cf. A. W. Hofmann, Ber., 15, 411 (1882), who reports that NaOI did not produce an amine on reaction with acetamide.

(7) R. T. Arnold and P. Morgan, This Journal, 70, 4248 (1948).

(8) M. Hauptschein, R. L. Kinsman and A. V. Grosse, ibid., 74, 849 (1952).

(9) M. Hauptschein, E. A. Nodiff and A. V. Grosse, ibid., 74, 1347 (1952).

(10) J. H. Simons and T. J. Brice, U. S. Patents 2,554,219 (May 22, 1951), 2,614,131 (October 14, 1952); J. H. Simons, T. J. Brice, and W. H. Pearlson, This Journal, 68, 968 (1946).

(11) By analogy of the brominating properties of CF₃CONHBr, J. D. Park, H. T. Gerjovich, W. R. Lycan and J. R. Lacher, ibid., 74, 2189 (1952).

(12) A. H. Ahlbrecht, D. R. Husted, T. S. Reid and G. H. Smith, Jr., ibid., 76, in press (1954); the isocyanate reacts with water to produce an amide containing one less carbon atom, cf., A. H. Ahlbrecht, D. R. Husted, U. S. Patent 2,617,817 (Nov. 11, 1952).

(13) D. R. Husted and A. H. Ahlbrecht, 116th Meeting A.C.S., Atlantic City, N. J., 1949, Abstracts p. 10K, paper No. 17.

(14) H. Gilman and R. G. Jones, This Journal, 65, 1458 (1943).

(15) A. F. Benning and J. D. Parks, U. S. Patent 2,348,321 (May 9, 1944); C. A., 39, 625 (1945).

responding n-1,1-dihydroperfluorobutyl bromide, $C_3F_7CH_2Br$, a known compound.[16]

Reaction 1c is also thought to be improbable because under the conditions of the Hofmann reaction all free bromine has disappeared before the amide is added.

Since it was known that n-hydroperfluoropropane could be produced from a perfluoro acid (see Experimental section) the second mechanism was also adaptable to direct test. A sample of N-bromoperfluorobutyramide was synthesized, and tested for stability to boiling water and boiling 30% aqueous sodium hydroxide. It was found to be stable to boiling water for several minutes, but to decompose slowly on continued refluxing to yield free bromine and perfluorobutyramide. The action of refluxing 30% aqueous sodium hydroxide caused decomposition with the production of perfluoropropyl bromide, presumably by the reaction

$$C_3F_7CONHBr + NaOH \longrightarrow$$
$$\overset{O}{\overset{\|}{C_3F_7Br}} + [HOCNH_2] \longrightarrow CO_2 + NH_3 \quad (5)$$
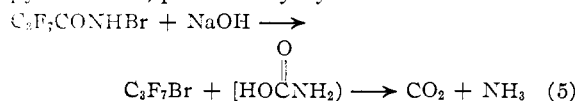
This mechanism is supported by the isolation of carbon dioxide and ammonia as by-products from some of the original Hofmann reactions.

To further test this new theory of the reaction, two more N-halogenated amides, N-bromoperfluoroacetamide and N-iodoperfluorobutyramide, were prepared and treated with alkali.

The preparation of N-bromoperfluoroacetamide and the subsequent alkali treatment went smoothly to produce bromotrifluoromethane, but the N-iodoperfluorobutyramide was difficult to isolate.

The dry mixture of N-iodoperfluorobutyramide and silver iodide when heated in an ampoule produced the compound, C_3F_7I. The reaction of N-iodoperfluorobutyramide with hot 30% aqueous sodium hydroxide produced first free iodine followed by n-hydroperfluoropropane, C_3F_7H, and perfluoropropene, C_3F_6, the amount of the latter two products depending somewhat on the degree of heating of the alkaline solution. Similarly, distillation to dryness of perfluorobutyramide in 30% sodium hydroxide solution produced n-hydroperfluoropropane, C_3F_7H, in small yield.
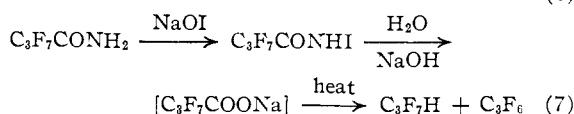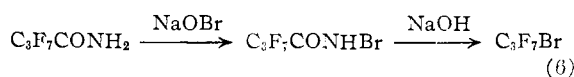
Reaction 2a was tested further by refluxing a sample of sodium perfluorobutyrate in strong alkali solution. The n-hydroperfluoropropane produced was identified by infrared absorption spectral analysis. It had already been shown that perfluorobutyramide was converted in part to sodium perfluorobutyrate under the conditions of the reaction (section 3 of the experimental).

Reaction sequence 3 was ruled out because of the failure to obtain brominated products by the reaction of sodium perfluorobutyrate and sodium hypobromite.

Reaction sequence 4 was ruled out because of the inability to brominate perfluorobutyramide by the Park procedure (Ag_2O, Br_2, CF_3COOH)[11] since unreacted amide was recovered.

Thus it appears that the path of the long-chain amide reaction is according to equations 6 and 7.

(16) G. V. Tiers, H. A. Brown and T. S. Reid, Fluorine Symposium, 124th A.C.S. Meeting, Chicago, Ill., September, 1953; THIS JOURNAL, **75**, 5978 (1953).

$$C_3F_7CONH_2 \xrightarrow{NaOBr} C_3F_7CONHBr \xrightarrow{NaOH} C_3F_7Br \quad (6)$$

$$C_3F_7CONH_2 \xrightarrow{NaOI} C_3F_7CONHI \xrightarrow[NaOH]{H_2O}$$

$$[C_3F_7COONa] \xrightarrow{heat} C_3F_7H + C_3F_6 \quad (7)$$

While for trifluoroacetamide the first step (equation 8) of the reaction does not take place.

$$CF_3CONH_2 \xrightarrow{NaOBr} \not\longrightarrow CF_3CONHBr \quad (8)$$
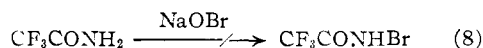
since it was shown that the necessary second step will occur (equation 9)

$$CF_3CONHBr \xrightarrow[NaOH]{} CF_3Br \quad (9)$$
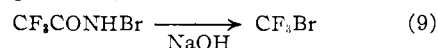
and the products reported[5] were probably formed according to equation 10.[17]

$$CF_3CONH_2 \xrightarrow{NaOBr} CF_3COONa \xrightarrow{\Delta}$$
$$CF_3-CF_3 + Na_2CO_3 + {}^1/_2O_2 \quad (10)$$
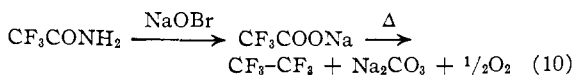
Experimental

Preparation of n-Perfluoropropyl Bromide.—In a 500-ml. 3-necked flask fitted with a tight sleeve stirrer, a thermometer dipping into the liquid, and a reflux condenser vented through a Dry Ice–acetone cooled trap, was placed 36 g. (0.90 mole) of sodium hydroxide and 100 ml. of water. The solution was cooled to 0° and 28.8 g. (0.18 mole) of bromine added dropwise, keeping the temperature of the solution below 5°. After the bromine was added and the red color had disappeared, 32 g. (0.150 mole) of perfluorobutyramide[13,18,19] and 50 ml. more water was added. The mixture was stirred for 1 hour, then the ice-bath was removed and the mixture allowed to warm to 20° over a period of 1 hour, after which the solution was heated to 95° (reflux) for about 2.5 hours. The liquid which collected in the cold trap was redistilled and the fraction boiling 10–15° (742 mm.) collected and redistilled. The product was n-perfluoropropyl bromide, b.p. 15–15.2° (742 mm.); yield about 16 ml., 65–70%. Infrared curve corresponded to that obtained by Hauptschein[9] and to samples prepared in this laboratory by other methods. It contained the characteristic absorption band at 1103 and 1190 cm.$^{-1}$.

Anal. Calcd. for C_3BrF_7: mol. wt., 249; Br, 32.1. Found: mol. wt., 248; Br, 32.3.

Preparation of Perfluoropropyl Chloride.—The reaction was carried out in a 1000-ml. flask similar to that described above, except that the dropping funnel was replaced by a gas inlet tube dipping into the liquid. To 80 g. (2 moles) of sodium hydroxide and 200 ml. of water was added 28 g. (0.396 mole) of chlorine and 71.2 g. (0.33 mole) of perfluorobutyramide. After about 15 minutes, the contents of the flask set to a gel. The reaction mixture was heated to 105° for 8 hours. About 5 ml. of liquid which collected in the Dry Ice–acetone cooled trap was vaporized and washed by passing through dilute hydrochloric acid to remove any ammonia present, and then was further purified by distillation in a low temperature still, b.p. 8–14° (740 mm.). About 1.5 ml. of liquid was obtained. Infrared absorption spectral curves indicated the presence of approximately 10% of normal monohydroperfluoropropane, C_3F_7H,[20,21] as an impurity.

Anal. Calcd. for C_3ClF_7: Cl, 17.3; mol. wt., 204.5. Found: Cl, 18.2; mol. wt., 200.

(17) A. D. Kirschenbaum, A. G. Streng and Murray Hauptschein, ibid., **75**, 3141 (1953).

(18) A. R. Diesslin, E. A. Kauck and J. H. Simons, U. S. Patent 2,567,011 (Sept. 4, 1951).

(19) Brochure on Perfluorobutyric Acid, Minnesota Mining & Mfg. Co., St. Paul, Minnesota, p. 7 (1949).

(20) W. H. Pearlson, "Fluorine Chemistry," Ch. 14, Editor, J. H. Simons, Academic Press, Inc., New York, N. Y., 1950, p. 469.

(21) D. G. Weiblen, 116th Meeting ACS, Atlantic City, N. Y., 1949, p. 29K, Paper No. 48.

The water solution remaining in the still was cooled and extracted with ether, but on evaporating the ether, the absence of solid remaining behind indicated complete reaction of the amide starting material. The water solution was distilled to dryness with the still vent connected to a Dry Ice–acetone cooled trap. A small amount of liquid collected in the trap and was identified as containing approximately 66% monohydroperfluoroethane, C_2F_5H,[22] and 34% perfluoropropylene, C_3F_6,[23,24] by infrared absorption spectral analyses. The white residue was a mixture of sodium chloride, sodium fluoride and some unidentified material. A sulfuric acid distillation of the solid yielded an unidentified red liquid, but no further information on the unknown component.

Perfluoroethyl hydride and the perfluoropropylene may arise from the heating of the sodium salt of the acid formed by the hydrolysis of the amide.[25,26]

Preparation of n-Perfluoropropyl Hydride.—The reaction was carried out in a manner similar to that described in the preceding paragraphs using 36 g. (0.9 mole) of sodium hydroxide, 100 ml. of distilled water, 45.6 g. (0.18 mole) of crystalline iodine and 32 g. (0.15 mole) of perfluorobutyramide, and followed by distillation to dryness. A small amount of material collected in the Dry Ice trap which on distillation yielded a portion of n-perfluoropropyl hydride, identified by molecular weight and the infrared absorption spectral curve.[20,21,27]

Anal. Calcd. for C_3HF_7: mol. wt., 170. Found: mol. wt., 165.

Only a small amount (25–40%) of the starting material was converted to the n-perfluoropropyl hydride and several unidentified products were obtained. Approximately 50% of the starting material was recovered in the form of the acid or sodium salt, and some ammonium fluoride (10% based on starting material) was obtained, indicating deep-seated decomposition. Other products isolated during the investigation included ammonia, carbon dioxide, iodine, and ammonium chloride.

Preparation of Pentafluoroethyl Bromide.—In a manner similar to that described above 36 g. (0.9 mole) of sodium hydroxide, 100 ml. of water, 28.8 g. (0.18 mole) of bromine and 24.5 g. (0.15 mole) of perfluoropropionamide[28] were allowed to react. About 10 to 12 ml. of liquid collected in the cold trap which on distillation yielded perfluoroethyl bromide, b.p. −18.5 to −17.5°.[12,29] The infrared absorption spectral curve contained no bands characteristic of CH, CN, NH or C=O

Anal. Calcd. for C_2BrF_5: mol. wt., 198.98. Found: mol. wt., 198.9.

Perfluoroacetamide.—Using a 0.5-mole run and a procedure similar to that described in the first paragraph of the experimental, no bromotrifluoromethane was isolated, and no evidence for its presence was found in the infrared spectral curves. Ammonia and an inert gas which appeared to be carbon monoxide were detected.

N-Bromotrifluoroacetamide.—The material was prepared by the procedure of Park,[11] m.p. 63°, lit. 63°.

N-Bromoperfluorobutyramide.—The above procedure of Park did not work well for the preparation of this compound. Instead N-silver perfluorobutyramide was prepared by refluxing a 100-ml. ether solution of 21.3 g. (0.1 mole) of perfluorobutyramide and 11.3 g. (0.05 mole) of silver oxide with stirring until the silver oxide disappeared and white crystals formed in the mixture (about 36 hours). (The preparation

may also be carried out in water solution, but the purification is slightly longer.) The crystals of N-silver perfluorobutyramide were removed by filtration, washed with ether, air-dried, then dissolved in trifluoroacetic acid and bromine added according to Park's[11] procedure. The product was purified by high vacuum sublimation, m.p. 78–79.2° (uncor.).

Anal. Silver salt: Calcd. for C_4HONF_7Ag: N, 4.25. Found: N, 4.25. Debye–Scherrer X-ray powder pattern— 4 most prominent lines: I, 11.94, v.s.; II, 9.017, v.s.; III, 13.80, s.; IV, 10.16, s.. Bromo compound: Calcd. for $C_4HONBrF_7$: Br, 27.38; N, 4.79; Found: Br, 27.34; N, 4.79. Debye–Scherrer X-ray powder pattern—4 most prominent lines: I, 2.49, v.v.s.; II, 14.24, v.v.s.; III, 17.65, v.s.; IV, 3.10, v.s.

N-Iodoperfluorobutyramide.—Neither of the above procedures was satisfactory since after purification only perfluorobutyramide was recovered. Equimolar amounts of N-silver perfluorobutyramide and silver oxide were finely ground in a mortar in a dry atmosphere, and allowed to stand 72 hours in a stoppered bottle. There was a considerable evolution of heat on mixing, indicating rapid reaction. Attempts to isolate the pure N-iodoperfluorobutyramide by high vacuum $(10^{-4}$ mm.) sublimation results in the production of iodine, and finally of a pure sample of perfluorobutyramide, m.p. and mixed m.p. 105°. Attempted recrystallization resulted in loss of iodine to the solvent. Examination of the mixture by the petrographic microscope showed the presence of silver iodide and a new compound not perfluorobutyramide or N-silver perfluorobutyramide. An X-ray Debye–Scherrer fine powder pattern confirmed these observations. On the theory that perhaps we had a mixture of starting materials, a sample had been previously sealed in a heavy wall ampoule and heated at 100° for 72 hours to complete the reaction. On opening the tube it was found to contain n-iodoperfluoropropane, C_3F_7I, identified by its infrared absorption curve.[10,30] Determination of the capillary m.p. resulted in decomposition at about 110–120°. From these results it was concluded that the N-iodoperfluorobutyramide had formed and was very unstable. The reaction mixture itself was used for the aqueous alkali hydrolysis.

THREE MOST PROMINENT DEBYE–SCHERER X-RAY POWDER LINES

	I	II	III	IV
Mixture	2.27v.s.	3.69s.	1.94s.	3.91w.
$C_3F_7CONH_2$	6.65v.s.	2.61s.	2.49s.	2.97s.
$C_3F_7CONHAg$	11.94v.s.	9.017v.s.	13.80s.	10.16s.
AgI	3.74v.s.	1.95s.	2.29s.	
C_3F_7CONHI (by subtraction)	2.27v.s.	3.69s.	3.91w.	

Alkaline Hydrolysis of N-Bromoperfluorobutyramide.— In a 20-ml. flask fitted with a reflux condenser connected to a liquid air cooled trap was placed 0.4 g. (0.0014 mole) of N-bromoperfluorobutyramide and 25 ml. (0.25 mole) of 30% aqueous sodium hydroxide. After refluxing for 5 hours the contents of the trap were removed and the infrared absorption spectral curve determined. It was found to contain n-bromoperfluoropropane, identified by the infrared absorption spectral curve.

Alkaline Hydrolysis of N-Bromoperfluoroacetamide.— The reaction was carried out by placing 1 g. (0.005 mole) of the bromoamide and 2 ml. (0.013 mole) of 30% aqueous sodium hydroxide in a Claisen flask whose receiver was connected to a liquid air cooled trap. The contents of the still were distilled practically to dryness (no charring), and the contents of the liquid air trap were identified as bromotrifluoromethane by the use of the infrared absorption spectra.

Alkaline Hydrolysis of N-Iodoperfluorobutyramide and of Perfluorobutyramide.—The hydrolysis was carried out as described for N-bromotrifluoroacetamide above. N-Iodoperfluorobutyramide yielded n-hydroperfluoropropane, C_3F_7H; perfluoropropylene, C_3F_6; and ammonia. Perfluorobutyramide yielded n-hydroperfluoropropane and ammonia. The isolated yields were small; for example, 2.75 g. (0.004 mole) of C_3F_7CONHI + AgI mixture yielded

(22) J. H. Simons, W. H. Pearlson, T. J. Brice, W. A. Wilson and R. D. Dresdner. *J. Electrochem. Soc.*, **95**, 59 (1949).

(23) W. F. Edgell, 114th Meeting A.C.S., Portland, Ore., 1948, Abs. p. 42-O, Paper No. 67

(24) W. F. Edgell, THIS JOURNAL, **70**, 2816 (1948).

(25) L. J. Hals, T. S. Reid and G. H. Smith, Jr., *ibid.*, **73**, 4054 (1951).

(26) J. F. Dowdall, this Laboratory. private communication, states that a water solution of perfluorobutyric acid heated to 150–200° in a sealed tube produces n-monohydroperfluoropropane, C_3F_7H. The perfluoropropionic acid could arise from the reaction mentioned in ref. 12.

(27) R. N. Haszeldine. *J. Chem. Soc.*, 2789 (1950).

(28) D. R. Husted and A. H. Ahlbrecht. THIS JOURNAL, **75**, 1605 (1953).

(29) T. J. Brice, W. H. Pearlson and J. H. Simons, *ibid.*, **68**, 968 (1946).

(30) M. Hauptschein and A. V. Grosse. *ibid.*, **73**, 2461 (1951).

300 ml. (96 mm., 27°) (0.00154 mole, approx. 38% yield) of C₃F₇H.

Stability of N-Bromoperfluorobutyramide to Water.— This was determined by boiling in water several minutes and determining the m.p. It was unchanged after two minutes, and after 30 minutes refluxing had risen only to 83°, indicating that hydrolysis was not yet complete. After refluxing 8 hours perfluorobutyramide was obtained. The results with N-bromotrifluoroacetamide were similar.

Stability of N-Iodoperfluorobutyramide to Water.— The compound was found to be so unstable to water that it could not be handled in humid atmosphere long enough to prepare an infrared sample without decomposing with the production of iodine.

Reaction of Sodium Perfluorobutyrate with Sodium Hydroxide and with Sodium Hypobromite.— In a 50-ml. flask fitted with a reflux condenser whose outlet was connected with a liquid air cooled trap protected by a Drierite trap was placed 5 g. (0.0233 mole) of perfluorobutyric acid and 6.19 mole of 33% aqueous sodium hydroxide (0.07 mole NaOH). The alkaline solution was refluxed for 8 hours. The trap was removed and replaced by a fresh one and an additional 10 ml. of 33% aqueous sodium

hydroxide solution added and refluxed an additional 8 hr. Both traps contained n-hydroperfluoropropane, C_3F_7H, identified by infrared absorption spectral curve. The yields were low, for example, 50 ml. (78 mm.).

The reaction with sodium hypobromite was carried out in a similar manner except that the bromine was dissolved in cold alkali before addition of the acid. The quantities used were: sodium hydroxide, 7.35 ml. (0.12 mole); bromine, 1.86 g. (0.023 mole); perfluorobutyric acid, 5 g. (0.233 mole). The product was n-hydroperfluoropropane. The infrared absorption spectra showed no evidence for the presence of any brominated product.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Absorption Spectra of Some p-Aminoaryldiazonium Derivatives

BY LEIGH C. ANDERSON AND JOHN W. STEEDLY, JR.[1,2]

p-Aminoaryldiazonium salts and some of their derivatives are exceedingly stable compounds when compared to the majority of simple diazonium compounds. Their color, instability to light and coupling properties render them of great value in photochemical reproduction processes. The visible and ultraviolet absorption spectra of p-amino-, p-methylamino- and p-phenylaminophenylenediazoimine, the corresponding diazonium salts as well as the salt of p-dimethylaminobenzenediazonium chloride and a number of metal salt complexes of the latter compounds have been studied. A comparison of their absorption spectral curves with those of diphenylquinomethane indicates that these diazonium compounds should be assigned a quinonoid structure.

p-Aminoaryldiazonium salts are a group of exceedingly stable compounds when compared to simple diazonium salts. They are usually yellow or orange in color while the great majority of other diazonium compounds are colorless. The p-amino or p-monosubstituted aminoaryldiazonium salts are precursors of the p-diazoimines which are quite unstable and yet colored like the parent diazonium salts. The unique stability of these p-aminoaryldiazonium salts in conjunction with their color prompted this investigation to determine what constitutional differences between these compounds and other diazonium salts are responsible for the observable differences in properties. The p-amino-aryldiazonium salts have considerable value in photochemical reproduction processes, because they are decomposed by the long wave ultraviolet light which they absorb whereas the simple colorless diazonium compounds are decomposed very slowly by this radiation. The p-diazoimines are characterized by their yellow to orange-red color, relative instability to heat and light with comparatively low explosion temperatures, ready conversion to the p-aminoaryldiazonium salts on treat-

ment with mineral acids, and ease of coupling with arylamines and phenols.

It would seem reasonable that the structure of the p-diazoimines would be closely related to that of the analogous diazophenols. Previous investigators have presented evidence for and against the assignment of the quinonoid structure to these latter compounds as well as the corresponding diazonium salts. Anderson and Roedel[3] have presented absorption spectral data indicating that the diazophenols have a quinonoid structure. It would appear, therefore, contrary to the statement of Saunders in 1936[4] regarding the imino compounds, "... and the question as to whether their structure is benzenoid or quinonoid has been settled in favor of the former," that the p-diazoimines may have the quinonoid structure as originally proposed by Hantzsch[5] although definite proof has been lacking up to the present time. The formation of metallic salt complexes is reputed to give even greater stability to these diazonium salts in the dry state. No absorption spectral studies of the p-diazoimines have been made up to the time of this study.

On Fig. 1 the quantitative absorption spectral curve of a water solution p-phenylenediazoimine, $HNC_6H_4N_2$, is compared to that of an ether solution

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(2) Presented in part before the Division of Organic Chemistry at the 119th Meeting of the American Chemical Society at Cleveland, Ohio, April, 1951.

(3) L. C. Anderson and M. J. Roedel, THIS JOURNAL, **67**, 955 (1945).

(4) K. H. Saunders, "The Aromatic Diazo Compounds," Arnold and Co., London, 1936, p. 18.

(5) A. Hantzsch, *Ber.*, **35**, 888 (1902).