[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Fluorocarbon Bromides

BY T. J. BRICE, W. H. PEARLSON AND J. H. SIMONS

The series of alkyl fluorocarbons has been previously reported[1] and numerous chlorine containing fluorocarbons are reported in the literature. Only two dibromo fluorocarbons are recorded, namely, dibromodifluoromethane[2] and *sym*-dibromotetrafluoroethane.[3] There is no record in the literature of the preparation and properties of any of the monobromo compounds. Henne[4] reports an unsuccessful attempt to prepare bromotrifluoromethane by the photochemical bromination of fluoroform.

A general method for the preparation of fluorocarbon bromides has now been found which consists of the thermal bromination of the corresponding hydrogen containing fluorocarbon, *i. e.*, CF_3Br from CF_3H, C_3F_7Br from C_3F_7H, etc. A method of preparing fluoroform has been previously described[5] and the detailed preparation and properties of this and other hydrogen containing fluorocarbons will be described in a subsequent paper. Direct thermal chlorination was found to proceed in a similar manner.

The method consists of passing a gaseous mixture of the hydrogen containing fluorocarbon and bromine through a hot tube and condensing the product. The mixture obtained by passing the gaseous starting material through an electrically heated bubbler containing bromine maintained at 40 to 50° was passed through the reaction chamber, a 30-centimeter length of 19-millimeter Pyrex tubing packed with short lengths of 6-millimeter Pyrex tubing to provide surface contact. The tube was heated by an electric furnace and the temperature was maintained at about 600°. The products were collected in a series of three traps. The first one was cooled with ice, the second with Dry Ice–acetone, and the third with liquid air. The flow rate employed was between 0.2 and 0.4 moles per hour. The condensate was allowed to warm slowly and the vapors passed through a basic bisulfite solution, then through concentrated sulfuric acid for drying, and recondensed. Final purification was accomplished by distillation in a suitable helix-packed fractionating column.

In Table I examples of the results of this method are given. The boiling points were taken at 740 mm. and the molecular weights were obtained by a vapor density balance previously described.[6] The yield of CF_3Br from CF_3H was about 90% and that of C_3F_7Br from C_3F_7H was about 80%. Other yields were similar but not determined.

The bromides obtained are colorless gases which condense to colorless highly mobile liquids. A tendency to congeal to glasses on cooling prevented obtaining accurate freezing points. The monobromides are stable to light and heat and inert to ordinary reagents. The dibromides, even when sealed in glass, tend to release bromine and become colored after a few days at room temperature.

Analysis was accomplished by a method similar to that employed previously for the fluorocarbons,[1] consisting of decomposition over hot sodium, solution of the residues, and the determination of the bromine by the Volhard method.

Similar to that which has been found previously for the chlorine containing fluorocarbons, the bromine containing fluorocarbons appear more stable and less reactive than the corresponding alkyl bromides and they also have much lower boiling points. For example, CF_3Br with a molecular weight of 149 boils at −60° whereas methyl bromide with a molecular weight of 95 boils at 4.5, and *sym*-dibromotetrafluoroethane with a molecular weight of 260 boils at 46.4° whereas ethylene dibromide with a molecular weight of 188 boils at 131.6. It has been found, however, that some of these bromine compounds are sufficiently reactive to undergo certain reactions. For example, C_3F_7Br has been found to react with magnesium in the presence of ether but only when extreme precautions were taken to remove traces of moisture. The formation of the Grignard reagent was demonstrated by its hydrolysis with water to C_3F_7H, which was identified by its known boiling point −21° and molecular weight, as determined by the vapor density in a gas density balance[6] of 168 (calcd. 170). The product failed to react with bromine at room temperature.

A sample of the material of the composition $C_3F_6Br_2$ when treated with zinc and glacial acetic acid at room temperature gave a sample of gas which had a molecular weight of 150 and boiling point −29°. *Anal.* Found: C, 23.6%. Calcd. for C_3F_6 (molecular weight 150): C, 24.0. This gas also reacted with bromine.

TABLE I

Compound	B. p., °C.	Molecular weight Found	Molecular weight Calcd.	% Bromine Found	% Bromine Calcd.
CF_3Br	−60.5 to −59.0	149	149	53.4	53.7
C_2F_5Br	−23.0 to −21.0	201	199	39.7	40.2
C_3F_7Br	11.0 to 12.0	248	249	31.8	32.1
$C_3F_6Br_2$	71.0 to 71.5	308	310	51.1	51.6
C_3F_6HBr	31.5 to 33.0	228 to 235	231	34.3	34.6
				H. 0.40	0.43

This work was done under the sponsorship of

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Summary

Five new fluorocarbon bromides have been prepared by the thermal reaction of the corresponding hydrogen containing fluorocarbon with bromine.

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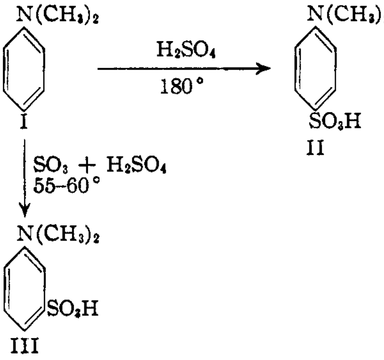
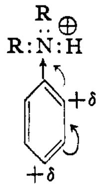
Mechanism of the Sulfonation of Aromatic Amines. I. Sulfonation with Fuming Sulfuric Acid

BY ELLIOT R. ALEXANDER[1]

It is well known that the sulfonation of aromatic amines produces different isomers depending upon the experimental conditions employed. Thus when the acid sulfate of dimethylaniline is heated to 180° it is transformed into dimethylsulfanilic acid (II),[2] while sulfonation with fuming sulfuric acid at 55–60° produces dimethylmetanilic acid (III).[3] Under these conditions the reactions are clean cut and the isomers are obtained in pure form.

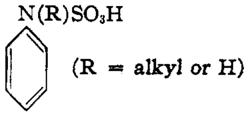


Theoretically the formation of *para* substitution products is somewhat surprising in view of the fact that a positively charged nitrogen atom would be expected to deactivate the aromatic nucleus and to cause *meta* orientation by the electronic mechanism (IV).



IV

For aniline and secondary aromatic amines a mechanism for *para* sulfonation has been advanced which is based upon the rearrangement of arylsulfamic acids (V), which were postulated as intermediates.[4]



V

This mechanism, however, is not completely satisfactory because it cannot be applied to the *para* sulfonation of tertiary aromatic amines where such intermediates are impossible, and it has been pointed out that there is evidence that the formation of arylsulfamic acids does not occur at low temperatures when the amine is present as a salt.[5]

Accordingly as a preliminary step in the investigation of the mechanism of the "baking process," a study of the effect of temperature upon the position of the entering group in the sulfonation of aniline was undertaken since there was available a quantitative method for distinguishing between *ortho–para* and *meta* sulfonation[6] and since it was reported possible to convert aniline into either *ortho*, *meta* or *para*-aminobenzenesulfonic acid.[7]

In Table I is shown a summary of sulfonation experiments carried out with aniline at temperatures ranging from 10 to 95°. It is quite surprising that in all cases the ratio of *meta* to *ortho–para* derivatives is less than one. This clearly indicates either that the anilinium ion is not the only reacting species or that there is a difference between the mechanism of the sulfonation of aniline and dimethylaniline.

It appeared at first that possibly the minute amount of undissociated aniline in solution might be responsible for this anomalous behavior. Undissociated aniline by virtue of its unshared electron pair would be expected to facilitate the attack of electrophilic reagents by mechanism VI, and even though if only present in very small amounts, the greater reactivity of this molecule with respect to the anilinium ion might be sufficient to overbalance the ratio of isomers formed in favor of *ortho–para* substitution. Experiments

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(1) Frank B. Jewett Fellow. Present address: Department of Chemistry, University of California, Berkeley, California. Presented before the Division of Organic Chemistry at the 109th Meeting of the American Chemical Society, April, 1946, Atlantic City, New Jersey.

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