[CONTRIBUTION FROM VENEREAL DISEASE EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

# The Reaction Between Diazonium Fluoborates and Arsenic Trichloride in Organic Solvents[1]

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The reaction between diazonium fluoborates and arsenic trichloride in organic solvents and in the presence of certain catalysts has been studied. Both primary arsonic and secondary arsinic acids are formed. The total yield of the two acids and the ratio between the yields varies with the solvent and the catalyst used. Alcohols appear to be the most useful solvents for this reaction. Copper and its salts are the most satisfactory catalysts; ferrous chloride, potassium iodide and hydroquinone are less effective. A relationship between oxidation-reduction potential and catalytic effect is suggested. By use of this reaction, several new secondary arsinic acids have been prepared and characterized.

Replacement of a diazo group by a metal is one method for establishing a carbon-metal bond. This method, when applicable, can be used for preparing aromatic organometallic compounds containing a wide variety of functional groups. A large number of organic arsenic and antimony compounds have been prepared in this manner. The reaction has also been applied, under special conditions, to the preparation of compounds of mercury,[2] tin,[3] lead[4] and bismuth.[5] The preparation of arsenic compounds is usually performed in aqueous alkaline solution (the Bart reaction). A useful modification was introduced by Scheller[6] in which an aromatic amine is diazotized in an organic solvent in the presence of arsenic trichloride. The reaction was subsequently extended to the preparation of aromatic stibonic acids.[7] Several attempts in this Laboratory to prepare bismuth and phosphorus compounds under the conditions of the Scheller reaction have not been successful. The possibility exists, however, that if this reaction were performed under anhydrous conditions, its usefulness might be extended. Such a procedure would necessitate the use of stable, dry diazonium salts, such as diazonium fluoborates. These diazo compounds have been used previously in the preparation of organometallic compounds, but the reaction was usually conducted in aqueous solution.[8]

We have undertaken an investigation of the reaction between the halides of certain elements and dry diazonium fluoborates in organic solvents. The reaction was first attempted with arsenic trichloride and *p*-nitrobenzenediazonium fluoborate in absolute alcohol, with cuprous bromide as the catalyst. Since excellent yields of arsonic acids can be obtained by other methods, we had originally planned only a few orienting experiments with arsenic trichloride. It was found, however, that using *p*-nitrobenzenediazonium fluoborate, both *p*-nitrobenzenearsonic and bis-(*p*-nitrophenyl)-arsinic acids were obtained in yields of 47 and 4%, respectively.[9] As the customary preparation of secondary arsinic acids involves a number of steps, we have investigated the effect of various solvents and catalysts on the yields of secondary acids.

## Experimental

**Reagents.**—The diazonium fluoborates used in the present investigation were prepared by one of two procedures, methods IB and IIA, described by Roe.[10] The salts obtained by either procedure gave identical results in the following reactions. For analysis of the diazonium compounds the procedure of Siggia[11] was adapted to a semi-micro scale. It was found necessary to substitute a Dry Ice source[12] for the carbon dioxide cylinder. In place of the hydrochloric acid and water used in Siggia's procedure we employed a solution of cuprous chloride in 10% hydrochloric acid. The solution was boiled to remove air, was cooled in an atmosphere of carbon dioxide, and was finally stored under a layer of mineral oil in an aspirator bottle. When this reagent was used, the blank determination was found consistently to be about 0.2 ml. Analysis of the diazonium fluoborates used in this investigation indicated that they were reasonably pure (90–100%). The solvents were reagent grade and were not specially dried. The catalysts were commercial C.P. chemicals except for anhydrous ferrous chloride, which was made in this Laboratory.

**Procedure.**—*p*-Nitrobenzenediazonium fluoborate (0.1 mole) was suspended in 125 ml. of the solvent in a 2-necked flask equipped with a sealed stirrer and an outlet tube connected to a water trap. Arsenic trichloride (0.1 mole) and catalyst (2 g.) were added and stirring was begun. In the majority of experiments nitrogen was evolved immediately and the reaction was complete in less than one hour. In a few cases no reaction occurred until the mixture was heated on a steam-bath.

After the evolution of nitrogen the mixture was steam distilled to remove the organic solvent and volatile byproducts of the reaction. The residual liquid in the flask was evaporated to 100 ml.; on cooling a precipitate separated which was removed by filtration. The solid was dissolved in sodium carbonate solution and the solution filtered from a small amount of undissolved material. No tertiary arsine oxide was found in this insoluble residue. The filtrate was acidified to congo red with concentrated hydrochloric acid and the mixture of *p*-nitrobenzenearsonic and bis-(*p*-nitrophenyl)-arsinic acids removed by filtration. The mixture was extracted with boiling water. The primary acid crystallized out of this solution and was purified by two recrystallizations from hot water. The water-insoluble portion, which consisted of crude secondary acid, was recrystallized from hot alcohol.

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[1] Presented before the Organic Division of the American Chemical Society at Boston, Mass., April, 1951.

[2] A. N. Nesmejanow, *Ber.*, **62**, 1010 (1929); A. N. Nesmejanow and E. J. Kahn, *ibid.*, **62**, 1018 (1929).

[3] A. N. Nesmejanow, K. A. Kozeschkow and V. A. Klimova, *ibid.*, **68**, 1877 (1935); K. A. Kocheshkov, A. N. Nesmeyanov and V. A. Klimova, *J. Gen. Chem.* (*U.S.S.R.*), **6**, 167 (1936); *C. A.*, **30**, 4834 (1936).

[4] K. A. Kocheshkov, A. N. Nesmeyanov and N. K. Gipp, *J. Gen. Chem.* (*U. S. S. R.*), **6**, 172 (1936); *C. A.*, **30**, 4834 (1936).

[5] H. Gilman and H. L. Yablunky, THIS JOURNAL, **63**, 949 (1941).

[6] E. Scheller, German Patent 522,892 (1926).

[7] G. O. Doak and H. G. Steinman, THIS JOURNAL, **68**, 1987 (1946).

[8] M. F. W. Dunker, E. B. Starkey and G. L. Jenkins, *ibid.*, **58**, 2308 (1936); M. F. W. Dunker and E. B. Starkey, *ibid.*, **61**, 3005 (1939); A. W. Ruddy, E. B. Starkey and W. H. Hartung, *ibid.*, **64**, 828 (1942); F. A. Bolth, W. M. Whaley and E. B. Starkey, *ibid.*, **65**, 1456 (1943).

[9] M. Ya. Kraft and S. A. Rossina, *Compt. rend. acad. sci., U. R. S. S.*, **55**, 821 (1947); *C. A.*, **42**, 531 (1948), have recently reported the formation, in the Bart reaction, of trace amounts of secondary arsinic acids and tertiary arsine oxides.

[10] A. Roe in "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 193.

[11] S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 78.

[12] E. Stehr, *Ind. Eng. Chem., Anal. Ed.*, **18**, 513 (1946).

In addition to the arsenic compounds described above, a water-insoluble material separated from the steam distillate. This product was crystallized one or more times from ether or other organic solvents. *p*-Nitrochlorobenzene was isolated from all reactions and was usually the sole reaction product found in the steam distillate. When cuprous bromide was used as the catalyst, *p*-nitrobromobenzene was also formed; this was isolated by fractional crystallization of the products which separated from the steam distillate.

In several cases the steam distillate was extracted with ether after removal of water-insoluble material. The ether layer was dried and distilled. *p*-Nitrofluorobenzene was found in trace amounts in this fraction and was identified by ultraviolet absorption spectra and by mixed melting point with an authentic sample. In those reactions in which no arsenical was formed a large amount of oily material separated from the steam distillate. Fractional crystallization of this material yielded *p*-nitrochlorobenzene and a large amount of *p*-nitrophenetole.

## Results and Discussion

A change in the ratio of arsenic trichloride to diazonium fluoborate was without significant effect on the yield of either primary or secondary acid. However, there was a marked effect on the yields of *p*-nitrobenzenearsonic and bis-(*p*-nitrophenyl)-arsinic acids by substituting other solvents for absolute ethanol. The following solvents increased the yield of secondary acid and decreased the yield of primary acid: methanol, *i*-propanol, *n*-butanol, *t*-butanol, *n*-pentanol, ethyl acetate, *i*-propyl acetate, aqueous ethanol (95%, 80%, or 70%) and aqueous *t*-butanol (80%). Acetone and dioxane gave lower yields of both acids. Aqueous ethanol and aqueous *t*-butanol in the concentrations used were superior to all the dry solvents for the production of the secondary acid. A maximum yield (21%) was obtained with 80% ethanol; *t*-butanol, the best anhydrous solvent, gave a 14% yield.

Substitution of other catalysts for cuprous bromide had a striking effect on the yields of both acids. Both cupric and cuprous chloride increased the yield of primary acid but reduced the yield of secondary acid to less than 1%. In contrast, copper bronze reduced the yield of primary acid but increased the yield of secondary acid from 4 to 14%.

Although copper and its salts were the most effective catalysts, other compounds, namely, anhydrous ferrous chloride, potassium iodide and hydroquinone, led to the formation of organic arsenic compounds. The reaction did not yield organic arsenicals in the absence of a catalyst or in the presence of anhydrous ferric chloride, manganous chloride or chromous chloride. It may be significant that all effective catalysts can in aqueous solution participate in oxidation–reduction systems whose potentials lie within a relatively small range (−0.34 to −0.77 volt).[13] The catalysis by cupric chloride is in contrast to the results of Voight[14] who reported that only reducing agents were catalysts for the formation of primary stibonic and secondary stibinic acids.

Since 80% ethanol was the best solvent (in the presence of cuprous bromide) and since copper bronze was the best catalyst (in absolute alcohol), it seemed reasonable to use copper bronze in 80% ethanol. This combination, however, reduced the yield of primary acid to 13% and gave a yield of secondary acid of only 9%. The most favorable reaction conditions for the formation of secondary acid were, therefore, 80% ethanol and cuprous bromide; for the formation of the primary acid, absolute ethanol and cupric chloride. Accordingly, both sets of reaction conditions were tried with several substituted benzenediazonium fluoborates. The results obtained are listed in Table I. We were unable to prepare either primary or secondary acids from the diazonium fluoborates derived from aniline or *o*-nitroaniline. Analytical data and melting points for compounds not previously reported are listed in Table II.

TABLE I

ARYLARSONIC AND DIARYLARSINIC ACIDS PREPARED FROM DIAZONIUM FLUOBORATES[a]

| $RC_6H_4N_2BF_4$ R = | 80% EtOH and CuBr Arsonic acid, yield, % | | Abs. EtOH and $CuCl_2$ Arsonic acid, yield, % | |
|---|---|---|---|---|
| | Arsonic acid, yield, % | Arsinic acid, yield, % | Arsonic acid, yield, % | Arsinic acid, yield, % |
| *o*-Cl | 19 | 13 | 45 | 2 |
| *m*-Cl | 39 | 18 | 62 | Trace |
| *p*-Cl | 23 | 14 | 62 | 0 |
| *m*-$NO_2$ | 21 | 17 | 42 | 0.8 |
| *p*-$NO_2$ | 19 | 21 | 54 | 0.7 |

[a] The following quantities of reactants were used: 0.1 mole diazonium fluoborate, 0.1 mole arsenic trichloride, 125 ml. solvent, 2 g. catalyst.

TABLE II

ANALYSES AND MELTING POINTS OF BIS-(CHLOROPHENYL)-ARSINIC ACIDS

| $R_2AsO_2H$ R = | M.p., °C. | Formula | Analyses, % | | Neutral equivalent | |
|---|---|---|---|---|---|---|
| | | | Calcd. | Found | Calcd. | Found |
| *o*-$ClC_6H_4$– | 245–248 | $C_{12}H_8AsO_2Cl_2$ | 22.63 | 22.19 | 331.0 | 331.3 |
| *m*-$ClC_6H_4$– | 150–152 | $C_{12}H_8AsO_2Cl_2$ | 22.63 | 22.47 | 331.0 | 328.8 |
| *p*-$ClC_6H_4$– | 177–179 | $C_{12}H_8AsO_2Cl_2$ | 22.63 | 22.40 | 331.0 | 328.3 |

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(13) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938.

(14) A. F. Voight, *Acta Chem. Scand.*, **1**, 118 (1947).