be obtained from this substance by the Doak–Freedman method. *m*-Ethylphenyldiazonium fluoborate was prepared conventionally, but this proved to be even less stable than its tolyl analog. Usually within 15 minutes of isolation by filtration from the reaction mixture, the colorless solid showed signs of vigorous decomposition, being transformed to a red liquid. An attempt to employ this fluoborate for the preparation of the phosphonic acid, after rapid drying by washing with ether, failed to yield any of the desired product.

Determination of Apparent Dissociation Constants.—The technique of the determinations as well as the apparatus and the mode of calculations were precisely as described in an earlier paper from this Laboratory.[1]

Determination of Apparent Molecular Weights.—The determinations by lowering of freezing points were run as described earlier.[3] Di-*p*-*t*-butylbenzene was used as the standard for calibration. The boiling point determinations were made in the conventional Cottrell apparatus.

The molal constants were determined experimentally. These were: 7.20 for naphthalene, 39.7 for camphor, 1.55 for acetone and 1.86 for water.

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

The Preparation of Arsenic and Phosphorus Compounds from Stable Diazonium Salts

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Diazonium fluosilicates or chlorozincates can be used for the preparation of organoarsenic and organophosphorus compounds. The yields of these compounds are compared with the yields obtained from the corresponding diazonium fluoborates.

Aromatic compounds of arsenic, phosphorus and antimony can be prepared readily through the use of diazonium fluoborates.[1] It was of interest to determine whether other stable diazonium salts could be used in place of fluoborates. In particular, the diazonium fluosilicates seemed worth considering since they are, at least in some cases, more stable[2] and easier to isolate[3] than the corresponding fluoborates.

Table I compares the yields of phosphonic and phosphinic acids obtained from diazonium fluosilicates with the yields obtained from the corresponding diazonium fluoborates. Although the end results are similar, the reactions of the diazonium fluosilicates were less vigorous, and the organophosphorus compounds obtained were purified with less difficulty.

TABLE I

YIELDS OF ARYLPHOSPHONIC AND DIARYLPHOSPHINIC ACIDS PREPARED FROM DIAZONIUM SALTS[a]

$RC_6H_4N_2X$ R =	Yield from diazonium fluosilicate, % Phosphonic acid	Phosphinic acid	Yield from diazonium fluoborate,[b] % Phosphonic acid	Phosphinic acid
H	19	10	17	4
m-Cl	35	9	43	7
m-O_2N	48	3	37	6
p-O_2N	50	3	47	6

[a] The following quantities of reactants were used: 0.1 equivalent of diazonium salt, 0.1 mole of phosphorus trichloride, 125 ml. of ethyl acetate, 2 g. of cuprous bromide. The yield data in this and succeeding tables were, in most cases, obtained from single experiments. However, enough of the reactions were run in duplicate to indicate that the yields given can probably be reproduced to about 3 absolute %. [b] These results are taken from ref. 1b.

Organoarsenic compounds also can be prepared by the use of diazonium fluosilicates. For example, *p*-nitrobenzenearsonic and bis-(*p*-nitrophenyl)-arsinic acids were obtained in 1 and 14% yields, respectively, when arsenic trichloride reacted with *p*-nitrobenzenediazonium fluosilicate in 80% alcohol in the presence of cuprous bromide. The fluoborate under the same conditions gave 19% arsonic acid and 21% arsinic acid.[1a]

The diazonium fluosilicates also were used for the preparation of phosphinic acids from phenyldichlorophosphine; the yields obtained are given in Table II. Also given in Table II are the results we obtained using fluoborates and considerably less catalyst than previously employed. Evidence was presented previously[1d] which indicates that the unsymmetrical phosphorus compounds disproportionate to some extent under the conditions of the reaction. It seems reasonable to suggest that the lower temperatures prevailing in the diazonium fluosilicate reactions lead to less disproportionation and hence to higher yields of unsymmetrical phosphinic acids. This view is consistent with the fact that the use of 0.8 g. of cuprous bromide per 0.1 mole of diazonium fluoborate moderates the violence of the reaction with phenyldichlorophosphine and, in three out of four cases, increases the yields of the unsymmetrical acids (*cf.* Table II).[4]

Because of their stability and ease of isolation, diazonium chlorozincates (zinc chloride double salts of diazonium chlorides) have been used for many purposes.[5] We have found that these salts also can be used for the preparation of arsenic and phosphorus compounds but they offer no advantage over the fluoborates or fluosilicates. Table III

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[1] (a) G. O. Doak and L. D. Freedman, THIS JOURNAL, **73**, 5656 (1951); (b) *ibid.*, **73**, 5658 (1951); (c) G. O. Doak, L. D. Freedman and S. M. Efland, *ibid.*, **74**, 830 (1952); (d) L. D. Freedman and G. O. Doak, *ibid.*, **74**, 2884 (1952); (e) G. O. Doak and L. D. Freedman, *ibid.*, **75**, 683 (1953); (f) L. D. Freedman, H. Tauber, G. O. Doak and H. J. Magnuson, *ibid.*, **75**, 1379 (1953).

[2] R. D. Beaty and W. K. R. Musgrave, *J. Chem. Soc.*, 875 (1952).

[3] G. F. Hawkins and A. Roe, *J. Org. Chem.*, **14**, 328 (1949).

[4] Unpublished work from this Laboratory indicates that the yields of phosphonic acids obtained from diazonium fluoborates and phosphorus trihalides are unaffected by using 0.8 g. of cuprous bromide instead of the usual 2.0 g. per 0.1 mole of diazonium fluoborate. However, such a decrease makes these reactions less vigorous. Thus, using the smaller ratio of catalyst to fluoborate, we have found that two moles of *p*-nitrobenzenediazonium fluoborate can react safely with phosphorus trichloride in a 12-l. flask equipped with an 18-mm. gas outlet tube.

[5] K. H. Saunders, "The Aromatic Diazo-Compounds and Their Technical Applications," 2nd edition, Edward Arnold and Co., London, 1949, p. 78.

TABLE II

YIELDS OF DIARYLPHOSPHINIC ACIDS PREPARED FROM DIAZONIUM SALTS AND PHENYLDICHLOROPHOSPHINE^a

Phosphinic acid	Yield from diazonium fluosilicate, % 2 g. CuBr/0.1 equiv.	Yield from diazonium fluoborate, % 0.8 g. CuBr/0.1 equiv.	2 g. CuBr/0.1 equiv.^{b}
$(C_6H_5)_2PO_2H$	33	40	42
$(m\text{-}ClC_6H_4)C_6H_5PO_2H$	41	68	27
$(o\text{-}BrC_6H_4)C_6H_5PO_2H$	29	31	15
$(m\text{-}O_2NC_6H_4)C_6H_5PO_2H$	41	47	36
$(p\text{-}O_2NC_6H_4)C_6H_5PO_2H$	32	30	30

[a] The following quantities of reactants were used: 0.1 equivalent of diazonium salt, 0.1 mole of phenyldichlorophosphine, 125 ml. of ethyl acetate, 2 (or 0.8) g. of cuprous bromide. [b] These results are taken from ref. 1d.

reports the yields of both primary and secondary acids from the chlorozincates; it is seen that the yields are rather low.

TABLE III

ORGANOARSENIC AND ORGANOPHOSPHORUS COMPOUNDS PREPARED FROM DIAZONIUM CHLOROZINCATES^a

$(RC_6H_4N_2)_2ZnCl_4$ R =	Yield using arsonic trichloride,^{b} % Arsonic acid	Arsinic acid	Yield using phosphorus trichloride,^{c} % Phosphonic acid	Phosphinic acid
p-Br	35^d	3^d	18^e	0^e
p-O_2N	21	3	^{f}	1

[a] The following quantities of reactants were used: 0.1 equivalent of diazonium salt, 0.1 mole of arsenic (or phosphorus) trichloride, 125 ml. of solvent, 2 g. of cuprous bromide. [b] The solvent used was absolute ethanol. [c] The solvent used for the *p*-bromo compound was ethyl acetate; the solvent used for the *p*-nitro compound was isopropyl acetate. [d] Analytical data and other properties of *p*-bromobenzenearsonic and bis-(*p*-bromophenyl)-arsonic acids will be given in a later paper. [e] The preparation of *p*-bromobenzenephosphonic and bis-(*p*-bromophenyl)-phosphinic acids from the corresponding diazonium fluoborate is described in reference 1e. [f] Although a small amount of phosphonic acid was isolated, it could not be purified by Procedure B as previously described; *cf.* ref. 1b.

Because diarylarsinic acids were obtained in the reaction between arsenic trichloride and diazonium fluoborates or fluosilicates or chlorozincates, we suspected that arsinic acids are probably formed also in the customary Scheller reaction procedure,[6] which involves the reaction of diazonium chlorides or sulfates with arsenic trichloride. However, no one has reported the isolation of arsinic acids from this reaction although it has been used for about 25 years. We have now found that arsinic acids can be obtained in low yields from the Scheller reaction. Thus, under the conditions previously employed,[6] *p*-nitrobenzenediazonium sulfate gives a 7% yield of bis-(*p*-nitrophenyl)-arsinic acid and a 45% yield of *p*-nitrobenzenearsonic acid; using 80% alcohol and cuprous bromide, we obtain 3% arsinic acid and 10% arsonic acid.

Experimental

The diazonium fluoborates,[7] diazonium fluosilicates[8] and diazonium chlorozincates[9] were prepared by known methods and analyzed as described in an earlier paper[1a] from this Laboratory. The phenyldichlorophosphine was kindly furnished us by the Victor Chemical Works. The solvents and other chemicals were reagent grade and were not further purified.

The compounds prepared in this investigation, with the exception of bis-(*p*-bromophenyl)-arsinic acid, have been reported previously. The apparatus and procedure employed were similar to those developed in this Laboratory for the preparation of arsenic and phosphorus compounds from diazonium fluoborates.[1]

o-Nitrobenzenediazonium fluosilicate could not be obtained by the procedure employed for the other diazonium fluosilicates; the compound decomposed rapidly in suspension when the temperature was allowed to rise to about 30°. The reaction mixture was steam distilled, and a large quantity of nitrobenzene was isolated from the distillate.

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[6] G. O. Doak, THIS JOURNAL, **62**, 167 (1940).

[7] A. Roe, method II A in "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 204.

[8] P. H. Cheek, R. H. Wiley and A. Roe, THIS JOURNAL, **71**, 1863 (1949).

[9] W. E. Hanby and W. A. Waters, *J. Chem. Soc.*, 1029 (1946).