Reduction of 1,1,1-Tribromo-3-methanesulfonylpropane.—This compound (1 g.) was added to 15 ml. of ethanol (95%) followed by the addition of zinc dust (1–2 g.). To catalyze the reduction, 1 ml. of a 5% solution of copper sulfate was added and the mixture was refluxed gently with shaking for 30 minutes. The alcohol solution was filtered while hot, and evaporated under vacuum. About 0.5 ml. of a yellow liquid remained. This was purified by micro-distillation. It was found to have a boiling point of 129–130° (19 mm.) and a refractive index, n^{20}_D 1.4493. This was identical with the physical constants of methyl *n*-propyl sulfone prepared independently by the following process: Iodopropane (10 g.) and 5.1 g. of sodium methanesulfinate[28] were dissolved in 50 ml. of absolute ethanol. The solution was refluxed with stirring for 6 hours. The salt (NaI) formed was filtered off and the solution was distilled under vacuum. After removal of ethanol, a high boiling colorless liquid was obtained, b.p. 128–129° (19 mm.), n^{20}_D 1.4503. The yield was 53.4%.

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[28] Supplied by J. P. Milionis, this Laboratory.

LAFAYETTE, INDIANA

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

A New Synthesis of Unsymmetrical Phosphinic Acids

BY LEON D. FREEDMAN AND G. O. DOAK

RECEIVED NOVEMBER 26, 1951

A number of diaryl- and arylalkylphosphinic acids have been prepared by the reaction between diazonium fluoborates and dichlorophosphines in ethyl acetate in the presence of cuprous bromide. Evidence is presented which indicates that unsymmetrical phosphorus compounds disproportionate to symmetrical compounds under the conditions of this reaction. Several aminophosphinic acids have been obtained by reduction of the corresponding nitro compounds.

The synthesis of arylphosphonic and diarylphosphinic acids by the reaction between diazonium fluoborates and phosphorus trichloride has been described in recent papers[1] from this Laboratory. The major reaction product was invariably the phosphonic acid; however, by proper choice of solvent and catalyst, a fair yield of the symmetrical phosphinic acid could be obtained. We have now found that the phosphinic acid can be obtained as the main product of the reaction between diazonium fluoborates and aromatic or aliphatic dichlorophosphines. By means of this reaction, symmetrical diaryl-, unsymmetrical diaryl- and arylalkylphosphinic acids can be readily prepared. No phosphine oxide was isolated in any reaction so far investigated.

The unsymmetrical phosphinic acids were isolated in somewhat smaller yields than the total yields of organophosphorus compounds obtained in the reaction described earlier.[1a] This decrease is due not only to a lower yield of crude product, but also to greater difficulties experienced in the purification of the unsymmetrical compounds. These difficulties are associated with the presence of symmetrical phosphinic acids in reaction products in which only unsymmetrical acids should be expected. Thus, from the reaction between *p*-nitrobenzenediazonium fluoborate and ethyldichlorophosphine, we have isolated not only (*p*-nitrophenyl)-ethylphosphinic acid but also a small amount of bis-(*p*-nitrophenyl)-phosphinic acid. From the reaction between *m*-nitrobenzenediazonium fluoborate and ethyldichlorophosphine, we obtained a 4% yield of bis-(*m*-nitrophenyl)-phosphinic acid and none of the expected (*m*-nitrophenyl)-ethylphosphinic acid.

The symmetrical compounds are probably formed by a reaction of the type

$$2RR'PX_3 \rightleftharpoons R_2PX_3 + R'_2PX_3$$

Similar redistribution reactions of lead and mercury compounds have been extensively studied by Calingaert.[2] The disproportionation of aromatic dichlorophines has been postulated by Kosolapoff and Huber.[3]

The unsymmetrical nitro substituted phosphinic acids were reduced to amino derivatives by the method previously used.[1b] Since (*p*-aminophenyl)-ethylphosphinic acid was rather soluble in water, it was found convenient to reduce the corresponding nitro compound in methanol. After removal of the catalyst by filtration, the amino acid was obtained by vacuum concentration of the filtrate. The crude product was recrystallized from methanol.

The compounds prepared, together with their analyses, yields, and m.p.'s, are listed in Table I. With the exception of diphenylphosphinic acid, none of these compounds have previously been described.

Materials.—All of the phosphinic acids described in the present paper, with the exception of the amino compounds, were prepared by the reaction between phenyl- or ethyldichlorophosphine and the appropriate diazonium fluoborate. The phenyldichlorophosphine was kindly furnished us by the Victor Chemical Works. The ethyldichlorophosphine was prepared by the method of Kharasch, Jensen and Weinhouse.[4] The tetraethyllead needed for this preparation was obtained through the courtesy of the Ethyl Corporation. The diazonium fluoborates were prepared and analyzed as described in an earlier paper[5] from this Laboratory. The solvents and other chemicals used were reagent grade and were not further purified.

Experimental

The apparatus and procedure employed were similar to those developed in this Laboratory for the preparation of arylphosphonic and symmetrical diarylphosphinic acids.[1a] A short lag period (30 minutes or less) after mixing the solvent, diazonium fluoborate, dichlorophosphine and catalyst, was followed by a violent reaction. The residual liquid, after the steam distillation, was evaporated to approximately

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[1] (a) G. O. Doak and L. D. Freedman, THIS JOURNAL, **73**, 5658 (1951); (b) G. O. Doak and L. D. Freedman, *ibid.*, **74**, 753 (1952).

[2] G. Calingaert and H. A. Beatty, in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1806.

[3] G. M. Kosolapoff and F. W. Huber, THIS JOURNAL, **69**, 2020 (1947).

[4] M. S. Kharasch, E. V. Jensen and S. Weinhouse, *J. Org. Chem.*, **14**, 429 (1949).

[5] G. O. Doak and L. D. Freedman, THIS JOURNAL, **73**, 5656 (1951).

TABLE I

PHOSPHINIC ACIDS RR'PO_2H

R	R'	Yield, %	M.p.,[a] °C.	Formula	P analyses, % Calcd.	P analyses, % Found	Neutral equivalent[b] Calcd.	Neutral equivalent[b] Found	N analyses, % Calcd.	N analyses, % Found
C_6H_5	C_6H_5	42[c]	192–195	$C_{12}H_{11}O_2P$	14.20	14.10	218.2	219.3		
m-ClC_6H_4	C_6H_5	27[c]	159–162	$C_{12}H_{10}ClO_2P$	12.26	12.21	252.6	252.4		
o-BrC_6H_4	C_6H_5	15[c]	206–209	$C_{12}H_{10}BrO_2P$	10.43	10.39	297.1	299.2		
m-$NO_2C_6H_4$	C_6H_5	36[c]	166–167	$C_{12}H_{10}NO_4P$	11.77	11.81	263.2	263.4	5.32	5.22
p-$NO_2C_6H_4$	C_6H_5	30[c]	153–154	$C_{12}H_{10}NO_4P$	11.77	11.59	263.2	264.1	5.32	5.29
m-$NH_2C_6H_4$	C_6H_5	89	260–263 dec.	$C_{12}H_{12}NO_2P$	13.28	13.19	233.2	233.3	6.01	6.01
p-$NH_2C_6H_4$	C_6H_5	84	210–211.5	$C_{12}H_{12}NO_2P$	13.28	13.17	233.2	233.4	6.01	6.04
o-BrC_6H_4	C_2H_5	9[c]	98–101	$C_8H_{10}BrO_2P$	12.44	12.66	249.1	250.3		
p-$NO_2C_6H_4$	C_2H_5	15[c]	127–130	$C_8H_{10}NO_4P$	14.40	14.14	215.1	216.8	6.51	6.50
p-$NH_2C_6H_4$	C_2H_5	69	172–173	$C_8H_{12}NO_2P$	16.73	16.65	185.2	183.7	7.57	7.60

[a] Melting points were taken as previously described; *cf.* ref. 1. [b] Phenolphthalein was used as the indicator. [c] These yields were obtained by the use of ethyl acetate as the solvent and cuprous bromide as the catalyst.

100 ml. for preparations on a 0.1 mole scale. The crude phosphinic acid, which crystallized when this solution was cooled, was removed by filtration. The solid was dissolved in 10% sodium hydroxide solution and the solution filtered from a small amount of undissolved material. No phosphine oxide was ever found in this insoluble residue. The alkaline filtrate was treated with Darco, again filtered, and the phosphinic acid reprecipitated by the addition of concentrated hydrochloric acid. The phosphinic acid was finally purified by recrystallization from appropriate solvents.

Diphenylphosphinic acid was readily purified by the recrystallization from aqueous alcohol. The unsymmetrical diarylphosphinic acids were more difficult to purify. Repeated recrystallizations from aqueous alcohol were necessary in order to remove traces of symmetrical diarylphosphinic acids. The arylethylphosphinic acids were even more difficult to obtain in a pure state. Neither aqueous alcohol nor ether were satisfactory recrystallizing solvents. Ethyl acetate proved to be the solvent of choice for the two arylethylphosphinic acids studied.

In two cases symmetrical phosphinic acids were isolated from reactions of ethyldichlorophosphine with diazonium fluoborates. In one experiment 6.2 g. of crude (*p*-nitrophenyl)-ethylphosphinic acid was recrystallized from 50% aqueous alcohol and then extracted with ether in a Soxhlet apparatus for 72 hours. The insoluble residue (0.25 g.) was shown to be bis-(*p*-nitrophenyl)-phosphinic acid by analysis and mixed m.p. with an authentic sample. An attempt to prepare (*m*-nitrophenyl)-ethylphosphinic acid yielded a phosphinic acid, which was recrystallized from 95% alcohol. The recrystallized material was identified as bis-(*m*-nitrophenyl)-phosphinic acid by analysis and mixed m.p. with an authentic sample. It is possible that the desired unsymmetrical acid was formed in small amount, and was lost in the purification process.

Analysis for Phosphorus.—Phosphorus was determined by a modification of the method of Bachofer and Wagner.[6] Details of this modification will be reported elsewhere.

Acknowledgment.—The authors wish to thank Miss Sadie Herndon for performing the analyses necessary for this research and Miss Stella Efland for skilled technical assistance.

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[6] M. D. Bachofer and E. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **15**, 601 (1943).

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

Condensation of Saturated Halides with Unsaturated Compounds. VIII. Condensation of Dihaloalkanes with Ethylene and Chloroethylenes[1]

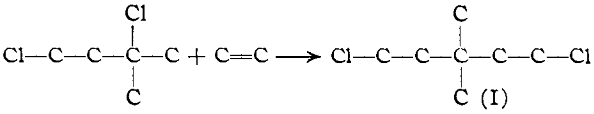
BY LOUIS SCHMERLING AND JAMES P. WEST

RECEIVED NOVEMBER 19, 1951

The metal chloride-catalyzed condensation of ethylene and chloroethylenes with dichloroalkanes in which at least one chlorine atom is attached to a tertiary carbon atom results in the formation of polychloroalkanes containing quaternary carbon atoms. For example, the reaction of the readily prepared isoprene dihydrochloride (or the analogous dibromide) with ethylene offers a convenient means for the preparation of 1,5-dihalo-3,3-dimethylpentane, from which a number of heterocyclic compounds with *gem*-dimethyl groups have been synthesized. Two new spiro hydrocarbons, 8,8-dimethylspiro[4,5]-2,4-decadiene and 8,8-dimethylspiro[4.5]decane are described.

In previous papers in this series it was shown that alkyl halides (chlorides and bromides) containing at least three carbon atoms add to olefins[2] and haloölefins[3] in the presence of metal halide catalysts of the Friedel–Crafts type. The present communication describes the extension of the reaction to dihaloälkanes, at least one halogen atom of which is held by a tertiary carbon atom.

The reaction of 1,3-dichloro-3-methylbutane (isoprene dihydrochloride) with ethylene in the presence of aluminum chloride at −12° resulted in a 68% yield of 1,5-dichloro-3,3-dimethylpentane (I). It is apparent that the chlorine atom attached to the tertiary carbon atom is much more reactive than that attached to the primary carbon atom. This finds analogy in the results with the alkyl halides; in general the best yields were obtained with the tertiary alkyl halides and the poorest with the primary isomers.



$$\mathrm{Cl{-}C{-}C{-}\overset{\displaystyle Cl}{\underset{\displaystyle C}{C}}{-}C + C{=}C \longrightarrow Cl{-}C{-}C{-}\overset{\displaystyle C}{\underset{\displaystyle C}{C}}{-}C{-}C{-}Cl}\quad \text{(I)}$$

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[1] (a) Presented at the XIIth International Congress of Pure and Applied Chemistry, New York, September 10–13, 1951. (b) Preceding paper in this Series, THIS JOURNAL, **71**, 753 (1949).

[2] (a) L. Schmerling, *ibid.*, **67**, 1152 (1945); (b) *ibid.*, **69**, 1121 (1947); (c) L. Schmerling and E. E. Meisinger, *ibid.*, **71**, 753 (1949).

[3] L. Schmerling, *ibid.*, **68**, 1650, 1655 (1946); **71**, 701 (1949).