

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

The Synthesis of Arylphosphonic and Diarylphosphinic Acids by the Diazo Reaction¹

BY G. O. DOAK AND LEON D. FREEDMAN

A number of arylphosphonic and diarylphosphinic acids have been prepared by the reaction between diazonium fluoroborates and phosphorus trichloride in organic solvents and in the presence of copper salts. The solvents used include dioxane and several aliphatic acetates. Two procedures are described for the isolation and purification of the phosphonic acids.

A study of the reaction between the halides of certain elements and dry diazonium salts in organic solvents has been initiated in this Laboratory. The first paper of this series describes the results obtained using arsenic trichloride and diazonium fluoroborates.² The present paper reports an extension of this reaction to phosphorus trichloride.

Several methods have been previously used for the preparation of arylphosphonic acids.³ None of these reactions has been found convenient for preparing a wide variety of such compounds. Previous attempts to prepare phosphonic acids by means of the diazo reaction have been unsuccessful.^{4,5} We have now prepared a series of arylphosphonic and diarylphosphinic acids from the corresponding aryldiazonium fluoroborates by the use of the general method described in the previous paper.² The melting points of many of the compounds prepared by this method are significantly higher than the melting points previously reported; this fact, we believe, reflects the increased purity of these compounds as compared with those prepared by older methods.

Since most of the phosphonic acids are extremely soluble in water and in many organic solvents, the isolation and purification of these acids has offered considerable difficulty. The hemi-sodium and hemi-potassium salts are less soluble than the free acids; we have used this fact to facilitate isolation. The barium salts were also used, but generally have proved less satisfactory.

Experimental

Reagents.—All of the diazonium fluoroborates used were analyzed by the method described in the previous paper.² The solvents and other chemicals were reagent grade and were not specially purified.

Procedure.—The reaction was carried out in a hood, because boron trifluoride was evolved. The diazonium fluoroborate (0.2 mole) was suspended in 250 ml. of the organic solvent in a 3-necked flask, equipped with a sealed stirrer, a wide-bore gas outlet tube connected to a water-trap, and a thermometer which dipped beneath the surface of the liquid. Stirring was begun and then phosphorus trichloride (0.2 mole) and 4 g. of the catalyst were added. There was at this point a slight rise in temperature, usually followed by a lag period, during which time no visible reaction occurred. This lag period varied from 15 minutes to 2 hours, and was followed by a sudden evolution of gas and a rapid increase in

temperature. It was often necessary to cool the mixture at this point to prevent the reaction from becoming violent.⁶ In a few cases no reaction occurred until the mixture was heated to about 50° on a water-bath.

When gas was no longer evolved, the thermometer was removed and a dropping funnel substituted; 50 ml. of water was added dropwise to the stirred solution. The addition of water was performed carefully as considerable heat was generated. The reaction mixture was then steam distilled until approximately 1 liter of distillate had been collected. In this manner the solvent and volatile by-products of the reaction were removed. The residual liquid in the flask was then transferred to a beaker and evaporated on a steam-bath in a hood to approximately 200 ml. The diarylphosphinic acid crystallized when this solution was cooled. The crude acid was removed by filtration and dissolved in 10% sodium hydroxide solution. The alkaline solution was treated with Darco, filtered, and the acid reprecipitated by the addition of concentrated hydrochloric acid. The diarylphosphinic acid was purified by recrystallization. Aqueous alcohol was used for all the secondary acids except for bis-(*m*-nitro-

TABLE I

THE EFFECT OF VARIOUS SOLVENTS AND CATALYSTS ON THE YIELDS OF *p*-NITROBENZENE^aPHOSPHONIC AND BIS-(*p*-NITROBENZENE)-PHOSPHINIC ACIDS

$\text{O}_2\text{NC}_6\text{H}_4\text{PO}_3\text{H}_2$ yield, %	$\text{O}_2\text{NC}_6\text{H}_4)_2\text{PO}_3\text{H}$ yield, %	Solvent	Catalyst
47	6	EtOAc ^b	CuBr
35	14	<i>i</i> -PrOAc ^c	CuBr
23	7	<i>n</i> -BuOAc ^c	CuBr
34	0	Dioxane ^d	CuBr
38	7	EtOAc ^b	Cu bronze
46	0.2	EtOAc ^b	CuCl

^a Isolated by procedure B. ^b Eastman Kodak Co., white label (anhydrous). ^c Carbide and Carbon Chemicals Corporation. ^d Eastman Kodak Co. white label.

TABLE II

ARYLPHOSPHONIC AND DIARYLPHOSPHINIC ACIDS PREPARED FROM DIAZONIUM FLUOROBORATES WITH THE USE OF CUPROUS BROMIDE AS THE CATALYST

R	Isolation procedure	RPO_3H_2 yield, %	$\text{R}_2\text{PO}_3\text{H}$ yield, %
C_6H_5	A	17	3.8
<i>o</i> -ClC ₆ H ₄	B	44	10
<i>m</i> -ClC ₆ H ₄	A	43	7.0
<i>p</i> -ClC ₆ H ₄	A	50	7.0
<i>m</i> -NO ₂ C ₆ H ₄	B	37	5.5
<i>m</i> -NO ₂ C ₆ H ₄	B	27 ^a	26 ^a
<i>p</i> -COOH C ₆ H ₄	A	39	0 ^b
<i>p</i> -SO ₂ NH ₂ C ₆ H ₄	A	50	0
<i>p</i> -CH ₃ C ₆ H ₄	A	42	0 ^b

^a These yields were obtained by the use of isopropyl acetate as the solvent; all other yields listed in this table were obtained using ethyl acetate. ^b Based on a single synthesis.

(6) The reaction has been successfully carried out with 0.5 mole of diazonium fluoroborate in a 5-liter flask equipped with an 18 mm. gas outlet tube. Because of the vigor of the reaction, syntheses on a large scale might prove hazardous.

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

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

(3) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, Chapter 7.

(4) D. R. Nijk, *Rec. trav. chim.*, **41**, 461 (1922); V. M. Piets, *J. Gen. Chem. (U. S. S. R.)*, **7**, 270 (1937).

(5) V. M. Piets, *ibid.*, **7**, 84 (1937), has reported the preparation of arylphosphonous acids from diazonium salts and sodium hypophosphite. Other investigators (*cf.* G. M. Kosolapoff, *ref. (3)*, p. 142), have been unable to duplicate these results.

TABLE III
ANALYSES AND MELTING POINTS OF ARYLPHOSPHONIC AND DIARYLPHOSPHONIC ACIDS

RC ₆ H ₄ (PO ₃ H) ₂ R =	M.p., ^a °C.	Formula	P analyses, %		Neut. equiv., ^b	
			Calcd.	Found	Calcd.	Found
H ^{c,d}	162.5-163	C ₆ H ₇ O ₃ P	19.60	19.23	79.0	79.2
<i>o</i> -Cl	182-184	C ₆ H ₅ ClO ₃ P	16.09	15.81	96.3	96.1
<i>m</i> -Cl ^e	137-137.5	C ₆ H ₅ ClO ₃ P	16.09	16.16	96.3	96.6
<i>p</i> -Cl ^{f,g}	187-188.5	C ₆ H ₅ ClO ₃ P	16.09	16.13	96.3	96.0
<i>m</i> -NO ₂ ^{h,i}	155-156	C ₆ H ₅ NO ₃ P	15.25	14.73	101.5	101.6
<i>p</i> -NO ₂ ^j	197-198	C ₆ H ₅ NO ₃ P	15.25	15.36	101.5	101.5
<i>p</i> -COOH ^k	>300	C ₇ H ₇ O ₃ P	15.33	15.04	67.4	67.1
<i>p</i> -SO ₂ NH ₂ ^l	224-225	C ₆ H ₅ NO ₆ PS	13.06	12.75	118.6	m
<i>p</i> -CH ₃ ⁿ	198-199	C ₇ H ₉ O ₃ P	18.00	17.61	86.1	86.7
(RC ₆ H ₄) ₂ PO ₃ H, R =						
H ^o	192-193.5	C ₁₂ H ₁₁ O ₃ P	14.20	13.95	218.2	219.4
<i>o</i> -Cl ^p	233-236	C ₁₂ H ₉ Cl ₂ O ₃ P	10.79	10.68	287.1	286.7
<i>m</i> -Cl	164-165	C ₁₂ H ₉ Cl ₂ O ₃ P	10.79	10.52	287.1	292.2
<i>p</i> -Cl ^q	145-146	C ₁₂ H ₉ Cl ₂ O ₃ P	10.79	10.49	287.1	289.2
<i>m</i> -NO ₂ ^{r,s}	271-273	C ₁₂ H ₉ N ₂ O ₆ P	10.05	9.89	302.2	t
<i>p</i> -NO ₂ ^u	275-277	C ₁₂ H ₉ N ₂ O ₆ P	10.05	9.80	308.2	307.8

^a Melting points were taken on a Fisher melting point block. The thermometer was calibrated against U.S.P. melting point reference standards, cf. Rosin, *J. Am. Pharm. Assoc. Sci. Ed.*, **35**, 56 (1946). ^b The indicator used for the primary acids was thymolphthalein; the indicator used for the secondary acids was phenolphthalein. ^c Previously prepared by A. D. F. Toy, *THIS JOURNAL*, **70**, 186 (1948), and other workers. Highest previously reported m.p. 161-162°. ^d Calcd.: C, 45.58; H, 4.46. Found: C, 45.23; H, 4.33. ^e Previously prepared by G. M. Kosolapoff, *ibid.*, **70**, 3465 (1948); m.p. 136-137. ^f Previously prepared by H. Bauer, *ibid.*, **63**, 2137 (1941), and other workers. Highest previously recorded m.p. 188°. ^g Calcd.: Cl, 18.41. Found: Cl, 18.36. ^h Previously prepared by D. R. Nijk, *Rec. trav. chim.*, **41**, 461 (1922), and other workers. Highest previously reported m.p. 140°. ⁱ Calcd.: N, 6.90. Found: N, 7.02. ^j Calcd.: N, 6.90. Found: N, 6.78. ^k Previously prepared by A. Michaelis and Cl. Paneck, *Ber.*, **14**, 405 (1881). ^l Calcd.: C, 30.38; H, 3.40; N, 5.91. Found: C, 30.27; H, 3.37; N, 5.96. ^m A sharp end-point could not be obtained with this compound using thymolphthalein. ⁿ Previously prepared by A. Michaelis and Cl. Paneck, *Ber.*, **13**, 653 (1880), and other workers. Highest previously reported m.p. 189°. ^o Previously prepared by G. M. Kosolapoff, *THIS JOURNAL*, **64**, 2982 (1942), and other workers. Highest previously reported m.p. 195-196°. ^p Previously reported by V. M. Plets, Dissertation, Kazan, 1938; cf. Kosolapoff, ref. 3, p. 170; m.p. 212-214°. ^q Previously prepared by Kosolapoff, ref. o; m.p. 133-135°. Also reported by Plets, ref. p; m.p. 208-210°. ^r Previously prepared by C. Dörken, *Ber.*, **21**, 1505 (1888); m.p. 268°. ^s Calcd.: N, 9.09. Found: N, 9.05. ^t Consistent neutral equivalent results on this compound could not be obtained. ^u Calcd.: N, 9.09. Found: N, 9.00.

phenyl)-phosphonic acid, which was recrystallized from glacial acetic acid.

The original filtrate from the diarylphosphonic acid was evaporated to 50 ml. and cooled whereupon the crude arylphosphonic acid crystallized from solution. The crystalline acid was dissolved in that amount of 20% sodium or potassium hydroxide necessary to give a solution of approximately pH 8. This solution was filtered from the precipitated copper hydroxide and the filtrate treated with Darco. The charcoal was removed and the filtrate acidified to congo red with concentrated hydrochloric acid. The hemi-sodium (or hemi-potassium) salt immediately precipitated. The mixture was cooled and the salt removed by filtration. In order to isolate the free phosphonic acid from its salt, one of two methods (Procedures A and B below) was used.

With the *m*- and *p*-chloro derivatives, a mixture of arylphosphonic and diarylphosphonic acid was obtained when the residual liquid from the steam distillation was evaporated in 200 ml. In these cases the liquid was evaporated to 50 ml. and cooled. The solid which separated was removed by filtration and dissolved in 10% sodium hydroxide; this solution was treated with Darco and filtered. The filtrate was acidified to congo red with concentrated hydrochloric acid whereupon the diarylphosphonic acid and the hemi-sodium salt of the arylphosphonic acid precipitated. The solid was removed by filtration and then extracted with boiling 6 *N* hydrochloric acid. The arylphosphonic acid dissolved leaving the diarylphosphonic acid as an oil. On cooling the solution the phosphonic acid crystallized out. The diarylphosphonic acid solidified on cooling and was then purified by recrystallization from aqueous alcohol.

Procedure A.—When the phosphonic acid was only slightly soluble in the cold, the hemi-sodium salt was dissolved in hot 6 *N* hydrochloric acid. On cooling the solution, the crystalline acid separated and was recrystallized one or more times from dilute hydrochloric acid. (It was found that the hemi-sodium salt was preferable for this procedure. When the hemi-potassium salt was used the phosphonic acid was usually contaminated with potassium chloride.)

Procedure B.—When the phosphonic acid was very soluble in hydrochloric acid the following procedure was used. The hemi-potassium salt (which was less soluble than the corresponding sodium salt) was dissolved in an excess of hot 6 *N* hydrochloric acid. The solution was evaporated to dryness on a steam-bath, and the residue further dried in a desiccator over sodium hydroxide. The solid was extracted with ether in a soxhlet apparatus until the material in the thimble gave no acid reaction. The phosphonic acid crystallized readily from the ether solution and a second crop could usually be obtained by evaporating the ether to a small volume.

Analysis.—Two methods of determining phosphorus in the purified compounds were used, namely, the procedure of Bachofer and Wagner⁷ and a similar method using an electric ignition macro bomb. With both methods the phosphorus values obtained tended to be slightly lower than theoretical.

Results

The total yield and the ratio between the yields of *p*-nitrobenzenephosphonic acid and bis-(*p*-nitrophenyl)-phosphonic acid was found to vary with the solvent and catalyst used. These results are shown in Table I. The yields obtained with other diazonium fluoroborates are shown in Table II. Analyses and melting points of all compounds prepared are given in Table III. Only in the case of *o*-nitrobenzenediazonium fluoroborate has the reaction failed to produce the expected arylphosphonic acid. Attempts to prepare this compound under a variety of reaction conditions always yielded a large quantity of tar. Although a small amount of phosphonic acid was isolated in each

(7) M. D. Bachofer and B. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **35**, 601 (1940).

case, analysis, both Kjeldahl and Dumas, indicated that this material did not contain nitrogen. We have not yet identified this substance.

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The Thermal Degradation of Polyesters

BY HERBERT A. POHL

The general character of thermal degradation in hot polyesters has been examined. In particular the degradation of molten terephthalic acid/ethylene glycol polyester is shown to involve considerable main chain cracking resulting in lowered molecular weight. Study of a number of polymers of varied structure has thrown some light on the probable weak points for their thermal degradation. The carboxyl group, $-\text{CO}-\text{O}-$, is considered to be an active center for the degradation reaction as polymer without this group but otherwise similar in structure is considerably more stable. It is further evident that the presence of a $-\text{CH}_2-$ group two carbon atoms removed from the ether oxygen of the carboxyl, is a key weak point and that replacing the H's by CH_3 on this $\beta\text{-CH}_2$ group considerably increases the thermal stability of the polyester.

I. General Character of Polymer Degradation

As H. Melville recently explained¹ the degradation of polymers to monomer may in general follow three courses (Fig. 1).

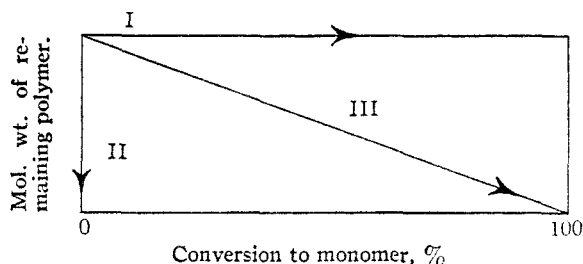


Fig. 1.

Types of Polymer Degradation.—Type I degradation, in which particular polymer molecules depolymerize practically completely to monomer while the remaining polymer molecules stay essentially unchanged in size, is common in vinyl addition polymers. It is typical of a "zipper-like" reverse polymerization preceded by activation of an end group.

Type II degradation is typical of random chain cracking where relatively few chain breaks cause a large drop in molecular weight. Thermal degradation of most polyesters which cannot form cyclic monomer and of polythene is of this type (e.g., terephthalic acid/glycol polyesters).

Type III degradation is typical of main chain cracking in which the zipper effect goes in one direction only from the split, or proceeds to a limited extent to leave fragments of relatively large but reduced molecular weight together with many monomer fragments. Certain vinyl polymers degrade in this manner¹ as well as certain polyesters and polyanhydrides which produce cyclic monomer at relatively low temperatures.^{2,3}

II. Broad Aspects of Thermal Degradation in Polyesters

A. Depolymerization to Monomer.—To an extent limited essentially by the end-group content, condensation

polymers can in general be heated to yield small amounts of monomer. This reaction tends to increase the molecular weight, except in the cases noted where cyclic monomer can be split out in analogy to reverse addition polymerization.

For example, polyethyleneterephthalate, the monomeric unit of which cannot exist as a cyclic structure, under molecular distillation conditions yields only a few-tenths per cent. of material containing 1, 2 or 3 monomer units. On the other hand, polytrimethylene carbonate under similar conditions easily produces much larger (up to 50%) yields of cyclic monomer.^{4,5}

B. Chain Cracking.—The most important mode of polymer degradation, as far as molecular weight or chain size is concerned, is chain-cracking. This may occur in polyesters as a direct thermal cracking or as a result of hydrolysis by water produced by other reactions. The chemical attack by oxygen is excluded from this discussion.

C. Conversion of Main Chain Groups.—In polyethyleneterephthalate there is good evidence that in at least two instances the nature of groups in the main chain are rather simply altered, causing only slight change in the chain length, although the by-products of these reactions may presumably act to split other chain links. In the first instance, the ester link is known in this polymer to be convertible to an anhydride link. This conclusion is based on direct chemical and on infrared spectroscopic evidence. In the second instance, color formation, the colored residues can be shown by selective solubility experiments to be converted members of the chain which are still attached to the main chain. To prove this second case, a terephthalic acid/glycol polyester, which was colored because of thermal degradation, was dissolved to form a 10% solution in liquefied phenol (ca. 10% H_2O). This solution was mixed with a similar 10% solution of colorless nylon (hexamethylenediamine adipamide) in the same solvent. The mixture resuspended into two layers, the lower containing the polyester. That the color of the polyester is firmly fixed onto the long polyester chains was evidenced by the observation that the color remained associated with the polyester layer instead of becoming distributed between the two layers as small molecules would do.

III. The Effect of Structure on Thermal Stability

In order to better understand the source of degradation and site of weak spots in polyesters, a number of polyesters were prepared from carefully purified intermediates and the thermal degradation studied and compared with that of a pure hydrocarbon polymer. In these experiments the degradation was determined by measurement of the rate of total gas evolution, coloration, and acid end-group formation. The hydrocarbon polymer, polyethylene of a low degree of branching, was employed as a comparison compound to allow better understanding of the role of the ester linkage in degradation.

A. Experimental

Measurement of the rate of gas produced was made in an isoteniscope. One-gram samples of polymer were placed in

(1) H. Melville, *Science Progress*, **38**, 1-9 (1950), No. 149, January.
(2) W. H. Carothers and E. W. Spanagel, *ibid.*, **38**, 664 (1936).
(3) W. H. Carothers and J. W. Hill, *This Journal*, **58**, 5081 (1936).