Organometallic Azides. III. Methylphenylphosphinic Azide and Related Compounds[1,2]

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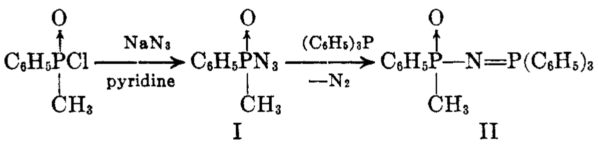
The prototype of arylenebis(methylphosphinic azides), methylphenylphosphinic azide, has been synthesized and found to be thermally stable. The thermal reorganization of phosphorus trichloride and *p*-phenylenebis(diphenylphosphine) provides a convenient route to *p*-phenylenebis(phosphonous dichloride), a reactive intermediate for the synthesis of a variety of derivatives leading to arylenebis(methylphosphinic azides). The use of alkyl tosylates in the Michaelis-Arbusov reaction has been invesigated as a route to synthetic intermediates.

In previous papers from this laboratory we have described the syntheses and properties of *p*-phenylenebis(methylphosphinic acid)[4] as well as several diarylphosphinic azides,[5a] and arylphosphonic diazides.[5b] More recently the syntheses of several arylenebis(phenylphosphinic acids) have been reported.[6] As the result of an effort to further expand the field of organophosphorus azide chemistry toward thermally stable polymeric materials, we wish now to report on the synthesis and properties of methylphenylphosphinic azide. Additionally, we would like to present a preliminary account of new routes to arylenebis(methylphosphinic acids), the precursors of arylenebis(methylphosphinic azides).

General Approach

Methylphenylphosphinic Azide.—Prior to the preparation of arylene bis(methylphosphinic azides) for use in the syntheses of polyphosphorane polymers, it was considered prudent from both a safety and a synthetic point of view to prepare and characterize a prototype compound, methylphenylphosphinic azide (I). Following the previously described method,[5a] we treated methylphenylphosphinic chloride with sodium azide in pyridine to obtain I, the first example of a mixed alkylarylphosphinic azide.

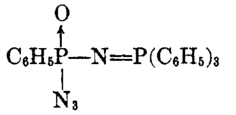
Initially as a further safety precaution, a small quantity of I was distilled at reduced pressure without incident. The azide I was found not to detonate in a drop-weight test and to burn only slowly in air. Thus, I appeared to be qualitatively as stable as the previously prepared diarylphosphinic azides.[5a] Further evidence of the stability of I was obtained when it was observed that the reaction with triphenylphosphine proceeded only slowly in pyridine at room temperature. In contrast, the diarylphosphinic azides reacted exothermically and more rapidly with triphenylphosphine.[5a] In pyridine at the reflux temperature or in a sealed tube at 125°, the reaction of I with triphenylphosphine took place at a convenient rate and we obtained a quantitative yield of nitrogen and were able to isolate the phosphorane II, P-methyl-P-phenyl-N-triphenylphosphoranylidinephosphinic amide. Thermogravimetric analysis (TGA) indicated that II was qualitatively as thermally stable as the fully phenylated analog and, thus, that the methylphenylphosphinic group could be introduced into polyphosphorane compositions to vary possibly the physical properties. The preparation of methylphosphinic azide (I) and its conversion to II are summarized in eq 1.



$$C_6H_5\overset{O}{\overset{\uparrow}{\underset{CH_3}{\underset{|}{P}}}}Cl \xrightarrow[\text{pyridine}]{NaN_3} C_6H_5\overset{O}{\overset{\uparrow}{\underset{CH_3}{\underset{|}{P}}}}N_3 \xrightarrow[-N_2]{(C_6H_5)_3P} C_6H_5\overset{O}{\overset{\uparrow}{\underset{CH_3}{\underset{|}{P}}}}{-}N{=}P(C_6H_5)_3 \quad (1)$$

I II

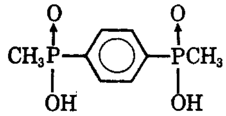
The azide asymmetric stretching absorption in the infrared spectrum of I was observed at 2137 cm^{-1} which represents a slight shift of this absorption band previously observed at 2155–2165 for the arylphosphonic diazides,[5b] 2150 for the diarylphosphinic azides,[5a] and about 2140 cm^{-1} for the azidophosphorane III.[5b] Therefore, it appears that the decrease in the reactivity of phosphorus (+5) azides with triphenylphosphine can be correlated with the slight shifts in the azide asymmetric absorption to the lower frequencies. A similar correlation is found in the data obtained by Thayer and West[7] for the series of triphenylazido compounds of silicon (2149 cm^{-1}), germanium (2100 cm^{-1}), tin (2093 cm^{-1}), and lead (2046 cm^{-1}). An even more dramatic decrease in the reactivity of some of these azides with triphenylphosphine was observed as no reaction occurred with the latter two azides even at 180°.



$$C_6H_5\overset{O}{\overset{\uparrow}{\underset{N_3}{\underset{|}{P}}}}{-}N{=}P(C_6H_5)_3$$

III

Arylenebis(methylphosphinic acids).—In view of the above results, we desired to prepare arylenebis(methylphosphinic azides) for evaluation in polyphosphorane compositions. However, since of this series of acids only *p*-phenylenebis(methylphosphinic acid) (IV) has



IV

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[1] Presented in part at the First Annual Western Regional American Chemical Society Meeting, Los Angeles, Calif., Nov 18–20, 1965. For previous papers in this series, see ref 5.

[2] This work was supported by the U. S. Air Force, under Contracts AF 33(657)-11296, -11129, and AF 33(615)-3570, monitored by the Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio.

[3] Chemistry Research Laboratory, Rocketdyne, a Division of North American Aviation, Inc., Canoga Park, Calif. 91304.

[4] E. M. Evleth, Jr., L. D. Freeman, and R. I. Wagner, *J. Org. Chem.*, **27**, 2192 (1962).

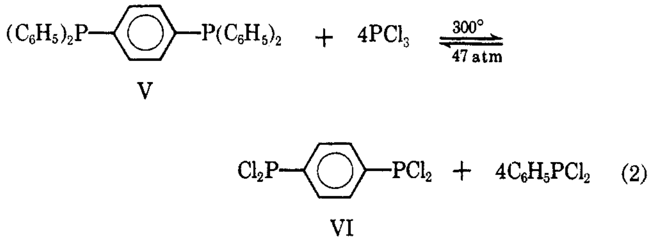
[5] (a) R. A. Baldwin and R. M. Washburn, *ibid.*, **30**, 3860 (1965); (b) R. A. Baldwin, *ibid.*, **30**, 3866 (1965).

[6] R. A. Baldwin and M. T. Cheng, *ibid.*, **32**, 1572 (1967).

[7] J. S. Thayer and R. West, *Inorg. Chem.*, **3**, 406 (1964).

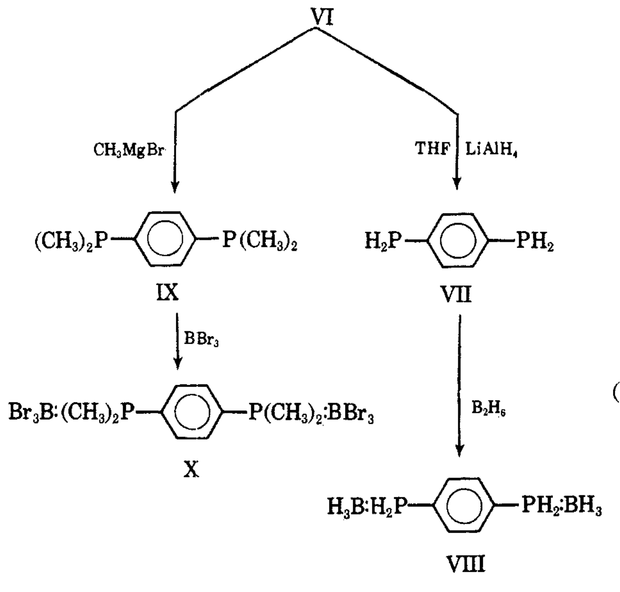
been previouly prepared *via* a circuitous route[4] which was subject to synthetic difficulties,[6] it was first deemed necessary to investigate new routes to IV as well as other arylenebis(methylphosphinic acids).

The key step in the new, alternate route to *p*-phenylenebis(methylphosphinic acid) (IV) was the successful thermal reorganization of *p*-phenylenebis(diphenylphosphine) (V) and phosphorus trichloride. A high conversion of V to *p*-phenylenebis(phosphonous dichloride) (VI) was obtained (eq 2) if at least a 500% excess of phosphorus trichloride was used.



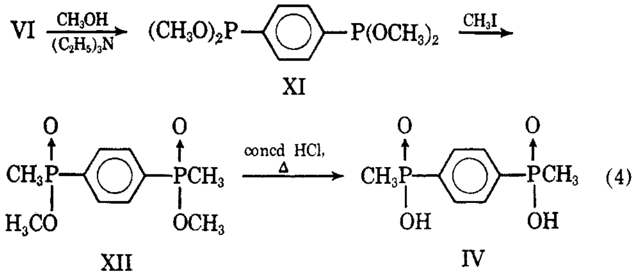
(2)

Although not isolated and characterized, *p*-phenylenebis(phosphonous dichloride) (VI) in the residue obtained from the reaction described above was confirmed by its reduction with lithium aluminum hydride in tetrahydrofuran to give a 38% yield of *p*-phenylenebis(phosphine) (VII; *cf.* 20% yield using diethyl ether as the solvent[4]) and subsequent conversion of VII to the bis(borane) adduct VIII.[8] Thus this new method offers a greatly shortened route to VI and many of its derivatives with higher over-all yield. Further characterization of VI was effected by preparing *p*-phenylenebis(dimethylphosphine) (IX) and its bis(tribromoborane) adduct (X). These reactions are summarized in eq 3.



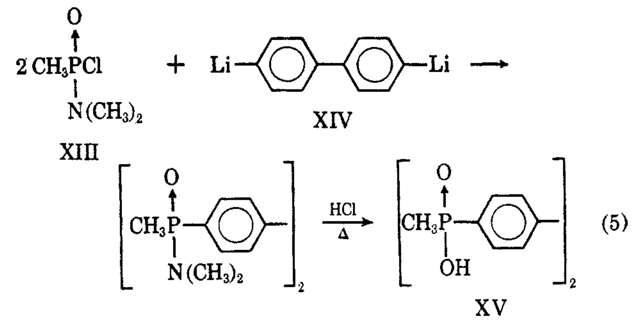
(3)

With the improved synthesis of *p*-phenylenebis(phosphonous dichloride) (VI), an alternate and potentially high yield route to *p*-phenylenebis(methylphosphinic acid) (IV) was available as illustrated in eq 4. Treatment of the crude reaction product VI with methanol and triethylamine resulted in the formation of colorless, liquid tetramethyl *p*-phenylenebis(phosphonite) (XI) isolated in 21–22% yield. Infrared absorptions associated with the phosphonite ester at about 1031 and 1010 as well as *para* substitution at 820 cm^{-1} were observed for XI. Subsequent reaction of XI with methyl iodide in refluxing benzene resulted in a 58% yield of the Michaelis–Arbusov product, dimethyl *p*-phenylenebis(methylphosphinate) (XII) as a white, solid product. Hydrolysis of XII was effected by refluxing with concentrated hydrochloric acid to give a 64% yield of beautifully crystalline *p*-phenylenebis(methylphosphinic acid) (IV).



(4)

The more direct reaction sequence involving a phosphorous-substituted methylphosphonic chloride and *p*-phenylenedilithium or di Grignard was not investigated in view of the results obtained previously in similar preparations.[4,6] Thus, low yields and byproducts such as (4-bromophenyl)phenylphosphinic acid obtained in the synthesis of *p*-phenylenebis(phenylphosphinic acid) from *p*-phenylenedilithium and N,N-dimethylphenylphosphonamidic chloride made this approach to *p*-phenylene derivatives unattractive. However, illustrative of the more direct synthesis is the reaction of N,N-dimethylmethylphosphonamidic chloride (XIII) with 4,4′-biphenylenedilithium (XIV) to give only an 11% yield of 4,4′-biphenylenebis(methylphosphinic acid) (XV, eq 5). No attempt was made to isolate the intermediate bis(phosphinic amide). The low yield of XV was not the result of a low conversion of 4,4′-dibromobiphenyl to XIV since high yields (>90%) of 4,4′-biphenylenebis(diphenylphosphine) have been obtained from XIV.[6] The recent observation of the lability of both the chloro and dimethylamino groups of XIII in reactions with phenols and anilines[9] suggests similar displacements occurred in eq 5 to give tertiary phosphine oxide instead of the acid XV, and, thus, the low yield of XV.



(5)

Of note in the synthetic sequence used to prepare N,N-dimethylmethylphosphonamidic chloride (XIII), used above in eq 5, from trimethyl phosphite was an improved procedure for the utilization of alkyl tos-

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(8) The utilization of VIII in the preparation of polyborphosphane resin composites has been recently described by F. X. Maggio and C. O. Wilson, Jr., First Annual Western Regional American Chemical Society Meeting, Los Angeles, Calif., Nov 18–20, 1965.

(9) N. N. Mel'nikov, A. F. Grapov, and N. V. Lebedeva, *Zh. Obshch. Khim.*, **36**, 457 (1966).

TABLE I

PRODUCTS OF TOSYLATE–PHOSPHITE REACTIONS

Tosylate	Phosphite	Molar ratio, T/P	% content by vpc analysis			
			$CH_3P(O)(OCH_3)_2$	$CH_3P(O)(OC_2H_5)_2$	$C_2H_5P(O)(OCH_3)_2$	$C_2H_5P(O)(OC_2H_5)_2$
CH_3 Tos[a]	$(CH_3O)_3P$	1/14	98.9	...	...	...
CH_3Bs[b]	$(CH_3O)_3P$	1/10	99	...	...	...
C_2H_5 Tos	$(C_2H_5O)_3P$	1/14	...	...	...	94.7[c]
CH_3 Tos	$(C_2H_5O)_3P$	1/1	...	74.0	21.5	2.7
C_2H_5 Tos	$(CH_3O)_3P$	1/1	42.1	...	43.5	...
CH_3 Tos	$(C_2H_5O)_3P$[d] (1)	2/1	...	43.6	46.0	...
	(2)		...	63.3	33.3	...
C_2H_5 Tos	$(CH_3O)_3P$[e]	2/1	30.6	10.2	39.2	...

[a] Where Tos = p-$OSO_2C_6H_4CH_3$. [b] Where Bs = $OSO_2C_6H_5$. [c] Impurity from phosphite amounted to 4.8% diethyl phosphite. [d] Distillation cut into two fractions. [e] Also noted was 9.8% trimethylphosphite.

ylates[10] (*i.e.*, alkyl *p*-toluenesulfonates) in place of alkyl iodides in the Michaelis–Arbusov conversion of trialkyl phosphites to the corresponding alkylphosphonate esters. Utilizing a mole ratio of trimethyl phosphite to methyl tosylate of 14:1, we found it was necessary to warm the mixture only to the reaction point (~100–110° in this system) at which point a brief but vigorous exothermic reaction occurred. Infrared examination of the cooled reaction mixture then revealed an extremely strong P→O absorption. Fractional distillation of the reaction mixture resulted in a nearly quantitative yield of dimethyl methylphosphonate and recovery of methyl tosylate. Methyl benzenesulfonate could also be used without a decrease in yield of the same ester. Triethyl phosphite and ethyl tosylate reacted similarly to yield diethyl ethylphosphonate. That the esters were obtained in high purity also was confirmed by vapor phase chromatography (see Table I).

Attempts to carry out a mixed reaction between, for example, methyl tosylate and triethyl phosphite, led to a complex mixture of products even though the reaction ratio was 1:1 or 2:1. The results of these studies are given in Table I. Additionally, ethyl diphenylphosphinate and methyl toluate failed to react with triethyl phosphite and trimethyl phosphite, respectively, and were quantitatively recovered. Not unexpectedly, an attempt to rearrange a phenyl group from phenyl tosylate to triethyl phosphite also failed. Clearly then, the use of alkyl tosylates in the Michaelis–Arbusov reaction is synthetically limited to components which contain the same alkyl groups. Thus the availability of a particular like phosphite–tosylate pair is a limiting factor in this approach to the preparation of of synthetic intermediates.

Experimental Section

Infrared spectra of liquid samples were determined on a Beckman IR-5 spectrophotometer as thin films. The spectra of solids were determined as potassium bromide pellets on a Perkin-Elmer Model 21 instrument. Melting points, taken in a Thomas-Hoover capillary melting point apparatus, and boiling points are not corrected. Vapor phase chromatography was done on a Perkin-Elmer 801 gas chromatograph using 6-ft glass columns packed with 10% tricresyl phosphate on 60–80 mesh Gas Pack F. Neutralization equivalent titrations were carried out using a Beckman Model Zeromatic II pH meter. The mass spectrum of phosphorane II was determined with a Hitachi mass spectrometer (Model RMU-60).

Methylphenylphosphinic Azide (I).—Methylphenylphosphine was oxidized[4] using aqueous iodic acid to give a 48% yield of methylphenylphosphinic acid melting at 136.2–137° (lit.[4] mp 134–136°). Subsequent reaction of the acid with excess thionyl chloride resulted in a 35% yield of methylphenylphosphinic chloride, bp 95° (>1 mm) [lit.[11] bp 98° (0.5 mm)].

A solution of 16.5 g (0.094 mole) of methylphenylphosphinic chloride dissolved in 40 ml of pyridine was added to a slurry of 7.7 g (0.118 mole, 25% excess) of sodium azide in 200 ml of pyridine and stirred at ambient temperature for 18 hr. At this point the solution was slightly pink in color and the presence of I was indicated by the strong azide absorption in the infrared spectrum of the mixture. After removal from the by-product salt and solvent, one-fifth of the crude azide I was quantitatively distilled at 65° at about 0.3 μ. Neither the crude nor the distilled methylphenylphosphinic azide showed any shock sensitivity (50 cm with 2 kg) and burned only slowly in air. Distillation of the remaining crude azide resulted in an over-all yield of 78%. The distilled azide I contained a strong asymmetric azide absorption at 2137 cm^{-1}.

Anal. Calcd for $C_7H_8N_3OP$: N_3, 23.20; mol wt, 181.1. Found: N_3, 23.6; mol wt, 185.

As an additional quantitative test for the azide content of I, a mixture of 104.5 mg (0.577 mmole) of I, 265.4 mg (1.052 mmoles, 82.3% excess) of triphenylphosphine, and 3 ml of pyridine was sealed at −78° under vacuum in a tube. After 18 hr at 110–120° the tube was opened on a vacuum line and the evolved nitrogen was collected by means of a Sprengel pump, and measured as 13.1 cc (0.587 mmole. 101.7%) (see also below).

P-Methyl-P-phenyl-N-triphenylphosphoranylidinephosphinic Amide (II).—The reaction of 6.94 g (0.0383 mole) of methylphenylphosphinic azide with 10.05 g (0.0383 mole) of triphenylphosphine in toluene at ambient temperature was slow and incomplete after 1.5 hr at 50°. After 2 hr at the reflux temperature, the evolution of nitrogen was 846 cc (0.0378 mole, 98.7%, cor). The solvent was removed under reduced pressure to give a white powder. After a washing with dilute ammonium hydroxide and drying followed by trituration with methylcyclohexane, the dried, white powder melted at 116–119°. The yield was only 64%. Further washing with dilute ammonium hydroxide increased the melting point to 119–121°.

Anal. Calcd for $C_{25}H_{23}NOP_2$: C, 72.28; H, 5.58; N, 3.37; P, 14.91; mol wt, 415.4. Found: C, 72.35; H, 5.54; N, 3.22; P, 14.8; mol wt, 395.

Further evidence in support of the expected product, P-methyl-P-phenyl-N-triphenylphosphorylidinephosphonic amide, was obtained from the mass spectrum of II. The parent group of peaks in the region of m/e 415 substantiated the molecular weight. Confirmation of the declared structure for II was indicated by the most prominent peaks at m/e 399 and 400, probably representing a mixture of the ions, $CH_3(C_6H_5)PN{=}P(C_6H_5)_3^+$ and $C_6H_5P(O)N{=}P(C_6H_5)_3^+$, respectively. Large peaks occurred also at m/e 322 and 338 for the probable ions, $CH_3PN{=}P(C_6H_5)_3^+$, and $CH_3P(O)N{=}P(C_6H_5)_3^+$, respectively.

***p*-Phenylenebis(phosphonous dichloride)** (VI).—In a typical preparation, 390.5 g (0.875 mole) of *p*-phenylenebis(diphenylphosphine) and 2202 g (16.03 moles, 458% excess) of phosphorus trichloride were charged into a heavy wall cylindrical tube (capacity 2700 ml). The mixture was cooled to −78° and the tube was sealed under about 10 mm of dry nitrogen gas. The glass tube was submerged in about 2 l. of benzene (as a pressure-equalizing medium) within a large, high-pressure steel reactor, which was sealed and heated at 300° for 30 hr. The dark solution

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[10] T. C. Meyers, S. Preis, and E. V. Jensen, *J. Am. Chem. Soc.*, **76**, 4172 (1954).

[11] M. Green and R. F. Hudson, *J. Chem. Soc.*, 1004 (1963).

was removed from the glass tube by pressure siphon to a distilling flask, from which 1739 g (12.66 moles) of phosphorus trichloride was recovered. Based on the amount of phosphorus trichloride consumed, 463 g (3.37 moles), the reaction had proceeded (eq 2) 96.3% toward completion to form *p*-phenylenebis(phosphonous dichloride) and phenyldichlorophosphine. However, only 529 g (2.96 moles, 84.6%) of the latter product was isolated from the reaction mixture by vacuum distillation, bp 96° (14 mm), and was identified by infrared analysis. *p*-Phenylenebis(phosphonous dichloride) was not isolated, measured quantitatively, or characterized as such, but its presence as a major product was demonstrated during the following synthetic sequence.

Reduction of VI to *p*-Phenylenebis(phosphine) (VII).—A portion of the liquid residue considered to be mainly VI and to contain about 212 g (0.760 mole) of crude VI was diluted to a volume of 740 ml with tetrahydrofuran and filtered to remove a small amount of finely divided carbonaceous material. The clear, dark solution was added dropwise to a solution of 35.2 g (0.930 mole, 12.1% excess) of lithium aluminum hydride which had been dissolved in about 2400 g of refluxing tetrahydrofuran before cooling. The resultant reaction mixture tested positively for the presence of excess hydride ion.

About 1650 g of the tetrahydrofuran solvent was removed from the reaction mixture by distillation before 800 ml of 6.1 *M* hydrochloric acid was added to the reaction residue. A heavy, green emulsion formed and broke on standing. The organic layer was removed by pressure siphon and the aqueous portion was washed with ether. The combined organic ethereal solutions were dried over 194 g of anhydrous sodium sulfate for over 60 hr. Ether and tetrahydrofuran were removed from the dried solution by distillation to a head temperature of 68°. The residue was subjected to high-vacuum sublimation. Two traps (at 0° and −78°, respectively) were attached in series between the vessel holding the residue and the source of high vacuum. In the trap at 0° was collected, over a period of 2 days, 41.7 g (0.292 mole, 37.6%) of *p*-phenylenebis(phosphine), mp about 70° (lit.[4] mp 69.0–70.5°).

***p*-Phenylenebis(phosphine borane) (VIII).**—When a mixture of 7.6 g (0.054 mole) of *p*-phenylenebis(phosphine) (VII) dissolved in 34.7 g of benzene was contacted with gaseous diborane, 1113 cc (0.050 mole, 92.6%) of diborane was absorbed. The bisadduct VIII was only slightly soluble in benzene.

Tetramethyl *p*-Phenylenebis(phosphonite) (XI).—A quantity of crude, black *p*-phenylenebis(phosphonous dichloride) thought to contain about 0.3 mole of the tetrachloro compound and 122 g (1.2 moles) of triethylamine dissolved in a mixture of ether and tetrahydrofuran (to aid in the solution of starting material) was cooled to 10° prior to the slow addition of 38.7 g (1.2 moles) of methanol. During the exothermic reaction, a thick, white precipitate formed which was very difficult to stir. After removal of the amine hydrochloride and concentration of the mixture at reduced pressure, the black residual liquid was fractionally distilled at about 0.1 to 0.2 mm. About 16.8 g (0.064 mole, 21%) of colorlesss tetramethyl *p*-phenylenebis(phosphonite) (XI) boiling at 94–97° with n^{20}_D 1.5479 was recovered.

Anal. Calcd for $C_{10}H_{16}O_4P_2$: C, 45.81; H, 6.15. Found: C, 45.90; H, 6.00.

Dimethyl *p*-Phenylenebis(methylphosphinate) (XII).—A benzene solution containing 10.3 g (0.039 mole) of tetramethyl *p*-phenylenebisphosphinate and 2 ml of methyl iodide were stirred at about 36° for 1 hr and then at reflux for 4 hr. A small quantity of white, insoluble material was removed by filtration prior to removal of the benzene at reduced pressure. The residue was washed with ether and water and then vacuum dried to give 6.0 g (0.023 mole, 58%) of XII melting at 107–109°.

Anal. Calcd for $C_{10}H_{16}O_4P_2$: C, 45.81; H, 6.15. Found: C, 45.61; H, 6.44.

***p*-Phenylenebis(dimethylphosphine) (IX).**—Approximately 234 g (0.836 mole) of *p*-phenylenebis(phosphonous dichloride) (VI) dissolved in 300 ml of anhydrous diethyl ether was slowly added to 3.34 moles of methylmagnesium bromide in 1200 ml of the ether held at 0–5°. After 1 hr at reflux, the reaction was cooled and treated with about 200 ml of saturated ammonium chloride solution. The ether was decanted from the solids, which were subsequently broken up under nitrogen and further extracted with additional ether. The combined ether was concentrated to yield a small quantity of black liquid residue. It was fractionally distilled, bp 66–70° (0.01 mm), to yield only 11 g of the colorless product, n^{24}_D 1.5890. The infrared spectrum did not exhibit any PO absorptions in the region near 1250 cm^{-1}.

A bis(tribromoborane) adduct[12] was prepared by adding an excess quantity of boron tribromide to a petroleum ether (bp 30–60°) solution of IX held at −78°. The derivative, *p*-phenylenebis(dimethylphosphine tribromoborane) (X), a white powder, melted at about 305–315° dec.

Anal. Calcd for $C_{10}H_{16}B_2Br_6P_2$: B, 3.09; Br, 68.6; P, 8.86; B:P:Br ratio, 1:1:3. Found: B, 3.11; Br, 67.9; P, 9.26; B:P:Br ratio, 1:1.04:2.96.

Preparation of Synthetic Intermediates by the Michaelis–Arbusov Reaction. A. Dimethyl Methylphosphonate.—Under a nitrogen atmosphere, 462 g (3.72 moles) of trimethyl phosphite and 50 g (0.07 mole) of methyl *p*-toluenesulfonate were mixed and sampled for an infrared spectrum. The absence of any absorption near 1250 cm^{-1} permitted following the course of the reaction since the product phosphonate would contain a PO absorption at or close to 1250 cm^{-1}. The mixture was heated slowly to about 100–110° and a vigorous reaction occurred raising the temperature of the mixture to 185°. After the mixture was cooled and sampled for an infrared spectrum which revealed a strong P$\rightarrow$O absorption at 1240 cm^{-1}, it was distilled through a 12-in. Vigreux column. Four fractions of dimethyl methylphosphonate, bp 70–73° (18 mm), n^{20}_D 1.4128–1.4132, weighed 452 g (3.62 moles, 98%). Further distillation of the residual liquid remaining after removal of the phosphonate resulted in recovery of 91% of the methyl *p*-toluenesulfonate.

In a similar experiment, 62.0 g (0.50 mole) of trimethyl phosphite and 8.6 g (0.05 mole) of methyl benzenesulfonate (n^{20}_D 1.5151) were allowed to react (~110°) to yield 62.0 g (0.50 mole, 100%) of dimethyl methylphosphonate, bp 75–77° (19 mm), n^{20}_D 1.4136. The residue from the distillation was found to be slightly impure methyl benzenesulfonate, n^{20}_D 1.5088.

The infrared spectra of the products from these two preparations were superimposable with the spectrum of dimethyl methylphosphonate prepared *via* methyl iodide and trimethyl phosphite. The purities of these products as determined by vapor phase chromatography (vpc) may be reviewed in Table I.

B. Diethyl Ethylphosphonate.—Following the same general tosylate procedure, 83.0 g (0.50 mole) of triethyl phosphite and 10.0 g (0.05 mole) of ethyl *p*-toluenesulfonate were heated together under nitrogen until an exothermic reaction took place. Fractional distillation of the reaction mixture yielded 76.1 g (0.458 mole, 91.6% yield) of diethyl ethylphosphonate boiling at 90–92° (18 mm), n^{20}_D 1.4156–1.4160. The recovery of ethyl *p*-toluenesulfonate, bp 108–110° (0.75 mm), n^{20}_D 1.5100, was 10 g (100%).

C. Mixed Tosylate–Trialkyl Phosphite Products.—In these reactions, in 1:1 or 1:2 mole ratios, triethyl phosphite was treated with methyl tosylate and trimethyl phosphite was treated with ethyl tosylate in the same manner as described above. The reaction products were distilled at about 18 mm and samples were analyzed by vapor phase chromatography. The results of these analyses are shown in Table I.

That the mixed dialkyl alkylphosphonates obtained were not artifacts formed in the vpc column was shown by analyzing a known mixture of dimethyl methylphosphonate and diethyl ethylphosphonate in the same column. There was not any evidence for mixed esters in the chromatogram obtained and the percentage of the components was not changed. Diethylphosphite, an impurity in the triethylphosphite, was also readily analyzed and identified on the same column used for the phosphonates. In addition, the mixed ester products which conceivably might be formed in the mixed phosphite–tosylate reactions were prepared *via* reaction of the appropriate alkyl iodide and the sodium salt of the secondary phosphite.[13] These samples were also analyzed by vpc to determine the relative retention times of all components.

Attempted Michaelis–Arbusov Reactions. A. Methyl *p*-Toluate and Trimethyl Phosphite.—A mixture of 7.5 g (0.05 mole) of methyl *p*-toluate and trimethyl phosphite was prepared under nitrogen and sampled for infrared examination. The mixture was slowly heated for over 2 hr to a mixture temperature of 115° at which time there was a gentle reflux in the attached Vigreux column. After 30 min, the reaction mixture was cooled and again sampled for infrared examination. Comparison of the

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[12] R. A. Baldwin, K. A. Smitheman, and R. M. Washburn, *J. Org. Chem.*, **26**, 3547 (1961).

[13] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p 123.

two spectra showed that no PO had formed in view of the absence of the expected strong absorption at 1240 cm^{-1}. Both reactants were subsequently recovered in nearly a quantitative amount.

B. **Triethyl Phosphite and Ethyl Diphenylphosphinate.**—In a similar manner, 41.5 g (0.25 mole) of technical grade triethyl phosphite and 6.6 g (0.027 mole) of ethyl diphenylphosphinate were mixed, sampled for infrared examination, and heated to gentle reflux over an 8.5-hr period. Distillation of the reaction mixture resulted in a 92% recovery of triethyl phosphite. The distillation residue was impure ethyl diphenylphosphinate, n^{20}D 1.5302.

C. **Triethyl Phosphite and Phenyl Tosylate.**—Equimolar quantities of triethyl phosphite (33.2 g, 0.2 mole) and phenyl tosylate (49.2 g, 0.2 mole) were heated to 173° over a 5-hr period, cooled, and distilled to yield 30.7 g (92.5% recovery) of triethylphosphite, bp 27° (0.75 mm). Recrystallization of the distillation residue yielded 45 g of white, crystalline phenyl tosylate (90% recovery).

4,4'-Biphenylenebis(methylphosphinic acid) (XV).—The 4,4'-biphenylenedilithium prepared in tetrahydrofuran by the interaction at −60° or lower of 0.2 mole of *n*-butyllithium and 31.2 g (0.10 mole) of 4,4'-dibromobiphenyl was immediately added to a second tetrahydrofuran solution also at −60° or lower containing 40.8 g (0.20 mole) of N,N-dimethylmethylphosphonamidic chloride (XIII). After the reaction mixture had warmed to ambient temperature, the solvents were removed at reduced pressure. The residue was digested in hot, concentrated hydrochloric acid for 4.5 hr. The mixture was next cooled, neutralized, filtered, and reacidified to precipitate crude XV. The acid obtained after two recrystallizations, 3.5 g (0.011 mole, 11%), melted at 307–310°.

Anal. Calcd for $C_{14}H_{16}O_4P_2$: C, 54.20; H, 5.20; neut equiv, 155. Found: C, 55.77; H, 5.31; neut equiv, 153.

N,N-Dimethylmethylphosphonamidic chloride (XIII), used above to prepare XV and obtained in 74% yield by the interaction of methylphosphonic dichloride and dimethylamine in ether at 0°, boiled at 72–75° (1.5 mm) [lit.[14] bp 74–75° (1.5 mm)]. The methylphosphonic dichloride was obtained in 33% yield as previously described[15] by treating dimethyl methylphosphonate with phosphorus pentachloride. Although the yield of methylphosphonic dichloride was low, its purity was high as it solidified to a beautiful, crystalline mass melting at about 30°.

***p*-Phenylenebis(methylphosphinic acid) (IV).**—A 3.0-g (0.0114 mole) quantity of dimethyl *p*-phenylenebis(methylphosphinate) (XII) and 25 ml of concentrated hydrochloric acid were heated at the reflux temperature for 4 hr and then allowed to stir overnight at ambient temperature. Excess acid and water were removed at reduced pressure to yield an off-white solid which on recrystallization from ethanol and Norit A yielded 1.4 g (0.006 mole, 52%) of beautiful, crystalline *p*-phenylenebis(methylphosphinic acid) (IV) melting at 233–235° (lit.[4] mp 231–236°). The neutralization equivalent was determined to be 117.4 (theory, 117.1). From the mother liquor there was obtained an additional 0.3 g of IV melting at 232–234°. The total yield was 63.6%.

Registry No.—I, 4583-37-3; II, 10561-78-1; VI, 10498-56-3; IX, 10498-57-4; X, 10498-58-5; XI, 10498-59-6; XII, 10580-44-6; XV, 10498-60-9; dimethyl methylphosphonate, 756-79-6; diethyl ethylphosphonate, 78-38-6; ethyl diphenylphosphinate, 1733-55-7; triethyl phosphite, 122-52-1.

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Application of the Hammett Equation to Organophosphorus-Substituted Phosphinic and Benzoic Acids[1]

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Organophosphorus-substituted benzoic and phosphinic acids have been readily obtained from (4-bromophenyl)diphenylphosphine. From correlations with the Hammett equation, it has been possible to compute Hammett σ and Taft σ^0 values for the p-$(C_6H_5)_2P$, p-$(C_6H_5)_2P(S)$, and p-$(C_6H_5)_2P(O)$ groups. In the systems studied, the p-$(C_6H_5)_2P$ group is found to be almost neutral in its electrical effects, the p-$(C_6H_5)_2P(S)$ group is found to be a moderate electron acceptor, and the p-$(C_6H_5)_2P(O)$ group is a moderately strong electron acceptor.

The effect of structure on acidities of a variety of phosphorus acids has been recently extensively reported[2] and the Hammett equation has been applied to both substituted arylphosphonic[3] and arylphosphinic acids.[4] From these studies it was then possible, using arylphosphonic and phosphinic acids containing phenolic and carboxylic groups, to determine Hammett substituent (σ) constants for the PO_3H^-, $PO_3{}^{2-}$, and the PO_2H_2 groups[3,4] as well as the diethoxyphosphono group.[5] More recently polar-substituent constants (σ^*) have been determined for several phosphonium, dialkoxyphosphono, and diphenylphosphono groups.[6] From the analysis of C^{13} nmr spectra of organophosphorus compounds, tentative assignments of both σ and σ^+ values for ten phosphorus groups, including the $(C_6H_5)_2P$ and $(C_6H_5)_2P(O)$ groups, have been made recently.[7] We wish to report in this paper the syntheses of several organophosphorus-substituted diarylphosphinic acids as well as the evaluation of both Hammett σ and Taft σ^0 constants for the p-$(C_6H_5)_2P$, p-$(C_6H_5)_2P(S)$, and p-$(C_6H_5)_2P(O)$ groups. These new substituent constants were then successfully applied

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