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# OXIDATIVE PHOSPHONYLATION OF AROMATIC COMPOUNDS

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Summary - Aryl phosphonates can be prepared in good yield from the respective arenes and tri- or dialkylphosphites by either chemical or anodic oxidation. The anodic oxidation proceeds either via phosphinium radical cations, which then attack the arenes electrophilically, or via arene radical cations, which add the trialkylphosphite as nucleophile. Aryl phosphonates are also obtained in good yield by chemical oxidation with peroxodisulfate/$AgNO_3$ in acetonitrile/water or glacial acetic acid. The diethylphosphinium radical cation, formed from diethylphosphite by oxidation with Ag(II), is supposed to be the reactive species in this process. Raising the silver salt concentration leads to an increase in polyphosphonylation. Selectivity ratios were determined for the oxidative phosphonylation process.

## INTRODUCTION

In contrast to the introduction of e.g. halo, sulfur, or nitrogen substituents into aromatic substrates, the introduction of phosphorus substituents poses a difficult problem. The electrophilic potential of the known phosphonylation agents as a rule is not sufficient for electrophilic substitution. In this respect, the situation is analogous to the preparation of aryl silanes[1] which likewise are not accessible via regular Friedel-Crafts type electrophilic substitution. The following procedures have been described in the literature for preparation of aromatic and/or heterocyclic phosphonates:

a) electrophilic reaction of arenes with phosphorus pentoxide,[2a] phosphorus pentasulfide,[2b] or phosphorus trichloride (with or without addition of $AlCl_3$ as FC catalyst)[3] all of which, however, require rather drastic conditions;

b) reaction of metallated arenes (lithio or Grignard compounds) with phosphorus halides;[4]

c) phosphonylation via radical intermediates,[5] e.g. reactions of aryl halides with phosphorus nucleophiles under irradiation;[6-8]

d) preparations via aryl diazonium salts[9] or by metal ion-catalyzed reaction of aryl halides with phosphorus nucleophiles;[10]

e) direct substitution of acceptor activated arenes[11] or hetarenes[12] with phosphorus nucleophiles.

Most of these reactions are not generally applicable, however, or require specific activation of the aromatic substrate. Especially with arenes of intermediate reactivity, phosphorus substituents can be introduced only via diazonium salts or organometallic precursors. Both procedures can be rather tedious and often are thwarted by the presence of other reactive substituents in the substrate. There is great interest, therefore, in the development of new preparative methods for introducing phosphorus substituents into arenes and hetarenes. In the case of other functions which are hard to introduce electrophilically, such as the hydroxy or amino group, an oxidative pathway has been applied successfully.[13,14] The neutral reagent is transformed, by either chemical or anodic oxidation, into a radical cation which, as the reactive intermediate, then forms the desired

new bond with a suitable nucleophile.
There are two ways to realize this process for the introduction of phosphorus substituents into aromatic substrates:
a) oxidizing the aromatic substrate to the corresponding radical cation and trapping it by a phosphorus nucleophile;
b) oxidizing a suitable neutral phosphorus compound to the respective phosphinium radical cation which then attacks the aromatic substrate.
Anocid oxidative phosphonylation of arenes has been reported recently,[15,16] phosphonylation by chemical oxidation so far has not been described. We want to report here oxidative arene phosphonylation by anodic as well as chemical means.

## Anodic Phosphonylation of Arenes

Yu. M. Kargin, E.V. Nikitin et al.[15a] and M. Masui et al.[16] have independently reported the preparation of aryl phosphonium salts and/or aryl phosphonates by anodic oxidation of trialkylphosphites in the presence of benzene or hetarene derivatives. Both groups of authors formulate the phosphonylation via primary oxidation of the trialkylphosphite and follow-up reactions of the electrochemically generated phosphorus radical cations with the aromatic substrate. The aryl phosphonium salts thus formed are converted, in part during work-up, in full by the final treatment with nucleophiles, into the corresponding aryl phosphonates. These, as a rule, were the products isolated from the oxidative phosphonylation of arenes and hetarenes.

$$(RO)_3P - e^- \longrightarrow (RO)_3P^{+\cdot}$$
$$(RO)_3P^{+\cdot} + ArH \longrightarrow (RO)_3\overset{\cdot}{P}Ar + H^+$$
$$(RO)_3\overset{\cdot}{P}Ar - e^- \longrightarrow (RO)_3\overset{+}{P}Ar$$
$$(RO)_3\overset{+}{P}Ar + RONa \longrightarrow ArP(O)(OR)_2 + ROR + Na^+$$

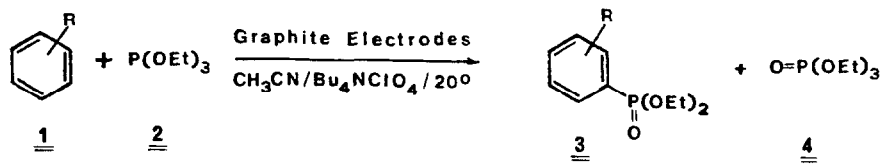
Masui et al.[16] report exclusive ortho and para substitution for alkyl benzenes, and thence conclude that the arene is attacked electrophilically by a phosphorus radical cation. Nikitin et al.[15c,d] on the other hand, find a relatively high ratio of meta phosphonylation. In addition, they have also determined a very low selectivity value for trialkylphosphite radical cations ($\rho = -1.46$) from competitive reactions.[15d]

In connection with our general research interest in aromatic substitution,[17] the controversial reports on the isomer distribution in anodic phosphonylation of alkyl benzenes have prompted us to reinvestigate this reaction. Especially, we wanted to explore the potential preparative scope of both the chemical and the anodic oxidative phosphonylation of aromatic substrates, and also to obtain some definite information about the actual reaction mechanism.

By systematic variation of the individual parameters for the anodic oxidation, with p-xylene (1e) as model substrate, we have found that the results of the oxidative phosphonylation with triethylphosphite depend mainly on substrate concentration, residual oxygen content, and on the solvent system. The following standard reaction conditions were derived from these model investigations: electrode material, graphite; supporting electrolyte, tetrabutylammonium perchlorate; solvent, acetonitrile; educt concentration, equimolar; reaction temperature, 20°C. Under these standard conditions, the diethyl arylphosphonates 3, besides small amounts of triethylphosphate (4), were obtained from the oxidative phosphonylation of several benzene derivatives and of naphthalene (1m) with triethyl phosphite (2) in a thermostated, undivided electrolysis cell (Table 1).
The potentials for the onset of oxidation (onset potential, see also ref.[18]) of both aromatic substrate and triethylphosphite were determined prior to each preparative electrolysis under standard conditions. Oxidation was then performed at an anode potential halfway between the two onset potentials (current strength ≈ 100 mA ≙ current density ≈ 5 mA/cm$^2$ electrode). Thus, it was

ascertained that a radical cation was generated only from the educt with the lower oxidation potential while the other substrate, with higher potential, reacts as nucleophile.

Table 1. Electrochemical Phosphonylation of 1




1 2 3 4

| Arene R | | Potential[a] (mv) 1 | 2 | Applied Electrolytic Potential (mV) | | Products[b] Diethyl-phosphonate (Ratio of Isomers) | Conv. (%) | Yield[d] (%) |
|---|---|---|---|---|---|---|---|---|
| 1a | H | 1350 | 900 | 1050 | 3a | phenyl- | | 38 |
| 1b | Me | 1350 | 950 | 1100 | 3b | 2(3,4)-tolyl- (40:23:37) | | 40 |
| 1c | 1,2-$Me_2$ | 1250 | 850 | 1000 | 3c | 2,3(3,4)-dimethylphenyl- (40:60) | | 53 |
| 1d | 1,3-$Me_2$ | 1300 | 910 | 1180 | 3d | 2,6(2,4/3,5)-dimethylphenyl- (16:74:10) | | 49 |
| 1e | 1,4-$Me_2$ | 1260 | 930 | 1090 | 3e | 2,5-dimethyl- | 74 | 62 |
| 1f | 1,3,5-$Me_3$ | 1250 | 900 | 1050 | 3f | mesityl- | 70 | 67 |
| 1g | OMe | 1150 | 900 | 1050 | 3g | 2(3,4)-anisyl- (41:8:51) | 76 | 73 |
| 1h | $C_6H_5$ | 1300 | 950 | 1150 | 3h[c] | biphenyl-2(3,4)-yl (60:9:31) | 72 | 69 |
| 1i | $NHCOCH_3$ | 1000 | 870 | 960 | 3i | 2(3,4)-acetamidophenyl- (63:1:36) | 62 | 92 |
| 1k | 1,3,5-$(OMe)_3$ | 660 | 940 | 820 | 3k | 2,4,6-trimethoxyphenyl- | 62 | 67 |
| 1l | 1,4-$(OMe)_2$ | 580 | 900 | 750 | 3l | 2,5-dimethoxyphenyl- | 76 | 73 |
| 1m | naphthalene | 1100 | 850 | 1050 | 3m[c] | 1(2)-naphthyl- (75:25) | 69 | 40 |

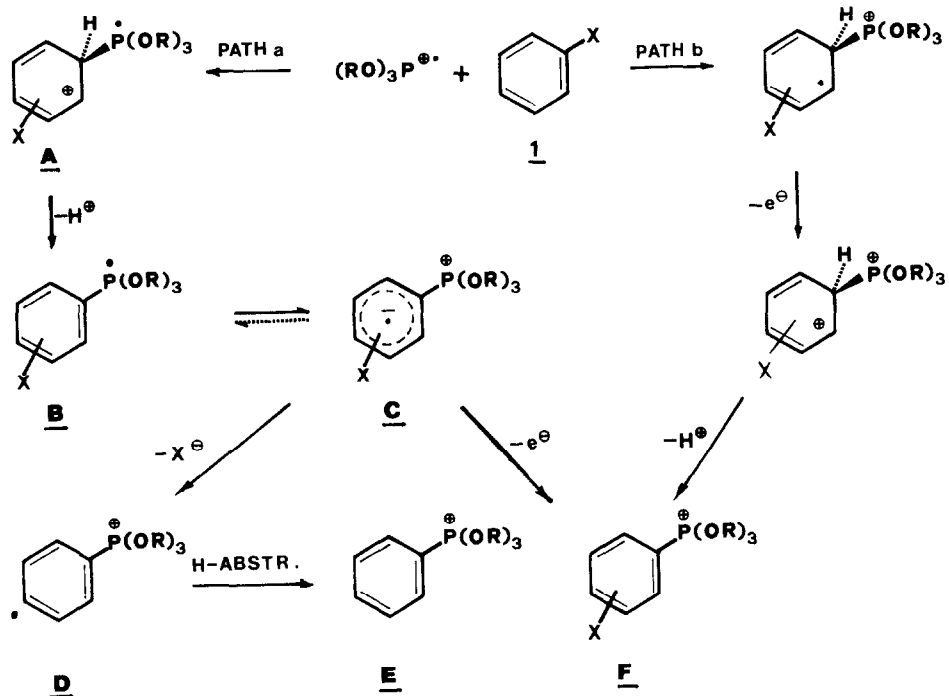
[a] Potential of U/I curve at starting oxidation. - [b] In addition 10-26% triethyl phosphonate (4). - [c] After dehydrogenation with DDQ. - [d] Based on converted aromatic substrate.

After work-up, the isolated compounds were identified spectroscopically. In mixtures of isomers, the isomers and their ratios were established by GLC with reference substances. In case of anodic phosphonylation of 1h and 1m with 2 in addition partly hydrogenated compounds were obtained which could be oxidized by DDQ to 3h and 3m, respectively (see experimental section).

Mechanism of the Anodic Phosphonylation of Aromatic Substrates with Triethylphosphite

In the literature reports on anodic phosphonylation,[15c,16] it was assumed that primarily the trialkylphosphite is oxidized to a phosphinium radical cation which, as reactive species, then attacks the aromatic substrate. This mechanism in fact seems to prevail for the phosphonylation of the substrates 1a-i (Table 1) which all have a higher half-wave potential than 2. In the subsequent attack on the aromatic substrate (Scheme 1), the P radical cation can react either as an "electrophile" (path a), or as a "radical" (path b). Recent ESR investigations[19] have shown that the SOMO of phosphinium radical cations is localized mainly on the phosphorus atom.

The experimental isomer distribution, and the selectivity values derived therefrom (Table 1), would bear out both mechanistic alternatives, i.e. reaction of the phosphinium radical cations as electrophiles of low selectivity, or as electrophilic radicals. For the phosphonylation of chlorobenzene, however, the electrophilic mechanism (path a) must hold since the isolated aryl phosphonate no longer contains chlorine. The halogen elimination could be rationalized as follows (Scheme 1):



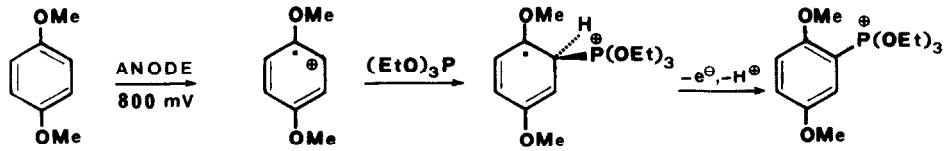

**SCHEME 1**

The Wheland intermediate A is rapidly deprotonated to the phosphoranyl radical B, which then "rearranges" into the more stable electronic configuration C.[20] B and C are truly isomeric structures, and not resonance hybrids, since ligand configuration at the phosphorus is definitely tetrahedral in C, and most probably trigonal-bipyramidal in B. If $X^{\ominus}$ is a good leaving group, it is expelled from C, a well established process for such radical anions.[21] The aryl radical D thus liberated is stabilized by H abstraction; e.g. from the solvent, under formation of the halogenfree phosphonium salt E. †

In the case of electron-rich arenes, in contrast, the aromatic substrates are oxidized directly to the corresponding radical cations under our standard conditions for the anodic phosphonylation. If equimolar amounts of hydroquinonedimethylether, p-xylene and triethylphosphite are electrolyzed at low electrode potential (800 mV), the phosphonylation product of hydroquinonedimethylether is formed almost exclusively (Scheme 2).
If a phosphonium radical cation, with well established low selectivity, had been formed, at least a small amount of 2,5-dimethylphenyl phosphonate should have been isolated from the competitive

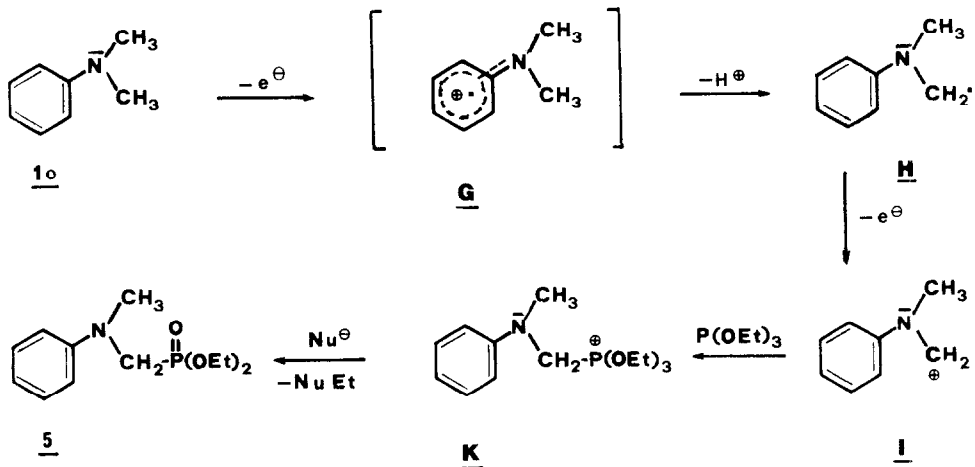
† We gratefully acknowledge helpful discussion with Prof. P. Tordo, Université de Provence, Marseille-Cedex, France.

reaction of the two aromatic substrates. The anode potential in this case was markedly lower than that of triethylphosphite.




**SCHEME 2**

In the reaction of N,N-dimethylaniline (1o) only diethyl(N-methyl-N-phenyl)aminomethylphosphonate (5) is formed besides triethylphosphate (Scheme 3).




**SCHEME 3**

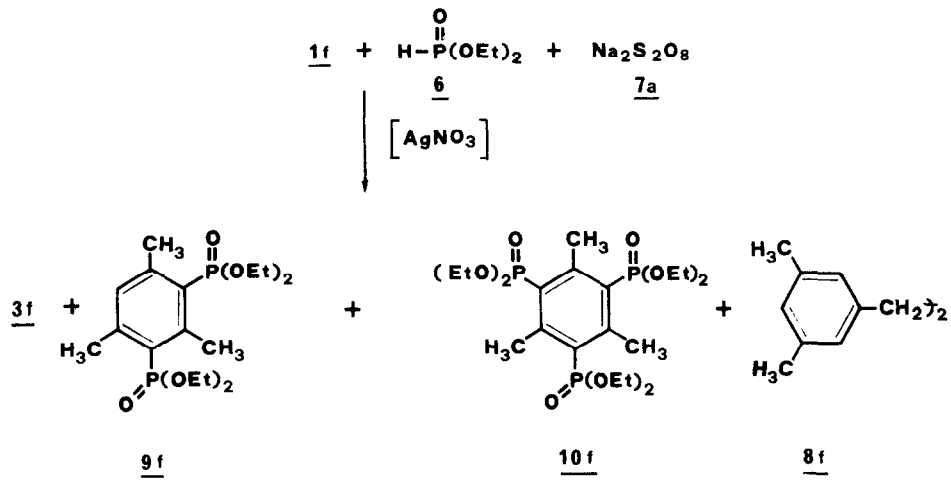
This result again can be rationalized only in terms of a primary oxidation of dimethylaniline to the radical cation G, which then reacts - via H, I and K - to 5. An analogous product has been isolated from the reaction of N,N-dimethylmesidine.[22]
These experiments clearly demonstrate that arenes with an oxidation potential lower than that of triethylphosphite react via primary oxidation of the aromatic substrate.

Phosphonylation of Aromatic Compounds by Chemical Oxidants

As noted above, no phosphonylation of aromatic substrates with chemical oxidants has been reported so far. Peroxodisulfates are widely used as oxidants for aromatic compounds.[13,23] We have therefore investigated the oxidative phosphonylation with tri- and diethylphosphite (2,6), respectively, and sodium peroxodisulfate (7a) with mesitylene (1f) as model substrate.[24]

The first prerequisite for a successful phosphonylation, as we have found, is the additional presence of silver ions. Our effective phosphonylation reagent thus comprises the three-component system alkyl phosphite/peroxodisulfate/silver nitrate. Furthermore, a delicate balance must be maintained between the stability of the phosphonylation agent and the efficiency of the oxidant in the respective reaction medium. No phosphonylation products, for instance, were obtained from

reactions without solvent or in acetonitrile alone. In water/acetonitrile (5:1), 1f is effectively phosphonylated to 3f in presence of 10 mol% $AgNO_3$. 1,2-Bis(3,5-dimethylphenyl)ethane (8f) is formed as by-product by oxidative coupling of 1f. At higher silver nitrate ratios, di- and triphosphonylated products 9f and 10f respectively are formed increasingly (Scheme 4). In glacial acetic acid, an equimolar concentration of silver nitrate is required for 3f to be formed in good yield. Concomitantly, formation of 8f is suppressed at higher $Ag^+$ concentrations. 8f can be prepared in good yield directly from mesitylene with sodium peroxodisulfate alone.[25] In both solvent systems the yield of 3f can likewise be enhanced by using an excess of 6.




**SCHEME 4**

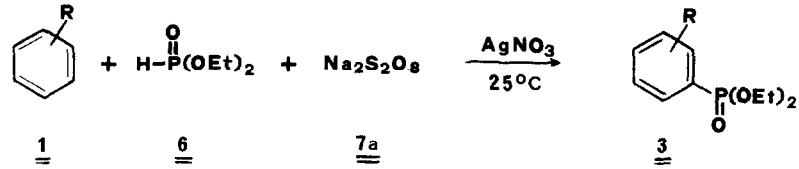
Triethylphosphite (2) is unstable in both media. In aqueous acetonitrile, it is rapidly hydrolyzed to 6, in acetic acid, 2 is completely transformed into diethyl(1-diethylphosphorylethyl)phosphonate within two hours, analogous to the behavior observed for trimethylphosphite.[26] If diethylphosphite (6) is employed directly, 1f can be phosphonylated successfully in both solvent systems, though again only in the presence of silver nitrate.

Other metal ions, which are likewise suitable for persulfate cleavage,[23] displayed little ($Ce^{3+}$) or no effect (e.g. $Fe^{2+}$, $Cu^+$). Combinations of these ions have been employed successfully in the persulfate-initiated hydroxylation of aromatic compounds[13b,27] (effectivity $Fe^{2+}/Cu^{2+} > Ag^+/Cu^{2+} >> Ag^+$). In phosphonylation, though, they are far less effective than silver nitrate ($Ag^+ > Ag^+/Cu^{2+} >> Fe^{2+}/Cu^{2+}$).[24] In aqueous systems, the yield of 3f is drastically decreased at higher temperatures (80°C), due probably to increasing hydrolysis of 6 and to decomposition of the arylphosphonate 3f. In acetic acid, mesitylene underwent oxidative acetoxylation. Even at 80°C, though, i.e. under conditions favorable for a persulfate cleavage, arene phosphonylation was observed only in the presence of $Ag^+$. Generally, lower reaction temperatures have proven advantageous even though the necessary longer reaction times (48-60h) favor oxidation of the alkylaryl phosphonate products. Stability tests with diethyl 4-tolylphosphonate have shown formation of aldehydes and carboxylic acids.

Under optimized phosphonylation conditions, the diethyl arylphosphonates 3a-i, m, n, p, q were obtained (Table 2) from the corresponding aromatic substrates, together with usually less than 10% of oligophosphonylation products. To circumvent hydrolysis of 2, we also carried out oxidative phosphonylation with 2 and tetrabutylammonium persulfate in absolute acetonitrile; this - hitherto unknown - peroxodisulfate is sufficiently soluble in anhydrous acetonitrile. In the case of aromatic substrates with half-wave potentials higher than that of 2, only triethylphosphate (4) was

formed in quantitative yield. From N,N-dimethylaniline (1o), on the other hand, 5 was formed via primary oxidation of 1o to the radical cation, in a yield comparable to that for the anodic phosphonylation.

Table 2. Chemical Phosphonylation of Arenes 1




1 6 7a 3

| Arene | Method A[a] Educt 1 (%)[c] | 3 | (Ratio of Isomers) | Conv. (%) | Yield[x] (%) | Method B[b] Educt 1 (%)[c] | 3 | (Ratio of Isomers) | Conv. (%) | Yield[x] (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1a benzene | | 3a | | | 48 | | 3a | | | 48 |
| 1b toluene | 1b 10 | 3b | (47:20:33) | 90 | 58[d] | 1b 12 | 3b | (58:19:23) | 88 | 58 |
| 1c 1,2-xylene | 1c 9 | 3c | (26:74) | 91 | 60[e] | | | | | |
| 1d 1,3-xylene | 1d 2 | 3d | (9:85:6) | 98 | 60 | 1d 20 | 3d | (40:54:6) | 80 | 87 |
| 1e 1,4-xylene | 1e 12 | 3e | | 88 | 52[f] | | | | | |
| 1f mesitylene | 1f 18 | 3f | | 82 | 74[g] | 1f 13 | 3f | | 87 | 92[h,i] |
| 1g anisole | 1g 38 | 3g | (62:15:23) | 62 | 85 | 1g 32 | 3g | (63:11:26) | 68 | 84[k] |
| 1h biphenyl | 1h 58 | 3h | (26:8:66) | 42 | 76 | 1h 42 | 3h | (51:12:37) | 58 | 86 |
| 1i acetanilide | 1i 72 | 3i | (80:4:16) | 28 | 50 | | 3i | (95:1:4) | | 11 |
| 1m naphthalene | 1m 68 | 3m | (90:10) | 32 | 87 | 1m 34 | 3m | (88:12) | 66 | 89 |
| | | Diethyl 2(3,4)-phenylphosphonate | | | | | | | | |
| 1n chlorobenzene | 1n 63 | 3n | -chloro- (37:21:42) | 37 | 54 | | | | | |
| 1p fluorobenzene | | 3p | -fluoro- (41:35:24) | 29 | 29 | | 3p | (50:26:24) | | |
| 1q benzonitrile | 1q 62 | 3q | -cyano- (21:13:66) | 38 | 40 | | 3q | (28:18:54) | | 5 |

[a]Method A: in $CH_3CN/H_2O$ with 10 mol-% $AgNO_3$, 48h. - [b]Method B: in $CH_3COOH$ with 100 mol-% $AgNO_3$, 60h. - [c]GLC yields. - [d]Polyphosphonylated products neglected. - [e-h]In addition [e]1,2-Bis(2-tolyl)ethane (8c)(12%), [f]1,2-Bis(4-tolyl)ethane (8e)(12%), [g]1,2-Bis(3,5-dimethylphenyl)-ethane (8f)(10%), tetraethyl mesityldiphosphonate (9f)(10%) and hexaethyl mesityltriphosphonate (10f)(2%), [h]8f (6%) and 9f (10%). - [i,k]Preparative yields: [i]3f (64%), [k]3g (57%). - [x]Based on converted aromatic substrate.

Mechanism of the Chemical Phosphonylation

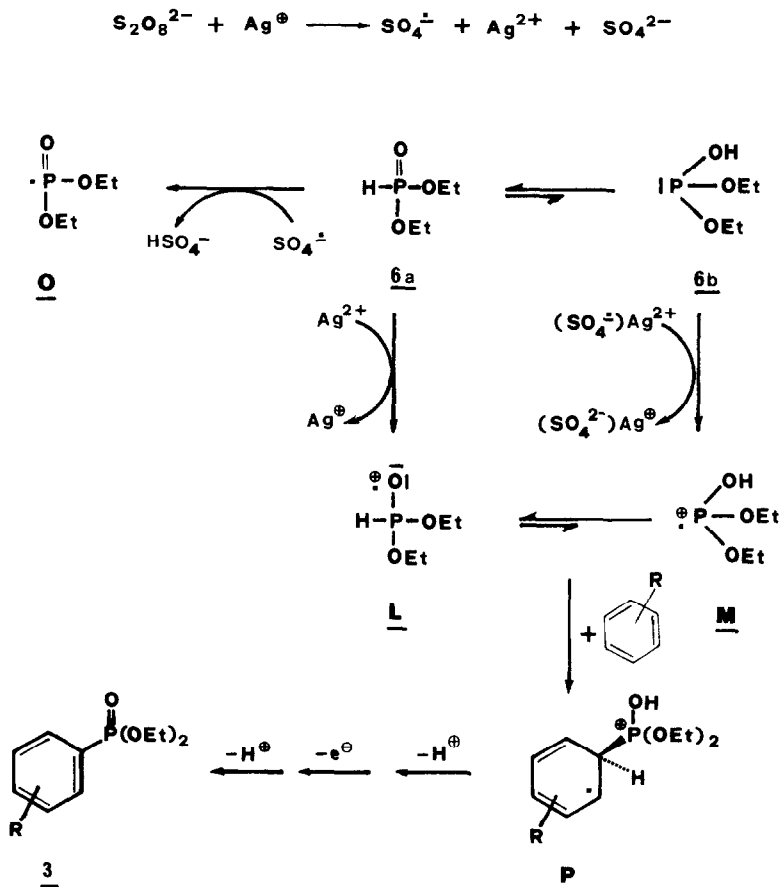
Both $Ag^{2+}$ and $SO_4^{\cdot -}$ can act as effective oxidants in the peroxodisulfate/silver nitrate system. This system is characterized by such a high oxidation potential[23] that a selective oxidation of aromatic compounds or alkylphosphites, respectively, is highly unlikely. Rather than the relative half-wave potentials of the two substrates, follow-up reactions of the different reactive intermediates, formed from oxidant and substrates, will therefore decide on the actual product formation.

Diphenylethanes and -methanes as well as acetoxylated derivatives are formed in the reaction of alkylbenzenes with $Ag^+$/peroxodisulfate/diethylphosphite in acetic acid. This clearly indicates intermediate formation of aromatic radical cations. They cannot be intercepted by 6 under formation of an aryl-C-phosphorus bond, however, since diethylphosphite exists mainly in the tautomeric

form 6a and thus no longer represents a P nucleophile.[28] By the same token intermediate formation of silver diethylphosphite, $(EtO)_2\bar{P}OAg$),[29] is improbable, proved by our own investigations since this would be an even better phosphorus nucleophile than 6.

There are two further strong arguments against the intermediacy of aromatic radical cations in arylphosphonate formation by chemical oxidation: (a) The isomer distribution differs markedly from that found for reactions with established addition of nucleophiles to aromatic radical cations.[13a,30] (b) Increasing amounts of oligophosphonylated products are formed at higher $Ag^+$ concentrations. Introduction of a diethylphosphonyl group should deactivate the aromatic substrate almost as much as a nitro group,[31] and thus effectively prevent both the reaction with an electrophile and further oxidation under the standard reaction conditions employed.

Based on these experimental findings, we propose the mechanism, outlined in Scheme 5, for the phosphonylation of aromatic compounds with diethylphosphite (6)/silver nitrate/peroxodisulfate. We consider silver(II)ions as the only species with a sufficiently high potential for the oxidation of 6; in the absence of silver ions, phosphonylation does not occur even if sulfate radical anions are present. The phosphorus radical cation L or M, respectively, generated in the first oxidative step, then attacks the aromatic substrate as a radical, forming the intermediate P (and thence the arylphosphonates 3) rather than as electrophile via the intermediate C as in the anodic phosphonylation (see Scheme 1). Thus, formation also of oligophosphonylation products is easily rationalized.




**SCHEME 5**

Attack of L/M at the aromatic substrate as a radical is also supported by the fact that no chloride elimination at all is observed in the phosphonylation of chlorobenzene, in sharp contrast to the anodic process (see above). Since the triethylphosphinium radical cation and the radical cation M (see Schemes 1 and 5, respectively) should display comparable reaction behavior, the divergent results for the chlorobenzene phosphonylation show that the tautomeric equilibrium L/M must be shifted extremely in favor of L.

Phosphonylation by the phosphonyl radical O can be ruled out because both $Ag^{2+}$ and $SO_4^{\cdot -}$, as typical electron transfer agents,[23] show little tendency for H-abstraction. As we could show in another context,[5] O which is definitely formed in the reaction of bis-tert.-butylperoxide and 6, in fact is a remarkably less effective phosphonylating agent.[24]

From the PE spectra of 6, we conclude that in the first oxidation step the electron is taken from the P=O $\pi$-orbital of 6 (as formulated in Scheme 5) which is localized primarily at the oxygen atom.[32]

In comparison to the known procedures, the oxidative phosphonylation of arenes, as described in this paper, has undoubtedly great preparative advantages for the introduction of phosphorus substituents into aromatic compounds. Investigations still in progress[33] show, that for the phosphonylation with chemical oxidants, Cerium(IV)salts give even better results than the silver/peroxodisulfate system.

Acknowledgement: We gratefully acknowledge the support by the "Deutsche Forschungsgemeinschaft" and the "Fonds der Chemischen Industrie".

## EXPERIMENTAL

Preparative column chromatography was done with silicagel S, 0.032-0.063 mm (Riedel-de Haën) using glass columns 35 cm x 5 cm and 20 cm x 3 cm. GLC analyses were performed with a Carlo Erba Fractovap GI, Brechbühler AG, Urdorf, equipped with a flame-ionization detector (FID) and a Spectraphysic Minigrator by using capillary columns 20 m (phase SE-52 and SE-54) and 20 m (phase Emulphor EM-ON D 1). Carrier gas: He (0.7 bar), thermoregulation SE-52: 5°/min, 10°/min, 50-250°, EM-ON: 5°/min, 50-170°, isotherm 150°. GLC yields refer to 1,4-dimethoxybenzene as internal standard, they are calibrated with identical reference substances. - $^1$H-NMR spectra were taken on Varian A-60 (60 MHz), Bruker WP 80 (80 MHz) and HX 90 (90 MHz) instruments, $^{13}$C-NMR spectra at 22.63 MHz on a Bruker HX 90 and at 75.47 MHz on a Bruker CXP 300 spectrometer where $CDCl_3$ was the solvent. $^{31}$P-NMR spectra were taken at 24.3 MHz on a Bruker WP60 and at 32.3 MHz on a Bruker WP 80 spectrometer.

Electrochemical investigations and preparative electrolyses were taken on a Wenking Potentiostat HP 72, equipped with a Wenking function generator, a Wenking current integrator SSI 70, a digital multimeter Kethley 169, an X,Y-recorder Philips 8141 and graphite electrodes. The reference electrode consisted of an internal silver system $Ag/Ag^+$ (Methrom EA 433) and a 0.1 N solution of $AgNO_3$ in $CH_3CN$.

General Method for Preparative Electrolyses. In an undivided electrolytical cell a solution of 100 ml of conducting salt in $CH_3CN$ was stirred for 15 min under dry $N_2$ (cell temperature was kept at 20° by a thermostat). After taking a voltammogram the educt (1 or 2) with the higher potential was added and the mixture stirred again for 10 min under dry $N_2$. Subsequently, a voltammogram was taken and then the same procedure was done with the other educt. The electrolysis was run at a constant anode potential until 2 F/mol have passed, $CH_3CN$ was removed at room temperature in a rotating evaporator, and about 200 ml ether were added to the dark brown oily residue. The precipitated conducting salt was filtered off and washed with ether, the combined ether layers were dried ($MgSO_4$), concentrated and worked-up by fractional distillation or by preparative column chromatography. Reference substances were synthesized by relevant literature methods and identified by $^1$H-, $^{13}$C- and $^{31}$P-NMR spectra for determination of 3 and the isomeric distribution.

Preparative electrolyses were done with each 25 mmol of 1 and 2 (4.0 g) and 100 ml of 1 N $Bu_4NClO_4$ in $CH_3CN$.

After work-up and A) fractional distillation were obtained:

from 1.95 g benzene (1a): 3a (2.0 g, 38%)b.p. 84°/$10^{-2}$ mm Hg (lit.(34)b.p. 96-98°/0.2 mm Hg) and 4 (1.2 g, 26%)b.p. 30°/$10^{-2}$mm Hg (lit.(35)b.p. 106-108°/24 mm Hg).

from 2.3 g toluene (1b): a mixture of the isomers 3b (2.3 g, 40%)b.p. 98°/0.08 mm Hg and 4 (1.2 g, 26%).

from 2.65 g 1,2-xylene (1c): a mixture of the isomers 3c (3.2 g, 53%)b.p. 93-95°/$10^{-3}$mm Hg and 4 (1.2 g, 26%).

from 2.65 g, 1,3-xylene (1d): a mixture of the isomers 3d (2.9 g, 48%)b.p. 84-86°/0.05 mm Hg and 4 (0.9 g, 20%).

from 2.65 g 1,4-xylene (1e): 3e (2.8 g, 46%)b.p. 103°/$10^{-2}$mm Hg, 1e (0.7 g, 26%) and 4 (1.05 g, 23%).

from 3.0 g mesitylene (1f): 3f (3.0 g, 47%)b.p. 102°/$10^{-3}$mm Hg (lit.(34)b.p. 111-112°/0.05 mm Hg), 1f (0.9 g, 30%) and 4 (0.8 g, 18%).
from 2.69 g anisole (1g): a mixture of isomers 3g (2.2 g, 36%)b.p. 108°/$10^{-3}$mm Hg, 1g (0.65 g, 24%) and 4 (0.5 g, 12%).
from 3.38 g acetanilide (1i): 4 (1.0 g, 22%) and by subsequent column chromatography of the residue with $CH_3CN$ 1i (1.3 g, 38%) $R_f(CH_3CN)$0.81, ortho-3i (2.45 g, 36%) $R_f(CH_3CN)$0.66 and para-3i (1.45 g, 21%) $R_f(CH_3CN)$0.37, m.p. 142° (lit.(11a) 138-140°).
from 4.2 g 1,3,5-trimethoxybenzene (1k): 4 (0.6 g, 13%) and by subsequent column chromatography of the residue 1k (1.6 g, 38%) $R_f(CH_2Cl_2)$0.72, and 3k (3.2g 43%) $R_f(CH_3COOEt)$0.35, m.p. 71-72.
from 2.8 g chlorobenzene (1n): 4 (2.5 g, 54%) and by subsequent column chromatography of the residue with $CH_3COOEt$ as the eluent 3a (0.78g,12%).

After work-up and B) preparative column chromatography were obtained:
from 3.85 g biphenyl (1h): 1h (1.1 g, 28%) $R_f(CH_2Cl_2)$1.0. Subsequently, the column was eluted with $CH_3CN$ and the eluate distilled to give 4 (0.8 g, 17%)b.p. 35°/$10^{-3}$mm Hg. The residue was determined by GLC with 1,4-dimethoxymethane as internal standard as a mixture of the isomers 3h and a diethyl tetrahydrobiphenyl-4-yl-phosphonate (57:11:15:16), which was dehydrogenated with 2,3-dichloro-5,6-dicyano-1,4-benzochinone (DDQ) (2.7 g, 12 mmol) in refluxing benzene (10 ml) for 2.5 h and then distilled to give a mixture of the isomers 3h (60:9:31) (3.3 g, 46%)b.p. 134-136°/$10^3$mm Hg.
from 3.20 g naphthalene (1m) as described above: 1m (1.0 g, 31%) $R_f(CH_2Cl_2)$1.0, 4 (0.9 g, 20%) and a mixture of the isomers 3m and a diethyl dihydro- and diethyl tetrahydro-1-naphthyl-phosphonate (10:7:7:4) which was dehydrogenated as described above and determined by capillar GLC (phase SE-54) as a mixture of the isomers 3m (75:25).
from 3.45 g 1,4-dimethoxybenzene (1l): 1l (0.82 g, 24%) $R_f(CH_2Cl_2)$0.68. Subsequently the column was eluted with $CH_3COOEt$ and the eluate fractionally distilled to give 4 (0.8 g, 17%) and 3l (3.8 g, 56%)b.p. 140°/$10^{-3}$mm Hg.
from 3.02 g N,N-dimethylaniline (1o): 1o (1.9 g, 63%) $R_f(CH_2Cl_2)$0.63. Subsequently the column was eluted with $CH_3COOEt$ and the eluate distilled to give diethyl (N-methyl-N-phenyl)amino-methylphosphonate (5) (1.9 g, 30%)b.p. 108°/$10^{-3}$mm Hg.

General method for phosphonylation of 1 with 6 and 7 in presence of $AgNO_3$ at 25°
A) in acetonitrile/water: In a three-necked flask, equipped with a gas inlet pipe, a reflux condenser and a gas outlet pipe with a bubble counter to a solution of 7a( 4.7 g, 20 mmol) in water (50 ml) the solution of 1 (10 mmol) in $CH_3CN$ (10 ml) and 6 (6.9 g, 50 mmol) was added. The mixture was stirred under dry $N_2$ for 20-30 min, the solution of $AgNO_3$ (0.34 g, 2 mmol) in water (10 ml) was added and the mixture stirred for 48 h at 25°.
Work-up: 1) The yellow colored layer was separated, the water layer extracted with ether or $CH_2Cl_2$. The solid was separated, the combined organic layers were neutralized with a solution of sodium carbonate in water, dried ($MgSO_4$), distilled and chromatographed.
2) If no organic layer was produced the solid was separated and extracted with $CH_2Cl_2$, the combined organic layers were worked-up as described above.
3) $CH_2Cl_2$ was added to the organic layers (see above, 1,2) to get a defined volume, then a defined amount of a standard was added and the products were determined by GLC.
B) in glacial acetic acid: ($CH_3COOH$) (fractionally distilled with a Fischer HMS 500, b.p. 118°/760 mm Hg): In a two-necked flask, equipped with a gas inlet and a gas outlet pipe with a bubble counter to the solution of 7a in $CH_3COOH$ 6 and 1 were added. The mixture was stirred under dry $N_2$ for 30 min, then $AgNO_3$ was added and the mixture stirred for 60 h at 25°. Subsequently the brown solid was filtered off and the $CH_3COOH$ distilled off at 25-35°/10-15 mm Hg. Water (100-200 ml) was added to the residue, the mixture was extracted with ether for several times, the combined ether layers were twice washed with water, neutralized with a solution of sodiumcarbonate in water, dried ($MgSO_4$) and distilled.

The general procedure A was employed for the reaction of:
benzene (1a)(0.78 g), toluene (1b)(0.92 g), 1,2-, 1,3- and 1,4-xylene (1c-e)(each 1.06 g), mesitylene (1f)(1.20 g), anisole (1g)(1.08 g), biphenyl (1h)(1.54 g), acetanilide (1i)(1.35 g), naphthalene (1m)(1.28 g), chlorobenzene (1n)(1.12 g), fluorobenzene (1p)(0.96 g) and benzonitrile (1q)(1.03 g), resp. After work-up the yields of 3 were determined by GLC with reference substances and 1,4-dimethoxybenzene as internal standard. The separation of the isomeric diethyl phosphonates 3b-d, g-i and m was done with capillary columns (phase SE-52 and SE-54), those of 3n, p and q with capillary columns (Emulphor EM-ON D 1).

The general procedure B was employed for the reaction of:
a) 1a, b, d, h, i, m, p, and q with 6 (6.9 g, 50 mmol), 7a (4.7 g, 20 mmol) and $AgNO_3$ (1.70 g, 10 mmol) in $CH_3COOH$ (50 ml). After work-up the yields of 3 (see Table 2) were determined by GLC as described above (A).
b) 1f (6.0 g, 50 mmol) and 1g (5.4 g, 50 mmol), resp. with 6 (34.5 g, 250 mmol), 7a (24.0 g, 100 mmol) and $AgNO_3$ (8.4 g, 50 mmol) in $CH_3COOH$ (250 ml). After work-up yielded:
1f (0.8 g, 13%), 3f (8.20 g, 64%)b.p. 102°/$10^{-3}$mm Hg and 9f (1.90 g, 11%)b.p. 155-158°/$10^{-3}$ mm Hg or 1g (1.7 g, 32%) and a mixture of the isomers 3g (7.07 g, 55%)b.p. 114°/$10^{-3}$mm Hg.

Phosphonylation of N,N-dimethylaniline (1o)(3.0 g, 25 mmol) with 2 (0.8 g, 5 mmol), 7b (6.80 g, 10 mmol) and $AgNO_3$ (0.17 g, 1 mmol) in $CH_3CN$ (30 ml):
7b was synthesized analogous lit. (36): To a solution of tetrabutylammoniumtetrafluoroborate (32.90 g, 100 mmol) in 50% ethanol (300 ml) the solution of potassiumperoxodisulfate (13.50 g, 50 mmol) in water (300 ml) was dropped at room temperature and stirred overnight in an ice bath. The precipitated potassiumtetrafluoroborate was filtered off and the filtrate was concentrated in a

rotating evaporator (T ≤ 30°). The light yellow oily residue was treated with $CH_2Cl_2$ (200 ml), the solid was separated and the filtrate concentrated in a rotating evaporator. The oily residue was dried in high vacuo at 30–40°/$10^{-3}$mm Hg to yield 7b (28.3 g, 83%) as a colorless powder, m.p. 95–96° (Found: C, 56.87; H, 10.59; N, 3.97; S, 9.29. Calcd. for $C_{32}H_{72}N_2O_8S_2$: C, 56.80; H, 10.65; N, 4.14; S, 9.48%). The reaction with 7b was done in an annealed and nitrogen degassed apparature, the solids were weighed in a glove box, the liquids injected by syringe over a septum. The mixture was stirred for 66 h at 25°, then the solvent was distilled off in a rotating evaporator and the brown viscous residue extracted with ether for several times. The solids were separated, the ether layers dried ($MgSO_4$) and distilled to give 5 (0.57 g, 45%)b.p. 126°/0.02 mm Hg.

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