

Mechanism of Dediazonation of Arenediazonium Salts with Triphenylphosphine and Trialkyl Phosphites. Generation of Cation Radicals from Trivalent Phosphorus Compounds and Their Reactions

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4-Nitro-, 4-methyl-, and 4-methoxy-benzenediazonium fluoroborates are readily dediazoniated with triphenylphosphine or trialkyl phosphites (alkyl = methyl or ethyl) in alcoholic solvents at room temperature in the dark under a nitrogen atmosphere to give the corresponding arenes and the corresponding oxidation product from the phosphine or the phosphites, triphenylphosphine oxide or trialkyl phosphates, respectively, along with a small amount of biaryls. In the reaction with the phosphite, dialkyl arylphosphonate is also formed. The stoichiometry of the reactions and the results of the reactions in deuteriated methanols, together with other evidence, indicate that the reactions proceed by a radical-chain mechanism initiated by single-electron transfer from the trivalent phosphorus compound to the diazonium salt, during which the cation radical is generated from the former. The product distribution shows that this cation radical reacts with the solvent alcohol to give a phosphoranyl radical, which eventually affords the final product, the phosphine oxide or the phosphate, from the phosphine or the phosphite, respectively. The cation radical from the phosphite also undergoes radical coupling with the aryl radical Ar[•] generated during the reaction to yield dialkyl arylphosphonate *via* a phosphonium intermediate, whereas no radical coupling of the cation radical from the phosphine with Ar[•] takes place.

Trivalent phosphorus compounds, which are easily converted into compounds of a higher oxidation state, readily form a fourth covalent bond at the phosphorus atom when treated with an electrophile. Examples include phosphorus-carbon bond formation during the Arbuzov^{1,2} and Wittig reactions,² phosphorus-nitrogen bond formation in the initial stage of the Mitsunobu esterification,³ and phosphorus-sulfur bond formation in the reductive cleavage of a disulfide⁴ or a trisulfide bond.⁵ The mechanism of these reactions has been supposed to involve direct nucleophilic attack of the phosphorus atom in a trivalent phosphorus compound on the electrophilic centre in the substrate, which leads to the formation of a phosphonium intermediate followed by its decomposition to a pentavalent phosphorus compound.²

Processes with single-electron transfer (SET) in organic reactions have recently been studied in detail, and evidence has been found that a radical pair is initially generated through SET during 'typical' nucleophilic reactions in which a carbon-carbon bond is formed: for example, S_N2 reactions,⁶ aldol condensations⁷ and the alkylation of olefins.⁸ Such a mechanism has been also postulated for carbon-hydrogen bond formation in the reduction of alkyl halides by lithium aluminium hydride.⁹ This easy occurrence of SET during the formation of carbon-carbon or carbon-hydrogen bonds calls attention to the phosphorus counterpart of such bond formation. That is, reactions of trivalent phosphorus compounds, for which a nucleophilic mechanism has been assumed, should be reinvestigated to determine whether SET is the first step of the reaction. If SET occurs, trivalent phosphorus compounds are necessarily converted to a cation radical in the first stage of the reaction, so the chemical properties of such radicals should be studied in such a reevaluation.

While electrochemical oxidation^{10,11} and γ -irradiation^{12,13} of phosphines or phosphites produce several kinds of trivalent

phosphorus cation radicals, the generation of cation radicals from trivalent phosphorus compounds during chemical reactions has been studied less often;¹⁴⁻¹⁷ the reaction of triphenylphosphine with 7,7,8,8-tetracyanoquinodimethane proceeds *via* triphenylphosphine cation radical as an intermediate;¹⁵ and the initial step of the photo-reduction of 10-methylacridinium ion with triphenylphosphine¹⁶ or a diphenylphosphinite derivative¹⁷ is SET from the latter to the former in the photo-excited state, through which the cation radical is generated from the trivalent phosphorus compound. The chemistry of such a cation radical, especially in terms of its chemical reactions, is not clear.

Since diazonium salts are good electron acceptors,¹⁸ efficient SET from trivalent phosphorus compounds to diazonium salts could take place, giving the cation radical as an incipient but discrete intermediate. Triphenylphosphine, as well as trialkyl phosphites, has been found to donate one electron to arenediazonium salts in the dark at room temperature in alcoholic solvents, which gives rise to the dediazonation of the diazonium salts through a radical-chain mechanism.¹⁹ The product distribution has been understood in terms of unit reactions of the cation radical generated from the phosphine or the phosphite during the reaction. Thus, this reaction system is useful for examinations of the chemical behaviour of trivalent-phosphorus cation radicals.

In this article, we present further evidence for a radical-chain mechanism in the dediazonation of arenediazonium salts with triphenylphosphine or trialkyl phosphites, which confirms that cation radicals are generated from the trivalent phosphorus compounds during the reaction. We also discuss possible reaction pathways from such a radical species to the final products, based mainly on product analysis. To the best of our knowledge, this is the first report of an investigation of the chemical properties and the reactivity of trivalent-phosphorus cation radicals.

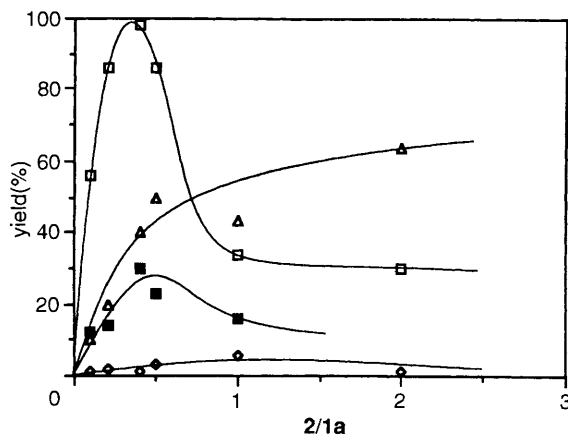
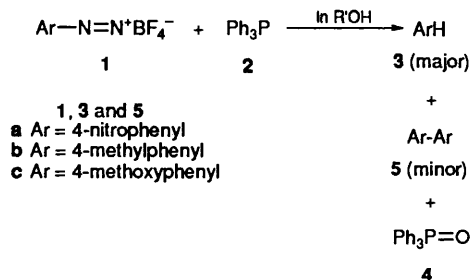


Fig. 1 Yields of products based on diazonium salt **1a** with different initial amounts of phosphine **2**. Initial amount of **1a**, 0.10 mmol, in 1.0 cm³ of methanol, reaction time, 30 min, in the dark at 20 °C. (□), (◇) and (△) denote yields of **3a**, **5a** and **4** under an N₂ atmosphere, respectively. (■), yield of **3a** under an O₂ atmosphere.

Results

Dediazoniating of 4-Nitrobenzenediazonium Fluoroborate 1a with Triphenylphosphine 2.—The reaction of the diazonium salt **1a** with the phosphine **2** was carried out in methanol at 20 °C in the dark under a nitrogen atmosphere for 30 minutes, and the reaction mixture was analysed on a gas chromatograph (GC) and a gas chromatograph–mass spectrometer (GC–MS) to show the formation of nitrobenzene **3a** and triphenylphosphine oxide **4**, along with a small amount of 4,4'-dinitrophenyl **5a** (Scheme 1). The yields of the products



Scheme 1

based on the initial amount of **1a**, listed in Table 1, were plotted against the ratio of the initial amount of **2** to that of **1a** (**2/1a**) in Fig. 1. Table 1 also shows that the reactions of **1a** with **2** in ethanol, propan-2-ol, and cyclohexanol under a nitrogen atmosphere likewise gave **3a**, **4** and **5a**. In the reactions in cyclohexanol, cyclohexanone, an oxidation product from the alcohol, was detected in addition to the above products (Table 1). In these reactions, an oxygen atmosphere suppressed the formation of **3a** and **5**, bringing about the quantitative oxidation of **2** to **4**.

Dediazoniating of 4-Methyl- and 4-Methoxybenzenediazonium Fluoroborate (1b and c) with Phosphine 2.—These arenediazonium salts were also dediazoniating with phosphine **2** under the same conditions as in the reaction of the 4-nitro derivative **1a**. The corresponding products were produced in yields comparable to those for the reaction of **1a** as listed in Table 2.

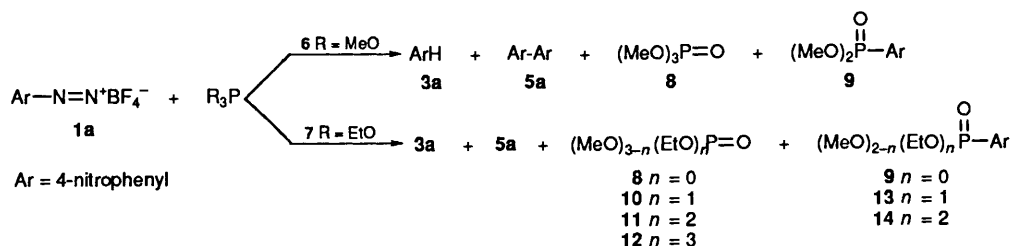
Dediazoniating of Diazonium Salts with Trimethyl Phosphite 6 and with Triethyl Phosphite 7.—The reactions of diazonium salt **1a** with trialkyl phosphites in methanol were carried out under the same conditions as described above. In the reaction of **1a** with trimethyl phosphite **6**, nitrobenzene **3a**, biaryl **5a**, trimethyl

Table 1 Reaction of 4-nitrobenzenediazonium fluoroborate **1a** with triphenylphosphine **2** in alcoholic solvents^a

Solvent	2:1a ^b	Atmosphere	Product yield (%) ^c			
			3a	5a	4 ^d	Other
Methanol	0.1	N ₂	56	<1	10 (100)	—
	0.1	O ₂	12	0	10 (100)	—
	0.2	N ₂	86	2	20 (100)	—
	0.2	O ₂	14	0	20 (100)	—
	0.4	N ₂	98	<1	40 (100)	—
	0.4	O ₂	30	0	40 (100)	—
	0.5	N ₂	86	3	50 (100)	—
	0.5	O ₂	23	0	50 (100)	—
	1.0	N ₂	34	6	43 (43) ^e	—
	1.0	O ₂	16	0	100 (100)	—
	2.0	N ₂	30	<1	64 (32) ^f	—
	10.0 ^g	O ₂	0	0	— (100)	—
Ethanol	0	N ₂	13	0	—	—
	0	O ₂	7	0	—	—
	0.1	N ₂	58	2	10 (96)	—
	0.1	O ₂	14	0	10 (100)	—
	0.3	N ₂	91	<1	26 (87)	—
	0.3	O ₂	36	0	30 (100)	—
	0.5	N ₂	78	8	32 (64)	—
	0.5	O ₂	29	0	50 (100)	—
	1.0	N ₂	31	5	29 (29)	—
	1.0	O ₂	13	0	100 (100)	—
Propan-2-ol	0	N ₂	13	0	—	—
	0	O ₂	6	0	—	—
	0.1	N ₂	61	3	9 (86)	—
	0.1	O ₂	16	0	10 (100)	—
	0.3	N ₂	96	<1	30 (100)	—
	0.3	O ₂	33	0	30 (100)	—
	0.5	N ₂	75	6	45 (89)	—
	0.5	O ₂	23	0	50 (100)	—
	1.0	N ₂	54	3	59 (59)	—
	1.0	O ₂	17	0	100 (100)	—
Cyclohexanol	0	N ₂	10	<1	—	12 ^h
	0	O ₂	0	0	—	0 ^h
	0.1	N ₂	38	<3	9 (93)	30 ^h
	0.1	O ₂	15	0	10 (100)	18 ^h
	0.3	N ₂	78	<6	30 (100)	69 ^h
	0.3	O ₂	27	0	30 (100)	30 ^h
	0.5	N ₂	93	<8	45 (89)	71 ^h
	0.5	O ₂	32	0	50 (100)	40 ^h
	1.0	N ₂	44	<1	25 (25)	38 ^h
	1.0	O ₂	22	0	100 (100)	34 ^h

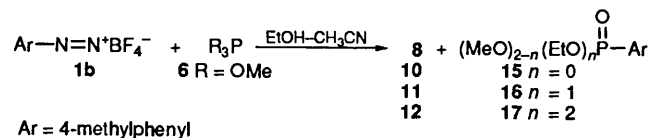
^a Initial amount of **1a**, 0.10 mmol, in 1.0 cm³ of solvent, reaction time 30 min, in the dark at 20 °C. ^b Ratio of the initial amount of **2** to that of **1a**. ^c Based on the initial amount of **1a**. ^d The values in parentheses are yields calculated based on the initial amount of **2**. ^e 30% of **2** was recovered. ^f 84% of **2** (based on the initial amount of **1a**) was recovered. ^g Initial amount of **1a**, 0.01 mmol, in 1.0 cm³ of methanol. ^h Yield of cyclohexanone.

phosphate **8**, and dimethyl 4-nitrophenylphosphonate **9** were obtained. In the reaction of **1a** with triethyl phosphite **7** in the same solvent, methanol, besides the same products mentioned above (**3a**, **5a**, **8** and **9**), ethyl dimethyl phosphate **10**, diethyl methyl phosphate **11**, triethyl phosphate **12**, ethyl methyl 4-nitrophenylphosphonate **13** and diethyl 4-nitrophenylphosphonate **14** were formed (Scheme 2). The reactions under an oxygen atmosphere gave the products in lower yields. The results in the reactions with **6** and with **7** in methanol are summarised in Tables 3 and 4, respectively. The reactions of 4-methylbenzenediazonium fluoroborate **1b** with **6** in ethanol–acetonitrile mixture under a nitrogen atmosphere afforded the mixture of the phosphates, **8**, **10**, **11** and **12**, and the mixture of phosphonates, dimethyl 4-methylphenylphosphonate **15**, ethyl methyl 4-methylphenylphosphonate **16**, and diethyl 4-methyl-



Scheme 2

phenylphosphonate 17 (Scheme 3). The results are listed in Table 5.



Scheme 3

The Reaction of 1a in Deuteriated Methanols.—The content of deuterium in the product, nitrobenzene 3a, formed in the reaction of diazonium salt 1a with phosphine 2 or phosphite 7 in differently deuteriated methanols was determined on a GC-MS as shown in Table 6. The results indicate that a methyl hydrogen of methanol was incorporated into 3a.

Controls.—The trivalent phosphorus compounds used here (2, 6 and 7) were stable in alcoholic solvent in the absence of the diazonium salt under either a nitrogen or an oxygen atmosphere within the test period. Neither the starting materials, the phosphites, nor the products, the phosphates and the phosphonates, underwent transesterification with the solvent alcohol. In the absence of the trivalent phosphorus compound, the dediazonation of diazonium salts 1 was not observed in methanol. The reactions of 1a in ethanol, 2-propanol, or cyclohexanol under a nitrogen atmosphere

afforded the dediazonation product, nitrobenzene 3a, in 10–13% yield (based on the initial amount of 1a) when the trivalent phosphorus compound was absent.

EPR Examination.—The reaction mixtures of diazonium salt 1a with phosphine 2 and of 1a with phosphite 7 in tetrahydrofuran (THF) were analysed by EPR spectroscopy. The signals for the former and the latter phosphorus compounds, respectively, had *g*-values of 2.004 and 2.005. The hyperfine structures were not recognised here.

Discussion

Under a nitrogen atmosphere, the yield of nitrobenzene 3a increases, reaches a maximum, and decreases, as the initial amount of the trivalent phosphorus compound R₃P [phosphine 2 (R = Ph), or phosphite 6 (R = MeO) or 7 (R = EtO)] increases (see Fig. 1, for example). Nitrobenzene 3a is formed in more than a stoichiometric amount when the ratio of the initial amount of R₃P to that of diazonium salt 1a is less than about 0.5, indicating that a chain reaction takes place during the dediazonation of 1a. The observation that an oxygen atmosphere suppresses the formation of 3a strongly

Table 2 Reaction of 4-substituted arenediazonium salts 1a, b and c with triphenylphosphine 2 in methanol^a

Arenediazonium	Product yield (%)		
	3	5	4
4-NO ₂ a ^b	34 ^c	6 ^d	43
4-Me b	28 ^e	< 1 ^f	27
4-MeO c	39 ^g	5 ^h	37

^a Initial amounts of 1 and 2, both 0.10 mmol, in 1.0 cm³ of methanol, reaction time, 30 min, under a nitrogen atmosphere in the dark at 20 °C. ^b Data taken from Table 1. ^c Nitrobenzene 3a. ^d 4,4'-Dinitrobiphenyl 5a. ^e Toluene 3b. ^f 4,4'-Dimethylbiphenyl 5b. ^g Anisole 3c. ^h 4,4'-Dimethoxybiphenyl 5c.

Table 3 Reaction of 4-nitrobenzenediazonium fluoroborate 1a with trimethylphosphite 6 in methanol^a

6: 1a ^b	Product yield (%) ^c		
	3	8 ^d	9 ^d
0.3	76	20 (66)	3 (11)
0.5	61	34 (68)	5 (11)
1.0	46	56 (56)	11 (11)
1.0 ^e	19	21 (21)	6 (6) ^f
2.0	13	89 (45)	23 (12) ^g

^a Initial amount of 1a, 0.10 mmol, in 1.0 cm³ of methanol, reaction time 30 min, in the dark at 20 °C under a nitrogen atmosphere. A trace amount of biaryl 5a was detected in each run. ^b Ratio of the initial amount of 6 to that of 1a. ^c Based on the initial amount of 1a. ^d The values in parentheses are yields calculated based on the initial amount of 6. ^e Under an oxygen atmosphere. ^f 29% of dimethyl methylphosphonate was obtained. ^g 16% (based on the initial amount of 1a) of dimethyl methylphosphonate was obtained.

Table 4 Reaction of 4-nitrobenzenediazonium fluoroborate 1a with triethyl phosphite 7 in methanol^a

7: 1a ^b	Product yield (%) ^c										
	3a	Phosphate					total ^d	Phosphonate			
		8	10	11	12	9		13	14	total ^d	
0.3	71	11	7	1	0	19 (65)	1	1	< 1	2 (7)	
0.5	62	24	7	3	2	36 (72)	3	2	< 1	5 (10)	
1.0	42	43	12	3	3	61 (61)	7	2	1	10 (10)	
2.0	17	58	31	7	4	100 (50)	22	8	3	33 (16)	

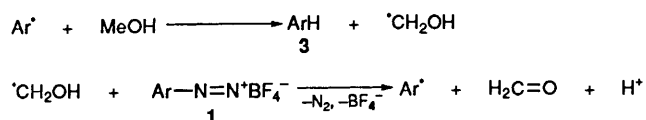
^a Initial amount of 1a, 0.10 mmol, in 1.0 cm³ of methanol, reaction time 30 min, in the dark at 20 °C under a nitrogen atmosphere. A trace amount of biaryl 5a was detected in each run. ^b Ratio of the initial amount of 7 to that of 1a. ^c Based on the initial amount of 1a. ^d The values in parentheses are yields calculated based on the initial amount of 7.

Table 5 Reaction of 4-methylbenzenediazonium fluoroborate **1b** with trimethyl phosphite **6** in ethanol-acetonitrile^a

EtOH (%)	Product yield (%)						
	Phosphate				Phosphonate		
	8	10	11	12	15	16	17
1	19	33	0	0	1	0	1
10	9	30	8	8	2	<1	1
50	0	17	11	15	2	2	2
100	0	15	15	32	2	3	2

^a Initial amounts of **6** and **1b**, both 0.10 mmol, in 1.0 cm³ of solvent, reaction time, 30 min, in the dark at 20 °C under a nitrogen atmosphere. A trace amount of biaryl **5b** was detected in each run.

suggests that this chain reaction is of a radical chain. The results obtained in the reactions of **1a** with phosphine **2** or phosphite **7** in deuteriated methanols, as shown in Table 6, indicate that a methyl hydrogen of methanol rather than an alcoholic hydrogen is incorporated into the product, nitrobenzene **3a**, which manifests that the radical chain involves propagation steps in which the aryl free-radical Ar[•] generated from **1a** abstracts a hydrogen from methanol to form hydroxymethyl radical as a chain-carrier (Scheme 4). The nearly quantitative



Scheme 4

incorporation of a methyl hydrogen from methanol into **3a** suggests that this process is the only path that gives **3a**. A similar process has been reported as a propagation step in the dediazonation of arenediazonium salts in the presence of an acid²⁰ or a one-electron donor.²¹ The formation of a small amount of biaryl **5a** also reflects the participation of Ar[•] in the reaction. According to Scheme 4, the solvent alcohol should be eventually oxidised to the corresponding carbonyl compound, and, in fact, when cyclohexanol is the solvent, not methanol, in the reaction with phosphine **2**, cyclohexanone is produced, its yield being roughly comparable to that of nitrobenzene **3a** at each concentration of **2**, as predicted (Table 1).

In the reaction of diazonium salt **1a** with phosphine **2** in ethanol, propan-2-ol, or cyclohexanol, the dependence of the yield of nitrobenzene **3a** on the molar ratio of the starting materials **2/1a** is similar to that observed in methanol, which, together with the inhibition of the formation of **3a** by oxygen, indicates that the reactions in these alcoholic solvents proceed by the same mechanism as in methanol. The results in Table 1 show that the yield of **3a** increases depending on the solvent alcohol in the order of methanol \cong ethanol < cyclohexanol < propan-2-ol when **1a** is treated with an equimolar amount of **2**. This order does not reflect the order of the polarity of the alcohols,²² but it seems compatible with the order of the stability of the corresponding α -hydroxyalkyl radicals which are crucial in the radical-chain reaction. These findings are evidence of the occurrence of the proposed radical-chain mechanism. Even in the absence of a trivalent phosphorus compound, ethanol, propan-2-ol and cyclohexanol give rise to the dediazonation of **1a** to afford a small amount of **3a**, as has been previously reported,^{*,23} but the contribution of this

* It is not known whether this alcohol-promoted dediazonation takes place *via* an ionic or a radical pathway.

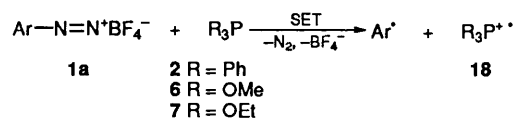
Table 6 Reactions of 4-nitrobenzenediazonium fluoroborate **1a** with trivalent phosphorus compounds in deuteriated methanols^a

Trivalent phosphorus	Solvent	D(%) in 3a ^b
Ph ₃ P 2	CH ₃ OD ^c	<0.5
	CD ₃ OD ^d	99.5
(EtO) ₃ P 7	CH ₃ OD ^c	<0.5
	CD ₃ OD ^d	99.5

^a Initial amounts of **1a** and the trivalent phosphorus compound, both 0.10 mmol, in 1.0 cm³ of solvent, reaction time 30 min, under a nitrogen atmosphere in the dark at 20 °C. ^b Deuterium content in the product, nitrobenzene **3a**, determined by GC-MS. ^c >99.5% D. ^d >99.8% D.

pathway to the formation of the products is too small to affect this discussion.

Since no reactions take place without a trivalent phosphorus compound R₃P in methanol, the chain reaction is most likely initiated by R₃P. There is little doubt that the initiation step of this radical-chain reaction is single-electron transfer (SET) from R₃P to the arenediazonium salt, which would be followed by delivery of a nitrogen molecule in a rapid reaction (Scheme 5). In fact, bubbling probably arising from the liberation of dinitrogen from the diazonium salt was observed when solutions of the starting materials were mixed. Thus, the radical-chain reaction can be summarised as in Schemes 4 and 5. The aryl free-radical Ar[•] and cation radical **18** are generated from the diazonium salt and R₃P, respectively, in the initiation step (Scheme 5).†



Scheme 5

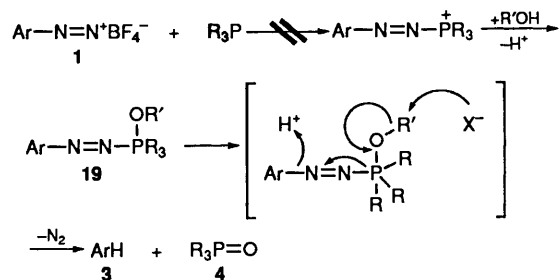
More direct evidence for this mechanism was provided by EPR examination. The *g*-value (2.004) observed in the reaction of diazonium salt **1a** with phosphine **2** in THF is within the range of those previously reported for triphenylphosphine cation radical (2.001–2.007).^{13,24} Although the datum for the phosphite **7** counterpart is not available, the signal at *g* = 2.004 observed in the reaction of **1a** with **7** can probably be assigned to the cation radical generated from **7**. Therefore, the formation of dimeric cation radical [(EtO)₃P–P(OEt)₃]^{•+}, the *g*-value of which has been reported to be 2.0017¹¹ or 2.000,²⁵ is precluded in this reaction.

The decrease in the yield of nitrobenzene **3a** with the increase of the initial amount of the trivalent phosphorus compound R₃P is attributable to the decomposition of Ar[•] or hydroxymethyl radical (or both) during radical scavenging by a surplus of R₃P to produce unexpected products. Several peaks were indeed found on the HPLC spectrum of the reaction mixture when an excess of R₃P was used; these products were not identified. A yield–substrate ratio profile similar to the profiles in Fig. 1 has been observed in the dediazonation of arenediazonium salts to the corresponding arenes by 1-benzyl-1,4-dihydrocinchonamide (BNAH) under a nitrogen atmosphere.²⁶ That observation has been cited as evidence for the radical-chain mechanism, and the

† The reaction of diazonium salt **1b** with phosphine **2** in methanol under a nitrogen atmosphere was analysed by GC-MS and a trace amount of bis(4-methylphenyl)diazene was detected. This suggests that the process shown in Scheme 5 is composed of two successive steps, in which the aryl diazenyl radical is formed before the liberation of a nitrogen molecule.

decrease in the yield of the corresponding arenes with the increase of the initial amount of BNAH has been discussed in the term of radical scavenging by a surplus of BNAH.

The ionic addition–elimination mechanism shown in Scheme 6 is unlikely. The ionic mechanism must include a phosphorane

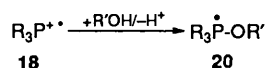


Scheme 6

intermediate **19**, the decomposition of which should afford the dediazonium product, nitrobenzene **3a**, with an alcoholic proton incorporated from the solvent alcohol. This is not the case. In addition, the ionic mechanism cannot account for the stoichiometry observed with respect to the yield of **3a**. That the substitution of ethyl groups by methyl groups in phosphite has a negligible effect on the yields of nitrobenzene **3a**, the phosphate, and the phosphonate is also incompatible with this ionic mechanism. Table 2 shows that the reactions of arenediazonium salts with an electron-releasing substituent such as 4-methyl- or 4-methoxy- (**1b** or **c**, respectively) and an equimolar amount of phosphine **2** gives the expected products, in comparable yields to the yield in the reaction of the 4-nitro-derivative **1a**. This result may eliminate the possibility that heterolytic cleavage of the arenediazonium salt gives an aryl cation intermediate, since this step would be rate-limiting and the yields of the products would be largely influenced by the substituent on the diazonium salt.²⁷

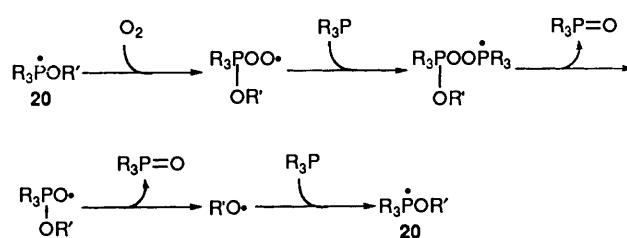
Thus, the dediazonation of the arenediazonium salts with the trivalent phosphorus compounds R_3P proceeds through the radical-chain mechanism initiated by SET from R_3P to the diazonium salt, generating cation radical **18** as well as aryl free-radical Ar^\bullet (Schemes 4 and 5). Now, the reactions of this cation radical can be discussed based on the product distribution.

The cation radical **18** interacts with the solvent alcohol to yield the corresponding phosphoranyl radical **20** (Scheme 7).^{15–17,28} Generation of **20** well explains the observation that



Scheme 7

the phosphine **2** and phosphite **6** are oxidised to the phosphine oxide **4** and phosphate **8**, respectively, under an oxygen atmosphere only when diazonium salt **1a** is present. That is, **20**, once formed, gives the corresponding oxidation product by the radical-chain procedure mediated by dioxygen (Scheme 8).²⁹ The oxidation of R_3P via **20** by the radical-chain under these

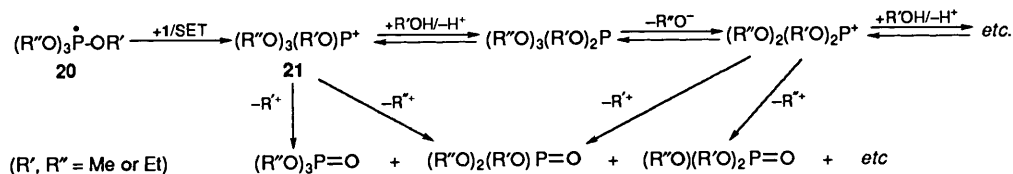


Scheme 8

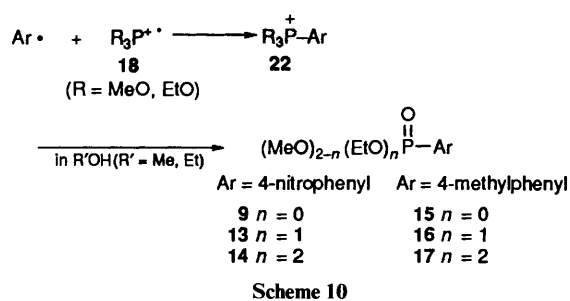
conditions is further confirmed by the fact that a catalytic amount of **1a** gives rise to the quantitative oxidation of **2** to **4** under an oxygen atmosphere (Table 1).

Under a nitrogen atmosphere, phosphoranyl radicals could decompose by several ways. β -Scission of **20**, with which a primary alkyl radical should be liberated, may be energetically disfavoured.³⁰ In fact, phosphates **8** and **10** obtained in the reaction of diazonium salt **1a** with triethyl phosphite **7** in methanol cannot be the products resulted from β -scission of the corresponding phosphoranyl radical (**20**, $\text{R} = \text{EtO}$, $\text{R}' = \text{Me}$ in Scheme 7). Alternatively, SET from **20** well accounts for the observed products. The ability of certain phosphoranyl radicals as reducing agents has been claimed.³¹ Thus, phosphoranyl radical **20** donates an electron to diazonium salt **1a** to give phosphonium ion **21**. Phosphonium ion **21** undergoes the successive reactions with solvent alcohol under the conditions,³² during which differently substituted phosphonium ions are formed *via* pentaoxyphosphorane intermediates. The elimination of the alkyl cation from each phosphonium ion in the Arbuzov fashion eventually affords the mixture of the phosphates (Scheme 9). This mechanism is confirmed by the results obtained in the reaction of diazonium salt **1b** with trimethyl phosphite (**6**) in ethanol–acetonitrile; thus, as shown in Table 5, the methoxy groups in the phosphates have been progressively replaced by the ethoxy group, with increasing the proportion of ethanol in the solvent.

Since phosphonate **9** is obtained in a lower yield during the reaction of diazonium salt **1a** with phosphite **6** under an oxygen atmosphere, the formation of the phosphonate under a nitrogen atmosphere results from another reaction of the cation radical generated from the phosphites. Under these conditions, the cation radical undergoes radical coupling with aryl radical Ar^\bullet to give phosphonium salt **22** (Scheme 10). The formation of **22** is suggested by the fact that phosphonates **9** and **13**, besides **14**, are formed in the reaction of diazonium salt **1a** with triethyl phosphite (**7**) in methanol (Table 4). That is, similarly to the decomposition of phosphonium ion **21**, the alkoxy group in **22** is replaced by that from solvent methanol through successive formations of tetraoxyaryloxyphosphoranes and trioxyaryloxyphosphonium ions; the decomposition of the latter results in the production of the mixture of the phosphonates. The solvent effect obtained in the reaction of diazonium salt **1b** with trimethyl phosphite (**6**) in ethanol–acetonitrile seems compatible with this mechanism, although the effect is small (Table 5); the yields of the ‘exchanged’ phosphonates (**16** and **17**) increase with an increase in the ethanol content in the



Scheme 9



solvent. It is thus evident that the cation radical from phosphite **6** or **7** couples with Ar \cdot to form phosphonium ion **22**.*

On the other hand, it is not easy to find out whether the cation radical from phosphine **2** reacts with Ar \cdot to afford the corresponding phosphonium ion **23**, because **23**, which does not react like phosphonium ion **22**, is not detectable by GC.



Then, we sought evidence of the formation of this type of phosphonium ion on the ^{31}P NMR spectrum of the reaction mixture of diazonium salt **1b** with an equimolar amount of phosphine **2** in [$^2\text{H}_4$]methanol or [$^2\text{H}_3$]acetonitrile, and found only a small signal at 39.5 ppm that could be assigned to 4-methylphenyltriphenylphosphonium ion **23** (Ar = 4-methylphenyl), besides the large signal of phosphine oxide **4** at 33.8 ppm.³³ This result shows that coupling between the cation radical from phosphine **2** and Ar \cdot takes place only to a small extent, if at all. In fact, **2** is quantitatively converted to **4** when the ratio **2/1a** is smaller than about 0.5, indicating that Ar \cdot undergoes abstraction of a hydrogen from methanol rather than coupling with the cation radical under these conditions. The yield of nitrobenzene **3a** is quite high at this ratio.

The lower reactivity of the cation radical from the phosphine than that from the phosphite toward Ar \cdot can be explained in terms of the spin distribution of these radical species; the unpaired electron of the cation radical from the phosphite (**18**, R = MeO or EtO) is centred on the phosphorus atom, whereas the unpaired electron of triphenylphosphine cation radical (**18**, R = Ph) is delocalised into the adjacent phenyl groups to reduce the radical character of this cation radical. A similar situation has been discussed for phosphoranyl radicals, based on EPR spectroscopy.³⁴ Steric factors could also account for the different behaviours of these cation radicals; phosphonium salt **23**, if formed, would be less stable than **22** because of its crowded structure as anticipated by the examination with Corey-Pauling-Koltun molecular models.

Conclusions

This study established that the dediazonation of arenediazonium salts with triphenylphosphine **2** or trialkyl phosphite **6** or **7** occurs by a radical-chain mechanism, and that during the reaction a cation radical is generated from the trivalent phosphorus compound. The product distribution suggests possible reaction pathways for the decomposition of the cation radical: (1) the cation radical generated from the phosphite undergoes competitively the ionic reaction with the solvent alcohol and the radical coupling with aryl radical Ar \cdot ; and (2) the cation radical generated from the phosphine undergoes the ionic reaction with the solvent alcohol, whereas

no coupling between the cation radical and Ar \cdot takes place probably due to delocalisation of the unpaired electron into the adjacent phenyl groups in this cation radical.

Experimental

Instruments.—GC analysis was performed with a Shimadzu GC-12A gas chromatograph and a Shimadzu GC-9A gas chromatograph GC-MS spectrometer fitted with a 25 m capillary column (OV-1; oven temperature 100–250 °C). HPLC analysis was performed with a TOSOH CCPD dual pump equipped with a UV-VIS detector (TOSOH UV-8000) on a Cosmosil 5-Ph column (4.6 × 150 mm) with water-methanol (20:80, v/v) as the eluent. ^{31}P NMR spectra were obtained on a Varian XL 200 NMR spectrometer under proton decoupling conditions. EPR spectra were taken with a JEOL JES-FE1XG spectrometer.

Materials.—Arenediazonium fluoroborates (**1a**, **b** and **c**) were prepared as described in the literature.³⁵ Trivalent phosphorus compounds (**2**, **6** and **7**) were obtained commercially (Wako Pure Chemical Industries, Ltd.). Triphenylphosphine (**2**) was purified by recrystallisation from hot ethanol prior to use, and trialkyl phosphites (**6** and **7**) were used without further purification. Alcoholic solvents were dehydrated on magnesium metal and distilled immediately prior to use. Deuteriated methanols were purchased (Aldrich Chemical Co.).

Reaction of Arenediazonium Salts with Trivalent Phosphorus Compounds.—In a test tube equipped with a septum were placed 0.10 mmol of the diazonium salt (**1a**, **b** or **c**), an appropriate amount of the phosphine **2**, and 0.10 mmol of dodecane as the internal standard for GC analysis under N₂ or O₂, and then 1.0 cm³ of alcohol as the solvent was added to the test tube through a syringe to resolve the materials. For the reaction of phosphite **6** or **7**, an appropriate amount of the phosphite was added to a solution of 0.10 mmol of the diazonium salt and 0.10 mmol of dodecane in 1.0 cm³ of solvent through a syringe under N₂ or O₂. After 30 min reaction time at 20 °C in the dark, the reaction mixture was analysed by GC and GC-MS. HPLC was also performed if necessary.

Reactions of **1a** with phosphine **2** or phosphite **7** in [$O\text{-}^2\text{H}$]methanol or [$^2\text{H}_4$]methanol were carried out as described above. The deuterium content in the product, nitrobenzene **3a**, was assayed by GC-MS.

EPR Spectroscopy.—In a sample tube for EPR measurement, 0.10 mmol of **1a** and 0.04 mmol of **2** or **7** were placed under N₂. Observation was made immediately after the addition of 1.0 cm³ of freshly distilled tetrahydrofuran (THF). The *g*-values were calculated with Mn^{II} salt as the standard.

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* It is not clear whether this coupling takes place in the solvent bulk or within the cage of the solvent.

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