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REACTION OF A CATION RADICAL GENERATED FROM TRIVALENT PHOSPHORUS COMPOUND THROUGH SINGLE-ELECTRON TRANSFER TO ARENEDIAZONIUM SALT

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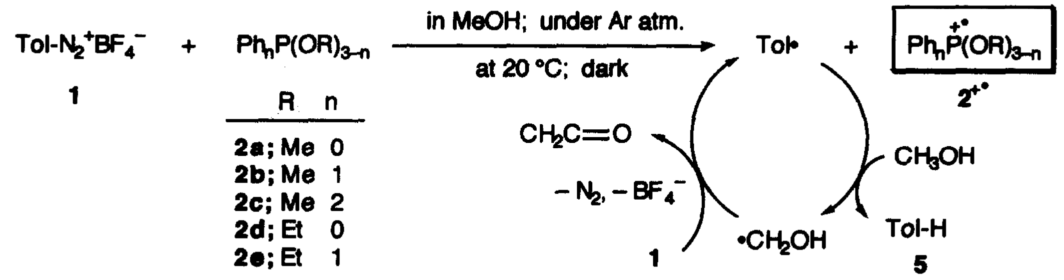
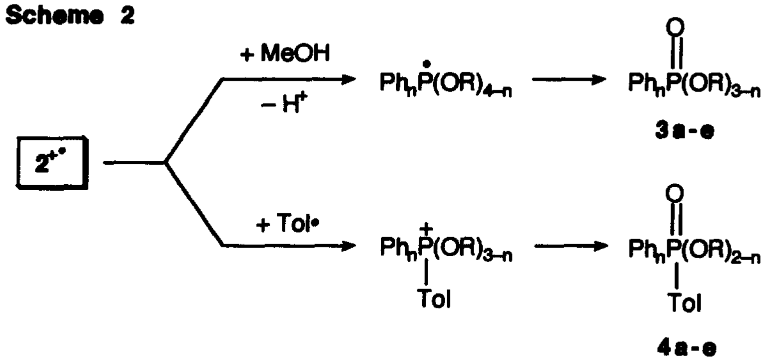
Abstract: *A cation radical generated from a trivalent phosphorus compound through single-electron transfer to an arenediazonium salt undergoes both ionic and radical reactions. Relative ease of these reactions depends mainly on the number of phenyl ligands on the phosphorus atom.*

A trivalent-phosphorus cation radical, when assumed as a transient intermediate in the oxidative conversion of a trivalent phosphorus compound into pentavalent one, is usually described as a cation, since its ionic reaction with a nucleophile well accounts for the observed product.1) However, the fact that such a cation radical is not simply a "cation" but also a "radical" in nature gives us questions: can a cation radical from a trivalent phosphorus compound behave as a radical species as well? If so, what factor determines relative ease of an "ionic" and a "radical" reactions? To answer these questions is crucial and urgent in the light of synthetic applicability of the reaction of such a cation radical, which was recently suggested for the stereospecific synthesis of a phosphorus compound related to cyclic nucleotide.2) We have found that trialkyl phosphite (**2a** and **2d**) as well as triphenylphosphine initiates radical-chain dediazoniation of arenediazonium salts in alcoholic solvent through single-electron transfer to the diazonium salt, during which cation radical $\mathbf{2}^{+\bullet}$ and aryl radical (*e.g.*, 4-methylphenyl radical Tol• when 4-methylbenzenediazonium fluoroborate (**1**) was reacted) are generated (Scheme 1).3) In this reaction, two types of products were formed from **2**, *i.e.*, the oxidation product **3** and the arylated product **4**. This result seems to answer the first question; cation radical $\mathbf{2}^{+\bullet}$ thus generated does undergo both an "ionic" and a "radical" reactions to give **3** and **4**, respectively (Scheme 2). This mechanism, however, should be tested more carefully because these products could result from some other reactions. We then investigated the reactions of diazonium salt **1** with trimethyl phosphite (**2a**), dimethyl phenylphosphonite (**2b**), and methyl diphenylphosphinite (**2c**), anticipating that cation radicals $\mathbf{2a\text{-}c}^{+\bullet}$, when formed, might exert different reactivity depending on the number of phenyl ligands. Survey of the results from these reactions will help to figure out the mechanism.

Scheme 1



Scheme 2



The reactions of **1** with **2a-c** were carried out in methanol at 20 °C in the dark under an argon atmosphere for 15 min. Product analysis based on GC and GCMS showed the formation of toluene (**5**), the dediazoniation product from **1**, as well as **3a-c** and **4a-c** (Table 1). In analogy with the reaction with triphenylphosphine or phosphites **2a** and **2d**,3) there is no doubt that the dediazoniation of **1** with phosphonite **2b** or phosphinite **2c** is also initiated by single-electron transfer from the latter to the former, generating cation radical $\mathbf{2}^{+\bullet}$ (Scheme 1). Radical-chain character of the reaction of **1** with **2a** was again confirmed here by the formation of **5** in more than a stoichiometric amount (entries 2 and 3) and inhibitory effect of oxygen on the formation of **5** (entry 4).

The reaction of phosphite **2a**, which has no phenyl group on the phosphorus atom, affords the largest value as the ratio of the yield of **4** to that of **3** (= **4**/**3**) (entry 1). This observation supports the proposed mechanism. Thus, the unpaired electron on cation radical $\mathbf{2a}^{+\bullet}$ (the number of phenyl substituent n = 0) is centered on the phosphorus atom, which facilitates radical coupling of $\mathbf{2a}^{+\bullet}$ with Tol•. On the other hand, the unpaired electrons of $\mathbf{2b}^{+\bullet}$ (n = 1) and $\mathbf{2c}^{+\bullet}$ (n = 2) are delocalized into adjacent phenyl groups to lower the radical character of the central phosphorus atom (entries 5 and 6). It has indeed been argued that phosphoranyl radicals with and without aryl ligand(s) exhibit small and large values for phosphorus coupling constant a_P, respectively, on ESR spectra indicating that unpaired electrons on the former and the latter phosphoranyl

Table 1. The dediazoniation of **1** with **2**.a)

entry	trivalent-phosphorus (**2**)	yield, %b)			4/3	a_P-value, Gc)
		3	**4**	**5**	**4/3**	
1	$P(OMe)_3$ (**2a**)	80.5	17.2	30.3	0.214	890 (**6a**)d)
2e)		12.5f)	9.1f)	34.6	0.728	-
3g)		N.D.h)	5.6f)	33.3	-	-
4i)		52.3	6.9	12.9	0.132	-
5	$PhP(OMe)_2$ (**2b**)	79.9	1.7	–j)	0.0212	9.25 (**6b**)k)
6	$Ph_2P(OMe)$ (**2c**)	52.0	1.7	–j)	0.0327	23.0 (**6c**)k)
7	$P(OEt)_3$ (**2d**)	88.2l)	9.4l)	37.8	0.107	-
8m)		71.5l)	8.3l)	32.2	0.116	-
9	$PhP(OEt)_2$ (**2e**)	85.2l)	5.3l)	–j)	0.0622	-
10m)		71.2l)	5.7l)	–j)	0.0800	-
11n)		79.3l)	1.6l)	53.3o)	0.0202	-

a)Initial amounts of **1** and **2**, both 1.00×10^{-1} mmol; in 1.0 ml of MeOH; reaction time, 15 min; in the dark at 20 °C under an argon atmosphere unless otherwise noted. b)Based on **1** used otherwise indicated; determined by GC. c)Values for the related phosphoranyl radicals designated in parentheses. d)From ref.5a. e)Initial amount of **2a**, 2.00×10^{-2} mmol. f)Based on **2a** used. g)Initial amount of **2a**, 1.00×10^{-2} mmol. h)Not detected. i)Under an oxygen atmosphere. j)Not determined. k)From ref.5b. l)Total yield of the ethyl ester and the esters in which one or more ethyl groups have been replaced by methyl group(s) from the solvent. m)In 1.0 ml of MeOH-MeCN (1:1). n)The reaction of 4-nitrobenzenediazonium fluoroborate (**7**) in MeOH. o)Yield of nitrobenzene.

$Ph_n\dot{P}(OBu^t)(OEt)_{3-n}$

6a; n = 0
6b; n = 1
6c; n = 2

radicals, respectively, are mainly located on the aryl ligand and on the central phosphorus.4,5) Table 1 lists the reported a_P-values for phosphoranyl radicals **6a-c**, the structures of which are related to those of **2a-c**$^{+\bullet}$, respectively.6) Obviously, the product ratios **4**/**3** observed in the reactions of **2a-c** correlate with these a_P-values, which clearly demonstrates that higher spin density on the phosphorus atom of cation radical **2**$^{+\bullet}$ results in more facile radical coupling.7) Certainly, the possibility that the reaction of **2** with Tol• eventually affords **4** is ruled out; upon the reaction with Tol•, trivalent phosphorus compound with higher number of phenyl ligands would give more stable phosphoranyl radical,8) favouring the formation of arylated product **4**, which is entirely against the results obtained here.

When the reaction of **1** with triethyl phosphite (**2d**) or diethyl phenylphosphonite (**2e**) was carried out in a methanol-acetonitrile mixture (1:1), slightly larger product ratio **4**/**3** than in the corresponding reaction in methanol was observed (compare entries 7 with 8, and 9 with 10). This result is also evidence for the mechanism proposed here; thus, lower concentrations of methanol as a nucleophile make the nucleophilic pathway unfavorable. In addition, when 4-nitrobenzenediazonium fluoroborate (**7**) was used in place of 4-methyl derivative **1**, yield of the arylated product **4** decreased (entry 11). 4-Nitrophenyl radical generated during the reaction may be stable enough to behave as a free-radical, more easily abstracting a hydrogen from the solvent. In fact, it has been shown that radical-chain is longer in the dediazoniation of diazonium salt **7** than of methyl derivative **1**.3)

In conclusion, a cation radical generated from a trivalent phosphorus compound acts as a cation, whereas the cation radical also acts as a radical species when another radical to be coupled with exists in the system; relative ease of ionic and radical reactions is determined mainly by spin density on the central phosphorus atom of the cation radical.

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6) Data from the references show that replacement of a methyl group in the phosphoranyl radicals by an ethyl group scarcely change the a_P-value.
7) Substitution of an alkoxyl group for a phenyl group may also cause change in the geometry of the cation radical, which may partly be responsible for its reactivity.
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