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DEDIAZONIATION OF ARENEDIAZONIUM SALT WITH TRIVALENT PHOSPHORUS COMPOUNDS BY ONE-ELECTRON TRANSFER MECHANISM

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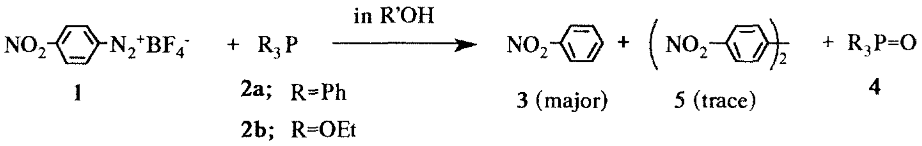
Abstract: *Trivalent phosphorus compounds, triphenylphosphine and triethyl phosphite, gave rise to dediazoniation of an arenediazonium salt in alcoholic solvent at ambient temperature in the dark. The reaction was well interpreted in terms of radical-chain mechanism initiated by an electron transfer from the trivalent phosphorus to a diazonium salt, which postulates a cation radical from the trivalent phosphorus as an intermediate.*

It has been widely accepted that exothermic conversion of a trivalent phosphorus compound to the corresponding pentavalent one takes place usually through nucleophilic attack of a trivalent phosphorus compound to a substrate.$^{1)}$ On the other hand, several examples have shown that a trivalent phosphorus acts as an electron donor to a good electron acceptor,$^{2)}$ which leads us to an idea that apparent nucleophilic attack of a trivalent phosphorus to a substrate may be composed of an electron transfer and a subsequent radical-pair coupling processes. In this matter, it is of special importance to evaluate intrinsic ability for a trivalent phosphorus compound to release an electron.

We have now found that a trivalent phosphorus compound gives rise to dediazoniation of an arenediazonium salt in an alcoholic solvent at ambient temperature in the dark. This brief report will present, for this reaction, a radical-chain mechanism initiated by an electron transfer from a trivalent phosphorus to the diazonium salt, with referring possible reactions of the postulated cation radical from the trivalent phosphorus compound.

4-Nitrobenzenediazonium fluoroborate (**1**) were allowed to react with an appropriate amount of triphenylphosphine (**2a**) or triethyl phosphite (**2b**) in an alcoholic solvent at 20 °C in the dark for 30 min. The analyses of the reaction mixture by a gas chromatograph (GC) and a gas chromatograph-mass spectrometer (GCMS) confirmed the formation of nitrobenzene (**3**) and the corresponding oxidized products from **2a-b**, triphenylphosphine oxide (**4a**) or triethyl phosphate (**4b**), respectively, along with a small amount of 4,4'-dinitrodiphenyl (**5**) (eq.1).$^{3)}$ The reaction with **2b** also gave a significant amount of diethyl 4-nitrophenylphosphonate (**6b**).



(eq.1)

The yields of the products determined by GC for the reactions in methanol were plotted against the ratio of an initial amount of 2 to that of 1 (2/1) (Figures 1A and B). Importantly, more than a theoretical amount of 3 was formed when the ratio 2/1 is less than *ca.* 0.5, which indicates participation of a chain process in the reaction. That the formation of 3 was suppressed under oxygen atmosphere suggests that this process is a radical-chain. As listed in Table 1, the results of the experiments in deuterated solvents clearly show that a hydrogen at the α-carbon rather than a hydroxyl hydrogen is introduced into 3, which is expected for the radical-chain mechanism where the aryl radical Ar· generated from 1 abstracts a hydrogen from the solvent alcohol forming an α-hydroxyalkyl radical as a chain-carrier. The formation of the dimeric product 5 is also in consistence with this mechanism. According to this mechanism, the solvent alcohol would eventually be oxidized to the corresponding carbonyl compound. The results in Table 2 show that the reactions in benzyl alcohol and cyclohexanol gave benzaldehyde and cyclohexanone, respectively, again verifying the radical-chain mechanism. Decrease in the yield of 3 after it reaches the maximum as the ratio 2/1 increases is

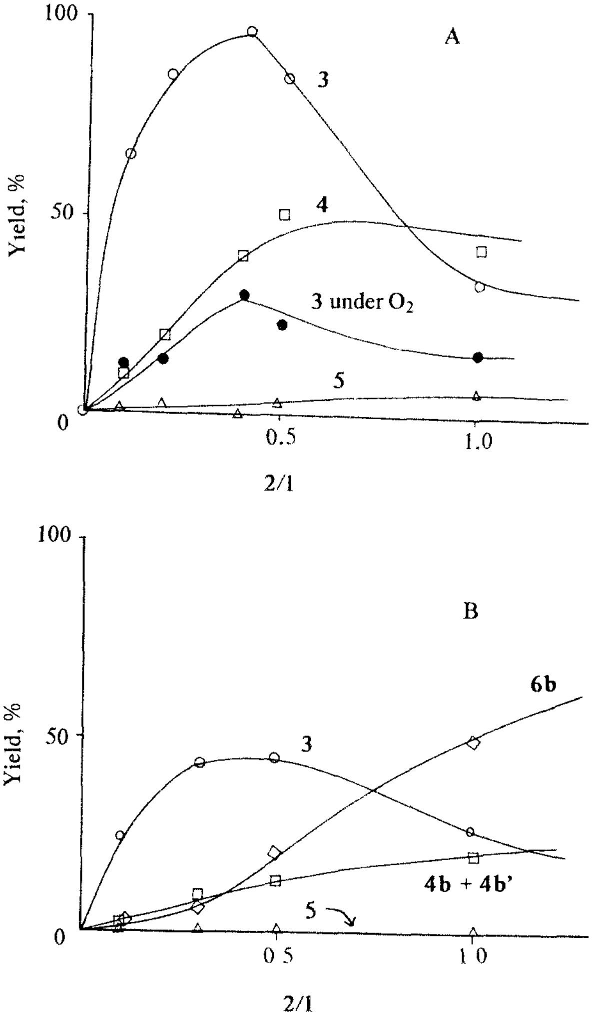


Figure 1. Yields of the products varying the initial amount of 2 based on 1. A and B represent the reactions with 2a and 2b, respectively. Initial amount of 1; 0.10 mmole in 1.0 ml of methanol. ○ , □ , △ , and ◇ denote the yields of 3, 4, 5, and 6b under N_2 atmosphere, respectively. ● denotes the yield of 3 under O_2 atmosphere

attributable to the consumption of **Ar·** by the attack to **2** when an excess amount of **2** exists in the reaction mixture, resulting in many unexpected reactions.[4] Similar yield-substrate ratio profile has been observed in the dediazoniation of **1** with 1-benzyl-1,4-dihydronicotinamide, where the reaction proceeds through a radical-chain mechanism.[5]

Table 1. Dediazoniation of **1** with **2** in deuterated methanols.[a]

trivalent-phosphorus	solvent	%D in **3**[b]
2a	CH_3OD	< 0.5
	CD_3OD	99.5
2b	CH_3OD	< 0.5
	CD_3OD	99.5

[a] 0.05 mmole of 1 and 2 were reacted in 0.5 ml of methanol. At 20°C under N_2 atmosphere in the dark. [b] Determined on GCMS.

Table 2. Solvent effect on product distribution in the reaction with **2a**.[a]

No	R' in R'OH	Yield, %[b] 3	4	5	C=O[c]
1	Me	34	43	6	d)
2	Benzyl	32	18	< 1	7
3	cyclo-Hex	44	25	< 1	38

[a] 0.10 mmol of **1** and **2a** were reacted in 1.0 ml of R'OH. At 20°C under N_2 atmosphere in the dark. [b] Based on **1** used. [c] Benzaldehyde and cyclohexanone for No. 2 and 3, respectively. [d] Yield of formaldehyde was not determined.

Now, the well established radical-chain mechanism for the present reaction in hand, we can unambiguously manifest that an electron transfer from **2** to **1** is the process that generates the radical **Ar·** as well as $\mathbf{2}^{+\bullet}$. It should be mentioned that no additive is required in this reaction. Thus, this chain process can be summarized as in eqs.2-4.

$$\mathbf{1} + \mathbf{2} \xrightarrow[-N_2,\ -BF_4^-]{\text{e-transfer}} Ar\cdot + \mathbf{2}^{+\bullet} \qquad \text{(eq.2)}$$

$$Ar\cdot + R''R'''CHOH \longrightarrow \underset{\mathbf{3}}{ArH} + R''R'''\dot{C}\text{-}OH \qquad \text{(eq.3)}$$

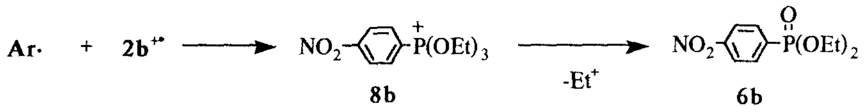
$$R''R'''\dot{C}\text{-}OH + \mathbf{1} \xrightarrow[-N_2,\ -BF_4^-]{} Ar\cdot + R''R'''C{=}O + H^+ \qquad \text{(eq.4)}$$

The cation radical $\mathbf{2}^{+\bullet}$ can interact with a solvent molecule to give phosphoranyl radical **7**, which collapses into the final product **4** (eqs.5 and 6).[6] Importantly, **2b** is converted into **4b** with transesterification to diethyl methyl 4-nitrophenylphosphonate (**4b'**) in methanol, supporting the existence of **7** as an intermediacy along this pathway. The product ratio **4b**:**4b'** = 23:77 was observed on GC, which roughly reapresents statistical distribution predicted by eq.6.

$$2a^{+\bullet} + R'OH \xrightarrow[-H^{+}]{} \underset{7a}{Ph_3\dot{P}OR'} \xrightarrow[-R'\cdot]{} \underset{4a}{Ph_3P{=}O} \qquad (eq.5)$$

$$2b^{+\bullet} + R'OH \xrightarrow[-H^{+}]{} \underset{7b}{(EtO)_3\dot{P}OR'} \xrightarrow[-R'\cdot \text{ or } -Et\cdot]{} \underset{4b}{(EtO)_3P{=}O} + \underset{4b'}{(EtO)_2(R'O)P{=}O} \qquad (eq.6)$$

The observation that the reaction with the phosphite **2b** affords the phosphonate **6b** as well (see Figure 1B) is also explained taking into account the radicals **Ar·** and $2^{+\bullet}$. Thus, this product is formed in the Arbuzov fashion if both radicals couple to give the phosphonium ion **8b** (eq.7). An ionic reaction between 1 and **2b**, if any, would afford an azo-compound such as $Ar\text{-}N{=}N\text{-}P^{+}R_3$ 7)



8b **6b** (eq.7)

In conclusion, we have verified the formation of the cation radical $2^{+\bullet}$ during the dediazoniation of an arenediazonium salt. More direct evidence will be available by ESR. The study is now in progress.

References and Notes

1) For example see; D. J. H. Smith, "Comprehensive Organic Chemistry, The Synthesis and the Reactions of Organic Compounds, Vol. 2" ed. by I. O. Sutherland, Pergamon Press, Oxford (1979), pp 1146 - 1156; R. S. Edmundson, *ibid.*, pp. 1203 - 1223.

2) S. Yasui and A. Ohno, *Tetrahedron Lett.*, 32, 1047 (1991); R. L Powell and C. D. Hall, *J. Am. Chem. Soc.*, **91**, 5403 (1969).

3) Arenediazonium salt with an electron-releasing substituent, 4-methoxylbenzenediazonium fluoroborate, was also dediazoniated by 2 to give 3 in comparable yield.

4) In fact, the chromatogram of HPLC for the reaction mixture showed some unidentified peaks as well.

5) S. Yasui, K. Nakamura, and A. Ohno, *J. Org. Chem.*, **49**, 878 (1984).

6) W. G. Bentrude and R. A. Wielesek, *J. Am. Chem. Soc.*, **91**, 2406 (1969); W. G. Bentrude and T. B. Min, *ibid.*, **94**, 1025 (1972).

7) D -L. F. DeTar and M. N. Turetzky, *J. Am. Chem. Soc.*, **77**, 1745 (1955); T. J. Broxton and M. J McLeish, *J. Org. Chem*, **48**, 191 (1983).

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