The Reaction of Alkylphosphite with Tris(*p*-bromophenyl)aminium hexachloroantimonate: An Efficient Chemical One Electron Oxidation for the Carbocation Formation

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Radical cations formed *via* one electron oxidations play as useful chemical reaction intermediates in subsequent reactions.[1] One of radical cation (**1**) formed from trialkylphosphites often generated electrochemically or photochemically, undergo a variety of substitution or addition reactions with nucleophiles or intramolecular Arbuzovs reaction.[2,3,4]

$$(RO)_3P: \rightarrow (RO)_3P^{+\cdot} + 1e \qquad (1)$$
$$\textbf{1}$$

If not trapped **1** react further with $(RO)_3P$ to give the σ^* phosphoranyl radical cation **2**, as shown by ESR measurements.[5,6]

$$[(RO)_3P\text{-}P(OR)_3]^{+\cdot} \quad (RO)_3\overset{+}{P}CH_2\dot{C}(Bu\text{-}t)_2 \quad (RO)_3\overset{+}{P}N=\dot{C}R'$$
$$\textbf{2} \qquad\qquad \textbf{3} \qquad\qquad \textbf{4}$$

In the presence of $t\text{-}Bu_2C=CH_2$ or RCN, **1** is intercepted to generate **3** or **4**.[6,7] Preparatively useful phosphorylations result from oxidation of trialkylphosphites in the presence of aromatics, the first step of which is most likely process A in Eq. (2).[8]

$$\textbf{1} + X\text{-}C_6H_5 \underset{A}{\rightarrow} (RO)_3P\text{-}Ph^{+\cdot} \rightarrow (RO_2)P(O)Ph \qquad (2)$$

Furthermore, $Ph_3P^{+\cdot}$ undergoes reaction with a nucleophile.[9]

We report here evidence that **1**, generated in the presence of the chloride ion, undergoes two competing reactions, combination with chloride ion to form a phosphoranyl radical **5**, and cleavage to phosphonyl radical **6** and a carbocation.

$$Cl\dot{P}(OR)_3 \underset{A}{\leftarrow} \textbf{1} \underset{B}{\rightarrow} (RO)_2\dot{P}=O + R^+ \qquad (3)$$
$$\textbf{5} \qquad\qquad\qquad \textbf{6}$$

Process B in Eq. (3) has no precedent for **1** to our knowledge. Recently, Yasuda and coworker suggested the possible carbocation formation from the radical cation formed in the photochemical electron transfer reaction of phosphonation.[3] The formation of neutral phosphoranyl radicals by combination of ions has received little attention, especially under chemical oxidation conditions.

Evidence for the competition between steps A and B in Eq. (3) can be explained by the product ratio obtained from one electron oxidation of a series of $ROP(OEt)_2$ in CH_2Cl_2. The tris(*p*-bromophenyl)aminium hexachloroantimonate, $(p\text{-}BrC_6H_4)_3\overset{+\cdot}{N}SbCl_6$ (**7**[+·]) served as an oxidant.[10] A weighed amount of phosphite, $ROP(OEt)_2$, was added *via* a septum to

Table 1. Products yield (%) of the reaction of phosphite[a] with $(p\text{-}BrC_6H_4)_3\overset{+\cdot}{N}SbCl_6$

phosphites	**11**[b]	**10**[b]	**11/10**	other products
$(EtO)_2POCH_2Ph$	66	0	100/0	$PhCH_2Cl$(68%), $PhCH_2OH$, $(PhCH_2)_2O$
$(EtO)_2POt\text{-}Bu$	83	4	95/5	$t\text{-}BuCl$, ⋊
$(EtO)_2POi\text{-}Bu$	18	59	23/77	$i\text{-}BuCl$, ⌇, ⌇, ⌇
$(EtO)_2POEt$	0[c]	75	0/100	

[a] in CH_2Cl_2. [b] by GC (capillary column, 30 m, SE-30, FID detector) with sensitivity calibrated internal standard based on the amount of added posphite. [c] trace amount was observed.

25 mL of an argon flushed 0.01 M CH_2Cl_2 solution of **7**[+·] stirred in an ice bath to give a solution equimolar in both phosphite and **7**[+·]. Partial fading of blue colour of **7**[+·] occurs almost instantaneously.

Products were identified by ^{31}P NMR and GLC (FID detector) analysis and quantitatively determined by GLC methods with internal standard calibration. Yields of the phosphorus-containing products $(EtO)_2P(O)Cl$, **10**, and $(EtO)_2P(O)H$, **11**, are recorded in the Table 1 along with RCl and other products. Reduction product $(p\text{-}BrC_6H_4)_3N$ was isolated from the reactions (GLC identification).

The distribution of products **10** and **11** and formation of RCl is interpreted *via* the Scheme 1. Conversion of radical cation **8** to phosphoranyl radical **9** is analogous to the proposed reaction of $Ph_3P^{+\cdot}$ by Cl^- to yield $Ph_3\dot{P}Cl$ which was supported by the formation of halophosphorane.[9] Process B competes with A in Scheme 1 according to the carbocation stability order for R^+: $PhCH_2^+ > t\text{-}Bu^+ > sec\text{-}Bu^+ > Et^+$.

Scheme 1

Once formed, phosphoranyl radical **9** undergoes β scission in the expected manner to yield the more stable radical, *i.e. t*-Bu· or *sec*-Bu· rather than Et·. Significantly, the competition between paths A and B of the Scheme 1 does not follow radical R· stability but instead is determined by the relative energies of the various carbocation R^+. Although the yield of **11** in R = CH_2Ph is less than the case of the R = *t*-Bu, the competition reaction ratio can be easily recognized by the ratio of the product **11/10**. That is, the competition ratio of the reaction is totally dependent on the stability of the carbocations on the basis of the product ratio (**11/10**) in the Table 1. Also consistence with the Scheme 1 is the ability of MeOH (MeOH/$PhCH_2OP(OEt)_2$ = 10/1) to intercept $PhCH_2^+$ to give $MeOCH_2Ph$. With *t*-$BuOP(OEt)_2$ evidence for *t*-Bu^+ formation came from the GLC identification of isobutylene. Although the formation of the alkyl chloride compounds and isobutylene could be explained by the S_N2 type reaction and elimination process between the radical cation and chloride ion, the appearance of the 1-butene, *cis*-, and *trans*-2-butene formed from the R = *i*-Bu can only be explained by the formation of the carbocation in the course of the reaction. Oxidation of $PhCH_2OP(OEt)_2$ in $CDCl_3$ gave deuterium NMR evidence for the formation of $(EtO)_2P(O)D$ (along with $(EtO)_2P(O)H$) as is consistent with the process $(EtO)_2\dot{P}(O)$ + $CDCl_3 \rightarrow (EtO)_2P(O)D$ + ·CCl_3.

In an earlier study of this cathodic oxidation of trialkyl phosphites, reaction (4) was suggested (R = Et, *n*-Bu, *i*-Pr).[11]

$$(RO)_3P\colon \xrightarrow[\text{(Et}_3\text{NH)}_2\text{SiF}_6]{-2e} (RO)_2P(O)F + RF \qquad (4)$$

Yields and relative amounts of the two products were not reported. It was proposed that $(RO)_3P^{\cdot\ddagger}$ is trapped by fluoride ion. Indeed, $(RO)_3\dot{P}F$ should yield $(RO)_2P(O)F$ on β scission. In the absence of quantitative data, it can not be ascertained whether RF could have resulted even in part from β scission of $(RO)_3P^{\cdot\ddagger}$. From the reported two-electron nature of the oxidation a likely source of RF is the process of the reaction (5).

$$R\cdot \xrightarrow[-e]{} R^+ \xrightarrow[\text{(Et}_3\text{NH)}_2\text{SiF}_6]{} RF \qquad (5)$$

$Et_4N^+BF_4^-$ was reported a less effective source of fluoride since its use in place of $(Et_2NH)_2SiF_6$ led to reduced yields.

The above results show that the reaction of phosphite with aminium antimonate radical cation could result in the carbocation and the efficiency of the result depend on the stability of the produced carbocation. This approach thus appears to be quite complementary to the other carbocation generation methods.

A further study in pursuit of applications of this reaction is in progress.

References

1. (a) Davidson, R. S. *Adv. Phys. Org. Chem.* **1983**, *19*, 1. (b) Chockalingam, K.; Pinto, M.; Bauld, N. L. *J. Am. Chem. Soc.* **1990**, *112*, 447 and references cited therein.
2. Effenberger, F.; Kottmann, H. *Tetrahedron* **1985**, *41*, 4171 and references cited therein.
3. Yasuda, M.; Yamashita, T.; Shima, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 938.
4. Bentrude, W. G.; Lee, S.-G.; Akutagawa, K.; Ye, W.-Z.; Charbonnel, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1577.
5. Gara, W. B.; Roberts, B. P. *J. Chem. Soc.* **1975**, 949.
6. Gara, W. B.; Roberts, B. P. *J. Chem. Soc. Perkin II* **1978**, 150.
7. Ohmori, H.; Sakai, K.; Nagai, N.; Mizuki, Y.; Masui, M. *Chem. Pharm. Bull.* **1985**, *33*, 373 and references cited therein.
8. Ohmori, H.; Nagai, S.; Masui, M. *J. Chem. Soc. Perkin I* **1979**, 2023.
9. Kargin, Y. M.; Nikitin, E. V.; Romanov, G. V.; Parakin, O. V.; Levshina, T. G.; Pudovik, A. N. *Zh. Obsh. Khim.* **1978**, *48*, 743.
10. (a) Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718. (b) Dinnocenzo, J. P.; Schmittel, M. *J. Am. Chem. Soc.* **1987**, *109*, 1561.
11. Nikitin, E. V.; Parakin, O. V.; Romanov, G. V.; Ignatev, Y. A.; Romakhin, A. S.; Kargin, Y. M.; Pudovik, A. N. *Dokl. Akad. Nauk. SSSR* **1980**, *252*, 929.