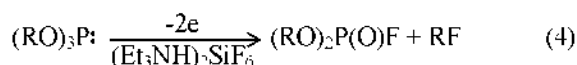


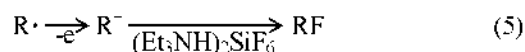


Once formed, phosphoranyl radical **9** undergoes  $\beta$  scission in the expected manner to yield the more stable radical, *i.e.* *t*-Bu $\cdot$  or *sec*-Bu $\cdot$  rather than Et $\cdot$ . Significantly, the competition between paths A and B of the Scheme 1 does not follow radical R $\cdot$  stability but instead is determined by the relative energies of the various carbocation R $^+$ . Although the yield of **11** in R = CH<sub>2</sub>Ph 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<sub>2</sub>OP(OEt)<sub>2</sub> = 10/1) to intercept PhCH<sub>2</sub> $^+$  to give MeOCH<sub>2</sub>Ph. With *t*-BuOP(OEt)<sub>2</sub> 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<sub>N</sub>2 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<sub>2</sub>OP(OEt)<sub>2</sub> in CDCl<sub>3</sub> gave deuterium NMR evidence for the formation of (EtO)<sub>2</sub>P(O)D (along with (EtO)<sub>2</sub>P(O)H) as is consistent with the process (EtO)<sub>2</sub>P(O) $\cdot$  + CDCl<sub>3</sub>  $\rightarrow$  (EtO)<sub>2</sub>P(O)D +  $\cdot$ CCl<sub>3</sub>.

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



Yields and relative amounts of the two products were not reported. It was proposed that (RO)<sub>3</sub>P $\cdot$  is trapped by fluoride ion. Indeed, (RO)<sub>3</sub>P $\cdot$  should yield (RO)<sub>2</sub>P(O)F on  $\beta$  scission. In the absence of quantitative data, it can not be ascertained whether RF could have resulted even in part from  $\beta$  scission of (RO)<sub>3</sub>P $\cdot$ . From the reported two-electron nature of the oxidation a likely source of RF is the process of the reaction (5).



Et<sub>3</sub>N $^+$ BF<sub>4</sub> $^-$  was reported a less effective source of fluoride since its use in place of (Et<sub>3</sub>NH)<sub>2</sub>SiF<sub>6</sub> 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.

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