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REACTION OF PHOSPHITES WITH METHYL p-TOLUENESULFONATE (1)

Donald B. Denney and Jack Giacin
Department of Chemistry, Rutgers, the State University
New Brunswick, New Jersey

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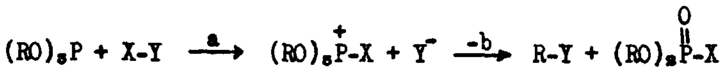
The general ubiquity of the Arbusov-Michaelis and related reactions in organophosphorus chemistry is well recognized (2). The general reaction involves a nucleophilic displacement by a phosphite (a) which gives an intermediate phosphonium salt (I). In most cases, when R = aliphatic,

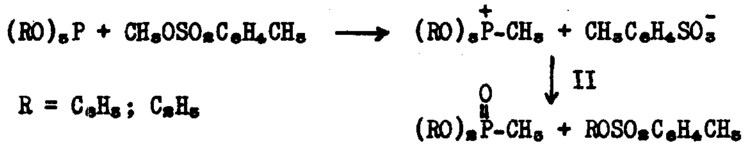


$$(RO)_3P + X\text{-}Y \xrightarrow{a} (RO)_3\overset{+}{P}\text{-}X + Y^- \xrightarrow{b} R\text{-}Y + (RO)_2\overset{O}{\overset{\|}{P}}\text{-}X$$

I

subsequent decomposition occurs by nucleophilic displacement by Y^- on R to give R-Y and the appropriate phosphorus-containing compound.

It is the purpose of this report to describe a novel reaction of this type. Methyl p-toluenesulfonate was heated with an equimolar amount of triphenyl phosphite for 72 hours at 130°. There were isolated from this reaction phenyl p-toluenesulfonate (III) (70%) and diphenyl methylphosphonate (IV) (65%). In an entirely similar reaction, triethyl phosphite and methyl p-toluenesulfonate yielded ethyl p-toluenesulfonate (48%) and diethyl methylphosphonate (56%) (3).



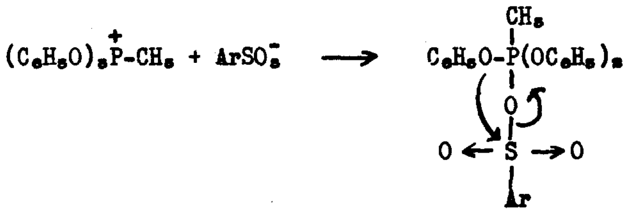
$$\begin{array}{ll} (RO)_3P + CH_3OSO_2C_6H_4CH_3 \longrightarrow & (RO)_3\overset{+}{P}\text{-}CH_3 + CH_3C_6H_4SO_3^- \\ & \qquad\qquad \downarrow \text{II} \\ R = C_6H_5;\ C_2H_5 & (RO)_2\overset{O}{\overset{\|}{P}}\text{-}CH_3 + ROSO_2C_6H_4CH_3 \end{array}$$

The first step in this conversion undoubtedly involves the formation of salts (II). Concrete evidence that this is the case was provided by treating triphenoxymethylphosphonium iodide with silver p-toluenesulfonate in acetonitrile. Removal of the silver iodide and acetonitrile afforded an oil which was heated at 130° for 72 hours. There were isolated

$$(C_6H_5O)_3\overset{+}{P}\text{-}CH_3 + I^- + Ag^+ + CH_3C_6H_4SO_3^- \longrightarrow \text{II} \longrightarrow \text{III} + \text{IV}$$

from this reaction mixture III (48%) and IV (56%).

Although the formation of salts (II) is not unexpected, their decomposition to the observed products is of particular interest. It is quite clear that nucleophilic attack by p-toluenesulfonate anion on a phenyl ring (step b in the usual decomposition) cannot account for product formation from II when R = phenyl. It is well known that p-toluenesulfonate



V

anion is a very weak nucleophile and that displacement on a phenyl group is a very high energy process (4). A much more likely path involves formation of the pentacovalent intermediate V. Decomposition of V could occur in two ways, intramolecular as illustrated or by loss of phenoxide ion which then attacks on sulfur. In the case of decomposition of II, R = C_2H_5, direct displacement by p-toluenesulfonate anion on an ethyl group becomes possible but does not seem likely in view of the weak nucleophilicity of the p-toluenesulfonate anion.

The results of these experiments serve to illustrate once again the importance of pentacovalent intermediates in organophosphorus chemistry and the tremendous driving force provided by the formation of the phosphorus oxygen double bond.

REFERENCES

1. Research supported by the National Science Foundation under grant GP-202.
2. J. I. G. Cadogan, Quart. Revs., 16, 208 (1962).
3. All compounds were characterized by n.m.r. and i.r. spectra as well as by comparison of melting points where possible.
4. J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 2d ed., 1962, p. 161 and chap. 17.