Tetrahedron Letters No.55, pp. 4799-4802, 1970. Pergamon Press. Printed in Great Britain.

THE MECHANISM OF THE REACTION BETWEEN TRIALKYL PHOSPHITES AND HALOGENOACETYLENES

P. Simpson and D. W. Burt

The Chemical Laboratory, School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ.

(Received UK 15 September 1970; accepted for publication 28 October 1970)

Fujii et al. (1) have recently published the results of their work on the reaction between triethyl phosphite and bromo- and chloroacetylenes. We now communicate the results of our own studies on this reaction which we have referred to on a previous occasion (2). Our approach is somewhat different and our results, obtained under different conditions, also differ somewhat from those of Fujii et al.

$$(RO)_3P + XC{\equiv}CPh \longrightarrow (RO)_2P(O)C{\equiv}CPh + RX \qquad [1]$$

We have studied reaction 1 (R = Et, Me; X = Cl, Br) by allowing reaction to take place in the presence of varying amounts of methanol or ethanol as trapping agents. We have plotted the number of moles of phenylethynylphosphonate and the number of moles of phenylacetylene produced per mole of halogenoacetylene, against the number of moles of trapping agent added per mole of halogenoacetylene. Diagrams of curves typical of cases where X = Cl, Br are presented in Figures 1 and 2 respectively. Maximum diversion of reaction 1, varying from 55-70% according to which reagents are involved, occurs in the presence of ca. two moles of trapping agent. We interpret this diversion as the interuption of a mechanism involving nucleophilic attack by phosphite on halogen (Scheme 1).

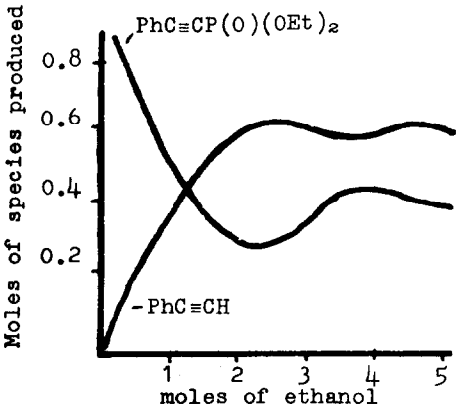


Figure 1. Curves for the system $(EtO)_3P/BrC{\equiv}CPh/EtOH$

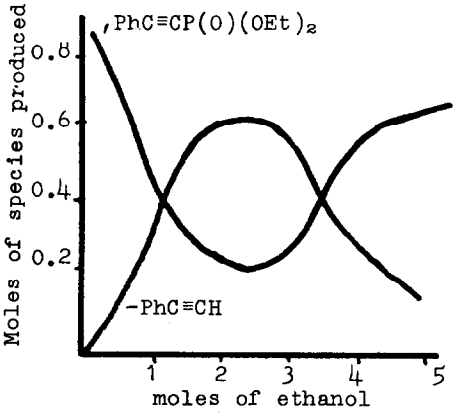
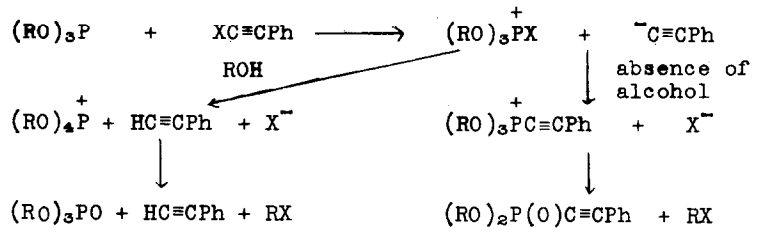


Figure 2. Curves for the system $(EtO)_3P/ClC{\equiv}CPh/EtOH$



Scheme 1

Where X = I, we were unable to make a full quantitative study, but two moles of ethanol suppressed phenylethynylphosphonate production from triethyl phosphite and iodoethynylbenzene by 80-85%.

We find solvent (trapping agent) dependance in cases where X = Cl to be high, but where X = Br it is lower. Our curves fail to

become linear and horizontal with increasing amounts of trapping agent, and ethanol is slightly more effective than is methanol in diverting the reaction.

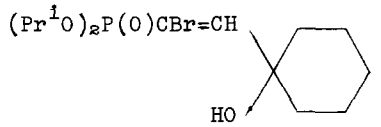
That at least one other mechanism is operating in all cases is clear from our curves, and like Fujii et al., we believe that this is an addition-elimination mechanism (Scheme 2). We have failed to find positive evidence for this mechanism in the case of

$$(RO)_3P + XC{\equiv}CPh \longrightarrow (RO)_3\overset{+}{P} - CX = \overset{-}{C}Ph$$

$$\longrightarrow (RO)_3\overset{+}{P}C{\equiv}CPh + X^- \longrightarrow (RO)_2P(O)C{\equiv}CPh + RX$$

Scheme 2

halogenoethynylbenzenes, but we do have evidence for it in the case of 1-bromoethynylcyclohexanol. We have identified the adduct I amongst the products of the reaction between this halogenoacetylene and tri-isopropyl phosphite.



(I)

We are indebted to the S.R.C. and Kesteven County Council for maintenance awards (to D.W.B.)

References

(1) A. Fujii, J. I. Dickstein, and S. I. Miller, Tetrahedron Lett., 3435 (1970).

(2) D. W. Burt and P. Simpson, J. Chem. Soc (C), 2273 (1969).