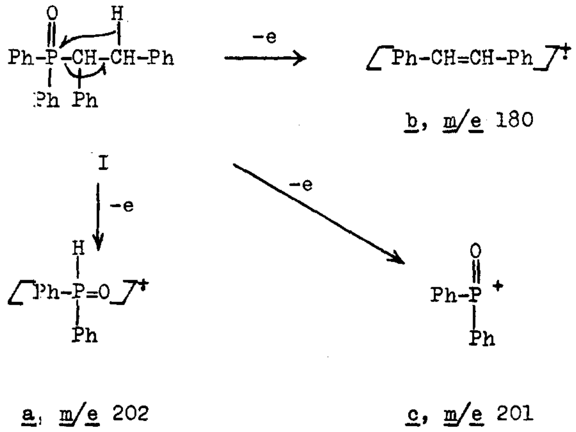
Tetrahedron Letters No.28, pp. 2361-2363, 1965. Pergamon Press Ltd.
Printed in Great Britain.

THE REACTION OF TRIPHENYLPHOSPHINE WITH PHENYLACETYLENE

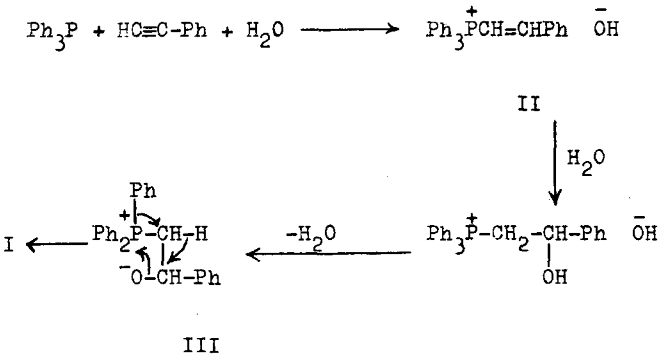
D. Allen and J. C. Tebby
Chemistry Department, North Staffordshire College
of Technology, Stoke-on-Trent
D. H. Williams
University Chemical Laboratory, Lensfield Road,
Cambridge.

(Received 21 May 1965)

Tertiary phosphines add to acetylenic bonds in the presence (1,2) and in the absence (1,3,4) of halogen acid. In these reactions the acetylenic bond has always required activation by a carbonyl, nitrile or phosphonium group. We now find that a phenyl group may be used to activate the triple bond towards nucleophilic attack by triphenylphosphine. The structure of the product obtained in 50% yield by the reaction of triphenylphosphine with phenylacetylene in refluxing wet diethyleneglycol was indicated by its NMR and mass spectrum and confirmed by comparison with an authentic specimen of 1,2-diphenylethyldiphenylphosphine oxide (I), m.p. and mixed m.p. 233-234° (5). The NMR spectrum of I contained three benzylic protons in the range $\delta = 3\text{-}4$ p.p.m., while the mass spectrum indicated a molecular weight of 382 and very specific fragmentation to a (m/e 202, base peak) and an ionised stilbene fragment b (m/e 180, 20% of base peak). The only other abundant ion (50%) in the spectrum corresponded to *c* (*m/e* 201). These assignments are supported by the mass spectrum of d_2-I, prepared using O-d_2-diethyleneglycol wet with deuterium oxide for the reaction. In the spectrum of d_2-I, *m/e* 201 (*c*) is unmoved, whereas *m/e* 202 (*a*) is predominantly shifted to *m/e* 203; *m/e* 180 (*b*) is split between *m/e* 181 and *m/e* 182.



Trippett and Walker have very recently isolated (5) the oxide (I) from the reaction of benzaldehyde with methyltriphenylphosphonium bromide in ethanolic sodium ethoxide and from the reaction of triphenylphosphine with styrene oxide. The course of the reaction of triphenylphosphine with phenylacetylene may involve the same betaine intermediate (III) suggested by these workers. If this is the case, the reactions should proceed via hydration of the intermediate vinylphosphonium hydroxide (II).



We thank Dr. S. Trippett for helpful discussions.

References

1. L. Horner and H. Hoffmann, Angew Chem., 68, 473 (1956).
2. H. Hoffmann and H. J. Diehr, Chem. Ber., 98, 364 (1965).
3. A. W. Johnson and J. C. Tebby, J. Chem. Soc., 2126 (1961).
4. G. S. Reddy and C. D. Weis, J. Org. Chem., 28, 1822 (1963).
5. S. Trippett and B. J. Walker, Chem. Comm., 106 (1965).
6. P. T. Keough and M. Grayson, J. Org. Chem., 29, 631 (1964).