Tetrahedron. 1967. Vol. 23. pp. 2795 to 2801. Pergamon Press Ltd. Printed in Northern Ireland

THE REACTION OF TRIARYLPHOSPHINES WITH PHENYLACETYLENE IN THE PRESENCE OF WATER

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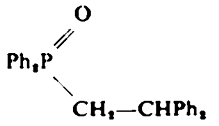
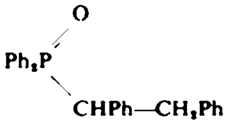
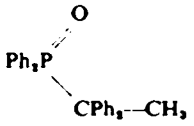
(*Received* 13 *October* 1966; *accepted for publication* 3 *November* 1966)

Abstract—Triphenylphosphine and tri-*p*-tolylphosphine react with phenylacetylene and water to produce 1,2-diphenylethyl-diphenylphosphine oxide and 2-phenyl-1-(*p*-tolyl)ethyldi-*p*-tolylphosphine oxide respectively. Two possible reaction pathways have been investigated.

IN AN earlier communication,[2] we reported on the reaction of triphenylphosphine with phenylacetylene and water in boiling digol. The product had the molecular formula $C_{28}H_{23}OP$, and was shown to be a very stable non-basic compound. It was recovered from boiling 10% aqueous sodium hydroxide, boiling 10% aqueous hydrochloric acid and boiling hydrogen peroxide in glacial acetic acid. The IR absorption spectrum showed the presence of a strong band at 1175 cm^{-1} which could be assigned to a P—O bond, and the UV spectrum contained a series of weak bands at 254, 260, 267 and 274 mμ similar to the spectra of triphenylphosphine oxide and diphenylphosphinic acid. These properties were in accordance with a phosphine oxide structure and three oxide structures I, II and III were considered. The ^1H NMR


I


II


III

spectrum contained an unresolved 3 proton multiplet centred at $\tau = 6{\cdot}6$ ppm and an unresolved 20-proton multiplet at $\tau = 2{\cdot}0$–$3{\cdot}0$ ppm. The spectrum was not in accord with III and this structure was therefore considered no further. The product was found to react readily with one equivalent of N-bromosuccinimide. A monobromo derivative was obtained which on treatment with sodium methoxide gave an olefinic compound. The olefin was hydrogenated to give the original phosphine oxide and was oxidized to give diphenylphosphinic acid and benzoic acid. Thus the olefin was diphenyl-1,2-diphenylvinylphosphine oxide (VI) and not the other isomeric possibility diphenyl-2,2-diphenylvinylphosphine oxide. The structure of the reaction product from triphenylphosphine, phenylacetylene and water was therefore shown to be II. This structure was confirmed by comparison of the product with an authentic sample of 1,2-diphenylethyldiphenylphosphine oxide.[3]

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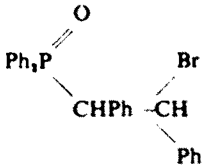
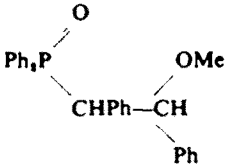
[1] Present address: Chemistry Department, University of Keele, Staffs.

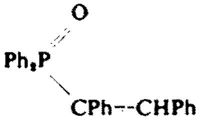
[2] D. Allen, J. C. Tebby and D. H. Williams, *Tetrahedron Letters* No. 28, 2361 (1965).

[3] S. Trippett and B. J. Walker, *Chem. Comm.* 106 (1965); *J. Chem. Soc.* (*C*) 887 (1966).

It has been shown that bromination occurred at the less hindered β position. The monobromo derivative possessed a poorly resolved ^{1}H NMR spectrum and was therefore converted to the corresponding methyl ether by solvolysis in boiling methanol.

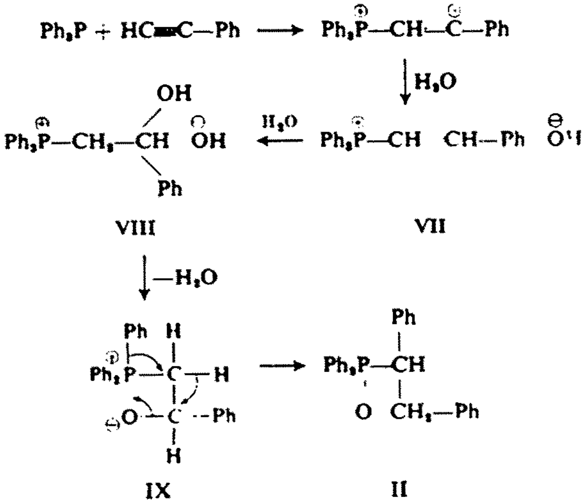

IV


V


VI

The ^{1}H NMR spectrum of the ether in deuterochloroform solution contained an unresolved 20 proton multiplet centred at $\tau = 2{\cdot}7$ ppm, a well-defined one-proton triplet centred at $\tau = 4{\cdot}92$ ppm (J = 6 c/s), a one-proton quartet centred at $\tau = 6{\cdot}25$ ppm and a three-proton singlet at $\tau = 6{\cdot}90$ ppm. The spectrum contained three types of aliphatic protons as required by a MeO group in the β position. Thus the methyl ether is represented by V, and its monobromo precurser by IV.

Trippett and Walker[3] have obtained 1,2-diphenylethyldiphenylphosphine oxide (II) from the reaction of triphenylmethylenephosphorane with benzaldehyde in ethanol and from the reaction of triphenylphosphine with styrene oxide. They showed that the betaine IX was an important intermediate and we have investigated the possibility that the betaine may also be a key intermediate in the reaction of triphenylphosphine with phenylacetylene and water. The reaction sequence may involve the betaine IX as shown in Scheme 1. This possibility was investigated by carrying out the reaction using deuterium oxide in place of water. The products were analysed by mass spectrometry. The results, which were reported in full in the first communication[2] were not conclusive due to a migration which occurred after electron impact in the spectrometer. We have therefore sought further evidence to establish the reaction pathway by attempting to prepare the proposed intermediate hydroxide VII. β-Styryltriphenylphosphonium bromide (X) was prepared from triphenylphosphine, phenylacetylene



Scheme 1

and hydrogen bromide in boiling diethylene glycol. Earlier workers[4] were unable to obtain the bromide X when ether was used as solvent. The bromide was characterized by conversion to the crystalline picrate salt.

The ^1H NMR spectrum of the picrate in deuterochloroform solution contained a 2 proton singlet at $\tau = 1.21$ ppm due to the picrate anion and a 22 proton multiplet at $\tau = 2.0$ to 3.3 ppm. The vinyl proton resonances could not be clearly distinguished from the phenyl resonances. The absence of terminal methylene resonances at $\tau =$ 4–5 ppm shows that the picrate is not the α-styrylisomer. The spectrum of 1,1-diphenylethylene for instance contains 2 vinyl protons at $\tau = 4.47$ ppm (singlet) and 10 phenyl protons at $\tau = 2.55$ ppm (singlet) and the vinyl protons of α-styrenephosphonic acid[5] appear as two doublets at $\tau = 4.07$ and 4.42 ppm. Aguiar and Daigle[6] have prepared *cis* and *trans* β-styryldiphenylphosphine oxide and observed four vinyl resonances for the *cis* isomer between $\tau = 3.37$ and 3.92 ppm. The vinyl resonances of the *trans* isomer were partially hidden by the phenyl resonances and occurred between $\tau = 2.8$ and 3.5 ppm. The vinyl resonances of *trans*-β-styrenephosphonic acid[5] also overlap the phenyl region. Comparison of these observations together with the spectra of *cis* and *trans* stilbene[7] which contain vinyl resonances at $\tau = 3.45$ and $\tau = 2.90$ ppm respectively, shows that the picrate is a *trans*-β-styryltriphenylphosphonium salt.

The preparation of the β-styryltriphenylphosphonium hydroxide was attempted by treating the bromide X with freshly prepared silver oxide. After removal of silver bromide and evaporation *in vacuo* a colourless oil was obtained. The oil, which gave an alkaline reaction in water, could not be converted into a crystalline picrate. This was possibly due to hydration of the β-styryltriphenyl phosphonium hydroxide (VII) to form some of the next intermediate VIII. When the oil was heated in wet digol no 1,2-diphenylethyldiphenylphosphine oxide (II) could be detected.

An alternative pathway shown in Scheme 2, involving a cyclic phosphorane intermediate, was also considered. Evidence has been put forward for the existence of triarylphosphoranes[8] and phosphocyclopropanes[9] as reactive intermediates. The last intermediate in Scheme 2 is the phosphonium hydroxide XI (shown in its pentacovalent form)[10] in which either of the P—C bonds of the three-membered ring may break to produce 1,2-diphenylethyldiphenylphosphine oxide. The reaction of tri-*p*-tolylphosphine, phenylacetylene and water was suitable to test this hypothesis since by this pathway the unsymmetrical intermediate XII would be formed, which upon cleavage would afford the two isomeric phosphine oxides XIII and XIV. However, when this reaction was carried out the product could not be separated into two isomers. Separation was attempted by TLC using a variety of supports and eluting solvent systems. The ^1H NMR spectrum measured in deuterochloroform contained only

[4] H. Hoffmann and H. J. Diehr, *Chem. Ber.* **98**, 364 (1965).

[5] G. L. Kenyon and F. H. Westheimer, *J. Am. Chem. Soc.* **88**, 3557 (1966).

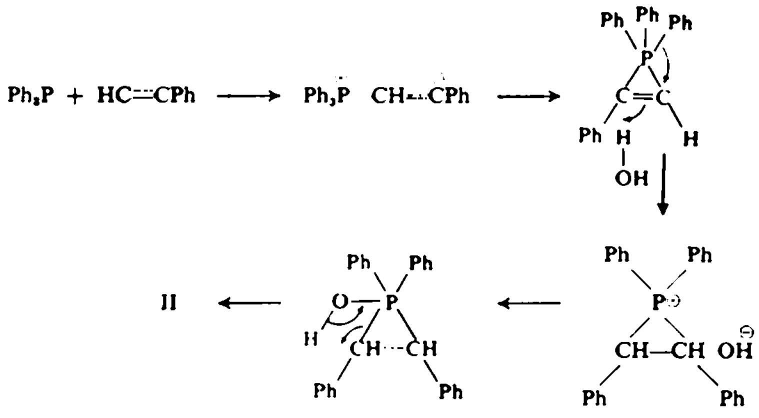
[6] A. M. Aguiar and D. Daigle, *J. Org. Chem.* **30**, 2826 and 3527 (1965).

[7] *Varian NMR Spectra Catalog* Vol. I, Spectra Nos 305 and 306. National Press, Palo Alto, Calif. (1962).

[8] D. Seyferth, W. B. Hughes and J. K. Heeren, *J. Am. Chem. Soc.* **87**, 2847(1965); *Ibid.*, **86**, 307 (1964).

[9] R. W. Turner and A. H. Soloway, *J. Org. Chem.* **30**, 4031 (1965).

[10] C. T. Eyles and S. Trippett, *J. Chem. Soc. (C)* 67 (1966).

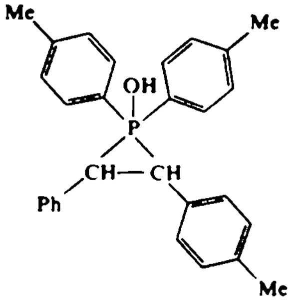


XI

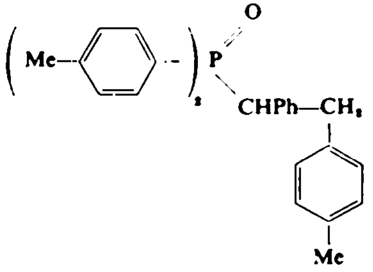
Scheme 2

two singlets (a and b) in the aromatic methyl region: (a) a six-proton singlet at $\tau = 7{\cdot}77$ ppm and (b) a three-proton singlet at $\tau = 7{\cdot}58$ ppm. A mixture of the isomers (XIII and XIV) was expected to give three singlets in the aromatic Me region. Finally the product was shown to be the same as the phosphine oxide XIV obtained from the reaction of tri-*p*-tolylphosphine with styrene oxide. Thus the reaction pathway is not that shown in Scheme 2.

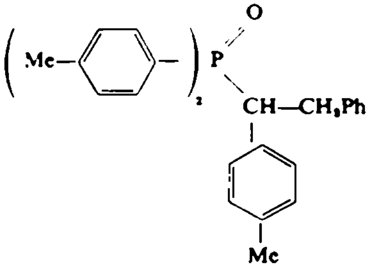
Since the reaction of triphenylphosphine with styrene oxide leads to the same product as that obtained from the phenylacetylene reaction it is very probable that a common intermediate, such as the betaine IX is involved. However we have been



XII

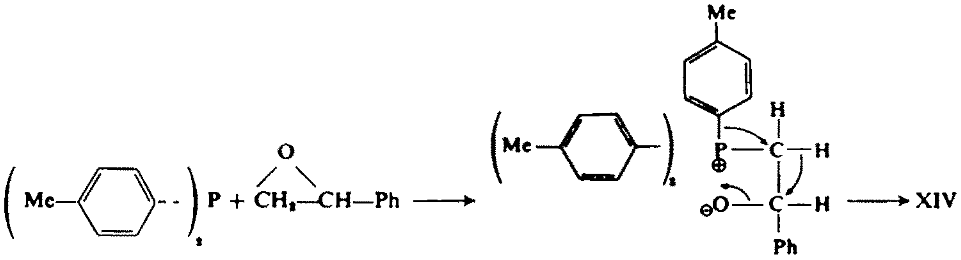


XIII



XIV

unable to establish that the reaction proceeds by the pathway shown in Scheme 1. Further studies are being made of a related reaction with methyl propiolate.



EXPERIMENTAL

M.ps were taken in capilliaries. The UV and IR spectra were determined on Unicam SP700 and SP200 spectrophotometers. NMR spectra were obtained in $CDCl_3$ using a Perkin-Elmer R10 spectrometer, with TMS as an internal reference.

Reaction of triphenylphosphine with phenylacetylene in the presence of water. A soln of triphenylphosphine (10 g, 0·038 mole), phenylacetylene (9·0 g, 0·088 mole) and water (3 ml) in diethylene glycol (75 ml) was refluxed for 8 hr. The solvent was removed by distillation under reduced press and the residue crystallized from benzene to give a crude product (7·2 g, 50%). After several recrystallizations from benzene, pure II was obtained as colourless crystals, m.p. 233–234° (Lit.[8] m.p. 232–233°). The analytical sample was prepared by sublimation at 220°/0·1 mm. (Found: C, 81·65; H, 5·90; P, 8·5; M (mass spectrometry) 382. Calc. for $C_{26}H_{23}OP$: C, 81·6; H, 6·04; P, 8·12%; M. 382.) ν_{max} (KBr) 1437(m), 1173(s), 1118(m), 1100(m), 792(m), 775(m), 747(m), 717(s), 697(s) cm^{-1}. λ_{max} (95% EtOH) 254, 260, 267, 274 mμ (ε 740). NMR spectrum: τ 2·0–3·0 (m, 20 aromatic protons) and 6·6 ppm (m, 3 benzylic protons).

Bromination of 1,2-*diphenylethyldiphenylphosphine oxide* (II). A mixture of N-bromosuccinimide (1·78 g, 0·01 mole), II (3·8 g, 0·01 mole) and CCl_4 (60 ml) was refluxed for 5 hr. The solvent was then distilled under reduced press and the residue boiled with acetone (60 ml) for 30 min to remove excess succinimide. The resulting soln was then cooled and filtered to give 2-*bromo*-1,2-*diphenylethyldiphenylphosphine oxide*, (IV) m.p. 182–183° (3·5 g, 76%). After several recrystallizations from benzene–EtOH, the product formed colourless crystals, m.p. 186–187°. (Found: C, 67·6; H, 5·00; Br, 17·3. $C_{26}H_{22}BrOP$ requires: C, 67·67; H, 4·77; Br, 17·3%.) ν_{max} 1180 cm^{-1}(s).

Preparation of the methyl ether V. Compound IV (0·5 g, 0·001 mole) dissolved slowly in MeOH (25 ml) when heated under reflux for 5 hr. Most of the MeOH was removed by distillation and the residual soln poured into water (100 ml). The ppt was filtered, washed with a little water, and dried m.p. 256–260° (0·44 g, 100%). After several recrystallizations from EtOH, 2-*methoxy*-1,2-*diphenylethyldiphenylphosphine oxide* (V) formed colourless crystals, m.p. 263–264°. (Found: C, 78·46; H, 5·91. $C_{27}H_{25}O_2P$ requires: C, 78·6; H, 6·06%.) ν_{max} (KBr) 1180(s), 1100(s) cm^{-1}. NMR spectrum: τ 2·7 (m, 20 aromatic protons), 4·92 (t, J = 6 c/s, one proton), 6·25 (q, J = 6 c/s, 1 proton) and 6·90 ppm (s, 3 protons).

Preparation of the olefin (VI). A soln of IV (1·0 g, 0·002 mole), NaOH (4·0 g) in MeOH (50ml) was refluxed for 4 hr. The soln was acidified with HCl and poured into water (150 ml). The ppt was filtered off, washed with a little water, and dried m.p. 156–158° (0·82 g, 100%). After recrystallization from 80–100° petroleum with the addition of a small quantity of EtOH 1,2-*diphenylvinyldiphenylphosphine oxide* (VI)[11] formed colourless crystals, m.p. 159–161°. (Found: C, 81·9; H, 5·55; M (mass spectrometry) 380. $C_{26}H_{21}OP$ requires: C, 82·09; H, 5·56%, M, 380.) ν_{max} (KBr) 1608(m), 1180(s) cm^{-1}. λ_{max} (95% EtOH) 268 mμ (ε 17,630).

Hydrogenation of the olefin (VI). Compound VI (0·3 g, 0·0008 mole) in abs EtOH (30 ml) was hydrogenated in the presence of PtO_2 (30 mg) for 30 hr. The resulting soln was filtered, and the solvent evaporated to low bulk, when the product crystallized. After several recrystallizations from EtOH, the product had m.p. 230–232°. The IR spectrum of the hydrogenation product was identical with that of II.

Oxidation of the olefinic compound (VI). Compound VI (0·56 g, 0·0015 mole) was suspended in refluxing acetone (20 ml), to which Na_2CO_3 (0·25 g) was added. $KMnO_4$ (4 g) was added in portions to the refluxing soln. After the addition of $KMnO_4$ was completed, the soln was refluxed for a further 6 hr. High flow supercell (1 g) was added and the suspension filtered hot. The filtrate was acidified with dil HCl, and extracted with Chf (2 × 10 ml). The Chf extract was dried and evaporated to yield a crystalline residue (81 mg). The residue was subjected to sublimation at 100°/0·1 mm. A highly crystalline sublimate was collected and was found to be identical with an authentic specimen of benzoic acid m.p. and mixed m.p. 121–122°. The non-volatile residue m.p. 192–193° was found to be diphenylphosphinic acid m.p. and mixed m.p. 192–193°.

The high-flow supercell filter aid added to collect the MnO_2 formed in the reaction was extracted with Chf. The dried Chf extract was evaporated to give the unchanged olefinic compound m.p. and mixed m.p. 159–161° (0·263 g).

*Reaction of tri-*p*-tolylphosphine with phenylacetylene in the presence of water.* A soln of tri-*p*-tolyl phosphine,[12] (1·0 g, 0·003 mole), phenylacetylene, (1·0 g, 0·009 mole) and water (0·5 ml) in diethylene glycol (5 ml) was refluxed for 6 hr. The solvent was removed by distillation under reduced press and the residue crystallized from benzene. The product was obtained as colourless crystals, m.p. 218–219° (0·64 g, 40%). Mixed m.p., TLC and the IR spectrum showed it to be identical with XIV prepared below.

*Preparation of 2-phenyl-1-(*p*-tolyl)ethyldi-*p*-tolylphosphine oxide* (XIV). This reaction was carried out according to the procedure of Trippett and Walker.[8] A soln of tri-*p*-tolylphosphine[12] (0·566 g, 1·86 mmole), styrene oxide (0·24 g, 2·0 mmole) in abs EtOH (5 ml) was refluxed for 2 hr. TLC examination of the reaction mixture showed the presence of tri-*p*-tolylphosphine oxide in addition to the required product. After evaporating the solvent, the residue was dissolved in Chf (2 ml) and purified by column chromatography on silica using AcOEt as eluent. Crystallization from benzene gave the *product* as colourless crystals, m.p. 218–219° (0·355 g, 45%). (Found: C, 82·4; H, 6·89. $C_{29}H_{29}OP$ requires: C, 82·09; H, 6·8%.) ν_{max} (nujol mull) 1170(s) cm^{-1}. NMR spectrum: τ 2·0–3·0 (m, 17 aromatic protons), 7·58 (s, 3 aromatic Me protons) and 7·77 ppm (s, 6 aromatic Me protons).

Synthesis of trans-*β-styryltriphenylphosphonium bromide* (X). This synthesis was achieved by a modification of the general procedure[4] for the synthesis of vinylphosphonium salts. Dry, bromine free, HBr gas was passed through a soln of triphenylphosphine (10 g, 0·038 mole) and phenylacetylene (10 g, 0·09 mole) in dry diethylene glycol (75 ml), whilst heating at reflux for 4 hr. The solvent was removed by distillation under reduced press to yield a black gum, which was heated on a steam-bath with water (100 ml) for 1 hr with constant stirring. The resulting mixture was allowed to settle and the aqueous soln decanted carefully, from the tarry residue. The aqueous extract was extracted with ether (2 × 20 ml) to remove non-ionic emulsified organic material, and then evaporated under reduced press to yield a pale-red gum. This gum was dissolved in Chf (50 ml), and the Chf soln dried over anhyd Na_2SO_4. The dried Chf soln was evaporated to yield trans-*β-styryltriphenylphosphonium bromide* (X) as a pale yellow gum (15·0 g, 88%). Attempted purification by crystallization from a number of solvents failed to give crystalline material. The salt was characterized by the formation of the corresponding *picrate* by treatment of an aqueous soln of the bromide with a saturated aqueous soln of sodium picrate. After several recrystallizations from EtOH, trans-*β-styryltriphenylphosphonium picrate* formed yellow crystals, m.p. 157–158°. (Found: C, 65·1; H, 3·90; N, 7·2; $C_{32}H_{24}N_3O_7P$ requires: C, 64·7; H, 4·05; N, 7·08%.) λ_{max} (95% EtOH) 276 (ε 26,510) and 363 mμ. (ε = 15,560). NMR spectrum: τ 1·21 (s, 2 aromatic protons), 2·0–3·3 ppm (m, 22 aromatic and vinyl protons).

Reaction of the phosphonium bromide (X) *with silver oxide.* The phosphonium bromide (15·0 g, 0·033 mole) was dissolved in water (50 ml) to which was added freshly prepared, washed, Ag_2O prepared from NaOH (6·0 g) and $AgNO_3$ (8·0 g). The suspension was agitated overnight, and

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[11] *Note added after submission of manuscript.* The diphenylvinyldiphenylphosphine oxide (VI) has been prepared in its *cis* and *trans* forms by A. M. Aguiar and T. G. Archibald [*Tetrahedron Letters* No. 45, 5541 (1966)] and the m.p. of our product corresponds to that of the *cis* isomer reported by these workers.

[12] F. G. Mann and E. J. Chaplin, *J. Chem. Soc.* 527 (1937).

filtered. The clear, alkaline filtrate was evaporated in a rotary evaporator at less than 30° to yield a colourless gum, which could be redissolved in water to yield a clear alkaline soln. Attempts to reconvert the phosphonium hydroxide into the corresponding picrate described above gave a product which could not be crystalliized. The phosphonium hydroxide (1·0 g) was refluxed (a) on its own and (b) in the presence of triphenylphosphine respectively in diethylene glycol containing water. The resulting solns were then examined by TLC using a silica support in an attempt to identify II. No trace of the latter could be observed in the developed chromatogram, which indicated the presence of triphenylphosphine oxide only.