The Rearrangement of Alk-2-enyl Diphenylphosphinites

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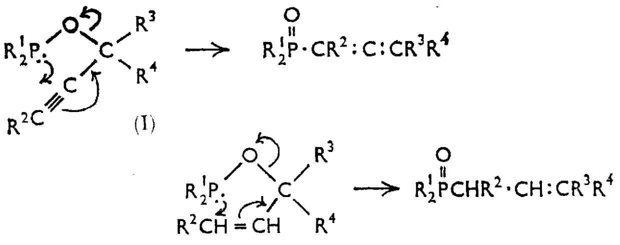
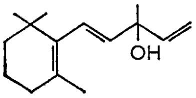
Several methods are described for the preparation of alk-2-enyl diphenylphosphinites which rearrange at *ca.* 140° to give alk-2-enyldiphenylphosphine oxides with inversion of the allyl group.

Alk-2-ynyl phosphites[1] (I; $R^1 = O$-alkyl) and diarylphosphinites[2] (I; $R^1 = Ar$) rearrange rapidly at room temperature to the corresponding alk-1,2-dienylphosphonates or alk-1,2-dienyldiphenylphosphine oxides presumably *via* five-membered transition states as shown. Alk-2-enyl phosphites (II; $R^1 = O$-alkyl) are much more thermally stable, but above 180° give alk-2-enylphosphonates with predominant inversion of the allyl group.[3] Arbusov and Nikonorov[4] prepared allyl diphenylphosphinite and showed that it rearranged on attempted distillation to give allyldiphenylphosphine oxide. We now report that alk-2-enyl diphenylphosphinites (II; $R^1 = Ph$) rearrange at or below 140° to give alk-2-enyldiphenylphosphine oxides (III; $R^1 = Ph$) with complete inversion of the allyl group, *e.g.*, cinnamyl diphenylphosphinite gives 1-phenylallyldiphenylphosphine oxide and 1-phenylallyl diphenylphosphinite gives cinnamyldiphenylphosphine oxide.

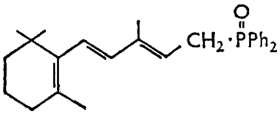
Four methods were used in preparing the phosphinites, which were rearranged at 140° without isolation. The methods are, in order of increasing utility, (*a*) addition of chlorodiphenylphosphine to a solution of the allylic alcohol in ether in the presence of one equivalent of pyridine,[4] (*b*) addition of chlorodiphenylphosphine to a



(II) (III)



(IV)



(V)

solution of the alcohol in pyridine or in 2,6-lutidine, (*c*) an exchange reaction between the alcohol and a

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[1] V. Mark, *Tetrahedron Letters*, 1962, 281.

[2] A. P. Boiselle and N. A. Meinhardt, *J. Org. Chem.*, 1962 **27**, 1828.

[3] A. N. Pudovik and I. M. Aladzheva, *Zhur. obshchei Khim.*, 1963, **33**, 3096; A. L. Lemper and H Tieckelmann, *Tetrahedron Letters*, 1964, 3053

[4] A. E. Arbusov and K. V. Nikonorov, *Zhur. obshchei Khim.*, 1948, **18**, 2008.

dialkylaminodiphenylphosphine at *ca.* 140°, and (*d*) treatment of the alcohol at room temperature or at 70° with acetoxydiphenylphosphine in the presence of an equivalent of triethylamine. Method (*a*) works well only with primary allylic alcohols; (*d*) would in general be the method of choice. The phosphine oxides were identified by synthesis and/or by their spectral properties. Although the possibility exists of *cis–trans* isomerism round the double bond which has migrated, in all cases the *trans*-form only was isolated. The results are summarised in the Table.

Preparation of phosphine oxides (III; R^1 = Ph) by rearrangement of phosphinites (II; R^1 = Ph)

R^2	R^3	R^4	% (III) (Method)
Me	H	H	60(*a*)
Ph	H	H	65(*a*)
H	Ph	H	4(*a*), 58(*b*), 60(*c*), 63(*d*)
H	Me	Me	4(*a*), 0(*b*), 10(*c*), 40(*d*)
H	C_5H_{10}		4(*a*), 45(*b*), 50(*c*)
H	PhCH:CH	H	2(*b*), 22(*c*), 15(*d*)
H	Me_2C:CH·CH_2·CH_2	Me	61(*c*)

None of the methods worked well on the allylic alcohol (IV) from β-ionone, the maximum yield of the pure phosphine oxide (V) being *ca.* 8%.

Acetoxydiphenylphosphine was prepared by the exothermic reaction of acetic anhydride with pyrrolidinyldiphenylphosphine. The accompanying *N*-acetylpyrrolidine could be separated by distillation but this led to extensive decomposition of the acetoxyphosphine and the reaction mixture was used directly. On heating with benzaldehyde, acetoxydiphenylphosphine gave α-acetoxybenzyldiphenylphosphine oxide.

Unsuccessful reactions of chlorodiphenylphosphine and allylic alcohols in the presence of pyridine gave as the major product a salt-like, high-melting substance, possibly $C_{35}H_{32}NO_6P_3$, of unknown structure.

EXPERIMENTAL

All reactions involving tervalent organophosphorus compounds were carried out under oxygen-free nitrogen. Light petroleum had b. p. 60—80°. N.m.r. spectra were recorded in deuteriochloroform with tetramethylsilane as internal standard on a Varian Associates A60 spectrometer. Mass spectra were recorded on an A.E.I. MS-9 spectrometer.

1-*Phenylallyldiphenylphosphine Oxide. Method* (a).—A solution of chlorodiphenylphosphine (11 g.) in ether (25 ml.) was added slowly to a stirred solution of cinnamyl alcohol (6·6 g.) and pyridine (9 ml.) in ether (50 ml.) cooled in ice. After 1 hr., the resulting suspension was filtered and the filtrate evaporated under reduced pressure. The residue was heated at 130° for 1 hr. and then recrystallised from benzene–ether to give 1-*phenylallyldiphenylphospine oxide* (10 g.), m. p. (from ethyl acetate) 193—193·5°, $\nu_{max.}$ 1175 (P:O), 990, 920 cm.$^{-1}$ (CH:CH_2) (Found: C, 79·1; H, 5·8; P, 9·6. $C_{19}H_{19}OP$ requires C, 79·4; H, 6·0; P, 9·75%).

In a similar way, crotyl alcohol (3·6 g.) gave 1-*methylallyldiphenylphosphine oxide* (7·5 g.), m. p. (from ether) 90—91°, $\nu_{max.}$ 1180 (P:O), 995, 920 cm.$^{-1}$ (CH:CH_2), quartet at τ 8·64 (J_{HH} = 7, J_{PH} = 16 c./sec.) (Found: C, 74·7; H, 6·6; P, 12·0. $C_{14}H_{17}OP$ requires C, 75·0; H, 6·65; P, 12·1%); 1-vinylcyclohexanol (2·8 g.) gave, after chromatography of the reaction mixture on alumina (60 g.), 2-cyclohexylidene-ethyldiphenylphosphine oxide (0·26 g.), m. p. (from benzene–light petroleum) and mixed m. p. 166—167°; 1-phenylallyl alcohol (2 g.) gave cinnamyldiphenylphosphine oxide (0·2 g.), m. p. (from benzene–light petroleum) and mixed m. p. 181—182°, and 2-methylbut-3-en-2-ol (4·2 g.) gave, after chromatography on alumina, 3-methylbut-2-enyldiphenylphosphine oxide (0·5 g.), m. p. (from benzene–light petroleum) and mixed m. p. 124—125°. The major product from the last three experiments was a substance, m. p. (from chloroform–ethyl acetate) 251—252° (Found: C, 64·3; H, 5·0; N, 1·9; P, 13·85%).

Cinnamyldiphenylphosphine Oxide. Method (b).—Chlorodiphenylphosphine (3·4 g.) was added slowly to a solution of 1-phenylallyl alcohol (2 g.) in pyridine (35 ml.) at room temperature and the solution set aside for 2 hr. and then heated under reflux for 1 hr. Pyridine was removed under reduced pressure and the residue, in chloroform, washed with dilute hydrochloric acid (3 ×), sodium hydrogen carbonate solution, and water. The solution was then dried and evaporated. The residue crystallised from benzene–light petroleum to give cinnamyldiphenylphosphine oxide (2·8 g.), m. p. and mixed m. p. 181—182°.

In a similar way, 1-vinylcyclohexanol (2·8 g.) gave 2-cyclohexylidene-ethyldiphenylphosphine oxide (3 g.), m. p. and mixed m. p. 166—167°.

2-*Cyclohexylidene-ethyldiphenylphosphine Oxide.*—A solution of 2-cyclohexylidene-ethyl bromide (0·88 g.) and methyl diphenylphosphinite (1 g.) in benzene (10 ml.) was heated under reflux for ½ hr., evaporated, and the residue crystallised from benzene–light petroleum to give 2-*cyclohexylidene-ethyldiphenylphosphine oxide* (0·85 g.), m. p. 166—167°, $\nu_{max.}$ 1180 cm.$^{-1}$ (P:O) (Found: C, 77·45; H, 7·4. $C_{20}H_{23}OP$ requires C, 77·4; H, 7·4%).

Similarly, cinnamyl bromide gave *cinnamyldiphenylphosphine oxide* (55%), m. p. (from benzene–light petroleum) 181—182°, $\nu_{max.}$ 1180 (P:O), 970 cm.$^{-1}$ (*trans*-CH:CH) (Found: C, 79·25; H, 5·8; P, 9·6. $C_{21}H_{19}OP$ requires C, 79·4; H, 6·0; P, 9·75%), and 3-methylbut-2-enyl bromide gave 3-*methylbut-2-enyldiphenylphosphine oxide* (72%), m. p. (from benzene–light petroleum) 124—125°, $\nu_{max.}$ 1180 cm.$^{-1}$ (P:O) (Found: C, 75·45; H, 7·1; P, 11·4. $C_{17}H_{19}OP$ requires C, 75·5; H, 7·0; P, 11·5%).

Geranyldiphenylphosphine Oxide. Method (c).—Linaloöl (2·25 g.) and dimethylaminodiphenylphosphine (3 g.) were heated at 130° for 24 hr. and the residue crystallised from benzene–light petroleum to give *geranyldiphenylphosphine oxide* (2·7 g.), m. p. 113—114°, $\nu_{max.}$ 1180 cm.$^{-1}$, quartet at τ 6·93 equivalent to two protons (J_{HH} = 7, J_{PH} = 15 c./sec.) (Found: C, 78·0; H, 8·0; P, 9·35. $C_{22}H_{27}OP$ requires C, 78·2; H, 8·0; P, 9·2%).

Similarly, 1-phenylallyl alcohol (3·0 g.) and dimethylaminodiphenylphosphine (5·1 g.) gave cinnamyldiphenylphosphine oxide (4·5 g.), m. p. and mixed m. p. 181—182°; the same alcohol (2·6 g.) and pyrrolidinyldiphenylphosphine (5 g.) gave the same phosphine oxide (3·6 g.); 2-methylbut-3-en-2-ol (2 g.) and dimethylaminodiphenylphosphine (7 g.) gave 3-methylbut-2-enyldiphenylphosphine oxide (0·5 g.), m. p. and mixed m. p. 124—125°; 1-vinylcylcohexanol (1·65 g.) and the same phosphine (3·0 g.) gave 2-cyclohexylidene-ethyldiphenylphosphine oxide (2·0 g.), m. p. and mixed m. p. 167—168°; and 1-phenylpenta-1,4-dien-3-ol (3·2 g.) and the same phosphine (4·6 g.) gave 5-*phenylpenta-*2,4-*dienyldiphenylphosphine oxide* (1·6 g.), m. p. (from benzene) 221—222°, $\nu_{max.}$ 1180 (P:O), 990 cm.$^{-1}$ (*trans*-CH:CH), quartet at τ 6·82 equivalent to two protons

(J_{HH} = 7, J_{PH} = 15 c./sec.), $\lambda_{max.}$ 292, 311 mμ (ε 48,500, 27,800 in ethanol) (Found: C, 80·2; H, 6·0. $C_{23}H_{21}OP$ requires C, 80·4; H, 6·1%).

1,6-*Diphenylhexa*-1,3,5-*triene*.—A suspension of sodium hydride (30 mg.) in dimethyl sulphoxide (50 ml.) was stirred at 60° for ½ hr.; 5-phenylpenta-2,4-dienyldiphenylphosphine oxide (0·4 g.) was added and the solution set aside at room temperature for ½ hr. Benzaldehyde (1·26 g.) was then added and the solution set aside at room temperature overnight, then poured into saturated brine (150 ml.). The mixture was extracted with ether (3 × 50 ml.) and the combined extracts washed with water, dried, and evaporated. Crystallisation of the residue from ethanol gave 1,6-diphenylhexa-1,3,5-triene (120 mg.), m. p. 200—202° (lit.,[5] m. p. 203°), having the recorded [5] ultraviolet spectrum.

3-*Methyl*-5-(2′,6′,6′-*trimethylcyclohex*-1′-*enyl*)*penta*-2,4-*dienyldiphenylphosphine Oxide* (V).—Dimethylaminodiphenylphosphine (10 g.) and vinyl-β-ionol (IV; 10 g.) were heated at 140° for 36 hr. The residue, in benzene, was chromatographed on neutral alumina (300 g.). Ether–0·5% methanol eluted the *phosphine oxide* (V; 1·4 g.), m. p. (from benzene–light petroleum) 126—127°, which gave only one spot on thin-layer chromatography; $\lambda_{max.}$ 260, 266·5, 273 mμ (ε 12,700, 13,000, 12,300 in ethanol), mass peak *m/e* 404, base peak *m/e* 201 (Ph_2PO), other significant peaks at *m/e* 389, 215, 202, quartet at τ 6·78 equivalent to two protons (J_{HH} = 8, J_{PH} = 15 c./sec.) Found: C, 80·1; H, 8·05. $C_{27}H_{33}OP$ requires C, 80·1; H, 8·2%).

Experiments with Acetoxydiphenylphosphine. Method (d).—Pyrrolidinyldiphenylphosphine (13·2 g.) and acetic anhydride (5·2 g.) were mixed and set aside until the temperature of the mixture, which rose to 70°, fell to 25°. The mixture then had $\nu_{max.}$ 1660 ($MeCO{\cdot}NC_4H_8$), 1750 cm.$^{-1}$ (Ph_2POAc).

The above product (2·8 g.), triethylamine (1·4 g.), and 1-phenylallyl alcohol (1·4 g.) were mixed and set aside at room temperature for ½ hr. The mixture, which then showed no absorption at 3300 or 1750 cm.$^{-1}$, was heated to 130° for 1 hr., cooled, and recrystallised from benzene–light petroleum to give cinnamyldiphenylphosphine oxide (2 g.), m. p. and mixed m. p. 183—184°. Similarly, 1-phenylpenta-1,4-dien-3-ol (1·6 g.) gave 5-phenylpenta-2,4-dienyldiphenylphosphine oxide (0·5 g.), m. p. and mixed m. p. 221—222°.

The above mixture of *N*-acetylpyrrolidine and acetoxydiphenylphosphine (2·8 g.), triethylamine (1·2 g.), and 2-methylbut-3-en-2-ol (0·86 g.) were mixed and kept at room temperature for 3 hr. The absorption at 3300 and 1750 cm.$^{-1}$ showed no diminution and the mixture was therefore kept at 70° for 3 hr. whereupon these absorptions had disappeared and intense absorption at 1180 cm.$^{-1}$ (P⁚O) had appeared. Recrystallisation of the product from benzene–light petroleum gave 3-methylbut-2-enyldiphenylphosphine oxide (1·2 g.), m. p. and mixed m. p. 123—124°.

The above mixture of *N*-acetylpyrrolidine and acetoxydiphenylphosphine (2·8 g.) was heated to 180° for ½ hr. with benzaldehyde (1·06 g.) and the product recrystallised from benzene–light petroleum to give α-acetoxybenzyldiphenylphosphine oxide (1·4 g.), m. p. and mixed m. p. 171—172° (lit.,[6] m. p. 175°).

We thank the S.R.C. for a Research Studentship, and Dr. F. R. Atherton for discussion.

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[6/555 *Received, May 9th*, 1966]

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