BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(4), 1173—1174 (1976)

Phosphinidenes and Related Intermediates. V.[1] Reactions of Phosphinylidenes with *cis*- and *trans*-Stilbene Oxides

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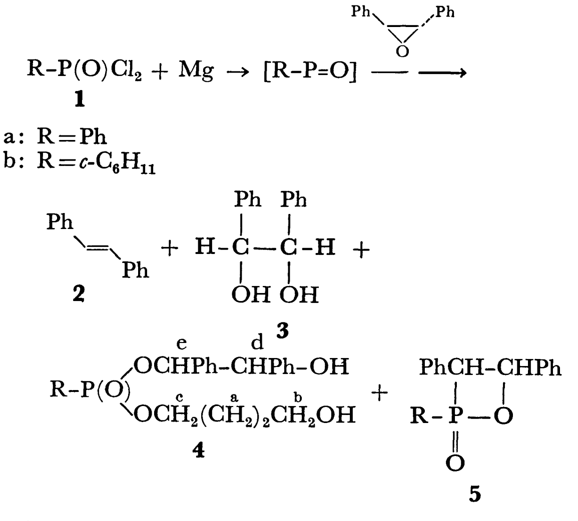
(Received January 16, 1976)

Synopsis. Reactions of phenyl- and cyclohexylphosphinylidenes with *trans*-stilbene oxide gave *trans*-stilbene and 4-hydroxybutyl 2-hydroxy-1,2-diphenylethyl phosphonate derivatives. In the case of cyclohexylphosphinylidene, 2-cyclohexyl-3,4-diphenyl-1,2-oxaphosphetane 2-oxide was also formed. Reactions with *cis*-stilbene oxide gave *cis*- and *trans*-stilbenes.

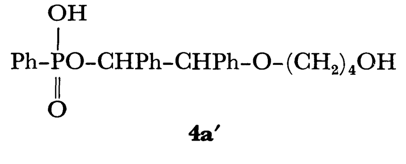
In the previous paper,[1] we reported that phosphinothioylidenes reacted with *cis*- and *trans*-stilbene oxides to give 1,3,2-oxathiaphospholane derivatives stereospecifically in most cases and *cis*- and/or *trans*-stilbenes. On the other hand, the reaction of phosphinylidenes gave different products except the formation of stilbenes.

Phenylphosphonic dichloride (**1a**) was allowed to react with magnesium in the presence of *trans*-stilbene oxide in tetrahydrofuran (THF) under nitrogen. *trans*-Stilbene (**2**), *meso*-1,2-diphenylethane-1,2-diol (**3**), and 4-hydroxybutyl 2-hydroxy-1,2-diphenylethyl phenylphosphonate (**4a**) were obtained in 10, 36, and 12% yields, respectively. A similar reaction using cyclohexylphosphonic dichloride (**1b**) gave 2,3,4-hydroxybutyl 2-hydroxy-1,2-diphenylethyl cyclohexylphosphonate (**4b**), and 2-cyclohexyl-3,4-diphenyl-1,2-oxaphosphetan 2-oxide (**5b**) in 11, 9, 12, and 8% yields, respectively.



The structures of **4** and **5** were determined by the elemental analyses and spectral data.

In the NMR spectrum of **4a**, the presence of the multiplet at δ 3.5—4.0 ppm would rule out another possible structure **4a′**.

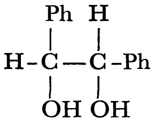


4a′

Comparison of the NMR spectrum of **4b** with that of **4a** suggests that **4b** is a mixture of isomers concerning with two methine parts (see Experimental). The IR spectrum of **5b** showed a strong broad band at 3150 cm^{-1} which is probably assignable to water of crystallization.

The fact that the reaction of *trans*-stilbene oxide with magnesium-magnesium(II) chloride did not give **3**[1] suggests a participation of phosphinylidene in the formation of **3**.

Reaction of phenylphosphinylidene with *cis*-stilbene oxide gave *cis*- and *trans*-stilbenes, *dl*-1,2-diphenylethane-1,2-diol (**6**), and *threo*-2-chloro-1,2-diphenylethanol (**7**), but the corresponding product of **4** could not be isolated in a pure state. A similar reaction of cyclohexylphosphinylidene gave *cis*- and *trans*-stilbenes and **7**.



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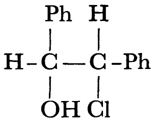

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Experimental

All reactions were carried out under nitrogen.

*Reaction of **1a** with Magnesium and* trans-*Stilbene Oxide.* A solution of **1a**[2] (3.90 g, 20 mmol) in THF (5 ml) was added dropwise to a stirred mixture of magnesium (0.53 g, 21.8 mmol) and *trans*-stilbene oxide[3] (2.00 g, 10.3 mmol) in THF (40 ml) at room temperature, and the mixture was stirred until exothermic reaction had ceased (*ca.* 1 h). Unchanged magnesium (10 mg) was filtered off and the solvent was evaporated ***in vacuo*** from the filtrate. The residue was extracted with $CHCl_3$. The extract was washed with aq. NH_4Cl and dried over $MgSO_4$. After evaporation, the residue was chromatographed on a silica gel dry column to give 0.13 g (0.7 mmol) of unchanged oxide, 0.18 g (1 mmol) of *trans*-stilbene (**2**), 0.74 g (3.5 mmol) of **3**, mp 136—138 °C (from CCl_4) (lit,[4] 137 °C), and 0.47 g (1.1 mmol) of **4a**. The yields of **2**, **3**, and **4a** were 10, 36, and 12%, respectively, based on *trans*-stilbene oxide consumed.

4a: mp 116—119 °C (from CCl_4); IR (KBr): 3345 (OH), 1218 (P=O), 1138 (P-Ph), 1000, and 988 cm^{-1} (P-O-C); NMR ($CDCl_3$): δ 1.4—1.8(m, 4H, $2CH_2$), 2.95(s, 2H, 2 OH), 3.2—3.5(m, 2H, $C\underline{H}_2OH$), 3.5—4.0(m, 2H, $POCH_2$), 4.95 (d, J_{HCCH} 5 Hz, 1H, $C\underline{H}PhOH$), 5.8(dd, J_{HCCH} 5, J_{POCH} 9 Hz, 1H, $POC\underline{H}Ph$), and 6.9—7.9(m, 15H, 3Ph); MS: *m/e* 338 ($PhP(OH)_2OCHPhCHPh^+$ or $PhP(OH)OCHPhCHPhOH^+$, 19%), 230 ($PhP(O)OCHPh^+$, 24), 178($PhC{\equiv}CPh^+$, 86), 167($PhP(O)OC_2H_3^+$, 72), 159 ($PhPO_3H_3^+$, 34), 141 ($PhPO_2H^+$, 61), 124 ($PhPO^+$, 31), and 77 (Ph^+, 100).

Found: C, 65.86; H, 6.46; P. 6.52%. Calcd for $C_{24}H_{27}O_5P \cdot 3/5H_2O$: C, 65.93; H, 6.50; P, 7.08%.

*Reaction of **1b** with Magnesium and* trans-*Stilbene Oxide.* A solution of **1b**[5] (4.02 g, 20 mmol) in THF (5 ml) was added dropwise to a stirred mixture of magnesium (0.53 g, 21.8 mmol) and *trans*-stilbene oxide (2.00 g, 10.3 mmol) in THF (40 ml) at room temperature, and the mixture was stirred overnight. After a usual treatment, dry column chromatography on silica gel gave unchanged oxide (0.52 g, 2.7 mmol), **2**(0.14 g, 0.8 mmol), **3**(0.14 g, 0.7 mmol), **4b**(0.40 g, 0.9 mmol), and **5b**(0.20 g, 0.6 mmol) in 11, 9, 12, and 8% yields, respectively, based on *trans*-stilbene oxide consumed.

4b: mp 113.5—116.5 °C (from hexane); IR (KBr): 3390 (OH), 1228, 1200 (P=O), 995, and 985 cm^{-1} (P–O–C); NMR ($CDCl_3$): δ 0.8—2.0(m, 15H, *c*-C_6H_{11} and $2CH_2$), 2.8(bs, 2H, 2 OH), 3.25—4.0(m, 4H, $2CH_2O$), 4.93 (d+d, $J_{H^dH^e}$ 6 and 4 Hz, 1H, H^d), 5.56(dd+t, $J_{H^dH^e}$ 6 and 4 Hz, J_{POCH^e} 14 and 4 Hz, 1H, H^e), and 6.9—7.6 (m, 10H, 2Ph); MS: *m/e* 344 (*c*-$C_6H_{11}P(OH)_2OCHPhCHPh^+$ or *c*-C_6H_{11}-$P(OH)OCHPhCHPhOH^+$, 10%), 178($PhC\equiv CPh^+$, 63), 163(*c*-$C_6H_{11}PO_3H^+$, 16), 91($C_7H_7^+$, 70), and 55($C_4H_7^+$, 100).

Found: C, 64.00; H, 7.44; P, 7.13%. Calcd for $C_{24}H_{33}O_5P\cdot H_2O$: C, 63.99; H, 7.83; P, 6.88%.

5b: mp 172—173 °C (from aq. EtOH); IR (KBr): 3150(br) (H_2O), 1213 (P=O), 1180, 1168, 1159, 1140, and 1090 cm^{-1} (P–O–C); NMR ($CDCl_3$): δ 0.8—2.4 (m, 11H, *c*-C_6H_{11}), 4.5—4.8 (m, 2H, 2CH), and 7.1—7.6 (m, 10H, 2Ph); MS: *m/e* 196 ($CHPhCHPhO^+$, 3%) and 167 ($PhC_2H_3O_2P^+$, 100).

Found: C, 72.35; H, 7.63; P, 8.86%. Calcd for $C_{20}H_{23}O_2P\cdot 2/5H_2O$: C, 72.01; H, 7.19; P, 9.29%.

*Reaction of **1a** with Magnesium and* cis-*Stilbene Oxide.* Dichloride **1a** (6.01 g, 30.8 mmol) in THF (5 ml) was added dropwise to a mixture of *cis*-stilbene oxide[6] (3.00 g, 15.3 mmol) and magnesium (0.81 g, 33.3 mmol) in THF (45 ml) with stirring at room temperature over 1 h and the mixture was refluxed for 3 h. After a similar treatment, the residue was chromatographed on a silica gel dry column to afford unchanged oxide (0.21 g, 1.1 mmol), *cis*-(0.24 g, 1.3 mmol, 4.4%), and *trans*-stilbenes (1.9 g, 1.1 mmol, 3.7%), and **6** (0.10 g, 0.5 mmol, 1.7%), mp 121.5—122.5 °C (from CCl_4) (lit,[4] 120 °C). An oily fraction analogous to **4** (0.7 g) was obtained, but could not be purified. In addition, **7** (0.6 g, mp 43—45 °C (from hexane) (lit,[7] 47 °C) was obtained. The yields were calculated based on *cis*-stilbene oxide consumed.

*Reaction of **1b** with Magnesium and* cis-*Stilbene Oxide.* The reaction was carried out in the same scale as that of **1a**, and *cis*-(0.68 g, 3.7 mmol, 11%) and *trans*-stilbenes (1.22 g, 6.8 mmol, 22%), and **7** (0.15 g, 1.1 mmol, 3.7%) were obtained.

This work was supported by a grant-in-aid from the Ministry of Education.

References

1) For Part IV see: S. Nakayama, M. Yoshifuji, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **48**, 3733 (1975).

2) A. D. F. Toy, *J. Am. Chem. Soc.*, **70**, 186 (1948).

3) D. J. Reif and H. O. House, *Org. Synth.*, Coll. Vol. 4, 860 (1963).

4) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **33**, 291 (1968).

5) R. Graf, *Chem. Ber.*, **85**, 9 (1952).

6) D. Y. Curtin and D. B. Kellom, *J. Am. Chem. Soc.*, **75**, 6011 (1953).

7) D. Reulos and S. Le Tellier, *C. R. Acad. Sci.*, **217**, 698 (1943); *Chem. Abstr.*, **39**, 926^4 (1945).