## DISPROPORTIONATION OF DI( $\alpha$ -HYDROXYALKYL)PHENYLPHOSPHINES AND THEIR DERIVATIVES

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 $Di(\alpha-hydroxyalkyl)$  phenylphosphines and their derivatives have been widely used in organic synthesis [1, 2], but the conditions under which these compounds disproportionate have not yet been studied. We investigated the products of acetylation  $\lfloor (I)-(IV) \rfloor$  in a mixture of acetic acid and acetic anhydride:



for (I) and (V), R = H, X = electron pair; for (II) and (VII), R = Me, X = electron pair; for (III) and (VI), R = Me, X = 0.

Acetylation of (I) and (III) yielded the acetates (V) and (VI), the structures of which were confirmed by elemental analysis and the intense absorption at 1752 cm<sup>-1</sup> in the IR spectra (the valence oscillation of the ester group). Acetylation of (IV) yielded the acetal (VII), as indicated by the elemental analysis and the absence of IR absorption in the 1600-1700 cm<sup>-1</sup> region. Reaction of (VII) with sulfur yielded two stereoisomeric sulfides with mp 88 and 165°C. The addition of sulfur proceeds stereospecifically [3]; consequently, the separation of stereoisomeric sulfides is evidence that (VII) is a mixture of stereoisomers. In the <sup>31</sup>P-<sup>1</sup>H NMR spectrum of (VII) (Fig. 1d) the 30 and 44 ppm signals correspond to them. The product of the acetylation of (II) is a mixture of three stereoisomers of the acetal (VII). The third stereoisomer, with a 34 ppm chemical shift in the <sup>31</sup>P-<sup>1</sup>H NMR spectrum (VII) (Fig. 1b), is present in such a small proportion that its sulfide could not be isolated.

Comparison of the NMR spectra of acetylation products of (I) and (IV), reaction mixtures (I) and (III), and also (II) and (IV) after neutralization in benzene shows that they are, respectively, identical. Allowing for the sensitivity of the method and the concentration of the solutions, this indicates that acetates predominate in the acetylation products of (I) and (III), and acetals in the acetylation products of (II) and (IV). Thus, in the

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Fig. 1. <sup>31</sup>P-<sup>1</sup>H NMR spectra: a) (V), liquid; b) VII from (II), liquid; c) (VI) in benzene; (VII) from (IV), liquid.

acetylation of  $\alpha$ -hydroxyalkyl derivatives of phenylphosphine the starting materials can disproportionate. In the series (I)-(IV) the direction of the reaction does not correlate with the inductive effect of the phosphorus-containing fragment, and is determined by steric effects in the intermediate stages of the concurrent reactions.

The differences of the constants of (I)-(IV) and their derivatives in the present work and in [4] is to be explained either by disproportionation or by the decomposition of the products under the reaction conditions described in [4]. During distillation, (I) may decompose to hydroxymethylphenylphosphine, (II) to  $\alpha$ -hydroxyethylphenylphosphine, and (IV) may disproportionate to acetal.

In connection with the fact that the composition of the starting materials and reaction products was controlled by the  ${}^{31}P^{-1}H$  NMR spectra, the spectrum of (II) is of interest (Fig. 2a). The location and the relative intensity of the signals does not depend on the way in which (II) was produced. The synthesis was carried out from PhPH<sub>2</sub> and MeCHO in ether, C<sub>6</sub>H<sub>6</sub>, MeOH, EtOH, in neutral medium and with acidification at various temperatures, and from (IV) by treatment with pyridine or aqueous KOH. Upon addition of sulfur, (II) is converted to the sulfide (VIII). In the reaction mixture of (VIII), one signal appears (Fig. 2b). Treatment of (II) with MeCHO in acidic medium gives (IV), in the spectrum of which there is also one signal (Fig. 2c). Oxidation of (II) yields a mixture of products. The oxide (III) which is separated from the mixture has one signal in the spectrum of (II) correspond to the d, *l*and the meso forms, and result from the diastereomeric anisochronicity [5, 6].

## EXPERIMENTAL

The  ${}^{31}P-{}^{1}H$  NMR spectra were obtained on a KGU-4 NMR spectrometer (10.2 MHz) with noise suppression of protons at a frequency of 25.2 MHz. Resolution was 40 Hz/cm. Concentration of solutions was 30-50%. Chemical shifts were measured relative to 85% H<sub>3</sub>PO<sub>4</sub>.

Di(hydroxymethyl)phenylphosphine (I). To a solution of 20 g (0.18 mole) of PhPH<sub>2</sub> in 10 ml of EtOH in a N<sub>2</sub> atmosphere was added dropwise a solution of 12 g (0.4 mole) of paraformaldehyde in 50 ml of MeOH at 35-40°C. Over a period of 1 h the alcohols were removed in vacuum (0.1 mm). The residue was a liquid, yield 100%;  $nD^{25}$  1.6064;  $d_4^{25}$  1.1887. <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum ( $\delta$ , ppm): 20. Found: C 56.83; H 6.50; P 18.40%. C<sub>8</sub>H<sub>11</sub>O<sub>2</sub>P. Calculated: C 56.47; H 6.47; P 18.23%. The product distilled with slight decomposition at 100°C (0.1 mm);  $nD^{27}$  1.6038;  $\delta$  20 ppm. Found: P 18.65%.

Di(hydroxymethyl)phenylphosphine Oxide. To 2 g of (I) in 5 ml of MeOH was added the calculated amount of 24% H<sub>2</sub>O<sub>2</sub> with cooling. The volatile components were removed in vacuum (0.1 mm). The residual liquid crystallized completely after 1 day, yield 100%. After washing with MeOH, mp 100-102°C;  $\delta$  -35 ppm. Found: C 51.40; H 6.04; P 16.47%. C<sub>8</sub>H<sub>11</sub>O<sub>3</sub>P. Calculated: C 51.60; H 5.96; P 16.65%.

Di(hydroxymethyl)phenylphosphine Sulfide. To 2.6 g (0.015 mole) of (I) in 2 ml of MeOH was added 0.5 g (0.015 mole) of powdered sulfur. The mixture was heated to 50°C and left



Fig. 2.<sup>31</sup>p-{<sup>1</sup>H} NMR spectra: a) (II), liquid; b) (VIII), liquid; c) (IV), liquid; d) (III), in MeOH.

over night. The solvent was removed in vacuum, yield 100%;  $\delta = -46$  ppm. Found: C 47.20; H 5.50; P 15.51%. C<sub>B</sub>H<sub>11</sub>O<sub>2</sub>SP. Calculated: C 47.52; H 5.44; P 15.34%.

<u>Tri(hydroxymethyl)phenylphosphonium Chloride.</u> To a solution of 5 g (0.045 mole) of PhPH<sub>2</sub> in 10 ml of EtOH in a N<sub>2</sub> atmosphere was added 4.1 g (0.14 mole) of paraformaldehyde in 35 ml of MeOH and 1 ml of conc. HCl at 35-40°C. Over a period of 1 h the volatile components were removed in vacuum (0.1 mm) at 100°C. The residue crystallized, yield 100%, mp 76°C;  $\delta$  -20 ppm. Found: Cl 15.11; P 13.01%. C<sub>9</sub>H<sub>14</sub>O<sub>3</sub>ClP. Calculated: Cl 14.99; P 13.09%.

 $\frac{\text{Di}(\alpha-\text{hydroxyethyl})\text{phenylphosphine (II).}}{\text{of ether in a N}_2 \text{ atmosphere was added 25 g (0.23 mole) of PhPH}_2 dropwise at -10°C.}$ The mixture was held for 2 h at 20°C, and the volatile components were removed in vacuum (0.1 mm). The residue was a liquid, yield 100%;  $n_D^{2^\circ}$  1.5760;  $d_4^{2^\circ}$  1.1238;  $\delta$  -2 and +12 ppm. Found: C 60.61; H 7.70; P 15.65%. C<sub>9</sub>H<sub>15</sub>O<sub>2</sub>P. Calculated: C 60.60; H 7.57; P 15.65%.

Distillation of (II) proceeds with decomposition, yielding  $\alpha$ -hydroxyethylphenylphosphine, bp 50°C (0.1 mm);  $n_D^{27}$  1.5755;  $\delta$  30 ppm. Found: C 61.56; H 7.07; P 20.34%. C<sub>10</sub>H<sub>15</sub>O<sub>2</sub>P. Calculated: C 62.33; H 7.14; P 20.13%.

<u>Di( $\alpha$ -hydroxyethyl)phenylphosphine Oxide (III)</u>. To a solution of 12 g (0.06 mole) of (II) in 20 ml of ether was added 20 g (0.07 mole) of 12% H<sub>2</sub>O<sub>2</sub> dropwise with mixing and cooling. At the end of the reaction the ether was removed in vacuum. A solid product precipitated from the aqueous solution, yield 11 g (84%), mp 153-154°C,  $\delta$  -44 ppm (C<sub>6</sub>H<sub>6</sub>). Found: C 56.20; H 7.00; P 14.55%. C<sub>10</sub>H<sub>15</sub>O<sub>3</sub>P. Calculated: C 56.07; H 7.01; P. 14.48%.

<u>Di( $\alpha$ -hydroxyethyl)phenylphosphine Sulfide (VIII)</u>. To 1 g (0.005 mole) of (II) in 5 ml of ether was added 0.16 g (0.005 mole) of powdered sulfur; the mixture was heated for 30 min at 35°C and held for 3 h at 20°C. The solvent was removed in vacuum. The residue was a viscous liquid, yield 100%;  $n_D^{22}$  1.5852;  $\delta$  -59 (C<sub>6</sub>H<sub>6</sub>). Found: C 52.50; H 6.51; P 13.27%. C<sub>10</sub>H<sub>15</sub>O<sub>2</sub>SP. Calculated: C 52.16; H 6.57; P 13.46%.

<u>Tri( $\alpha$ -hydroxyethyl)phenylphosphonium Chloride (IV).</u> To a solution of 45 ml (0.75 mole) of MeCHO in 30 ml of MeOH were added dropwise first 21 ml of conc. HCl, then in a N<sub>2</sub> atmosphere 20 g (0.18 mole) of PhPH<sub>2</sub> at -10°C and the mixture was stirred for 1 h at 20°C. The volatile components were removed in vacuum (0.1 mm). The residue was a viscous liquid, yield 100%,  $\delta$  -24 ppm.

<u>Acetylation of (I)-(IV)</u>. One mole of (I)-(IV) was heated with 2.5 moles of Ac<sub>2</sub>O and 2.5 moles of AcOH in a N<sub>2</sub> atmosphere for 1.5 h at 100°C; the mixture was cooled and evaporated in vacuum (0.1 mm). The acetylation products of (I), (II), and (IV) were dissolved in  $C_6H_6$ , washed with KOH solution and water until neutral; then the  $C_6H_6$  was distilled off in vacuum, and the residue was distilled. The acetylation product of (III) was dissolved in MeOH and the solvent was removed by evaporation.

In this manner the following were obtained:

1) Di(acetoxymethyl)phenylphosphine (V), bp 124-125°C (0.1 mm);  $n_{D}^{2^{\circ}}$  1.5380;  $d_{4}^{2^{\circ}}$  1.1640; yield 63%,  $\delta$  28 ppm. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1752 (C=O, in film). Found: C 56.76; H 5.99; P 12.54%. C<sub>12</sub>H<sub>15</sub>O<sub>4</sub>P. Calculated: C 56.67; H 5.96; P 12.19%.

2) Di( $\alpha$ -acetoxyethyl)phenylphosphine oxide (VI), bp 113°C (after washing with MeOH). Yield 60%,  $\delta$  -41 ppm (C<sub>6</sub>H<sub>6</sub>). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1753 (C=0, in oil). Found: C 56.00; H 6.40; P 10.72%. C<sub>12</sub>H<sub>15</sub>O<sub>5</sub>P. Calculated: C 56.35; H 6.43; P 10.39%.

3) 5-Pheny1-2,4,6-trimethy1-1,3,5-dioxaphosphinane (VII). (VII) was obtained from (IV), bp 87-88°C (0.1 mm);  $n_D^{2^\circ}$  1.5459;  $d_4^{2^\circ}$  1.1129. Yield 52%;  $\delta$  30 and 44 ppm. Found: C 64.06; H 7.70; P 13.44%. (VII) was obtained from (II), bp 88-89°C (0.1 mm);  $n_D^{2^\circ}$  1.5450. Yield 48%;  $\delta$  30, 34, and 44 ppm. Found: C 64.22; H 7.89; P 13.51%. C<sub>12</sub>H<sub>17</sub>O<sub>2</sub>P. Calculated: C 64.28; H 7.59; P 13.84%.

<u>5-Phenyl-5-thio-2,4,6-trimethyl-1,3,5-dioxaphosphinane.</u> An excess of sulfur was sprinkled on (VII). The next day the mixture was dissolved in MeCN and the unreacted sulfur was filtered off. Upon standing, a sulfide crystallized, mp 165°C. The solvent was evaporated; from the residue there slowly separated a sulfide, mp 88°C. Both sulfides were purified by washing with MeOH and MeCN. (VII) from (II) gave 32 and 24%, while (VII) from (IV) gave 84 and 2% sulfides with mp 88 and 165°C. The sulfide of mp 165°C has  $\delta$  -27 ppm. Found: C 56.75; H 6.91; P 12.55; S 12.74%. The sulfide of mp 88 has  $\delta$  -24 ppm. Found: C 56.20; H 6.49; P 12.35; S 12.60%. C<sub>12</sub>H<sub>17</sub>O<sub>2</sub>SP. Calculated: C 56.25; H 6.64; P 12.40; S 12.50%.

## CONCLUSIONS

When di( $\alpha$ -hydroxyethyl)phenylphosphine and tri( $\alpha$ -hydroxyethyl)phenylphosphonium chloride are heated with a mixture of acetic anhydride and acetic acid, they disproportionate to form 5-phenyl-2,4,6-trimethyl-1,3,5-dioxaphosphinane. Under the same conditions, di(hydroxymethyl)phenylphosphine and di( $\alpha$ -hydroxyethyl)phenylphosphine oxide are acetylated.

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