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EQUILIBRIUM OF STEREOISOMERS OF 2,4,5,6-TETRAPHENYL-1,3,5-DIOXAPHOSPHORINANE AND ITS DERIVATIVES

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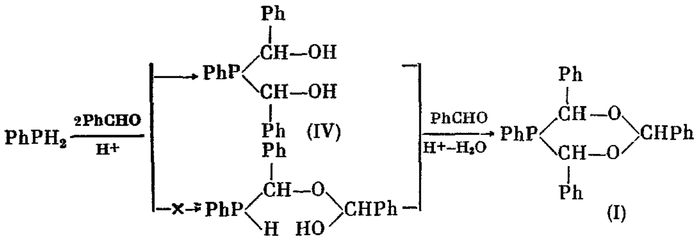
In connection with the results obtained in [1] for the equilibrium of 5-benzyl-5-oxo-2,4,6-triphenyl-1,3,5-dioxaphosphorinane, we studied the equilibrium of 2,4,5,6-tetraphenyl-1,3,5-dioxaphosphorinane (I), its oxide (II), and its sulfide (III). Compound (I) was obtained from $PhPH_2$ and PhCHO in acid medium as described in [2]. The reaction can go along two paths.



The intense signals of di(hydroxybenzyl)phenylphosphine (IV), with δ −10.6 ppm, appear first in the ^{31}P NMR spectrum of the reaction mixture, and then, as they decrease, the signal of (I) with δ 35 ppm begins to increase. The formation of (IV) indicates that a second PhCHO molecule also adds to the P atom, i.e., the reaction goes only along the first path depicted in the scheme. The direct reaction of (IV) with PhCHO in acid medium leads to the same product that is obtained from $PhPH_2$ and PhCHO.

The formation of the given (I) isomer in acid medium is amenable to thermodynamic control. This conclusion was made after studying the reaction of (IV) with PhCHO in neutral medium. Under these conditions the signals of three (I) stereoisomers with δ 30, 32, and 35 ppm are observed in the ^{31}P NMR spectrum of the reaction mixture. The stereoisomer with δ 35 ppm, which is also formed in acid medium, deposits from this reaction mixture on standing. The other two stereoisomers could not be isolated in the pure form. Heating the stereoisomer with δ 35 ppm and p-toluenesulfonic acid in C_6H_6 (80°C, 15 h) does not lead to the appearance of the other stereoisomers.

Compound (II) was obtained from (I) by oxidation with H_2O_2, as described in [2], and also by the reaction of di(hydroxybenzyl)phenylphosphine oxide (V) with PhCHO in acid medium. In both cases the product in the reaction mixture and in the pure form was the stereoisomer with δ −12 ppm. Isomerization was not observed when (II) was heated with p-toluenesulfonic acid in C_6H_6 (80°, 40 h). The equilibrium of 5-benzyl-5-oxo-2,4,6-triphenyl-1,3,5-dioxaphosphorinane is established in 24 h under such conditions. The reaction of di(hydroxybenzyl)benzylphosphine oxide with PhCHO in acid medium leads to a mixture of stereoisomers [1]. The above data indicate that the stereoisomer with δ −12 ppm is the most stable (II) stereoisomer. When (II) is isomerized in CF_3COOH it decomposes to (V) and PhCHO.

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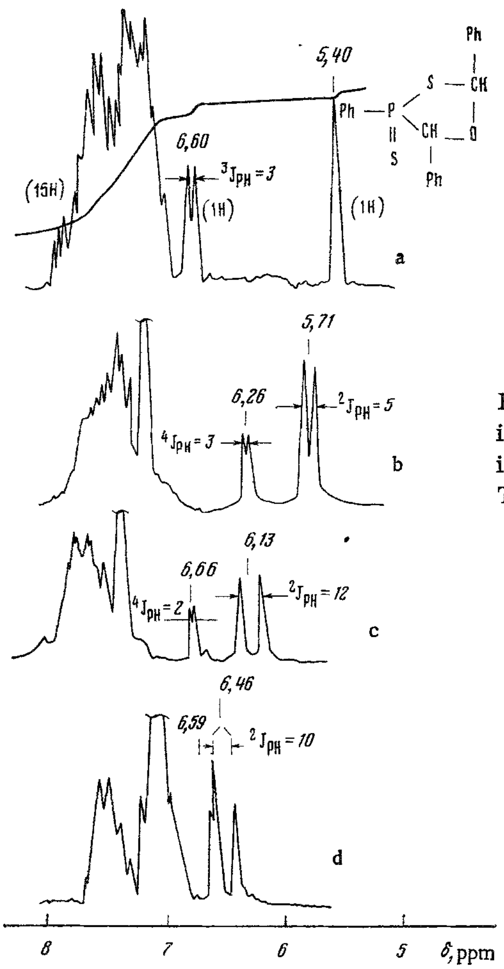

Fig. 1. PMR spectrum: a) (VI), in CCl_4; b) (I), in CH_3CN; c) (II), in DMSO; d) (III), in CH_3CN. The J values are given in Hz.

Compound (III) was obtained by the addition of sulfur to (I), δ −35 ppm. The isomerization of (III) was run in benzene in the presence of p-toluenesulfonic acid (80°, 15 h). In the ^{31}P NMR spectrum of the reaction mixture was observed a gradual decrease in the signal of (III) and the appearance of a signal with δ −87 ppm, while the signals of the other (III) stereoisomers were absent. On the basis of the elemental analysis data and the PMR spectrum (Fig. 1a) the product with δ −87 ppm was assigned the structure of 3-thio-2,3,5-triphenyl-1,4,3-oxathiaphospholane (VI). The PMR spectrum of this compound has the signals of three types of protons, with a relative intensity of 15 : 1 : 1. The signal of one of the protons, apparently at the C^5 atom [3, 4], is split from the coupling with the nucleus of the phosphorus atom.

The sulfides have a high nucleophilicity and are easily protonated. The rapid isomerization of the sulfides of 5-phenyl-2,4,6-trimethyl-1,3,5-dioxaphosphorinane was shown by us in [5]. The decomposition of (III) under conditions that favor isomerization, without the loss of stereohomogeneity, testifies to the greater thermodynamic stability of this stereoisomer.

A comparison of the PMR spectra of (I)-(III) (Fig. 1b-d) with the spectra of the previously studied model compounds [5] leads to the conclusion that in (I)-(III) the phenyls on the phosphorus atom and adjacent carbon atoms are found in the equatorial position. This confirms the stereospecificity of adding oxygen and sulfur to phosphines [6].

As a result, (II) is stereohomogenetic in the equilibrium state, which is sharply different from the equilibrium state of the isomeric 5-benzyl-5-oxo-2,4,6-triphenyl-1,3,5-dioxaphosphorinanes, where the stereoisomer with one axial phenyl and one equatorial phenyl on the 4,6 carbon atoms predominates. Consequently, in the discussed systems the reactions involving the benzyl and phenyl groups on the P atom are dissimilar.

EXPERIMENTAL

The ^{31}P NMR spectra were obtained on a KGU-4 NMR spectrometer (10.2 MHz) with noise suppression of the protons at a frequency of 24.3 MHz, and without suppression. The PMR spectra were recorded on a

Varian T-60 spectrometer at 34.5°; the IR spectra were recorded on a UR-10 spectrometer.

Di(hydroxybenzyl)phenylphosphine (IV). To 12.4 g of freshly distilled $PhPH_2$ in an argon atmosphere was added 35.8 g of freshly distilled PhCHO. The evolution of heat was observed. On standing overnight the mixture crystallized. The yield of (II) was 100%, mp 45-47°, δ −10.6 ppm. Found: C 74.50; H 5.98; P 9.42%. $C_{20}H_{19}O_2P$. Calculated: C 74.50; H 5.95; P 9.61%. When (IV) is vacuum-distilled it decomposes to PhCHO and $PhPH_2$.

Di(hydroxybenzyl)phenylphosphine Oxide (V). Compound (IV) is oxidized rapidly in the air and is converted quantitatively to (V), mp 162° (from MeCN), δ −38 ppm (in DMF). Found: C 71.17; H 5.64; P 9.35%. $C_{20}H_{19}O_3P$. Calculated: C 70.98; H 5.67; P 9.16%.

2,4,5,6-Tetraphenyl-1,3,5-dioxaphosphorinane (I). a) Using the method given in [2], we obtained (I) from $PhPH_2$ and PhCHO, and also from (IV) and PhCHO in acid medium; yield 40-50%, mp 205° (from MeCN) (cf. [2]), δ 35 ppm (in DMF). Found: C 79.13; H 5.56; P 7.57%. $C_{27}H_{23}O_2P$. Calculated: C 79.06; H 5.65; P 7.55%.

b) In an argon atmosphere, to 18.1 g of (IV) in 30 ml of ether was added 6.0 g of PhCHO. After 15 days the reaction mixture began to deposit crystals. After 24 days their yield was 4.4 g (20%), mp 205° (from MeCN), δ 35 ppm (in DMF). During the entire period the reaction mixture contained (IV) and a mixture of the three (I) stereoisomers with δ 30, 32, and 35 ppm.

5-Oxo-2,4,5,6-tetraphenyl-1,3,5-dioxaphosphorinane (II). a) Using the method given in [2], we obtained (II) from (I) by oxidation with H_2O_2, yield 82%, mp 248-249° (from MeCN) (cf. [2]), δ −12 ppm (in DMSO). Found: C 76.50; H 5.39; P 7.28%. $C_{27}H_{23}O_3P$. Calculated: C 76.03; H 5.44; P 7.27%.

b) To 1.1 g of (V) in 50 ml of abs. benzene were added 2.1 g of PhCHO and several crystals of p-toluenesulfonic acid. Using a Dean−Stark trap, the mixture was refluxed for 35 h. The benzene was removed in vacuo and the residue was recrystallized from MeCN. Yield 0.35 g (27%), mp 248-249°, δ −12 ppm (DMSO).

5-Thio-2,4,5,6-tetraphenyl-1,3,5-dioxaphosphorinane (III). To 1.5 g of (I) in 20 ml of MeCN was added 0.12 g of sulfur and the mixture was heated for 1 h at 80° until solution was complete. Then the mixture was cooled and the solvent was removed in vacuo. The residue was recrystallized from MeCN. Yield 1.4 g (73%), mp 223°, δ −35 ppm. (CH_3CN). Found: P 7.08%. $C_{27}H_{23}O_2P$. Calculated: P 7.00%.

The isomerization of (I)-(III) was run in C_6H_6 in the presence of p-toluenesulfonic acid.

3-Thio-2,3,5-triphenyl-1,4,3-oxathiaphospholane (VI). A solution of 8 g of (III) in 50 ml of C_6H_6 was refluxed in the presence of p-toluenesulfonic acid for 15 h. Then the solvent was removed in vacuo and the residual yellow oil was dissolved in hot MeOH. Crystals of (VI) deposited on cooling, yield 1.1 g (16%), mp 153°, δ −87 ppm (DMF). Found: C 65.57; H 4.57; P 8.49%. $C_{20}H_{17}OPS_2$. Calculated: C 65.20; H 4.66; P 8.41%.

CONCLUSIONS

The stereoisomers with an equatorial orientation of the phenyls on the phosphorus atom and on the carbon atoms of the ring predominate in the equilibrium of 2,4,5,6-tetraphenyl-1,3,5-dioxaphosphorinane, its oxide, and its sulfide.

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