

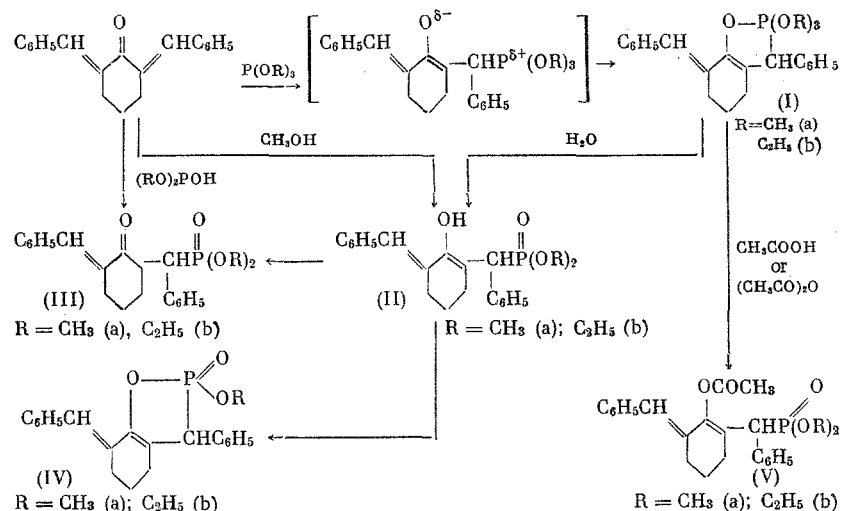
# REACTION OF 2,6-DIBENZYLIDENECYCLOHEXANONE WITH TRIALKYL PHOSPHITES AND DIALKYLPHOSPHOROUS ACIDS

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Many reactions of trialkyl phosphites with carbonyl [1-3], dicarbonyl [4-7], and  $\alpha, \beta$ -unsaturated carbonyl compounds [8-11], which lead to the formation of cyclic phosphoranes, are known at the present time. It was interesting to study the reaction of trialkyl phosphites with compounds in which the carbonyl group is found in conjugation with two benzylidene groups. We selected 2,6-dibenzylidenecyclohexanone [12] as such a compound.

In the present paper it was shown that the reaction of the trimethyl and triethyl phosphites with 2,6-dibenzylidenecyclohexanone leads to the formation of cyclic phosphoranes (Ia) and (Ib). The structure of the phosphoranes was proved by the data of the NMR and IR spectra. The absorption bands of the P=O and C=O groups are absent in the IR spectra of (Ia) and (Ib). Intense bands are present ( $\nu$ ,  $\text{cm}^{-1}$ ) at 1060, 1080, and 1110 (P-OC), and bands of average intensity are present at 1182 (P-O-CH<sub>3</sub>), 1110 (P-OC), and 1162 (P-O-C<sub>2</sub>H<sub>5</sub>); weak bands of the diene system are present at 1611 and 1655 (C=C). The chemical shift for the <sup>31</sup>P phosphorus nuclei, which was measured by the double nuclear resonance method relative to 85% H<sub>3</sub>PO<sub>4</sub>, is  $\delta_{31\text{P}} + 33$  ppm for (Ia), and  $\delta_{31\text{P}} + 32$  ppm for (Ib). The presence of a doublet in the NMR spectrum of (Ia)



with  $\delta$  3.56 ppm and a constant  $J_{\text{POCH}_3} = 11$  Hz, corresponding to three methoxyl groups, also corroborates the phosphorane structure.

Phosphorane (Ia) is easily hydrolyzed with an equimolar amount of water in benzene, in the presence of HCl, to give the dimethyl ester of 2-(6-benzylidenecyclohexanone)benzylphosphonic acid (IIIa). In the IR spectrum of (IIIa) are present the absorption bands ( $\nu$ ,  $\text{cm}^{-1}$ ): 1039, 1055 v.s. (P-O-C); 1230, 1250 m (P=O); 1188 m (P-O-CH<sub>3</sub>). Absorption at 1608 (C=C) and 1690  $\text{cm}^{-1}$  (C=O), which is of equal intensity, is characteristic for the s-cis forms of  $\alpha, \beta$ -unsaturated ketones [13].

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TABLE 1

Effect	T <sub>init</sub> , °C	T <sub>max</sub> , °C
I	90—96	120—127
II	165—170	195—200
III	195—200	235—239

TABLE 2

(RO) <sub>2</sub> P(O)H	Effect	T <sub>init</sub> , °C	T <sub>max</sub> , °C
R=CH <sub>3</sub>	I	142—145	200—202
	II	200—202	228—230
R=C <sub>2</sub> H <sub>5</sub>	I	140—145	208—212
	II	208—212	235—238

The hydrolysis of phosphorane (Ib) proceeds more easily. In ether solution, (Ib) is hydrolyzed even under the influence of atmospheric moisture. Based on the data of the IR spectra and the chemical properties (solubility in 5% aqueous caustic solution and a color with alcoholic FeCl<sub>3</sub> solution), the hydrolysis product has the structure of (IIb). The IR spectrum of (IIb) contains the absorption bands ( $\nu$ , cm<sup>-1</sup>): 1032, 1062 v. s. (P—O—C), 1205 s (P=O), attached to a hydrogen atom, 1605 and 1615 w (C=C); 3200–3400 (OH).

The enol form of (IIb) is unstable and either gradually (without a solvent or in ether) or rapidly (in benzene, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub>) changes to the keto form (IIIb). In the IR spectrum of (IIIb) this is indicated by the disappearance of the absorption band of the OH group, a shift of the P=O band toward the 1252 cm<sup>-1</sup> region, and the appearance of bands of equal intensity at 1602 (C=C) and 1685 cm<sup>-1</sup> (C=O).

In order to prove the structure of the phosphonic acid esters (III) we ran their counter synthesis from 2,6-dibenzylidenecyclohexanone and the appropriate dialkylphosphorous acids. It proved that the reaction proceeds in two directions, depending on the temperature. Compounds (IIIa and b) are formed when a mixture of 2,6-dibenzylidenecyclohexanone and the dialkyl phosphite in benzene is heated at 165–170°C. When the same reaction is run at 135–150° the cyclic esters (IVa and b) are formed in low yields, the structure of which was proved by the data of the IR and NMR spectra. In the IR spectra of (IV) are present the absorption bands ( $\nu$ , cm<sup>-1</sup>): 1049, 1060 (P—O—C); 1280 (P=O) (IVa); 1260 (P=O) (IVb); 1603, 1639 (C=C). The  $\delta_{31P}$  of (IVa) is -41 ppm, and the  $\delta_{31P}$  of (IVb) is -42 ppm. In the NMR spectrum of (IVa) are present a doublet of the CH<sub>3</sub>OP group, with  $\delta$  3.45 ppm and  $J_{POCH_3}$  = 10 Hz, and a doublet of the CH group, with  $\delta$  = 4.15 ppm and  $J_{PCH}$  = 21 Hz. The protons of the  $\alpha$ -methylene group of the cyclohexane ring give a triplet with  $\delta$  2.78 ppm; the  $\beta$ -methylene protons give a quintet with  $\delta$  1.80 ppm; the  $\gamma$ -methylene protons appear at  $\delta$  2.09 ppm (broad band). Ester (IVb) has a similar NMR spectrum.

Enol acetates (Va and b)\* are formed when the (I) phosphoranes are reacted with CH<sub>3</sub>COOH. The IR spectrum of these compounds contains the bands ( $\nu$ , cm<sup>-1</sup>): 1038, 1060 (P—O—C), 1196 (P—O—CH<sub>3</sub>), 1182 (P—O—C<sub>2</sub>H<sub>5</sub>), 1220, 1254 (P=O); 1628 (C=C); 1762 (C=O) (characteristic for acetyl carbonyl).

Enol acetates (Va and b) were obtained in higher yields by the reaction of acetic anhydride with 2,6-dibenzylidenecyclohexanone and trialkyl phosphites, and also by the reaction of acetic anhydride with phosphorane (Ia). The reaction of 2,6-dibenzylidenecyclohexanone with P(OCH<sub>3</sub>)<sub>3</sub> in the presence of excess methanol leads to the formation of phosphorane (Ia) and a small amount of enol (IIa).

In order to study the reaction of trialkyl phosphites and dialkylphosphorous acids with 2,6-dibenzylidenecyclohexanone we employed the thermography method. On the thermogram of the reaction with P(OCH<sub>3</sub>)<sub>3</sub> are observed three exo effects (Table 1). As a study of the reaction mixture disclosed, the first exo effect is caused by the formation of phosphorane (Ia). The nature of the subsequent exo effects was not ascertained. The exo effect of the reaction with trialkyl phosphites in the presence of proton-donor reagents (CH<sub>3</sub>COOH, alcohol) is observed in nearly the same temperature range. When the reaction was run in the presence of an equivalent amount of CH<sub>3</sub>COOH, after passing through the first exo effect, the enol acetates (V) were isolated. Enol (IIa) was isolated after thermographing a mixture of trimethyl phosphite with 2,6-dibenzylidenecyclohexanone in the presence of methanol up to the first exo effect. In the presence of acetic anhydride the exo effect of the reaction of trialkyl phosphites with 2,6-dibenzylidenecyclohexanone is observed in the same temperature range as in its absence. Enol acetates (V) were also isolated from the reaction mixture after passing through this effect.

The reaction of 2,6-dibenzylidenecyclohexanone with the dimethylphosphorous and diethylphosphorous acids proceeds at a higher temperature than when reaction is with trialkyl phosphites, and is accompanied

\*In the case of phosphorane (Ia), together with the main product (Va), a small amount of the cyclic ester (IVa) was isolated.

by two exo effects (Table 2). Study disclosed that the first exo effect is caused by the progress of two processes, namely the formation of enols and their cyclization to cyclic esters (IV). A small exo effect is also observed for enol (Iib) in the range 140–200°, and cyclic phosphonate (IVb) was isolated from the reaction mixture after passing through this effect. The nature of the second exo effect was not established.

## EXPERIMENTAL METHOD

2,6-Dibenzylidenecyclohexanone was obtained as described in [14]. The IR spectra were taken on a UR-10 spectrometer. The thermographing was run on a Kurnakov PK-52 pyrometer, equipped with a Chromel–Alumel thermocouple, in sealed Stepanov vessels (rate of heating = 4–6 deg/min). The NMR spectra were taken on a Varian NA-100 spectrometer (100 MHz), and the  $^{31}\text{P}$  NMR spectra were taken on a KGU-4 NMR spectrometer at a frequency of 10.2 MHz.

Reaction of 2,6-Dibenzylidenecyclohexanone with Trialkyl Phosphites. A mixture of 2.74 g of 2,6-dibenzylidenecyclohexanone and 1.86 g of  $\text{P}(\text{OCH}_3)_3$  was heated in a sealed ampul at 100° for 4 h, cooled, and allowed to stand overnight. The crystallized mass was washed with absolute ether. We obtained 2.66 g (67%) of 1-oxa-2,2,2-trimethoxy-2-phospha-3-phenyl-8-benzylidenebicyclo-(3)(4)-nonene 4-9 (Ia) as colorless crystals, mp 112–115°. Found: C 69.70; H 7.00; P 7.92%.  $\text{C}_{23}\text{H}_{27}\text{O}_4\text{P}$ . Calculated: C 69.32; H 6.83; P 6.78%.

In a similar manner, phosphorane (Ib) was obtained from 2.74 g of 2,6-dibenzylidenecyclohexanone and 2.49 g of triethyl phosphite (10 h at 100°). The excess phosphite was removed in vacuo by the repeated addition of dry benzene to the thick mass. Compound (Ib) was obtained as an oil. Found: C 70.63; H 7.22; P 6.69%.  $\text{C}_{26}\text{H}_{33}\text{O}_4\text{P}$ . Calculated: C 70.08; H 7.55; P 7.03%.

Hydrolysis of Phosphorane (Ia). To a solution of 0.9 g of (Ia) in 6 ml of absolute benzene were added 0.06 ml of distilled water with a micropipet and a drop of HCl solution. After two days the benzene was removed in vacuo. The residue when rubbed in petroleum ether (40–60°) gave (IIIa) as a pale yellow powder, mp 64–66°. Found: C 68.50; H 6.60; P 7.86%.  $\text{C}_{22}\text{H}_{25}\text{O}_4\text{P}$ . Calculated: C 68.73; H 6.55; P 8.06%.  $\delta_{31\text{P}}$  30 ppm.

Hydrolysis of Phosphorane (Ib). The crude phosphorane, obtained from 2.74 g of 2,6-dibenzylidenecyclohexanone and 1.7 g of triethyl phosphite, was treated with ether on a watch glass. Under the influence of atmospheric moisture, the enol (Iib) was gradually (~5 min) formed as a white powder, mp 107–108.5°. Found: C 69.66; H 7.06; P 6.88%.  $\text{C}_{24}\text{H}_{29}\text{O}_4\text{P}$ . Calculated: C 69.88; H 7.08; P 7.51%. Compound (Iib) when dissolved in benzene,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , or  $\text{CCl}_4$ , and also on long standing in ether, is converted to the keto form (IIIb). Compound (IIIb) was obtained as a thick yellow mass that would not crystallize. Found: P 7.49%.  $\text{C}_{24}\text{H}_{29}\text{O}_4\text{P}$ . Calculated: P 7.51%.  $\delta_{31\text{P}}$  28 ppm.

Reaction of Phosphorane (Ia) with Acetic Anhydride. To a solution of 1.35 g of (Ia) in 5 ml of absolute benzene, in a dry  $\text{N}_2$  stream, was added 0.346 g of freshly distilled acetic anhydride. The mixture was heated at 100° for 4.5 h. Then the benzene was removed in vacuo, and after standing for two days the residue crystallized. Recrystallization from cyclohexane gave (Va), mp 154–155°. Found: C 67.20; H 6.30; P 7.11%.  $\text{C}_{24}\text{H}_{27}\text{O}_5\text{P}$ . Calculated: C 67.58; H 6.38; P 7.26%. Compound (Va) is readily soluble in benzene, ether,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , or hot alcohol; it is insoluble in petroleum ether.

Reaction of 2,6-Dibenzylidenecyclohexanone with Trialkyl Phosphites in the Presence of Acetic Anhydride. A mixture of 2,6-dibenzylidenecyclohexanone, the trialkyl phosphite, and acetic anhydride, taken in a molar ratio of 1:2.5:1, was heated under thermographic control up to the first effect. On standing in the refrigerator the contents of the vessels crystallized. After recrystallization we isolated: 1.5 g (50%) of (Va), mp 154–155° (from cyclohexane), and 0.55 g (25%) of (Vb), mp 113–114° (from n-hexane). Compound (Vb) is readily soluble in ether,  $\text{CH}_2\text{Cl}_2$ , or  $\text{CCl}_4$ , or in hot alcohol or petroleum ether. Found (Vb): C 68.78; H 6.90; P 6.64%.  $\text{C}_{26}\text{H}_{31}\text{O}_5\text{P}$ . Calculated: C 68.70; H 6.87; P 6.82%.

Reaction of Phosphorane (Ia) with  $\text{CH}_3\text{COOH}$ . A mixture of 1.4 g of (Ia), 0.2 g of glacial  $\text{CH}_3\text{COOH}$ , and 2 ml of  $\text{CH}_2\text{Cl}_2$  was kept in a dry box for two days. After a part of the solvent was removed, the unreacted phosphorane and a small amount of (IVa) were filtered. From the filtrate by further evaporation we isolated (Va), mp 154–155°.

Reaction of 2,6-Dibenzylidenecyclohexanone with Trialkyl Phosphites in the Presence of  $\text{CH}_3\text{COOH}$ . A mixture of 1.67 g of 2,6-dibenzylidenecyclohexanone, 1.05 g of  $\text{P}(\text{OCH}_3)_3$ , and 0.377 g of glacial  $\text{CH}_3\text{COOH}$

was heated up to the first exo effect. On standing in the refrigerator the contents of the vessel crystallized. We obtained 0.65 g (40.7%) of (Va), mp 154-155° (from cyclohexane).

Compound (Vb) was obtained in a similar manner, and after repeated recrystallization from n-hexane it had mp 113-114°.

Reaction of 2,6-Dibenzylidenecyclohexanone with  $(\text{CH}_3\text{O})_2\text{POH}$ . Expt. 1. A mixture of 2 g of 2,6-dibenzylidenecyclohexanone, 1 g of  $(\text{CH}_3\text{O})_2\text{POH}$ , and 2 ml of benzene was heated in a sealed tube at 130° for 6 h, and then at 160° for 5 h. Evaporation in vacuo gave a mixture of crystals of the starting ketone and product (IVa). The mixture was washed with absolute ether. We obtained 0.5 g (20%) of (IVa), mp 184-186° (from cyclohexane). Found: C 71.87; H 6.29; P 8.89%.  $\text{C}_{21}\text{H}_{21}\text{O}_3\text{P}$ . Calculated: C 71.57; H 6.00; P 8.79%. Product (IVa) is readily soluble in benzene,  $\text{CH}_2\text{Cl}_2$ , or  $\text{CHCl}_3$ .

Expt. 2. Equimolar amounts of 2.74 g of 2,6-dibenzylidenecyclohexanone and 1.1 g of  $(\text{CH}_3\text{O})_2\text{POH}$  in 2 ml of absolute benzene was heated in a sealed tube at 160-165° for 9 h. The benzene was evaporated in vacuo. On standing in the air the residue solidified, and when rubbed in n-hexane it gave (IIIa) as a yellow powder, mp 64-66°. The latter is readily soluble in the common organic solvents. Found: P 7.99%.  $\text{C}_{22}\text{H}_{25}\text{O}_4\text{P}$ . Calculated: P 8.06%.

Reaction of 2,6-Dibenzylidenecyclohexanone with  $(\text{C}_2\text{H}_5\text{O})_2\text{POH}$ . A mixture of 2 g of 2,6-dibenzylidenecyclohexanone and 1 g of  $(\text{C}_2\text{H}_5\text{O})_2\text{POH}$  in 3 ml of absolute benzene was heated in a sealed tube at 130° for 2 h, and then at 150-165° for 9 h. The mixture was evaporated in vacuo. We isolated 0.4 g (15%) of (IIb), mp 173.5-175° (from cyclohexane). Found: C 72.44; H 6.54; P 8.26%.  $\text{C}_{22}\text{H}_{23}\text{O}_3\text{P}$ . Calculated: C 72.11; H 6.66; P 8.46%.

Reaction of 2,6-Dibenzylidenecyclohexanone with  $\text{P}(\text{OCH}_3)_3$  in the Presence of Methanol. A mixture of 1.38 g of 2,6-dibenzylidenecyclohexanone, 0.81 g of  $\text{P}(\text{OCH}_3)_3$ , and 0.33 g of absolute  $\text{CH}_3\text{OH}$  was heated in a Stepanov vessel. From the reaction mixture were isolated 1.1 g of phosphorane (Ia) and 0.15 g of (IIa), mp 114-116°. Found: C 68.75; H 6.66; P 7.83%.  $\text{C}_{22}\text{H}_{25}\text{O}_4\text{P}$ . Calculated: C 68.73; H 6.55; P 8.06%.

Thermographing of (IIb). Enol (IIb) (0.3727 g) was heated in a Stepanov vessel up to the first exo effect (190°). The contents of the vessel crystallized within 2 h after thermographing. The mixture was filtered and washed with absolute ether. We obtained 0.4 g (60%) of (IVb), mp 173.5-175°.

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## CONCLUSIONS

1. The reaction of 2,6-dibenzylidenecyclohexanone with trialkyl phosphites gave phosphoranes, and some of the properties of the latter were studied.

2. Depending on the temperature, 2,6-dibenzylidenecyclohexanone reacts with dialkyl phosphites to give the dialkyl esters of 2-(6-benzylidenecyclohexanone)benzylphosphonic acid, and also cyclic esters.

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