REACTION OF DIBENZALACETONE WITH TRIMETHYL PHOSPHITE AND DIMETHYLPHOSPHOROUS ACID

B. A. Arbuzov, V. M. Zoroastrova, G. A. Tudrii, and A. V. Fuzhenkova

Dibenzalcyclohexanone reacts with trimethyl phosphite (TMP) to give an adduct of the phosphorane type [1]. The reaction of dibenzalacetone (DBA) with trialkyl phosphites was not studied, which caused us to make the present study.

The reaction of DBA with TMP was checked by thermography. A small exo effect was observed on the thermcgram of the mixture, with an initial temperature (init. t.) of 55°C and a maximum temperature (max, t,) of 84° (Fig. 1a). This exo effect was reproduced on repeated thermographing of the same reaction mixture. After thermographing for 10 times a product with mp 121-122° was isolated, which proved to be phospherane (II). Phosphorane (II) is heat unstable and dissociates above 90-93° into the starting components. The thermogram of (II) reflects an endo effect with an initial temperature of 90-93° and a minimum temperature of 104°, which is the total effect of melting and dissociation. The dissociation of phosphorane (II) was confirmed by the IR spectra and by the isolation of DBA. Phosphorane (II) is also formed by the long standing of the mixture (3 weeks).

The structure of phosphorane (II) was confirmed by the NMR spectrum (δ_{3in} + 28 ppm) and the IR spectrum (the bands of the P = O and C = O groups are absent, and the frequencies characteristic for the P-OC group of phosphoranes are present at 1062, 1088 and 1102 cm⁻¹ [2]; bands of slight intensity are present at 1610 and 1648 cm^{-1} in the region of the double bonds). The structure of phosphorane (II) was also proved by its chemical transformations.



The hydrolysis of phosphorane (II) with water gave two compounds with mp 141-149 and 105-106.5°, that in their analysis corresponded to keto phosphonate (IV).

The IR spectrum of the product with mp 141-149° has bands at 1612 cm⁻¹ (C=C, intense) and 1705 cm^{-1} (C = O, medium intensity). Starting with the literature data [3-7] and the IR spectrum of the dimethyl ester of 2-(6-benzalcyclohexanone) benzylphosphonic acid, which has a fixed S-cis conformation of the C = Cand C = O bonds [1] [1608 (C=C) and 1690 cm⁻¹ (C=O)], the compound with mp 141-149° can probably be assigned the structure of keto phosphonate (IV) with an S-cis conformation. The IR spectrum of this compound has an absorption band in the 3300 $\rm cm^{-1}$ region that is analogous to the band of the enolic form of the diethyl ester of 2-(6-benzalcyclohexanone)benzylphosphonic acid [1], which testifies to the presence of a

A. M. Butlerov Chemical Institute of the V. I. Ul'yanov-Lenin Kazan State University, Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2581-2585, November, 1973. Original article submitted June 7, 1973.

© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

UDC 542,91:547.572:547.1'118



Fig. 1. Thermogram of a mixture of dibenzalacetone and $(CH_3O)_3P$ (a), and of the reaction of dibenzalacetone with $(CH_3O)_3P$ in the presence of CH_3COOH (b).

small amount of enol (III) in (IV). The 3300 cm⁻¹ band disappears in either benzene or CH_2Cl_2 solution, which indicates a transition of enol (III) to the keto form (IV).

The compound with mp 105-106.5° is probably the S-trans isomer of keto phosphonate (IV). Its IR spectrum has bands at 1630 (C=C) and 1660 cm⁻¹ (C=O, intense), and also an intense band at 990 cm⁻¹, which testifies to the trans-arrangement of the hydrogen atoms at the double bond [8]. The ratio in the intensities of the C=C and C=O bands, and $\Delta \nu$ < 75 cm⁻¹ [5, 7], both testify in support of the S-trans structure for (IV). In either benzene or CH₂Cl₂ the S-trans conformer changes partially to the S-cis conformer. A band at 1700 cm⁻¹ (C=O of the S-cis conformer) appears in the IR spectrum of the solutions, and the C=O band of the S-trans conformer shifts to the 1675 cm⁻¹ region. After removal of the solvent the IR spectrum is identical with the IR spectrum of the starting S-trans conformer.

The keto phosphonate (IV) with mp $105-106.5^{\circ}$ was also obtained by the reaction of DBA with either dimethylphosphorous acid or TMP in the presence of an equivalent amount

of CH₃COOH. On the thermogram in the latter case (Fig. 1b) the exo effect (init. t. 55°, max. t. 96°) nearly coincides with the exo effect of the reaction of DBA with TMP, but is larger in area, since in the presence of CH₃COOH the reaction proceeds almost to completion with the formation of keto phosphonate (IV).

The formation of the intermediate product, the bipolar ion (I), is also indicated by the formation of enol acetate (V) when DBA is reacted with TMP in the presence of $(CH_3CO)_2O$. Enol acetate (V) was obtained by counter synthesis from DBA and dimethyl acetylphosphite.

 $\begin{array}{c} C_6H_5CH=\!CH\!-\!C\!-\!CH=\!CHC_6H_5+(CH_3O)_2POCOCH_3\\ \|\\ O\\ \rightarrow C_6H_5CH=\!CH\!-\!C\!=\!CH\!-\!CHC_6H_5\\ H_5COOC & P(OCH_3)_2\\ \|\\ O\\ \end{array}$

If DBA is reacted with TMP at 100°, then phosphorane (II) is not formed, but rather an oil that cannot be distilled in a high vacuum, which, in its analysis and molecular weight, corresponds to the addition product of two molecules of DBA to one TMP molecule. A value of δ_{31P} + 30 ppm, the absence of frequencies that correspond to the P=O group, and the presence in the IR spectrum of bands at 1060, 1075 and 1100 cm⁻¹ (P-O-C), all indicate the phosphorane structure of the product. It is possible to assume that phosphorane (II) at 100° reacts with a second DBA molecule by the diene synthesis scheme:



Actually, (VIII) was isolated when phosphorane (II) was heated with DBA at 100°. We did not make a choice between structures a and b. As we indicated previously, at 90-100° the phosphorane dissociates into

the starting components, but with excess DBA some of the (II) succeeds in reacting with a second DBA molecule and in this way is removed from the equilibrium system: phosphate + DBA == phosphorane (II). Phosphorane (VIII) on hydrolysis gives a crystalline product with mp 135-137°, which corresponds to the phosphonic acid obtained from (VIII). The ability of phosphorane (II) to enter into the diene synthesis reaction is indicated by its reaction with α -naphthoquinone with the formation of the 1:1 adduct.

EXPERIMENTAL METHOD

The thermographic studies were run on a Kurnakov PK-52 pyrometer, equipped with a Chromel-Alumel thermocouple, in sealed Stepanov vessels. Fused magnesium oxide was used as the standard. The rate of heating the furnace was 4-5 deg/min. The DBA sample weighed 0.20-0.24 g, while the phosphite was taken in 2- to 3-fold excess. In individual cases, in order to accumulate the products, the amount of the starting materials was increased 5-6 times. The IR spectra were taken on a UR-10 spectrometer.

Synthesis of 2, 2, 2-Trimethoxy-3-phenyl-5- $(\beta$ -phenyl)vinyl-1, 2-oxa-4-phospholene (II). a) A mixture of DBA and TMP was thermographed up to the appearance of the exo effect (up to 94°). Crystals of DBA deposited on cooling. The mother liquor was evaporated in vacuo to remove the phosphite. The residue was also DBA. Phosphorane (I) was not detected.

b) The crystals that had deposited after the mixture had been chromatographed for 10 times were filtered and washed with absolute ether to remove the yellow needles of unreacted DBA. The colorless crystals of phosphorane (II) that remained on the filter had mp 121-122°; yield 5%. Phosphorane (II) was also obtained by keeping the reaction mixture at ~20° for 3 weeks. The yield of the phosphorane increases up to 66% if the mixture of DBA and TMP is first thermographed (up to 94°), and then kept at ~20° for 2 weeks. Found: C 67.10; H 6.51; P 8.66%. $C_{20}H_{23}O_4P$. Calculated: C 67.02; H 6.46; P 8.65%.

<u>Hydrolysis of 1, 2-Oxa-4-phospholene (II).</u> A drop of water was added to a solution of 0.17 g of (II) in 5 ml of benzene. After a day the solvent was removed in vacuo. The residual thick mass was treated with absolute ether. Here a colorless precipitate deposited, which was filtered quickly. We obtained 0.062 g (38.7%) of (IV), mp 141-149°. Found: C 66.07; H 6.21; P 8.92%. From the mother liquor, after a partial removal of the ether in vacuo, was obtained a second fraction (0.105 g, 65%) of (IV) as colorless crystals with mp 105-106.5° (from cyclohexane). Found: C 66.28; H 6.42; P 8.95%. $C_{19}H_{21}O_4P$. Calculated: C 66.28; H 6.14; P 9.00%.

Reaction of DBA with TMP in the Presence of CH_3COOH . Employing thermographic control, a mixture of DEA, TMP and CH_3COOH , taken in a 1:2:1 ratio, was heated up to the first exo effect. The contents of the vessel crystallized on standing in the refrigerator. The precipitate was washed with absolute ether, and then it was recrystallized from cyclohexane. We obtained a 35% yield of (IV) as colorless crystals with mp 105-106.5°. The mixed melting point with the product of the preceding experiment, mp 105-106.5°, was not depressed.

<u>Reaction of DBA with Dimethylphosphorous Acid.</u> A mixture of equimolar amounts of DBA and dimethylphosphorous acid in benzene (2 ml) was heated in a sealed ampul for 4 h at 140-160°. After the removal in vacuo of as much of the unreacted $(CH_3O)_2POH$ as possible the residual dark red mass was treated with absolute ether. We obtained (IV) as white crystals with mp 105-106.5° (from cyclohexane). The mixed melting point with the product of the preceding experiment was not depressed.

<u>Reaction of DBA with TMP in the Presence of $(CH_3CO)_2O$.</u> The vessel contents after thermographing a mixture of DBA and TMP in the presence of an equimolar amount of $(CH_3CO)_2O$ up to 122° was evaporated in vacuo. The obtained crystals were separated from the tarry portion by washing with absolute ether. We obtained (V) in 35% yield as mother-of-pearl needles with mp 135-136° (from cyclohexane). Infrared spectrum (ν , cm⁻¹): 1035, 1055 (P-O-C), 1186 (P-O-CH₃), 1249 (P=O), 1620, 1652 (C=C), 1757 (C=O). Found: C 65.87; H 6.02; P 8.07%. C₂₁H₂₃O₅P. Calculated: C 65.26; H 6.02; P 8.02%.

Reaction of DBA with Dimethyl Acetylphosphite. The reaction mixture, obtained when a mixture of DBA and $(CH_3O)_2POCOCH_3$ (slight excess) was thermographed up to the exo effect (max. t. 104°), was worked up the same as in the preceding experiment. Here we isolated (VII) with mp 135-136° (from cyclohexane). The mixed melting point with the product of the preceding experiment was not depressed.

Preparation of Phosphorane (VIII). A mixture of DBA and a 3-fold excess of TMP was heated in a sealed ampul at 100° for 10 h, after which it was diluted with absolute benzene, which was then removed in vacuo along with the excess TMP. The residual thick yellow oil was phosphorane (VIII). Found: P4.80%.

 $C_{37}H_{37}O_5P$. Calculated: P 5.23%. Infrared spectrum (ν , cm⁻¹): 1590 m, 1615 v.s (C = C), 1665 m, doublet 1680, 1692 v. s (conjugated C = O).

Hydrolysis of Phosphorane (VIII). To a benzene solution of 1.67 g of phosphorane (VIII) was added 1.5 ml of 1:1 HCl solution. The mixture was allowed to stand at ~20° for a day, after which a part of the benzene was removed by evaporation in vacuo. Here crystals appeared at the water-benzene interface. When the amount of crystals ceased to increase, they were filtered and washed with benzene. Lustrous needles with mp 135-137° were obtained. Found: C74.91; H6.64; P5.16%. C₃₆H₃₅O₅P. Calculated: C74 .72; H6.97; P5.35%. Infrared spectrum (ν , cm⁻¹): 1053 v.s (P-O-C), 1251 s (P = O), 1618 v.s (C=C), 1665 w, 1698 (conjugated C = O), 1720 (unconjugated C=O).

A product with mp 89-91° was obtained after treating the compound with mp 135-137° with CH_2Cl_2 , acetonitrile and hot benzene. Found: C 74.88; H 6.48; P 5.28%; mol. wt. 599.34; 619.32 (cryoscopically). $C_{36}H_{35}O_5P$. Calculated: mol. wt. 578.64. In the IR spectrum are observed an increase in the intensity of the 1665 cm⁻¹ band and a decrease in the intensity of the 1698 cm⁻¹ band. The 1720 cm⁻¹ band remains unchanged.

<u>Reaction of 1, 2-Oxa-4-phospholene (II) with 1, 4-Naphthoquinone</u>. An exo effect with init. t. 70° and max. t. 88-90° is observed when a mixture of phosphorane and α -naphthoquinone (in benzene) is thermographed. The vessel contents, a thick reddish mass, failed to crystallize after the solvent was removed. Infrared spectrum (ν , cm⁻¹): 1040, 1065, 1100 (P-O-C), 1190 s, (P-O-CH₃), 1630 (C=C), doublet 1680, 1700 s (C=O). The material on dehydrogenation [9] (by blowing air through an alcohol solution of the product in the presence of a drop of KOH solution) gave a brown powder with mp 141-144° (reprecipitation from benzene solution with petroleum ether). Found: P 6.51%. C₂₉H₂₁O₆P. Calculated: P 6.24%.

CONCLUSIONS

1. Trimethyl phosphite reacts with dibenzalacetone to give 2, 2, 2-trimethoxy-3-phenyl-5- $(\beta$ -phenyl)-vinyl-1, 2-oxa-4-phospholene (II).

2. The phosphorane ring is opened at the P-O bond when (II) is hydrolyzed with water, with the formation of two keto phosphonates, probably the S-cis and S-trans conformers.

3. Phosphorane (II) reacts with dibenzalacetone by the diene synthesis scheme.

LITERATURE CITED

- 1. B. A. Arbuzov, V. M. Zoroastrova, G. A. Tudrii, and A. V. Fuzhenkova, Izv. Akad. Nauk SSSR, Ser. Khim., 1972, 2545.
- 2. F. Ramirez, O. P. Madan, and S. R. Heller, J. Am. Chem. Soc., 87, 731 (1965).
- 3. K. Noack and R. N. Jones, Can. J. Chem., 39, 2201, 2225 (1961).
- 4. E. V. Sobolev and V. T. Aleksanyan, Izv. Akad. Nauk SSSR, Ser. Khim., 1963, 1336.
- 5. K. Nakanishi, Infrared Absorption Spectroscopy [Russian translation], "Mir" (1965), p. 11.
- 6. L. J. Bellamy, New Data on Infrared Spectra of Complex Molecules [Russian translation], "Mir" (1971), p. 172.
- 7. R. L. Erskine and E. S. Waight, J. Chem. Soc., 1960, 3425.
- 8. L. J. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], IL (1963), p. 68.
- 9. B. A. Arbuzov, Study of Isomeric Transformations of Bicyclic Terpene Hydrocarbons and Their Oxides [in Russian], Kazan (1936), p. 44.