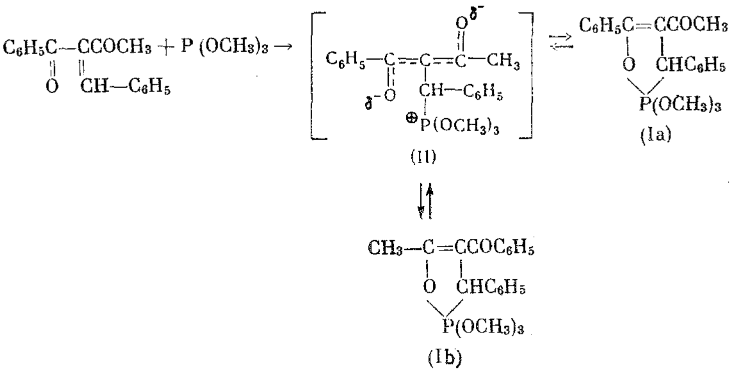
STRUCTURE AND PROPERTIES OF REACTION PRODUCTS OF BENZYLIDENEBENZOYLACETONE WITH TRIMETHYL PHOSPHITE AND DIMETHYLPHOSPHOROUS ACID

B. A. Arbuzov, N. A. Polezhaeva,
V. S. Vinogradova, G. I. Polozova,
and A. A. Musina

UDC 542.91:541.6:547.1'118

In previous papers we reported the synthesis of compounds with a phosphorane structure by the reaction of trialkyl phosphites with ethylideneacetylacetone [1, 2], and the ethylidene- [1, 2], benzylidene- [3], isopropylideneacetoacetic [4], and benzylidenebenzoylacetic [5] esters. In the present paper we studied the reaction of benzylidenebenzoylacetone with trimethyl phosphite and dimethylphosphorous acid.

Benzylidenebenzoylacetone reacts with trimethyl phosphite to give the 1 : 1 adduct (I) with mp 74-76°C and $\delta_{^{31}P}$ 27 ppm. The positive value of the ^{31}P chemical shift, the absence of the ν(P=O) band in the IR spectrum, the high values of the frequencies of the (POC) band (1080, 1107 cm^{-1}), and the easy hydrolyzability of (I) indicate that a compound with a pentacoordinated P atom is formed. Benzylidenebenzoylacetone, which has nonequivalent CO groups, can form two cyclic phosphoranes with trimethyl phosphite: 2,2,2-trimethoxy-3,5-diphenyl-4-acetyl-1,2-oxa-4-phospholene (Ia) and 2,2,2-trimethoxy-3-phenyl-4-benzoyl-5-methyl-1,2-oxa-4-phospholene (Ib)



The chemical properties of the obtained phosphorane do not permit making an unequivocal choice between forms (Ia) and (Ib). The reactions with proton-donor reagents lead to the same phosphonate independent of the structure of the phosphorane.

In the NMR spectrum of phosphorane (I), taken in CCl_4 (Fig. 1), the singlet with δ 1.70, the doublet with δ 2.13 with a slight splitting of ~1.0 Hz, and the doublet of multiplets with J_{PH} = 21 Hz, respectively, belong to the $CH_3-C=O$, $CH_3-C=$, and $C_6H_5-CH-C=$ groups. The fact that the doublet structure of the methyl at the double bond and the multiplet character of the component of the benzyl doublet are due to further proton–proton interaction via 5 bonds was shown by the double resonance experiment. It is interesting to mention that the CH_3O groups, attached to the pentacoordinated phosphorus, appear in the NMR spectrum as two doublets with δ 3.45 and 3.48 ppm ($^3J_{PH}$ = 12 Hz), with a relative intensity of 2 : 1. The presence of signals that correspond to the $CH_3-C=$ and $CH_3-C=O$ groups testifies to the presence of two phosphorane structures, (Ia) and (Ib), in the solution, which have the same chemical shift of the phosphorus

---

A. M. Butlerov Chemical Institute of the V. I. Ul'yanov–Lenin Kazan State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2071-2075, September, 1974. Original article submitted January 16, 1974.

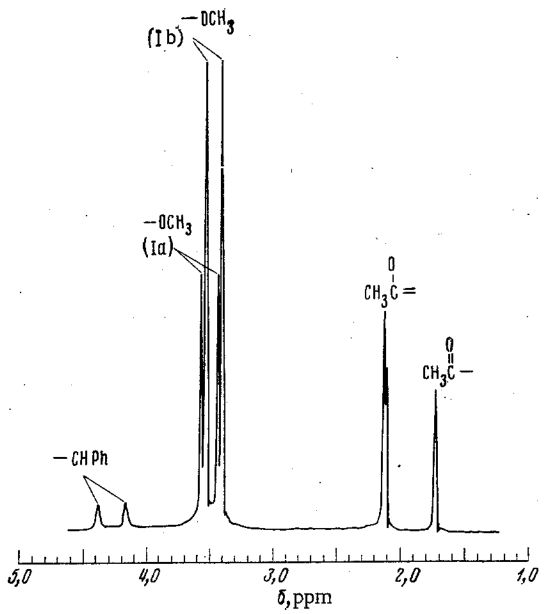


Fig. 1. NMR spectrum of phosphorane (I) in CCl_4.

nucleus. The indicated equilibrium, associated with a closure of the phosphorane ring at the different CO groups, can be accomplished via the bipolar ion (II), the concentration of which is so low that it is not recorded by the ^{31}P NMR spectra taken in various solvents. The possibility of the trimethylsilyl group migrating from the oxygen atom of one CO group to the oxygen of another in the enol ethers of β-dicarbonyl compounds was shown in [6].

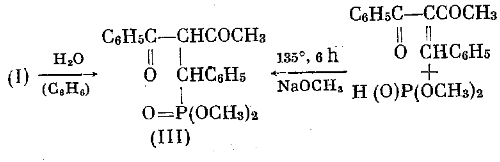
In the IR spectrum of (I) as a melt and in CCl_4 solution the absorption of the stretching vibrations is diffuse in the C=O and C=C regions. The complex band of medium intensity, with a doublet maximum of 1585 and 1598 cm^{-1}, coincides in shape and position with the analogous band in the spectrum of the liquid phosphoranes that contain an acetyl grouping [1, 2], and has additional weak shoulders at 1550 and 1648 cm^{-1}. The latter coincide with the bands in the spectrum of a phosphorane that contains a benzoyl group [7]. The character of the IR spectrum testifies to the presence of both forms (Ia) and (Ib) in solution or as a melt, in which connection each of these structures can exist as a mixture of two conformers with a variable orientation of the C=O and C=C groups. The doublet character of the bands in the region of the vibrations of the C=C and C=O groups in the IR and Raman spectra was observed by us previously for the liquid phosphoranes of close structure [2].

Phosphorane (I) is thermally unstable and at 100-120° it dissociates partially into the starting compounds, which complicates the NMR and IR spectra at elevated temperatures. The IR spectrum of the crystalline (I) is greatly simplified; strong narrow bands of the complex vibrations of the system of C=C–C=O bonds appear [8] at 1620, 1607, and 1573 cm^{-1}. The Raman spectrum* of the crystalline (I) has the lines: 1618 v.s. with a shoulder, 1630 w, 1600 m, and 1582 s. From a comparison of the IR spectrum of (I) with the spectra of the phosphoranes that contain an acetyl group in the side chain to the oxaphospholene ring [1, 2, 9] it may be concluded that the crystalline adduct exists in one form and is phosphorane (Ia), and apparently has the s-trans structure [10, 11]. The NMR spectra of α,β-unsaturated ketones do not permit distinguishing their s-cis and s-trans conformations [12], and the resonance bands correspond to a middle position between these two forms.

As a result, employing nuclear and vibrational spectroscopy, two kinds of equilibria are recorded for phosphorane (I): that associated with a closure of the phosphorane ring at different CO groups, and the equilibrium that corresponds to a variable mutual orientation of the C=O and C=C groups.

The UV spectral data are found to be in agreement with the above. In Fig. 2 (curve 1) is given the UV spectrum of phosphorane (I) in isooctane (λ_{max} 287.5 nm, log ε 3.95; λ_{min} 262.5 nm, log ε 3.70), which corresponds to a large amount of form (Ia) in isooctane. The spectrum does not have a maximum at ~250 nm, which is characteristic for the benzoyl group [7], and is close to the spectrum of 2,2,2-trimethoxy-3,5-dimethyl-4-acetyl-1,2-oxaphospholene [2]. The system of conjugated O–C=C–C=O bonds in the spectrum of the latter appears the same as the chelated system of the enolic form of acetylacetone [13]. The high value of ε in a broad range of the spectrum (~220-320 nm) indicates a greater redistribution of the electron density in the phosphorane molecule when compared with the enolic form of acetylacetone. The absorption curve of (I) is even higher in intensity and exhibits bathochromic shift.

The hydrolysis of phosphorane (I) leads to the dimethyl ester of 1-phenyl-2-acetyl-2-benzoylethylphosphonic acid (III). Phosphonate (III) is also obtained by the reaction of benzylidenebenzoylacetone with dimethylphosphorous acid



---

*The spectrum was obtained on a Coderg, Model PHO, laser Raman spectrometer.

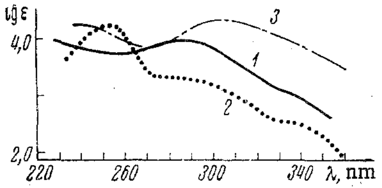
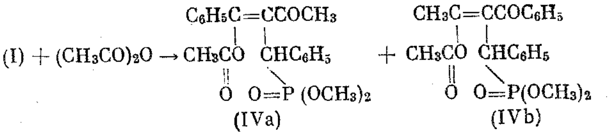


Fig. 2. Ultraviolet absorption spectra: 1) phosphorane (I) in isooctane; 2) dimethyl ester of 1-phenyl-2-acetyl-2-benzoylethylphosphonic acid (III) in CH_3OH; 3) (III) in $CH_3OH + CH_3ONa$, 1 : 2.

Based on the IR spectral data, phosphonate (III) in the crystalline state has a keto structure: absorption in the region of the vibrations of the C=C bond is absent in the spectrum, while stronger absorption is present at 1725 and 1680 (C=O), 1260 (P=O), and 1070, 1050 cm^{-1} (P–O–C).

It was interesting to study the possibility of the keto-enol tautomerism of the β-phosphono-substituted benzylbenzoylacetone (III) by the UV spectral method. The spectra were taken immediately after dissolving the compound, and after equilibrium had been established in solutions of isooctane, ether, alcohol, and water. The character of the absorption curves of (III) in all of the solvents is determined by the presence of the benzoyl group, and resembles the UV spectra of benzaldehyde, acetophenone, benzoylacetone, and C-methylbenzoylacetone [13]. Ultraviolet spectrum of (III) in CH_3OH (λ_{max}, nm): 252.5 (log ε 4.22), 285 (log ε 3.36), 320 (log ε 2.63) (see Fig. 2, curve 2); in $CH_3OH + CH_3ONa$: 240 (log ε 42.20), 305 (log ε 4.29); λ_{min} 270 (log ε 3.80) (see Fig. 2, curve 3). From the UV spectra it follows that the enolization of (III) is slight and shows little change with change in the polarity of the solvent. Phosphonate (III) exists in the enolate-ion form in methanol that contains CH_3ONa. Under the indicated conditions the UV spectrum of (III) is close to the spectrum of the enol form of benzoylacetone [13].

The treatment of phosphorane (I) with Ac_2O leads to the enol acetate. Since this reaction goes in the liquid phase, it is not excluded that a mixture of two acetates (IVa) and (IVb) is formed

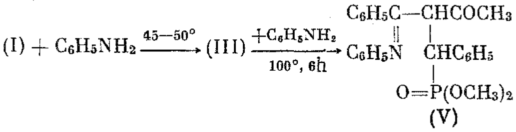


$$\text{(I)} + (CH_3CO)_2O \rightarrow \begin{array}{l} C_6H_5C{=}CCOCH_3 \\ CH_3COO\ \ CHC_6H_5 \\ \qquad O{=}P(OCH_3)_2 \end{array} + \begin{array}{l} CH_3C{=}CCOC_6H_5 \\ CH_3COO\ \ CHC_6H_5 \\ \qquad O{=}P(OCH_3)_2 \end{array}$$

(IVa) (IVb)

The IR spectrum confirms this. Besides bands at 1764 v. s. and 1630 w cm^{-1}, which are characteristic for enol acetates, the spectrum of the product has the bands of the C=O groups: acetyl at 1730 s, and benzoyl at 1678 v. s. cm^{-1}.

Aniline reacts with phosphorane (I) at 45-50°. Rupture of the P–O bond occurs first with the formation of ester (III), in which connection methylaniline is formed, which was identified as the hydrochloride. Stronger heating (100°, 6 h) leads to reaction with a second aniline molecule at the benzoyl group. However, the product could not be isolated in an analytically pure form. The IR spectrum of the crude (V) has absorption in the region of the C=O (1725) and C=N (1612 cm^{-1}) groups, while absorption in the region of the vibrations of the benzoyl and NH groups is absent



$$\text{(I)} + C_6H_5NH_2 \xrightarrow{45-50^\circ} \text{(III)} \xrightarrow[100^\circ,\ 6h]{+C_6H_5NH_2} \begin{array}{l} C_6H_5C{-}CHCOCH_3 \\ C_6H_5N\ \ CHC_6H_5 \\ \qquad O{=}P(OCH_3)_2 \end{array}$$

(V)

EXPERIMENTAL METHOD

Reaction of Benzylidenebenzoylacetone with Trimethyl Phosphite. To a solution of 2 g of benzylidenebenzoylacetone [14] in 10 ml of absolute CH_2Cl_2, in a dry N_2 atmosphere, at ~20°, was added 1 g of trimethyl phosphite in drops. The IR spectra of the reaction mixture (as a film) were taken after a day, 2 days, and 5 days. The bands of the starting benzylidenebenzoylacetone gradually disappear in the IR spectrum, and the bands of the reaction product appear. Removal of the solvent in vacuo left a viscous residue, which crystallized on long standing in hexane. We obtained 2.8 g of (I) as white crystals with mp 74-76°. Found: C 64.4; H 5.60; P 7.92%. $C_{20}H_{20}O_5P$. Calculated: C 64.69; H 5.40; P 8.35%.

Hydrolysis of (I). A mixture of 1.5 g of (I), 0.2 ml of water, and benzene was refluxed for 2 h. The residue crystallized after removal of the solvent in vacuo. We obtained 1 g of (III) as white crystals with mp 111-113° (petroleum ether–benzene). Found: P 8.53%. $C_{19}H_{21}O_5P$. Calculated: P 8.60%.

Reaction of (I) with Acetic Anhydride. To 2.6 g of (I) in a dry box at ~20° was added 0.7 g of Ac_2O in drops. The temperature rose by 6°. The mixture was heated in a dry N_2 atmosphere for 9 h at 100-105°. We obtained a viscous mass that could not be made to crystallize; n_D^{20} 1.5540. Found: P 7.56%. $C_{21}H_{23}O_6P$. Calculated: P 7.53%. An attempt to distill the product in a high vacuum resulted in decomposition.

Reaction of (I) with Aniline. A mixture of 1.9 g of (I) and 0.47 g of aniline was heated in an N_2 atmosphere at 45-50° for 16 h. We obtained (III), mp 113-114° (petroleum ether–benzene). Dry HCl was passed into the mother liquor. We isolated $C_6H_5NHCH_3 \cdot HCl$ with mp 118-120°.

Reaction of Benzylidenebenzoylacetone with Dimethylphosphorous Acid. A mixture of 1.3 g of benzylidenebenzoylacetone and 0.52 g of dimethylphosphorous acid was heated in a sealed tube at 160-170° for 8 h. We obtained 1.2 g of (III) as white crystals with mp 113-114° (petroleum ether–benzene). The mixed melting point with the hydrolysis product of the phosphorane was not depressed.

The authors express their gratitude to I. N. Shakirov for taking the Raman spectra, and to É. I. Gol'dfarb for taking the ^{31}P NMR spectra.

CONCLUSIONS

1. Trimethyl phosphite reacts with benzylidenebenzoylacetone to give the 1 : 1 adduct, which contains a pentacoordinated phosphorus atom.

2. In solution the obtained 1,2-oxaphospholene represents a mixture of two isomers, while in the solid state it has the structure of 2,2,2-trimethoxy-3,5-diphenyl-4-acetyl-1,2-oxa-4-phospholene.

3. The spectral and some of the chemical properties of the obtained phosphorane were studied.

4. Dimethylphosphorous acid adds to benzylidenebenzoylacetone to give the dimethyl ester of 1-phenyl-2-acetyl-2-benzoylethylphosphonic acid. Its keto-enol tautomerism was studied employing UV spectroscopy.

LITERATURE CITED

1. B. A. Arbuzov, N. A. Polezhaeva, V. S. Vinogradova, and Yu. Yu. Samitov, Dokl. Akad. Nauk SSSR, 173, 93 (1967).
2. B. A. Arbuzov, N. A. Polezhaeva, and V. S. Vinogradova, Izv. Akad. Nauk SSSR, Ser. Khim., 2281 (1967).
3. B. A. Arbuzov, É. N. Dianova, and V. S. Vinogradova, ibid., 1109 (1969).
4. B. A. Arbuzov, É. N. Dianova, V. S. Vinogradova, and M. V. Petrov, Dokl. Akad. Nauk SSSR, 195, 1094 (1970).
5. B. A. Arbuzov, É. N. Dianova, and V. S. Vinogradova, Izv. Akad. Nauk SSSR, Ser. Khim., 2543 (1970).
6. K. Kusnezowa, K. Rühlmann, and E. Gründemann, J. Organometal. Chem., 47, 53 (1973).
7. F. Ramirez, A. V. Patwardhan, and C. P. Smith, J. Org. Chem., 30, 2578 (1965).
8. E. V. Sobolev and V. G. Aleksanyan, Izv. Akad. Nauk SSSR, Ser. Khim.. 1336 (1963).
9. F. Ramirez, O. P. Madan, and S. R. Heller, J. Am. Chem. Soc., 87, 731 (1965).
10. K. Noack and R. Jones, Canad. J. Chem., 39, 2201, 2225 (1961).
11. K. Noack, Spectrochim. Acta, 18, 1625 (1962).
12. K. Jean, Bull. Soc. Chim. France, 704 (1965).
13. A. Gillam and E. Stern, Electronic Absorption Spectra of Organic Compounds [Russian translation], IL (1957), p. 314.
14. E. Knoevenagel, Ber., 36, 2134 (1903).