Reactions of 2,4-Dialkoxy-1,3-diphenyl-1,3,2,4-diazadiphosphetidines with Benzil, Benzalacetophenone, and *α*-Phenyliminobenzyl Phenyl Ketone

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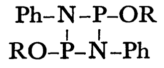
2,4-Diethoxy-1,3-diphenyl-1,3,2,4-diazadiphosphetidine (**1a**) reacted with benzil, benzalacetophenone, and α-phenyliminobenzyl phenyl ketone in refluxing *o*-dichlorobenzene to give 2-ethoxy-3,4,5-triphenyl-Δ^4-1,3,2-oxazaphospholine 2-oxide, 2-ethoxy-1,3,5-triphenyl-Δ^4-1,2-azaphospholine 2-oxide, and 2-anilino-3,4,5-triphenyl-Δ^4-1,3,2-oxazaphospholine 2-oxide, respectively. Under mild conditions, reaction of **1a** with benzil gave a Ramirez type 1:2 adduct, which thermally decomposed to give oxazaphospholine derivatives.

Mitsunobu and Mukaiyama[1)] have used "iminophosphite," ArN=POR, in phosphorylation of alcohols to dialkyl phosphites. However, analogous compounds usually exist as cyclic dimers, 1,3,2,4-diazadiphosphetidines.[2)] On heating, the dissociation of the dimer to the corresponding monomer may be expected to occur, the monomer being analogous to reactive intermediates such as phosphinylidenes (R–P=O) and phosphinothioylidenes (R–P=S).[3)]

In order to get information on these points, we investigated the structure of "alkyl phenyliminophosphites" and the reactions with 1,3-dienes and carbonyl compounds such as benzil, benzalacetophenone, and α-phenyliminobenzyl phenyl ketone.

Structure of "Alkyl Phenyliminophosphites." "Alkyl phenyliminophosphites," prepared by the reported method,[1)] were obtained as a viscous liquid, the ethyl derivative solidifying on standing for several weeks. No change of the spectral data was observed before and after solidification.



1

RO–P=N–Ph

1′

a, R=Et; b, R=Me

The mass spectrum of the ethyl derivative showed parent and base peaks at *m/e* 334 and 167, respectively, supporting the view that the structure is a cyclic dimer, 2,4-diethoxy-1,3-diphenyl-1,3,2,4-diazadiphosphetidine (**1a**). The ^{1}H-NMR spectrum showed two triplets centered at δ 1.22 and 1.25. The ratio of peak area of the triplet of δ 1.25 to that of δ 1.22 was *ca.* 1.4, indicating the existence of two ethoxy group in a different environment.

If we assume a rapid inversion on the nitrogen atoms,[4)] the existence of *cis* and *trans* isomers is possible with respect to two ethoxy groups. This was also supported by the ^{31}P-NMR spectrum. Two signals were observed at δ_P −134.9 and −182.0 ppm, the ratio of peak area being *ca.* 1.3. Since two phosphorus atoms are equivalent in this cyclic system, they should be assigned to signals of the phosphorus nuclei of *cis* and *trans* isomers.

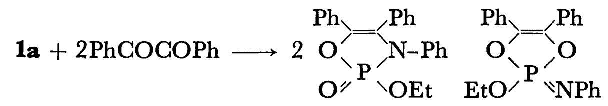
Nielsen and Pustinger[5)] observed two signals at δ_P −109.2 and −113.6 ppm in the ^{31}P-NMR spectrum of 2,4-dianilino-1,3-diphenyl-1,3,2,4-diazadiphosphetidine. It is expected in the *cis* isomer of **1a** that steric repulsion between two ethoxy groups causes repulsion of lone pair electrons on two phosphorus atoms and deshields the phosphorus nuclei. Thus, the signal in the *cis* isomer shifts considerably to a low field.

The ^{31}P-NMR spectrum of methyl derivative (**1b**) showed signals due to *trans* and *cis* isomers at δ_p −136.5 and −184.8 ppm, respectively.

Attempts to separate the *cis* and *trans* isomers of **1** were unsuccessful. The mixture was therefore used for reactions described below.

Attempted Reaction with Isoprene. If the dissociation equilibrium between **1** and **1′** was present, the resulting iminophosphite (**1′**) would be expected to undergo Diels-Alder type reaction with dienes analogously to R–P=S.[3a,c)] However, the reaction with isoprene in *o*-dichlorobenzene at 190 °C for one day in a sealed tube gave neither Diels-Alder adduct nor Ramirez type adduct, indicating that **1** does not dissociate to **1′** at 190 °C.

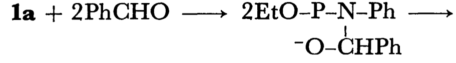
Reaction with Benzil. Under nitrogen atmosphere, benzil reacted with **1a** in refluxing *o*-dichlorobenzene to give 2-ethoxy-3,4,5-triphenyl-Δ^4-1,3,2-oxazaphospholine 2-oxide (**2**) in 17% yield. The structure was determined by elemental analysis and spectral data.



2 **3**

The IR and NMR spectra could not completely rule out another structure (**3**). However, the presence of peaks at *m/e* 268 (2,3-diphenylindole−H) and 180 (PhC≡N⁺–Ph) in the mass spectrum supports the structure **2**.

Structure **2** was also confirmed by an unequivocal synthesis by another route. The following reaction is expected to take place:[1)]



$$\mathbf{1a} + 2\mathrm{PhCHO} \longrightarrow 2\mathrm{EtO{-}\overset{+}{P}{-}N{-}Ph} \longrightarrow$$
$$\mathrm{^{-}O{-}CHPh}$$

2PhN=CHPh + 2EtO–P=O (or $(\mathrm{EtOPO})_n$)

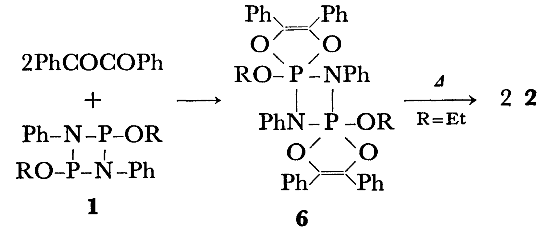
4

4 + PhCOCPh=NPh ⟶ **2**

5

Under nitrogen atmosphere, **1a** and benzaldehyde were refluxed in *o*-dichlorobenzene for 3.5 h, and then α-phenyliminobenzyl phenyl ketone (**5**) was added. After being refluxed for one day, **2** was obtained in 44% yield, the formation of *N*-benzylideneaniline being confirmed by NMR. Reaction of **4** with **5** is analogous to that of phosphinylidenes with benzil.[3b]

Under mild conditions, *viz*., in boiling benzene or in acetonitrile at room temperature, **1a** reacted with benzil to afford 5,7-diethoxy-2,3,6,9,10,12-hexaphenyl-1,4,8,11-tetroxa-6,12-diaza-5,7-diphosphadispiro[4.1.4.1]-dodeca-2,9-diene (**6a**), a Ramirez type adduct, in 44 or 18% yield, respectively.

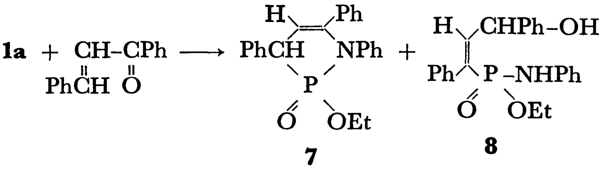


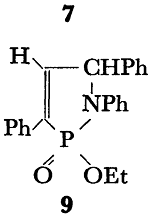
a, R=Et; b, R=Me

Similarly, **1b** reacted with benzil in acetonitrile at room temperature to give an analogous Ramirez type adduct (**6b**) in 12% yield. The ^{1}H-NMR spectrum showed complicated signals of methyl protons. These complexities can be attributed to virtual couplings observed in the ^{1}H-NMR spectra of some 2,2-diethoxy-1,3,5-triazatriphosphorine derivatives,[6] bis(dimethylamino)- and bis(methylthio)-1,3,2,4-diazadiphosphetidine 2,4-dioxides.[7]

Compound **6a** decomposed in refluxing *o*-dichlorobenzene to give **2** in 21% yield. It seems reasonable that **6** is an intermediate in the formation of **2**.

Reaction with Benzalacetophenone. Benzalacetophenone reacted with **1a** in refluxing *o*-dichlorobenzene to produce 2-ethoxy-1,3,5-triphenyl-Δ^4-1,2-azaphospholine 2-oxide (**7**) and an open-chain product (**8**), *O*-ethyl *N*-phenyl 1,3-diphenyl-3-hydroxy-1-propenylphosphonamidate, in 15 and 7% yields, respectively.



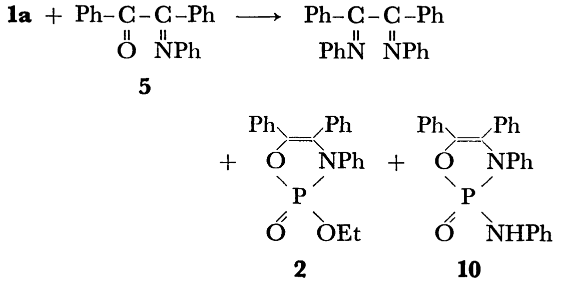


9

Another structure (**9**) is possible for **7**. The MS spectrum of **8** gave no parent peak, but the highest peak was observed at m/e 375 ($\mathrm{M^+-H_2O}$), which seems to be due to **9** formed by intramolecular dehydration of **8**. The fragmentation pattern differed from that of **7**, the base peak of **7** being at m/e 282 ($\mathrm{M^+-EtOPO-H}$), and that of **8** at m/e 193 ($\mathrm{Ph_2C_3H_3^+}$). NMR signals due to ethoxy protons exhibited doubling. This is explained by the presence of asymmetric carbon at the 2-position of **7**.

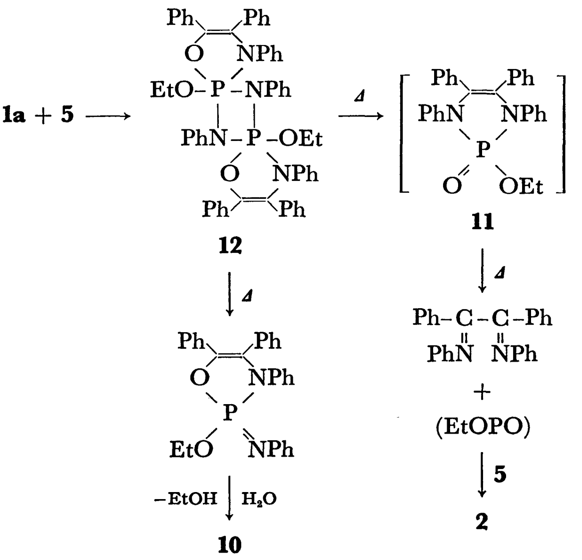
From the results, structure **7** is favored over structure **9**.

Reaction with α-Phenyliminobenzyl Phenyl Ketone. Under similar conditions, **1a** reacted with α-phenyliminobenzyl phenyl ketone (**5**) to afford α,α′-bis(phenylimino)bibenzyl, **2**, and 2-anilino-3,4,5-triphenyl-Δ^4-1,3,2-oxazaphospholine 2-oxide (**10**) in 20, trace, and 40% yields.



The expected product (**11**) corresponding to **2** and **7** was not obtained.

A possible mechanism is considered as follows, though an attempt to isolate the Ramirez type adduct (**12**) was unsuccessful.



Compound **1a** did not react with α-methoxyiminopropiophenone in a refluxing acetonitrile.

Experimental

All melting and boiling points are uncorrected. IR and mass spectra were recorded on a Hitachi EPI-G2 spectrophotometer and a Hitachi RMU-6L mass spectrometer, respectively. ^{1}H-NMR spectra were measured with Hitachi R-20 B, R-24 (60 MHz) and R-22 (90 MHz) spectrometers using TMS as an internal standard. ^{31}P-NMR spectra were determined with a Hitachi R-20 B-R-204-PB spectrometer using 85% phosphoric acid as an external standard.

All reactions were carried out under nitrogen atmosphere.

Materials. Benzil,[8] α-phenyliminobenzyl phenyl ketone,[9] and benzalacetophenone[10] were prepared by the methods given in the literature.

2,4-Diethoxy-1,3-diphenyl-1,3,2,4-diazadiphosphetidine (1a). Compound (**1a**) was prepared by the reported procedure,[1] bp 164 °C/0.2 mmHg (lit,[1]) 145—147 °C/0.08 mmHg). The viscous liquid solidified on standing for several weeks, mp 45 °C. MS: *m/e* 334 (M^+, 53%) and 167 ($M^+/2$, 100); ^{1}H-NMR (CCl_4): δ 1.22 (t, $J=7$ Hz), 1.25 (t, $J=7$ Hz), 4.1 (m, 2H, $\rangle$P–OC$\underline{H}_2$Me), and 6.7—7.35 (m, 5H, Ph). The area ratio of the signal at δ 1.25 to that at δ 1.22 was *ca.* 1.4; ^{31}P-NMR (PhH): δ_P −182.0 and −134.9 ppm. The area ratio of the signal at δ_P −134.9 to that at δ_P −182.0 ppm was *ca.* 1.3.

*2,4-Dimethoxy-1,3-diphenyl-1,3,2,4-diazadiphosphetidine (**1b**).* Compound (**1b**) was prepared by a procedure similar to that for **1a**, but could not be distilled under reduced pressure because of thermal decomposition. Thus it was used without further purification. ^{31}P-NMR (PhH): δ_P −184.8 and −136.5 ppm.

*Reaction of **1a** with Benzil.* *a) In* o*-Dichlorobenzene*: To a solution of benzil (4.20 g, 20.0 mmol) in *o*-dichlorobenzene (30 ml) was added **1a** (3.34 g, 10.0 mmol) in *o*-dichlorobenzene (10 ml) and the mixture was refluxed for 2 h. After removal of the solvent, the residue was chromatographed on a silica gel dry column with dichloromethane to afford 1.32 g (17%) of **2**, mp 146.0—146.5 °C (from ether); IR (KBr): 1650 (C=C), 1240 (P=O), and 1025 cm^{-1} (POC); NMR ($CDCl_3$): δ 1.29 (t, $J=7$ Hz, 3H, Me), 4.25 (dp, $J_{HCCH}=7$, $J_{POCH}=10$ Hz, 2H, OCH_2-), and 7.14—7.28 (m, 15H, 3Ph); MS: *m/e* 377 (M^+).

Found: C, 70.21; H, 5.11; N, 3.61%. Calcd for $C_{22}H_{20}NO_3P$: C, 70.02; H, 5.34; N, 3.71%.

b) In Benzene: To a solution of benzil (1.06 g, 5.0 mmol) in benzene (35 ml) was added **1a** (0.84 g, 2.5 mmol) in benzene (5 ml) with stirring. The mixture was refluxed for one day and the solvent was removed *in vacuo*. The residue was treated with ether to precipitate 0.835 g (1.1 mmol, 44%) of **6a**, mp 142—143 °C (dec) (from acetone). IR (KBr): 1650 (C=C) and 1020—1050 cm^{-1} (POC); ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 1.11 (t, $J=7$ Hz, 3H, $POCH_2C\underline{H}_3$), 1.24 (t, $J=7$ Hz, 3H, $POCH_2C\underline{H}_3$), 3.96 (m, 4H, $POC\underline{H}_2Me$), and 7.1—7.6 (m, 30H, 6Ph); ^{31}P-NMR (PhH): δ_P +62.8 ppm; MS: *m/e* 754 (M^+).

Found: C, 70.27; H, 5.36; N, 3.60%. Calcd for $C_{44}H_{40}N_2O_6P_2$: C, 70.02; H, 5.34; N, 3.71%.

c) In Acetonitrile: A mixture of **1a** (1.69 g, 5.05 mmol) and benzil (2.11 g, 10.0 mmol) in acetonitrile (30 ml) was stirred for one day at room temperature. The resulting precipitates were recrystallized from acetone to give **6a** (0.693 g, 18%).

*Alternative Preparation of **2**.* A mixture of **1a** (1.18 g, 3.5 mmol) and benzaldehyde (0.76 g, 7.2 mmol) in *o*-dichlorobenzene (40 ml) was refluxed for 3.5 h. To the reaction mixture was added a solution of α-phenyliminobenzyl phenyl ketone (2.00 g, 7.0 mmol) in *o*-dichlorobenzene (10 ml). The mixture was then refluxed for one day. After evaporation of the mixture, the NMR spectrum of the residue showed the presence of *N*-benzylideneaniline at δ 8.40 (s, Ph-C$\underline{H}$=). The residue was chromatographed on a silica gel dry column with dichloromethane to give crude **2** which was recrystallized from ether to give a pure sample (1.16 g, 3.1 mmol, 44%). Isolation of *N*-benzylideneaniline was unsuccessful because of the easy hydrolysis.

*Thermal Decomposition of **6a**.* A solution of **6a** (0.626 g, 0.83 mmol) in *o*-dichlorobenzene (30 ml) was refluxed for one day. After removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel dry column to afford **2** (0.131 g, 0.35 mmol, 21%).

*Reaction of **1b** with Benzil.* A solution of crude **1b** prepared from aniline (4.185 g, 45 mmol) and methyl phos phorodichloridite (2.00 g, 15 mmol) in acetonitrile (10 ml) was added to a solution of benzil (3.16 g, 15 mmol) in acetonitrile (40 ml) and the mixture was stirred for 2 days at room temperature. The resulting crystals were recrystallized from acetone to give **6b** (0.648 g, 0.89 mmol, 12%), mp 158.0—158.5 °C. IR (KBr): 1640 (C=C) and 1020—1050 cm^{-1} (POC); NMR ($CDCl_3$): δ 3.65 (m, 6H, POMe) and 7.1—7.6 (m, 30H, 6Ph); MS: *m/e* 726 (M^+).

Found: C, 69.18; H, 4.72; N, 3.60%. Calcd for $C_{42}H_{36}N_2O_6P_2$: C, 69.42; H, 4.99; N, 3.85%.

*Reaction of **1a** with Benzalacetophenone.* A solution of **1a** (1.67 g, 5.0 mmol) and benzalacetophenone (2.08 g, 10.0 mmol) in *o*-dichlorobenzene (45 ml) was refluxed for 9 h. After removal of the solvent *in vacuo*, the residue was chromatographed on a silica gel dry column with dichloromethane–carbon tetrachloride (1:1). Elution with ether from the partition of R_f 0.5—0.7 gave **7** (0.555 g, 1.47 mmol, 15%), mp 179—180 °C (from ether). IR (KBr): 1640 (C=C), 1218 (P=O), and 1038 cm^{-1} (POC); NMR ($CDCl_3$): δ 1.08, 1.32 (dt, $J=7$ Hz, 3H, $POCH_2C\underline{H}_3$), 4.07 (m, 2H, $POC\underline{H}_2CH_3$), 5.72 (d, $J_{PH}=20$ Hz, 1H, =CH–), 6.70 (m, 1H, $\rangle$CH–), and 7.0—7.7 (m, 15H, 3Ph); MS: *m/e* 375 (M^+, 75%) and 282 (PhC^+=CHCPh=NPh, 100).

Found: C, 73.84; H, 6.20; N, 3.87%. Calcd for $C_{23}H_{22}NO_2P$: C, 73.59; H, 5.91; N, 3.73%.

Elution with ethanol from the partition of R_f 0.7—0.9 gave 1.23 g of a tarry product. Treatment with a small amount of ethanol gave 0.284 g (7%) of **8**, mp 214 °C (from ethanol). An analytically pure sample could not be obtained. However, its structure was determined by the following spectral data. IR (KBr): 3260 (OH), 3100 (NH), 1630 (C=C), 1213 (P=O), and 1040 cm^{-1} (POC); NMR ($CDCl_3$): δ 1.00 (t, $J=7$ Hz, 3H, $OCH_2C\underline{H}_3$), 1.95 (s, 1H, OH), 3.64 (d, $J=7$ Hz, 1H, =CH–C$\underline{H}\langle$), 3.82 (dq, $J_{HH}=7$, $J_{PH}=10$ Hz, 2H, $POCH_2$), 6.10 (s, 1H, NH), 6.29 (t, $J_{HH}=J_{PH}=7$ Hz, 1H, =C$\underline{H}$–CH$\langle$), and 7.0—7.5 (m, 15H, 3Ph); MS: *m/e* 375 (M^+-H_2O, 47%) and 193 (100).

*Reaction of **1a** with α-Phenyliminobenzyl Phenyl Ketone.* A solution of **1a** (1.61 g, 4.8 mmol) and α-phenyliminobenzyl phenyl ketone (2.54 g, 8.9 mmol) in *o*-dichlorobenzene (40 ml) was refluxed for 24 h. After removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel dry column. Elution with dichloromethane from the first partition of R_f 0.7—1.0 gave 0.644 g (1.8 mmol, 20%) of α,α′-bis(phenylimino)bibenzyl, mp 147—148 °C (from ethanol) (lit,[11]) 142 °C); MS: *m/e* 360 (M^+). Elution with ether from the second partition of R_f 0.5—0.7 gave a trace of **2**. Elution with ether from the third partition of R_f 0.1—0.5 gave 1.66 g (3.9 mmol, 40%) of **10**, mp 164.5—165 °C (from ethanol). IR (KBr): 3150 (NH), 1640 (C=C), and 1235 cm^{-1} (P=O); NMR ($CDCl_3$): δ 6.7—7.1 (m, 10H, 2Ph), 7.24 (s, 10H, 2Ph), and 7.58 (bs, 1H, NH); MS: *m/e* 424 (M^+).

Found: C, 73.83; H, 4.95; N, 6.45%. Calcd for $C_{26}H_{21}N_2O_2P$: C, 73.58; H, 4.95; N, 6.60%.

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References

1) O. Mitsunobu and T. Mukaiyama, *J. Org. Chem.*, **29**, 3005 (1964).

2) H. W. Grimmel, A. Guenther, and J. F. Morgan, *J. Am. Chem. Soc.*, **68**, 539 (1946); J. Weiss and G. Hartmann, *Z. Naturforsch.*, **21b**, 891 (1966); E. H. M. Ibrahim, R. A. Shaw, B. C. Smith, C. P. Thakur, and M. Woods, *Phosphorus*, **1**, 153 (1971).

3) a) S. Nakayama, M. Yoshifuji, R. Okazaki, and N. Inamoto, *Chem. Commun.*, **1971**, 1186; b) M. Yoshifuji, S. Nakayama, R. Okazaki, and N. Inamoto, *J. Chem. Soc. Perkin Trans. 1* **1973**, 2065; c) S. Nakayama, M. Yoshifuji, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **48**, 546, 3733 (1975).

4) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5203 (1958).

5) M. L. Nielsen and J. V. Pustinger, Jr., *J. Phys. Chem.*, **68**, 152 (1964).

6) C. Hewlett and R. A. Shaw, *J. Chem. Soc.*, *A*, **1966**, 56.

7) M. Green, R. N. Haszeldine, and G. S. A. Hopkins, *J. Chem. Soc.*, *A*, **1966**, 1766.

8) R. Adams and C. S. Marvel, *Org. Synth.*, Coll. Vol. I, 94 (1941).

9) E. von Meyer and K. Voigt, *J. Prakt. Chem.*, **34**, 1 (1886).

10) E. P. Kohler and H. M. Chadwell, *Org. Synth.*, Coll. Vol. I, 78 (1941).

11) B. Lachowicz, *Monatsh. Chem.*, **14**, 283 (1893).