The Correct Structure of Cyclic Adducts of (Diphenylmethylene)oxophenylphosphorane with Aromatic Aldehydes

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Synopsis. The title cyclic adducts have been reported to be 4-aryl-2,3,3-triphenyl-1,2-oxaphosphetane 2-oxides. However, these compounds are concluded not to be the 1,2-oxaphosphetanes, but 1-aryl-3,4-diphenyl-3,4-dihydro-1*H*-2,3-benzoxaphosphorin 3-oxides from our detailed NMR studies and the investigation of the chemical behavior of the adduct of benzaldehyde.

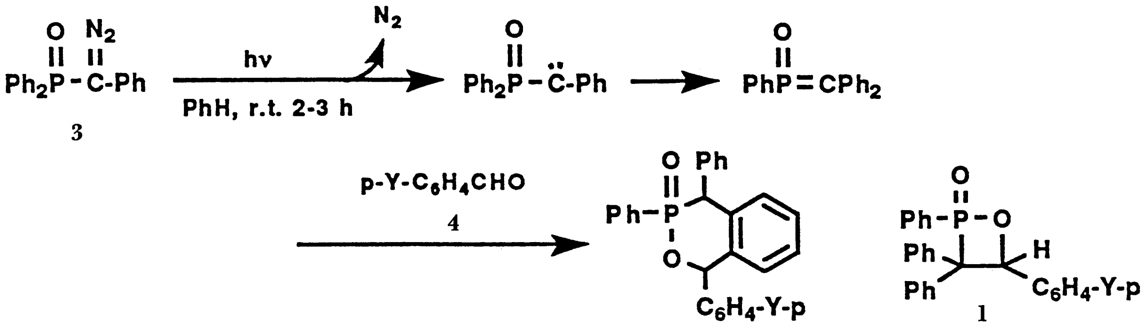
Recently, pentacoordinate 1,2-oxaphosphetanes have attracted much attention as the reactive intermediates of the Wittig reaction, which can be observed by the low temperature NMR spectroscopies.[1] 1,2-Oxaphosphetane 2-oxides, their tetracoordinate analogs, were known to be much more stable in the earlier time. Since the compound, which we reported previously as an example,[2] was not 1,2-oxaphosphetane 2-oxides, as mentioned in the preceding paper,[3] we decided to prepare 4-aryl-2,3,3-triphenyl-1,2-oxaphosphetane 2-oxides (**1**), which were reported as other examples of stable oxaphosphetane oxide,[4] in order to investigate their chemical behavior toward various nucleophiles. However, we have found that the compound prepared by the method reported in the literature are not 1,2-oxaphosphetane 2-oxides (**1**), but 3,4-dihydro-1*H*-2,3-benzoxaphosphorin 3-oxides (**2**). Here, we wish to report on the results.

Results and Discussion

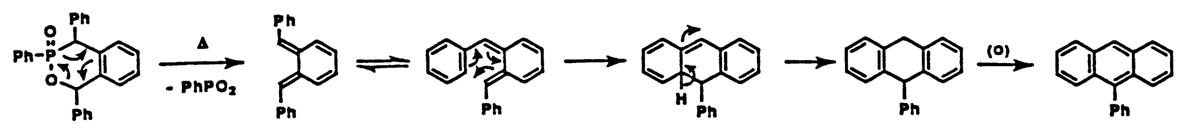
(Diphenylphosphinyl)phenyldiazomethane (**3**) was irradiated in benzene at room temperature in the presence of aromatic aldehydes (**4**) according to the literature,[4] to give a complex mixture, which was treated with MeOH to afford 1-aryl-3,4-diphenyl-3,4-dihydro-1*H*-2,3-benzoxaphosphorin 3-oxides (**2**) instead of 4-aryl-2,3,3-triphenyl-1,2-oxaphosphetane 2-oxides (**1**) as reported previously.[4]

In order to confirm the structure ^{13}C NMR spectrum was taken in various measuring modes. In the proton-noise decoupled ^{13}C NMR signals due to P$\underline{C}$ and $\underline{C}$O were observed at the expected positions for the structure of **1**, but these signals also appeared in its DEPT (distortionless enhancement by polarization transfer) spectrum, indicating that both of them are not signals due to quaternary carbon. In the detailed study of the ^{1}H NMR spectrum of **1a**, the existence of a doublet was elucidated in the region of aromatic protons. This coupling was confirmed to be that with a phosphorus nucleus by the ^{1}H-{^{31}P} NMR spectroscopy. Thus, it was clarified from both ^{1}H and ^{13}C NMR spectral data that this compound has two methine groups except aromatic protons in the molecule. In order to assign the signals, two-dimensional NMR spectra were taken. Figure 1 shows the C,H-COSY (correlation spectroscopy) spectrum of **2a**, indicating that two doublets at δ=4.7 and 6.7 correlate with two doublets at δ_C=49 and 78, respectively. From the magnitudes of coupling constants the following conclusion were drawn: one methine group is bonded directly with a phosphorus atom and the other is attached to an oxygen atom. These methines must not be bonded with each other. These facts cannot be explained from Structure **1**, but they are consistent with Structure **2**. Four continuous proton system of benzo moiety was elucidated by the H,H-COSY spectrum of **2a** as shown in Fig. 2.

Although the fragmentation pattern of mass spectrum was used as evidence for Structure **1**,[4] observation of the fragment (M$^+$-PhPO$_2$) can also be explained nicely as Structure **2**, by considering that the fragmentation takes place via the retro-Diels-Alder reaction. In order to undergo thermally this retro-Diels-Alder reaction **2a** was heated at 250 °C in toluene-d_8 in a sealed NMR tube. High-pressure liquid chromatography gave 9-phenyl-9,10-dihydroanthracene (**5**) and 9-phenylanthracene (**6**), oxidation product of **5**, in 26 and 13% yields, respectively. Dihydro compound **5** seems to be formed by the cyclization of the first product **7** of the retro-Diels-Alder reaction of **2a**. A similar result has been reported by Cava and his co-workers in the thermolysis of 1,3-



2 (a: Y=H; b: Y=OMe; c: Y=Cl)



2a 7 5 6

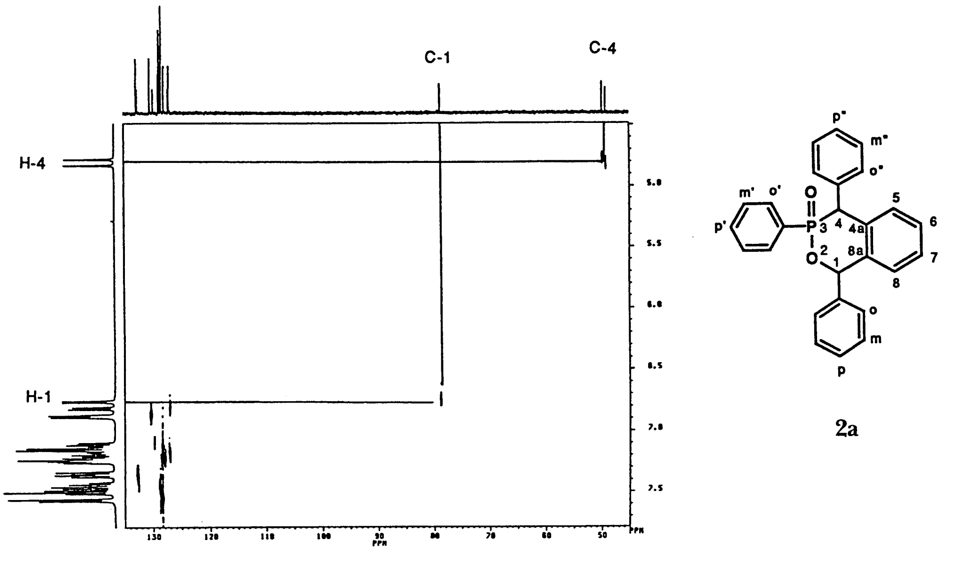


Fig. 1. The C,H-COSY Spectrum of 2a.

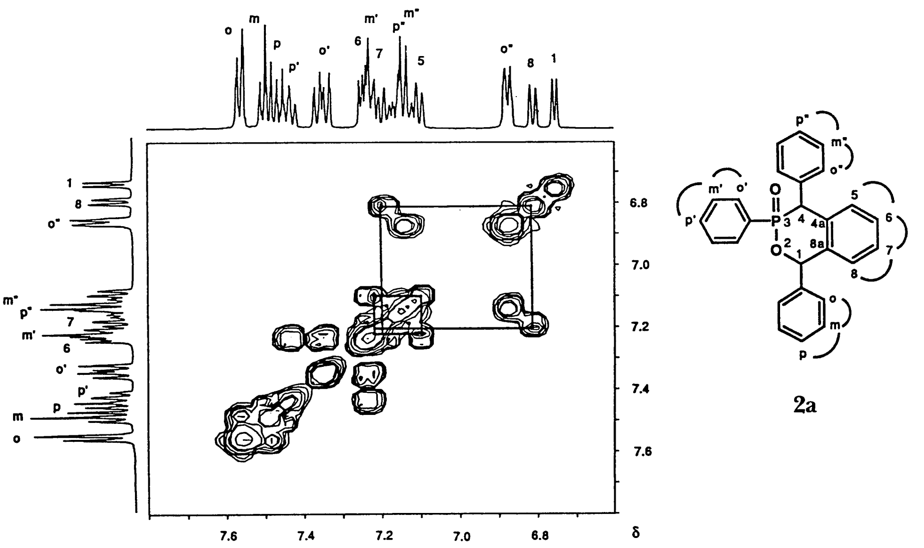


Fig. 2. The Partially H,H-COSY Spectrum of 2a.

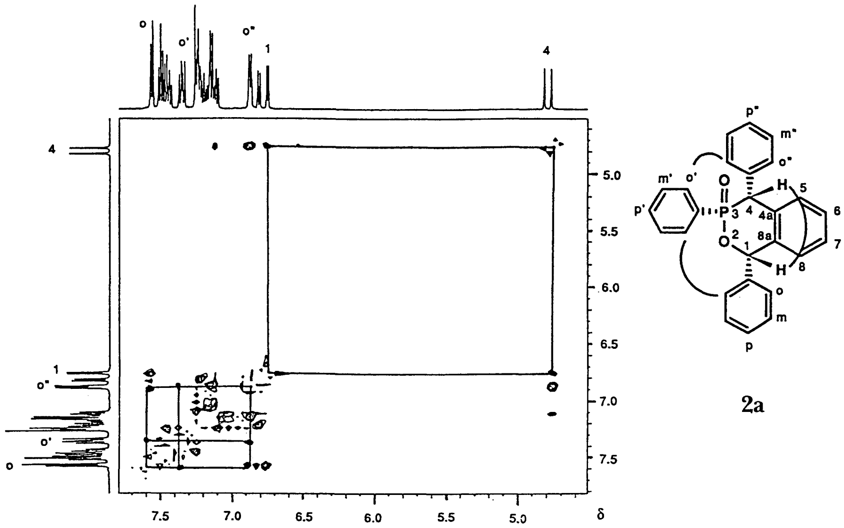
diphenyl-1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (**8**).[5] The structure with a fused benzene ring for **2a** is strongly supported by the fact that 9-phenyl-9,10-dihydroanthracene was obtained in its thermolysis. Judging from these spectral data and chemical behavior it is reasonably concluded that the compound is not 1,2-oxaphosphetane 2-oxide, but 2,3-benzoxaphosphorin 3-oxide. For 2,3-benzoxaphosphorin ring system only one example has been reported until now.[6]

The stereochemistry of **2a** was also studied. The NOESY (nuclear Overhauser effect spectroscopy) spectrum of **2a** (Fig. 3) shows the cross peaks between H-1 and H-4 and between ortho-protons of three phenyl groups, indicating that all phenyl groups are cis.

Experimental

All melting points are uncorrected. ^{1}H NMR spectra were measured with a Bruker AM-500 (500.13 MHz) spectrometer using tetramethylsilane (TMS) as an internal standard. ^{13}C NMR and ^{31}P NMR spectra were taken with a Bruker AM-500 (125.77 MHz) using TMS as an internal standard and with a JEOL FX-90Q spectrometer using 85% H_3PO_4 as an external standard, respectively. Mass spectra were recorded with a JEOL 300-D mass spectrometer.

Photolysis of (Diphenylphosphinyl)phenyldiazomethane (3) in the Presence of Aromatic Aldehydes (4). A benzene (20 ml) solution of **3** (0.207 g, 0.649 mmol), which was prepared by the method described in the literature using *n*-BuLi instead of PhLi,[7] and benzaldehyde (**4a**) (0.198 ml,



2a

Fig. 3. The NOESY Spectrum of 2a.

1.95 mmol) was irradiated with a 100-W medium-pressure mercury arc lamp for 2.5 h at room temperature under nitrogen atmosphere. After removal of the solvent the residue was treated with methanol to give crude 1,3,4-triphenyl-3,4-dihydro-1*H*-2,3-benzoxaphosphorin 3-oxide (**2a**), whose physical and spectral data agreed with those reported as 2,3,3,4-tetraphenyl-1,2-oxaphosphetane 2-oxide. Recrystallization from methanol afforded pure **2a** in 14% yield.

2a: mp 254—257 °C (decomp). ^{1}H NMR (CDCl$_3$)[8] δ= 4.80 (1H, d, $^{2}J_{\mathrm{H,P}}$=24.4 Hz, PC$\underline{\mathrm{H}}$Ph), 6.75 (1H, d, $^{3}J_{\mathrm{H,P}}$=5.8 Hz, POC$\underline{\mathrm{H}}$Ph), 6.81 (1H, d, $^{3}J_{\mathrm{H,H}}$=7.6 Hz, H-8), 6.86—6.89 (2H, m, ortho-H of C(4)-Ph), 7.10 (1H, d, $^{3}J_{\mathrm{H,H}}$=7.5 Hz, H-5), 7.11—7.27 (7H, m, H-6, H-7, meta and para-H of C(4)-Ph, and meta-H of P-Ph), 7.33—7.38 (2H, m, ortho-H of P-Ph), 7.41—7.52 (4H, m, para-H of P-Ph, meta and para-H of C(1)-Ph), and 7.54—7.58 (2H, m, ortho-H of C(1)-Ph). ^{13}C NMR (CDCl$_3$)[8] δ_{C}=49.47 (d,[9] $^{1}J_{\mathrm{C,P}}$=81.1 Hz, P$\underline{\mathrm{C}}$HPh), 78.73 (d, $^{2}J_{\mathrm{C,P}}$=8.0 Hz, PO$\underline{\mathrm{C}}$HPh), 127.04 (s, C-7 and C-8), 127.19 (d, $^{5}J_{\mathrm{C,P}}$=3.3 Hz, para-C of C(4)-Ph), 127.94 (d, $^{3}J_{\mathrm{C,P}}$=13.3 Hz, meta-C of P-Ph), 128.33 (s, ortho-C of C(1)-Ph), 128.35 (d, $^{4}J_{\mathrm{C,P}}$=3.8 Hz, meta-C of C(4)-Ph), 128.43 (d, $^{1}J_{\mathrm{C,P}}$=140.2 Hz, ipso-C of P-Ph), 128.50 (s, C-6), 128.90 (s, para-C of C(1)-Ph), 129.75 (d, $^{3}J_{\mathrm{C,P}}$=9.0 Hz, C-5), 130.35 (d, $^{3}J_{\mathrm{C,P}}$=5.2 Hz, ortho-C of C(4)-Ph), 132.51 (d, $^{4}J_{\mathrm{C,P}}$=2.7 Hz, para-C of P-Ph), 132.71 (d, $^{2}J_{\mathrm{C,P}}$=9.4 Hz, ortho-C of P-Ph), 134.17 (d, J=4.8 Hz), 134.82 (d, J=4.7 Hz), 137.29 (d, J=5.7 Hz) (C-4a, C-8a, ipso-C of C(1)-Ph), and 138.55 ($^{3}J_{\mathrm{C,P}}$=9.5 Hz, ipso-C of C(1)-Ph). ^{31}P NMR (CDCl$_3$) δ_{P}=35.47. Compounds **2b** and **2c** were obtained in 12 and 14% yields, respectively, as described above.[10]

Thermolysis of 2a. A solution of **2a** (10 mg, 0.025 mmol) in d_8-toluene (1 ml) was heated at 250 °C for 7 h in a degased sealed NMR tube until starting material disappeared completely. ^{1}H NMR showed a new AB quartet at δ=3.92. The solvent was distilled with a Kugelrohr to give tarry material, which was subjected to high-pressure liquid chromatography (column: Japan Analytical Industries: JAIGEL 1H, 2H) to afford 9-phenyl-9,10-dihydroanthracene (**5**)[11] and 9-phenylanthracene (**6**) in 26 and 13% yields, respectively. Besides these hydrocarbons some of unidentified products containing a phosphorus atom were obtained. Dihydro compound **5** was oxidized readily on silica gel to afford **6**.

5: ^{1}H NMR (CDCl$_3$) δ=3.91 (1H, d, $^{2}J_{\mathrm{H,H}}$=18.1 Hz, C$\underline{\mathrm{H}}$H'), 4.02 (1H, d, $^{2}J_{\mathrm{H,H}}$=18.1 Hz, CH$\underline{\mathrm{H'}}$), 5.26 (1H, s, C$\underline{\mathrm{H}}$Ph), 7.06—7.09 (2H, m, ortho-H of Ph), 7.12—7.16 (1H, m, para-H of Ph), 7.19—7.23 (6H, m, meta-H of Ph, H-1, H-2, H-7, H-8), 7.29—7.33 (4H, m, H-3, H-4, H-5, H-6). ^{13}C NMR (CDCl$_3$) δ_{C}=35.65 (t,[12] C-10), 51.42 (d, C-9), 126.19 (d), 126.35 (d), 126.40 (d), 127.75 (d), 128.04 (d), 128.41 (d), 128.43 (d), 136.42 (s), 139.48 (s), 143.57 (s). High-resolution mass spectrum (70 eV): m/z Found: 256.1244. Calcd for $\mathrm{C_{20}H_{16}}$: 256.1250. Compound **6** agreed with authentic sample.

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8) These assignments are supported by ^{1}H-{^{31}P} and ^{13}C-{^{31}P} NMR spectra and two-dimensional NMR (H,H-COSY and C,H-COSY) spectroscopies.

9) Abbreviations show a coupling manner with a phosphorus nucleus.

10) The physical and spectral data of **2b** and **2c** are deposited as Document No. 9100 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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12) Abbreviations show a coupling manner with proton.