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Reactions of Diphenylcyclopropenone with Trivalent Phosphorus Compounds*

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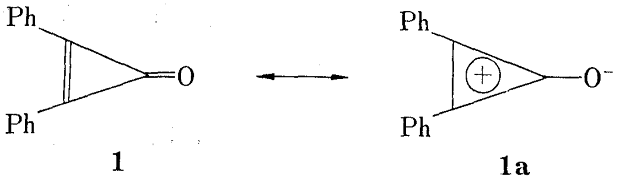
Diphenylcyclopropenone (**1**) reacted readily with trivalent phosphorus compounds (**2a**—**e**) to afford the new type of phosphoranes, ketene-phosphoranes (**4a**—**e**). These ketene-phosphoranes as intermediates further reacted with **1** to give five-membered unsaturated lactone derivatives (**9**, **15**) or rearranged to the novel phosphine (**13**).

The ketene-phosphorane (**4a**) derived from **1** and triphenylphosphine (**2a**) is the first example of the isolated phosphorane possessing the ketene group in a molecule, whose efficiency for the synthesis of cinnamic acid derivatives and the cyclobutenedione derivative is attractive.

Since the first preparation of diphenylcyclopropenone (**1**) by Breslow, *et al.*[2] and Vol'pin, *et al.*,[3] there have been reported many reactions involving an attack of nucleophilic reagents, such as diazomethane[4] and isonitrile,[5] on either the carbonyl carbon or the double bond, indicative of strong contribution of the polarized structure (**1a**).

We describe here the new type of reactions of **1** with trivalent phosphorus compounds (**2a**—**e**) to give interesting products, whose formations could be rationally explained by the route *via* the ketene-phosphoranes (**4a**—**e**).



1 **1a**

(I) Triphenylphosphine (2a)

The reaction of **1** with **2a** in a 1:1 molar ratio gave 92% yield of α-triphenylphosphoranylidenebenzylphenylketene (**4a**),[6] which was presumably formed *via* a betaine intermediate (**3**) as described in Chart 1. Thus, the first step was the nucleophilic attack of **2a** on the electrophilic cyclopropenone ring, followed by the cleavage of the cyclopropene ring. This reaction pattern is similar to that of **1** with isonitrile previously described.[5]

The structure of **4a** was established by the infrared spectrum which showed the strong ketene absorption at 2064 cm^{-1}, the elemental analysis and the molecular weight determination (M$^+$; 468) as well as the following reactions.

The reactions of **4a** with absolute methanol and α-phenyl-*trans*-cinnamic acid in dry benzene gave methyl α-phenyl-*trans*-cinnamate (**5**)[7] (89%) and α-phenyl-*trans*-cinnamic anhydride (**6**) (90%)[8] respectively, in addition to the quantitative recovery of **2a**. Similarly, 2,6-xylidine and 2,6-dimethylphenylisonitrile afforded N-(2,6-dimethylphenyl)-α-phenyl-*trans*-cinnamamide

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* Dedicated to the memory of Prof. Eiji Ochiai.

[1] Location: *Hongo 7-3-1, Bunkyo-ku, Tokyo.*

[2] R. Breslow, R. Haynie, and J. Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959).

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[5] N. Obata and T. Takizawa, *Tetrahedron Letters*, **1969**, 3403.

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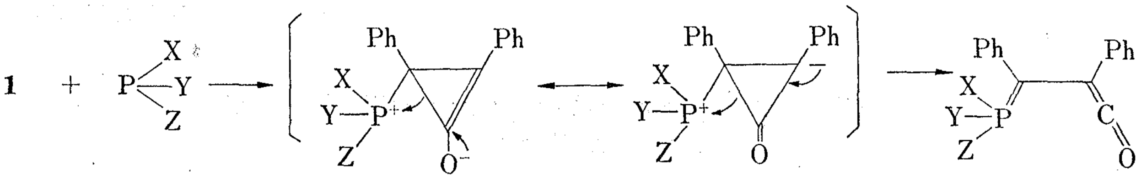

2a–e 3 4a–e

a: X=Y=Z=Ph b: X=Y=Z=OC_2H_5 c: X=Y=Z=$N(C_2H_5)_2$
d: X=Y=Ph, Z=$N(C_2H_5)_2$ e: X=Y=Ph, Z=Cl
Ph=phenyl

Chart 1

(**7**) (97%) and N-(2,6-dimethylphenylimino)-2,3-diphenylcyclobuten-1-one (**8**) (90%)[9] respectively.

The structure of **7** was confirmed by the elemental analysis, the molecular weight determination (M^+; 327) and the spectral data.

On the other hand, **4a** unlike usual ylides did not react with benzophenone and benzaldehyde. These facts indicate that the nucleophilic attack takes place preferentially on the ketene group rather than the ylide group. The reactions would proceed through the concerted pathway involving facile elimination of **2a** as illustrated in Chart 2.

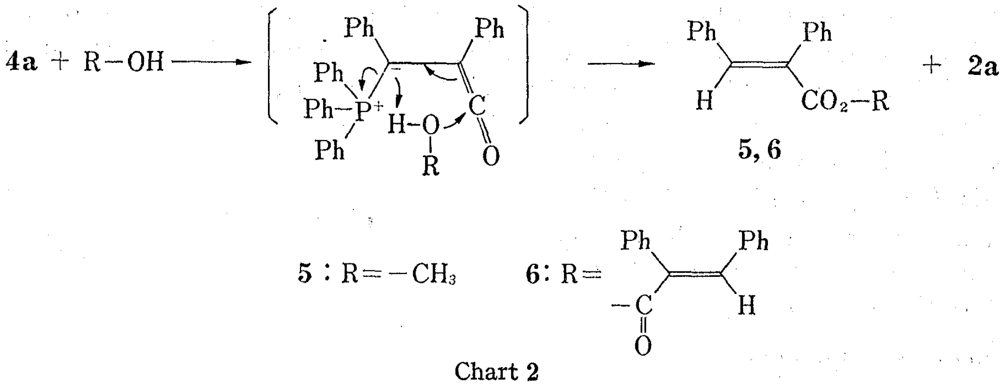

Chart 2

(II) Triethylphosphite (2b)

The treatment of **1** with an equimolar quantity of **2b** (60 hr) gave **9** (mp 183°, M^+; 412) in 6% yield, while at the molar ratio 1:0.06 (30 days), the yield increased to 60%. The spectral data of **9** [IR(KBr) cm^{-1}: 1810, 1740 and 1445. UV λ_{max}^{EtOH} mμ (log ε): 313 (4.45), 295 (4.59), 283 (4.55), 228 (4.58) and 220 (4.57).] were identical with those of the authentic sample prepared by the pyrolysis of **1**.[4] The presence of absolute methanol gave **5** (10.5%), ethyl α-phenyl-*trans*-cinnamate (**10**) (3%) and methyl 1,2-diphenyl-2-dimethoxyphosphinylpropionate (**11**) (80%). The structure of **11** was established by the elemental analysis, the molecular weight determination (M^+; 348) and its spectral data. The nuclear magnetic resonance (NMR) spectrum of **11** showed the signals of methoxy groups and not ethoxy groups. Further, the signal of proton a was observed at δ 4.62 (d.d. J=8 cps, P–CH_a) and that of proton b at δ 3.84 (d.d. J=19 cps, P–C–CH_b). The assignment of the protons a and b depended on the fact that the coupling constant between the phosphorus atom and the α proton is smaller than that between the phosphorus atom and the β proton in phosphorus compounds.[10]

The formation of **9** and **11** could be explained by the routes *via* the ketene-phosphorane (**4b**), of which existence in the reaction mixture was suggested by observation of an absorption at 2100 cm^{-1} in the infrared (IR) spectrum. The formation of **12** as a labile compound was supported by the NMR spectrum of crude products, which showed the signal due to the proton

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[9] N. Obata and T. Takizawa, *Tetrahedron Letters*, **1970**, 2231.
[10] M. Yoshifuji, *Yuki Gosei Kagaku Kyokai Shi*, **28**, 177 (1970).

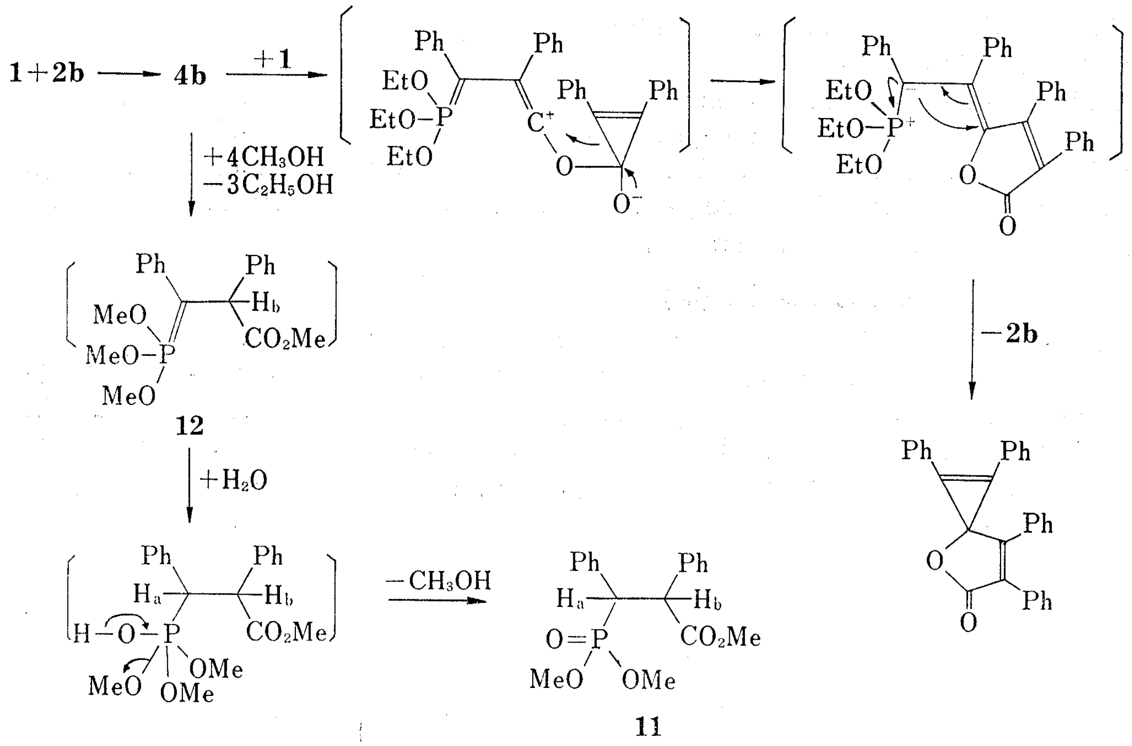

Chart 3

b at δ *ca*. 3.8 and the absence of ethoxy group. As shown in Chart 3, the addition of water to **12** at the stage of the separation by the column chromatography, followed by elimination of **16** methanol, gave **11** as an isolable product. The formation of **10** would be analogous to that of **5**, and the ethoxy group would come from the ethanol derived from transesterification of the P–OEt group with methanol.

(III) Tris(diethylamino)phosphine (2c) and Diphenyldiethylaminophosphine (2d)

In the reaction of **1** with **2c** at room temperature, the IR spectrum of the reaction mixture showed the strong absorptions at 2060 cm⁻¹ and 2140 cm⁻¹ (νC=C=O) after 2 min, and at 1630 cm⁻¹ (νC=O) after 10 min. The intensity of the absorption at 1630 cm⁻¹ increased gradually with decreasing of that of the ketene group, and the absorptions of **1** and the ketene group disappeared after 6 hr perfectly. This observation indicates the formation of **4c** and further rearrangement of the amino group to the ketene group. The reaction of **1** with **2d** afforded N,N-diethyl-α-phenyl-β-diphenylphosphino-*trans*-cinnamamide (**13**) in high yield, providing the proof of the rearrangement of the diethylamino group. The structure of **13** was established by the elemental analysis, the molecular weight determination (M+; 463) and its spectral data. The fact that the ultraviolet (UV) spectrum of **13** was similar to that of *cis*-stilbene indicated the intramolecular rearrangement of the amino group.

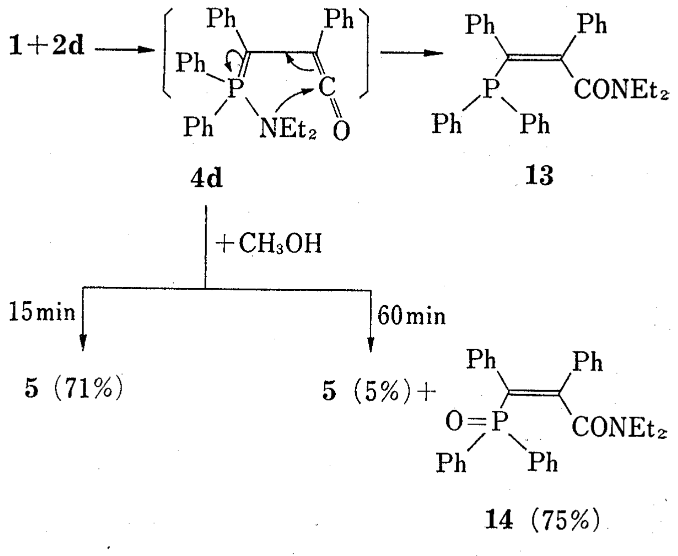

Chart 4

The formation of **13** could be reasonably explained by the route via the ketene-phosphorane (**4d**) as described in Chart 4.

Addition of methanol after 15 min, in the analogous reaction, gave **5** alone in 71% yield, but after 60 min gave N,N-diethyl-α-phenyl-β-diphenylphosphinyl-*trans*-cinnamamide (**14**) as the main product. This difference indicated the easy rearrangement of the amino group. The formation of the phosphine oxide (**14**) could be due to the air oxidation of **13** at the separation step by the column chromatography.

(IV) Diphenylphosphinous Chloride (2e)

The reaction of **1** with **2e** at molar ratio 2: 1 gave the dark red phosphorane derivative (**15**), α,β-diphenyl-γ-(1,2-diphenyl-1-diphenylchlorophosphoranylidene-2-ethylidene)-$\Delta^{\alpha,\beta}$-butenolide. In this case only the phosphorane (**15**) having a butenolide skeleton was obtained and neither rearrangement of chloride nor elimination of **2e** was observed. Hydrolysis of **15** with aqueous benzene afforded easily α,β-diphenyl-γ-(1,2-diphenyl-1-diphenylphosphinyl-2-ethylidene)-$\Delta^{\alpha,\beta}$-butenolide (**16**).

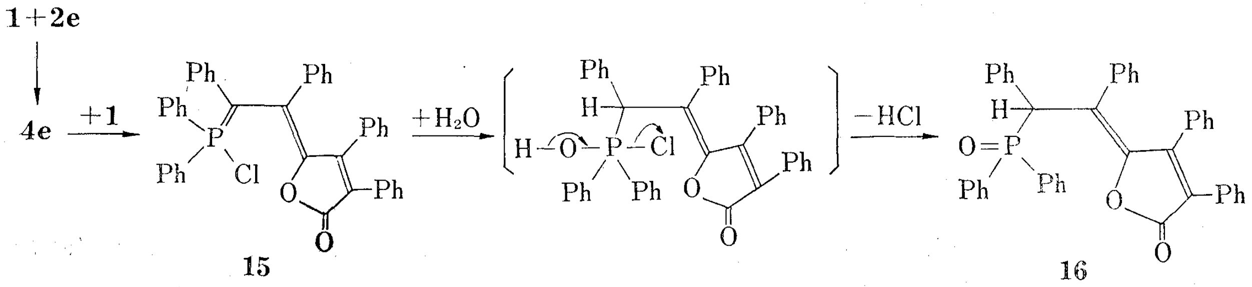

Chart 5

The structure of **16** was determined by elemental analysis, molecular weight determination by mass spectrometry, and its IR, UV and NMR spectral data. Although the data for determining the structure of **15** were not sufficient, because of the instability of **15**, the formation of **16** supported the structure of **15**. In the presence of absolute methanol the reaction of **1** with **2e** yielded methyl 1,2-diphenyl-2-diphenylphosphinylpropionate (**17**), and the mechanism for the formation of **17** would be analogous to that of **11**.

Experimental[11]

Materials——Diphenylcyclopropenone (1) was prepared according to the reported method.[4] Tris(diethylamino)phosphine (2c),[12] diphenyldiethylaminophosphine (2d)[13] and diphenylphosphinous chloride (2e)[14] were prepared by the reported method. Triphenylphosphine (2a) and triethylphosphite (2d) were obtained from Tokyo Chemical Industries, Ltd., and Wako Pure Chemical Industries, Ltd., respectively and the former was used without purification and the latter was purified by distillation.

Reaction of 1 with Triphenylphosphine (2a)——A dry benzene solution (30 ml) of **1** (2.06 g, 10 mmole) and **2a** (2.62 g, 10 mmole) was stirred at room temperature under nitrogen for 3 hr during which time the solution became orange. Removal of the solvent *in vacuo* and trituration of the residual oil with dry *n*-hexane and a small portion of dry CH_2Cl_2 afforded an orange solid, which was recrystallized under nitrogen

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11) All melting points were taken in Yanaco micro melting point apparatus and are uncorrected. The infrared spectra were recorded on a spectrophotometer, DS-402G, of the Japan Spectroscopic Co. The electronic spectra were measured on a Hitachi spectrometer, model EPS-3T. All NMR spectra were recorded on a Hitachi R-24 High Resolution NMR spectrometer, tetramethylsilane (TMS) being used as the internal standard.
The mass spectra were determined on a JEOL LTD, JMS-9-SG-2 mass spectrometer.

12) C. Stuebe and H.P. Laukelma, *J. Am. Chem. Soc.*, **78**, 976 (1956).

13) G. Ewart, D.S. Payne, A.L. Porte, and A.P. Lane, *J. Chem. Soc.*, **1962**, 3984.

14) L. Hornre, P. Beck, and V.G. Toscano, *Chem. Ber.*, **94**, 2122 (1961); C. Stuebe, W.M. Lesuer, and G.R. Norman, *J. Am. Chem. Soc.*, **77**, 3526 (1955).

from dry *n*-hexane–CH_2Cl_2 to give **4a**[15] as orange crystals; 4.35 g (92%) .mp 125—127°. IR (KBr) cm^{-1}: 2064, 1430, 1260 and 1180. Mol. wt. Calcd. for $C_{33}H_{25}OP$: 468. Found: 468 (by mass). *Anal.* Calcd. for $C_{33}H_{25}OP$: C, 84.61; H, 5.34. Found: C, 784.53; H, 5.52.

Reaction of 4a with Methanol——To a solution of **4a** (300 mg, 0.64 mmole) in 5 ml of dry benzene at room temperature was added 10 ml of absolute methanol. The reaction mixture was allowed to stand at room temperature for 1 hr and then the solvent was evaporated and the residue was chromatographed over silica gel, giving 160 mg (90%) of **2a** and 135 mg (89%) of **5**.

Reaction of 4a with α-Phenyl-*trans*-cinnamic Acid——To a solution of **4a** (468 mg, 1 mmole) in 10 ml of dry benzene and 10 ml of dry CH_2Cl_2 was added 224 mg (1 mmole) of α-phenyl-*trans*-cinnamic acid at room temperature under nitrogen. The reaction mixture was stirred at room temperature for 0.5 hr. The solvent was evaporated and the residue was chromatographed over silica gel, affording 260 mg (99%) of **2a** and 385 mg (90%) of **6**.

Reaction of 4a with 2,6-Xylidine——The solution of **4a** (586 mg, 1.25 mmole) and 303 mg of 2,6-xylidine in 10 ml of dry benzene was stirred at 50° under nitrogen for 19 hr. The solvent was evaporated and the residue was chromatographed over silica gel, giving 325 mg (99%) of **2a** and 396 mg (97%) of **7**. Recrystallization of **7** from *n*-hexane–benzene gave colorless needles; mp 132—133°. IR (KBr) cm^{-1}: 3380, 1660, 1615 and 1475. NMR ($CDCl_3$) δ: 7.96 (1H, s, –CH=), 7.6—7.0 (13H, m, aromatic), 6.90 (1H, broad s, NH) and 2.20 (6H, s, CH_3). UV $\lambda_{\max}^{\mathrm{CH_3CN}}$ mμ (log ε): 279 (4.35). Mol. wt. Calcd. for $C_{23}H_{21}ON$: 327. Found: 327 (by mass). *Anal.* Calcd. for $C_{23}H_{21}ON$: C, 84.34; H, 6.48; N, 4.28. Found: C, 84.12; H, 6.41; N, 4.41.

Reaction of 4a with 2,6-Dimethylphenylisonitrile——The solution of **4a** (260 mg, 0.56 mmole) and 2,6-dimethylphenylisonitrile (80 mg, 0.61 mmole) in 20 ml of dry benzene was stirred at room temperature under nitrogen for 2 hr. The solvent was evaporated and the residue was chromatographed over silica gel, affording 140 mg (96%) of **2a** and 175 mg (90%) of iminocyclobutenone (**8**).

Reaction of 1 with Triethylphosphite (2b)——A dry benzene solution (10 ml) of **1** (824 mg, 4 mmole) and **2b** (664 mg, 4 mmole) was allowed to stand at room temperature under nitrogen for 60 hr.

The solvent was evaporated and the oily product was chromatographed over silica gel, giving 50 mg (6%) of **9** (mp 183°, Lit.[4] 181—182°). At the molar ratio 1: 0.06, for 30 days, **9** was obtained in 60% yield.

Reaction of 1 with 2b in Methanol——To a solution of **1** (412 mg, 2 mmole) in 10 ml of absolute methanol was added 332 mg (2 mmole) of **2b**. The reaction mixture was stirred at room temperature under nitrogen for 15 hr. The solvent was evaporated and the residue was chromatographed on silica gel, giving 50 mg (10.5%) of **5**, 14 mg (3%) of **10** and 556 mg (80%) of **11**. The compound **10** was identified by the comparison with its authentic sample. The compound **5** and **10** could be separated by using the mixture of *n*-hexane and ether (19: 1) as the eluent.

Recrystallization of **11** from *n*-hexane–CH_2Cl_2 gave colorless needles; mp 148.0—148.5°. IR (KBr) cm^{-1}: 1735, 1455, 1270, 1245, 1210 and 1150. NMR ($CDCl_3$) δ: 7.6—7.2 (10H, m, aromatic), 4.62 (1H, d,d., $J=8$ and 12 cps, P–CH), 3.84 (1H, d.d., $J=19$ and 12 cps, P–C–CH), 3.32 (3H, s, CO_2CH_3), 3.10 (3H, d, $J=8$ cps, P–OCH_3) and 3.02 (3H, d, $J=8$ cps, P–OCH_3). UV $\lambda_{\max}^{\mathrm{CHCl_3}}$ mμ (log ε): 241 (2.76), 244 (2.66), 255 (2.66), 261 (2.84), 267 (2.76) and 272 sh (2.54). *Anal.* Calcd. for $C_{18}H_{21}O_5P$: C, 62.06; H, 6.08. Found: C, 62.08; H, 6.14.

Reaction of 1 with Tris(diethylamino)phosphine (2c)——To a solution of **1** (412 mg, 2 mmole) in 10 ml of dry tetrahydrofuran (THF) was added 494 mg (2 mmole) of **2c**. The reaction mixture was stirred at room temperature under nitrogen for 20 hr and 1 ml of methyl iodide was added and then the reaction mixture was stirred for additional 10 min. Solvent removal and chromatography on silica gel with elution by dry benzene gave 335 mg (29%) of colorless crystals[presumably methylbis(diethylamino)-β-N,N-diethylaminocarbonyl-*cis*-stilbenylphosphonium iodide]; mp 235—239°. IR (KBr) cm^{-1}: 3180, 2880, 1630, 1445, 1385, 1307 and 1150. UV $\lambda_{\max}^{\mathrm{CHCl_3}}$ mμ (log ε): 285 (3.93). *Anal.* Calcd. for $C_{28}H_{43}ON_3PI$: C, 58.02; H, 7.47; N, 7.25. Found: C, 58.33; H, 7.23; N, 7.92.

Reaction of 1 with Diphenyldiethylaminophosphine (2d)——A dry benzene solution (10 ml) of **1** (824 mg, 4 mmole) and **2d** (1028 mg, 4 mmole) was stirred at room temperature under nitrogen for 2 hr. The solvent was removed *in vacuo* and the residue was treated with dry *n*-hexane and filtered. Recrystallization of the solid from *n*-hexane–CH_2Cl_2 gave colorless crystals of **13** (1730 mg, 93%); mp 141—142°. IR (KBr) cm^{-1}: 1620, 1485, 1430, 1270, 1220, 1140, 830 and 745. NMR ($CDCl_3$) δ: 8.0—7.4 (20H, m, aromatic), 3.44 (2H, q, $J=8$ cps, –CH_2–), 3.41 (2H, q, $J=8$ cps, –CH_2–), 1.18 (3H, t, $J=8$ cps, –CH_3) and 0.86 (3H, t, $J=8$ cps, –CH_3). UV $\lambda_{\max}^{\mathrm{CHCl_3}}$ mμ (log ε): 261 (4.34). Mol. wt. Calcd. for $C_{31}H_{30}ONP$: 463. Found: 463 (by mass). *Anal.* Calcd. for $C_{31}H_{30}ONP$: C, 80.32; H, 6.52; N, 3.02. Found: C, 80.22; H, 6.81; N, 2.99.

Reaction of 1 with 2d in the Presence of Methanol——A dry benzene solution (20 ml) of **1** (412 mg, 2 mmole) and **2d** (514 mg, 2 mmole) was stirred at room temperature for 15 min and 5 ml of absolute methanol was added, and then the reaction mixture was stirred for additional 2 hr. Solvent removal and chromato-

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[15] **4a** is sensitive to moisture but could be stored at room temperature in dry condition for a week or so without any detective decomposition.

graphy on silica gel gave 340 mg (71%) of **5**. While methanol was added after 60 min, 23 mg (5%) of **5** and 717 mg (75%) of **14** were obtained.

The compound **14**; colorless crystals, mp 185—186° (from *n*-hexane–CH_2Cl_2). IR (KBr) cm^{-1}: 1620, 1590, 1570, 1480, 1435, 1270 and 1185. NMR ($CDCl_3$) δ: 8.0—6.7 (20H, m, aromatic), 3.28 (2H, broad s, $-CH_2-$), 3.04 (2H, broad s, $-CH_2-$), 1.04 (3H, t, $J=8$ cps, $-CH_3$) and 0.66 (3H, t, $J=8$ cps, $-CH_3$). UV $\lambda_{max}^{CHCl_3}$ mμ (log ε): 270 (4.30). *Anal.* Calcd. for $C_{31}H_{30}O_2NP$: C, 77.64; H, 6.30; N, 2.92. Found: C, 77.70; H, 6.15; N, 3.14.

Reaction of 1 with Diphenylphosphinous Chloride (2e)——To a solution of **1** (6.18 g, 0.30 mole) in 60 ml of dry benzene was added 3.30 g (0.15 mole) of **2e** at room temperature under nitrogen. The reaction mixture was stirred at room temperature. The solution turned to dark red with gradual formation of crystalline precipitates. After 20 hr the solution was condensed to *ca.* 20 ml and then 30 ml of dry ether was added to it. The dark red crystalline precipitates were removed by filtration and then washed with two 20 ml portions of dry benzene–ether under nitrogen. There was obtained 7.86 g (83%) of **15**16); mp 150—155°. IR (KBr) cm^{-1}: 1760, 1735, 1480, 1435 and 1245. Mol. wt. Calcd. for $C_{42}H_{30}O_2PCl$: 633. Found: 633 (by mass). *Anal.* Calcd. for $C_{42}H_{30}O_2PCl$: C, 79.67; H, 4.78. Found: C, 80.16; H, 5.24.

Hydrolysis of 15——Five ml of aqueous benzene was added to 500 mg (0.79 mmole) of **15** at room temperature. The solution was stirred for only 2 min and then evaporated. Recrystallization of the pale yellow residue from *n*-hexane–CH_2Cl_2 yielded 400 mg (82%) of **16** as pale yellow crystals; mp 215—217°. IR (KBr) cm^{-1}: 1760, 1485, 1435, 1180, 1000 and 753. NMR ($CDCl_3$) δ: 8.2—6.2 (30H, m, aromatic), and 5.82 (1H, d, $J=12$ cps, P–CH). UV $\lambda_{max}^{CH_3OH}$ mμ (log ε): 220 (4.64), 267 (3.87), 275 (3.87) and 333 (4.41). Mol. wt. Calcd. for $C_{42}H_{31}O_3P$: 614. Found: 614 (by mass). *Anal.* Calcd. for $C_{42}H_{31}O_3P$: C, 82.06; H, 5.08. Found: C, 81.85; H, 5.06.

Reaction of 1 with 2e in Methanol——To a solution of **1** (1030 mg, 5 mmole) in 10 ml of dry benzene was added 1100 mg (5 mmole) of **2e**. The reaction mixture was stirred at room temperature under nitrogen for 2 hr and then 10 ml of dry methanol was added to the reaction mixture. After 10 hr the solvent was evaporated and the residue was chromatographed on silica gel, giving 610 mg (28%) of **17**. Recrystallization of **17** from *n*-hexane–CH_2Cl_2 gave colorless crystals; mp 291—293°. IR (KBr) cm^{-1}: 1740, 1495, 1440, 1270, 1210, 1175, 1145 and 1075. UV $\lambda_{max}^{CHCl_3}$ mμ (log ε): 241 (3.78), 244 sh (3.70), 260 sh (3.35), 267 sh (3.27) and 274 sh (3.15). NMR ($CDCl_3$) δ: 7.6—6.8 (20H, m, aromatic), 4.78 (1H, d.d., $J=8$ and 12 cps, P–C–CH), 4.28 (1H, d.d., $J=4$ and 12 cps, P–CH) and 3.30 (3H, s, CO_2CH_3). Mol. wt. Calcd. for $C_{28}H_{25}O_3P$: 440. Found: 440 (by mass). *Anal.* Calcd. for $C_{28}H_{25}O_3P$: C, 76.35; H, 5.72. Found: C, 76.47; H, 5.95.

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16) Recrystallization of **15** was impossible because of its awful sensitivity to moisture.