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CYCLOADDITIONS AND OTHER REACTIONS OF PHOSPHOLES UNDER HIGH PRESSURES

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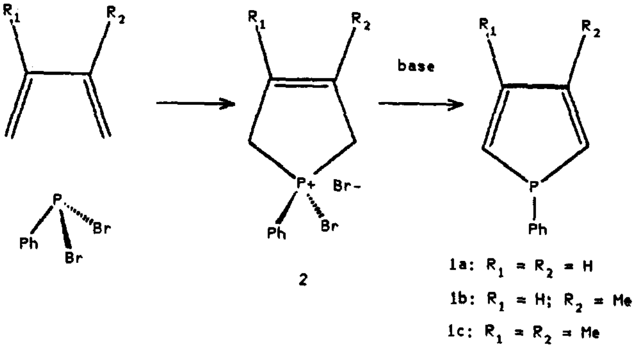
Abstract; Phospholes ,synthesised by an improved procedure, undergo Diels-Alder reactions at high pressure but not dipolar cycloadditions to nitrile oxides (which deoxygenate) or diazomethanes (which can, however, trap the phosphole oxides) . Diphenylketene gives an unexpected spirophosphorane with phospholes at 9 kbar.

Phospholes have been known only since 1959 [1] and 1-monosubstituted analogues only since the synthesis of 1-methylphosphole by Quin [2] in 1967. There is considerable controversy as to the extent of delocalisation of the phosphorus lone pair and the degree of aromaticity to be accorded to this ring system but the consensus of opinion seems to lie in favour of there being a small amount of aromatic character. Thus, the P-C$^{\alpha}$ bond length is about 7 pm shorter than normal [3]. The ^{31}P-NMR chemical shift is 30-50 ppm to the low-field side of typical resonances for phospholenes and phosphines, supportive though not conclusive of the presence of a ring current [4,5]. On the other hand, the geometry of the bonds at phosphorus is pyramidal indicating aromatic stabilisation being insufficient to overcome the strong barrier to inversion of phosphorus-(3). Recently a Diels-Alder reaction has been reported between 1-phenyl-2,3-dimethylphosphole,1c, and N-phenylmaleimide which argues in favour of diene character of the ring [6]. In an aromaticity index proposed by Bird [7], phosphole appears to be the least aromatic of the heterocycles; thiophene,pyrrole, furan, phosphole and this is supported by ab initio calculations of resonance energies -149, -124, -89 and -54 kJmol^{-1}, respectively [8,9]. The calculated inversion barrier of 66 kJmol^{-}1 is less than that of phosphines (ca. 150 kJmol^{-}1) which presumably results from a degree of overlap of n_P electrons with the ring. In view of these considerations it seemed likely that phospholes would show considerable diene character and that a variety of (4+2) and other cycloadducts would be possible especially under high pressure conditions. This communication reports on the extent to which this is borne out.

Experimental

3,4-Dimethyl-1-phenylphosphole was prepared by a modification of the method of McCormack, Scheme 1, [10]. Phenyldibromophosphine (5.57g, 20 mmol) was mixed with 2,3-dimethylbuta-1,3-diene (1.75g, 20 mmol) in hexane (10 mL). The mixture was maintained at a pressure of 4-5 kbar at 25^{o}C for 10h using the apparatus previously described [11]. The product was a

Scheme 1



granular white solid comprising almost quantitative conversion to the phospholenium bromide,2. Dichloromethane (10 mL) and hexane (20 mL) were added and a nitrogen atmosphere imposed. 2-Methylpyridine (3.9g, 40 mmol) was added with vigorous stirring and the stirring continued until the solid dissolved (about 1h) and the liquid separated into two layers, the upper yellow and the lower brownish. Hydrochloric acid (10 mL, 3M) was added with stirring over 10 min and the organic layer was separated, washed with water until neutral, dried (anhyd. sodium sulphate) and concentrated at reduced pressure at 30°C. The residual liquid was mixed with hexane (20 mL) causing precipitation of some polymeric byproducts which were removed by filtration through celite. Distillation under vacuum gave 3,4-dimethyl-1-phenylphosphole,1c, (2.6g, 70%) as a colourless, extremely odorous liquid, bp 80°C/0.2 mm; ^{1}H-NMR; ($CDCl_3$), δ 2.0 (d, 6H, J=2Hz);
δ 6.4 (d, 2H, J=36Hz) ; δ 7.2-7.4 (m, aromatic).

The above method carried out at high pressure has advantages over the reaction at 1 bar [10]. In the first place the rate is greatly accelerated , the addition at 1 bar taking about 12 days to accomplish. An estimate of the volume of activation yielded a value -60 cm^3mol^{-1}. Secondly the intermediate phospholenium salt,2, is obtained as a fine granular precipitate which readily undergoes elimination with 2-methylpyridine. In contrast, the intermediate obtained at 1 bar is a very hard aggregate, difficult to remove from the flask and needing fine grinding before further reaction which even then is slow.

In an analogous fashion, 3-methyl-1-phenylphosphole,1b, and 1-phenylphosphole,1a, were obtained by the use respectively of isoprene and 1,3-butadiene in place of 2,3-dimethylbutadiene.

3-Methyl-1-phenylphosphole had b.p. 70°C/0.1 mm and 1-phenylphosphole had b.p. 60°C/0.2 mm.

Rate measurements of the Reaction between Phenyldibromophosphine and 3,4-Dimethylbuta-1,3-diene.

A solution was made of phenyldibromophosphine (4.70g, 17.7 mmol) and dimethylbutadiene (1.48g, 17.7 mmol) with ether (10 mL). Aliquots of this mixture were pressurised for various times at a series of pressures up to 3.8 kbar.Each sample was removed diluted with

ether and the phospholenium salt filtered through a weighed crucible, washed, dried and the product weight, w, determined. The progress of reaction was fitted to a quadratic expression; $w = a + bt + ct^2$
from which the initial slopes, relative rates k_{rel} were obtained, Table 1. These were fitted to the expression; $\ln k_{rel} = A + Bp + Cp^2$
from which $B = d/dp(\ln k) = -\Delta V/RT$ and the volume of activation, ΔV, could be calculated [12]. Partial molar volumes of all reagents and products were obtained using a Paar high precision densimeter, Table 2.

Reaction between 3,4-dimethyl-1-phenylphosphole and fumaronitrile.

Freshly distilled 3,4-dimethyl-1-phenylphosphole (1.1g, 5.8 mmol) was mixed with fumaronitrile (0.47g, 6.0 mmol) in dichloromethane (3 mL) and the solution maintained at 9 kbar, 30°C for 24h . The solvent was removed under reduced pressure and ether added which precipitated a white solid. This was recrystallised from dichloromethane-ether (1:1) to obtain colourless crystals of 2,3-dimethyl-(trans)5,6-dicyano-7-phenylphosphabicyclo[2.2.1]hept-2-ene,3c, m.p. 154-155; yield,1.0g, 67%.
Found; C,71.65; H,5.32; N,10.37: $C_{16}H_{15}N_2P$ requires C,72.2; H,5.63; N,10.52%
The structure was further established by X-ray crystallography, Fig.1 .

Reaction between 3-methyl-1-phenylphosphole and fumaronitrile.

An analogous experiment was carried out using 3-methyl-1-phenylphosphole and a white crystalline precipitate obtained as before. However, this proved to be a mixture of the cycloadduct, 2-methyl-(trans)5,6-dicyano-7-phenylphosphabicyclo[2.2.1]hept-2-ene,3b, and the corresponding oxide,4c, evidently obtained during workup, and which proved difficult to separate; yield,0.77g, 60% . Evidently 3b is more susceptible to air oxidation than is 3a. The molecular formulae were established by mass spectroscopy of the molecular ions at m/e = 252 and 268 from 3b and 4b respectively;
Accurate mass calculated for $C_{15}H_{13}N_2P$ = 252.0811; found 252.0811.
Accurate mass calculated for $C_15H_{13}N_2PO$ = 268.0759;found 268.0755.

Reaction between 1-phenylphosphole and fumaronitrile.

An analogous experiment was carried out using 1-phenylphosphole,1a, and a white precipitate was obtained as before after 10h reaction time at 9kbar, 30°C. This was purified by solution in dichloromethane and careful precipitation by the addition of ether and had a melting range 120-142 °C indicative of a mixture. Mass spectrocopy revealed the product to be a mixture of the cycloadduct, (trans)5,6-dicyano-7-phenyl-7-phosphbicyclo [2.2.1]hept-2-ene,3a , and its oxide, 4a .
Accurate mass calculated for $C_{14}H_{11}N_2P$ (3a) = 238.0655; found 238.0655. Accurate mass calculated for $C_{14}H_{11}N_2PO$ (4a) = 254.0604;found 254.0605.

Reaction between 3,4-dimethyl-1-phenylphosphole and diphenylketen ; 3,4-dimethyl-1-phenylphosphole (2.0g, 10.6 mmol) was mixed with diphenylketen (2.1g, 10.8 mmol) in dichloromethane and the solution maintained at 9 kbar , 25°C for 10h. Addition of ether to the resulting solution precipitated a yellow solid which was filtered, washed with ether and purified by flash chromatography on silica using dichloromethane:pentane (2:1) as eluent. The yellow fraction was recrystallised from ether- dichloromethane (1:1) and yellow crystals of 5, m.p. 162-163 (dec) obtained ; yield, 0.7g, 30%. An accurate mass spectrum of the apparent parent ion had m/e = 496.159; $C_{34}H_{25}O_2P$ requires 496.158. However, this proved to be a fragment ion . The structure of was established by X-ray diffraction on a single crystal, Fig.2 .

The same compound was obtained when 3-methyl-1-phenylphosphole was used in place of the 3,4-dimethyl analogue confirming that all carbons of the phosphole ring and their substituents are lost in the formation of 5.

Reaction between 3,4-dimethyl-1-phenylphosphole and benzonitrile oxide .

Benzonitrile oxide (1.7g, 14.3 mmol) in ether (10 mL) was added dropwise to a solution of 3,4-dimethyl-1-phenylphosphole in ether (15 mL) at 0°C . An exothermic reaction occurred and a white precipitate formed which was filtered and recrystallised from dichloromethane-ether (1:1) ,m.p. 250-251 and identified as the dimer of the phosphole oxide,6.

Found; C,69.68;H,6.47 : $C_{2}4H_{26}O_2P_2$ requires C,70.58; H, 6.41%.

Accurate mass; found 408.145; required 408.14 .

Benzonitrile was identified in the filtrate by gas chromatography.

In analogous reactions between benzonitrile oxide with 3-methyl-1-phenyl phosphole and 1-phenylphosphole, only the dimers of the corresponding phosphole oxides were obtained.

Reaction between 3,4-dimethyl-1-phenylphosphole and diazomethane.

3,4-Dimethyl-1-phenylphosphole (3.57g, 19 mmol) was added to a solution of diazomethane (0.8g, 19mmol) in ether. The solution was maintained at 9 kbar, 25°C for 24 h. However, no reaction occurred and the reagents were unchanged. The reaction was repeated at 1 bar stirring the solution in the presence of air which was passed in a slow stream through the liquid. After 10h a yellowish solid formed which was filtered and recrystallised from ethyl acetate to obtain creamy-white crystals of 1,2-dimethyl-4- phospha-7,8-diazabicyclo [3.3.0]octa-2,7-diene P-oxide 7a , m.p. 139-140 (dec.). yield, 1.8g, 78%. Found, C,63.05; H,6.21; N,11.12: $C_{1}3H_{1}5N_{2}OP$ requires C,63.4;H,6.09;N,11.38%. Accurate mass calculated for $C_{13}H_{15}N_2OP$ is 246.0916; found, 246.0916.

^{1}H-NMR (220 MHz, $CDCl_3$); δ 1.7 (2,3H); δ 2.1 (q, 1H); δ 2.4 (s, 3H); δ 4.95 (m, 1H); δ 5.3 (t, 1H); δ 5.8 (d, 1H); δ 7.4-7.8 (m, 5H aromatic).

^{31}P-NMR; ($CDCl_3$, ext ref. 85% H_3PO_4) , δ +51.38 ppm.

The structure was confirmed by X-ray diffraction on a single crystal, Fig.3 .

In an analogous experiment, 3-methyl-1-phenylphosphole reacted with diazomethane in the presence of air to give 65% of the corresponding cycloadduct with the phosphole oxide,7b .

Reaction of 3,4-dimethyl-1-phenylphosphole with diphenyldiazomethane

3,4-Dimethyl-1-phenylphosphole (1.0g, 5.3 mmol) and diphenyldiazomethane (1.03g, 5.3 mmol) in ether (10 mL) was maintained at 9 kbar, 25°C for 24h at the end of which the reagents remained unchanged. The reaction was repeated at 1 bar and in a current of air when a small amount of white solid formed after 24h. This was filtered , recrystallised from dichloromethane-ether m.p.250 and shown to be the dimer of the phosphole oxide, 6.

Ultraviolet Irradiation of 7a .

A solution of 7a, (0.16g, 0.6 mmol) in acetonitrile (8 mL) was irradiated in Pyrex by a medium pressure mercury lamp for 10h. Gas bubbles were evolved during the irradiation and when this evolution ceased the solution was concentrated under reduced pressure to leave a viscous oil. On adding ether, the mass solidified and 1,2-dimethyl-4-phenyl-4-phosphabicyclo[3.1.0]hex-2-ene 4-oxide , 8a,was purified by solution in dichloromethane and careful precipitation by ether. The resulting white solid decomposed around 89 °C without melting.

Calculated mass for _$C_{13}H_{15}OP$ = 218.0856; found, 218.0839

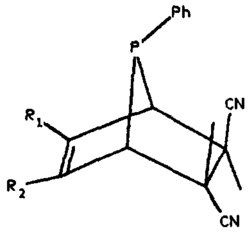
Reaction between 3,4-Dimethyl-1-phenylphosphole and benzaldehyde

3,4-Dimethyl-1-phenylphosphole (0.52g, 2.7 mmol) and benzaldehyde (0.58g, 5.4 mmol) in dichloromethane (2 mL) was maintained at 9 kbar, 30 °C for 48h. Ether was added causing the formation of a white precipitate of the phosphole oxide dimer. Excess aldehyde was removed from the filtrate by shaking with aqueous bisulphite and the organic layer washed, dried and concentrated under reduced pressure to leave a white solid m.p. 121-123 identified as trans-stilbene, 0.12g, 50%. The experiment was repeated using triphenylphosphine in place of the phosphole. A temperature of 50oC was required for 48h and a yield of 48% trans-stilbene was again isolated.

Discussion

This study has shown the value of high pressure conditions in the synthesis of phospholes both in the acceleration of the initial cycloaddition between diene and halophosphine and in the production of a finely divided phospholenium salt which rapidly undergoes elimination. As a result, the phospholes used in this work can be prepared in a morning as against 1-2 weeks by previous procedures. Measurement of the relative rates of the cycloaddition between 2,3-dimethylbutadiene and dibromophenylphosphine was carried out at a series of pressures between 1 bar and 3.8 kbar from which the volume of activation for this reaction was obtained, estimated at -60 +/- 5 cm^3mol^{-1}. This is a very large value , greater than that for either a neutral Diels-Alder reaction (ca. -35) or a Menshutkin reaction (-30 to -50) and is consistent with a reaction mechanism in which concerted cycloaddition occurs concurrent with the development of ionic charges which afford an additional reduction in volume by electrostriction. The overall volume of reaction is much less negative, -38 +/- 2 cm^3mol^{-1}, the reason for which is not clear. Ionogenic reactions as a rule have $|\Delta V| > |\Delta V^{\neq}|$ since electrostriction is not complete at the transition state.

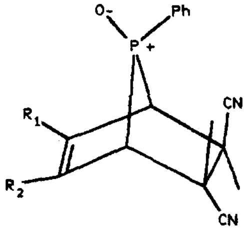
High pressure conditions increase the scope of (4+2)-cycloadditions to phospholes though the reaction is by no means a general one with the usual dienophiles. The adducts of the phospholes with fumaronitrile were the only new species of this type to be satisfactorily prepared and characterised. No reaction occurred at 10 kbar between the phospholes and either maleic anhydride or tetracyanoethylene despite both being normally considered more powerful dienophiles than fumaronitrile. Benzoquinone in the absence of solvent reacted violently with the phospholes and in solution gave only a black polymeric species and hydroquinone. Presumably electron transfer initiates these reactions. (2+2)-Cycloadditions



3a; $R_1 = R_2 = H$

3b: $R_1 = H$; $R_2 = Me$

3c: $R_1 = R_2 = Me$



4a: $R_1 = R_2 = H$

4b: $R_1 = H$; $R_2 = Me$

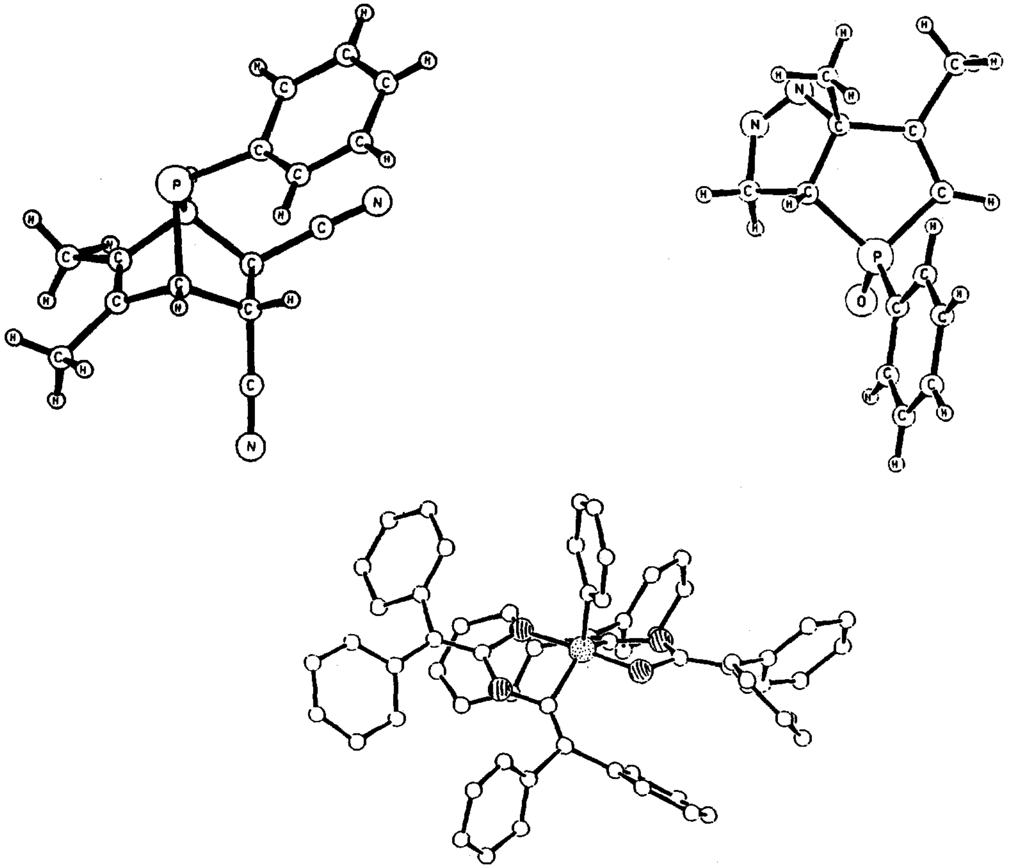
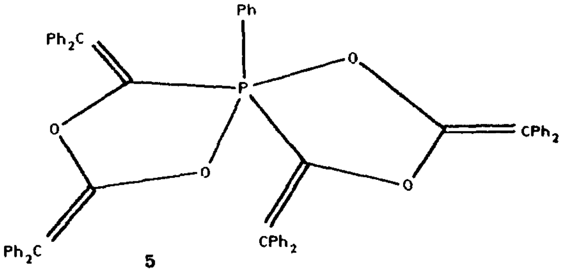


Fig.1: X-Ray Crystallographic Structures of Products. a, 3c; b, 7a; c,5.

analogous to those between cyclopentadiene and ketens were not achieved. The unusual course of the reaction between phospholes and diphenylketen has already been described but the route leading to the product,5 , is not known with certainty. The loss of the four-carbon unit from the phosphole suggests a (4+2)-cycloreversion possibly along the lines of Scheme 2. The weakness of this route, however, lies in the assumption of a (4+2) cycloaddition by the diphenylketen which appears to have no precedent. The yellow colour of these spirophosphoranes is of interest and arises from low intensity absorption centred around 350 nm extending into the visible region, presumably due to the chromophore; $Ph_2C=C(-O)-O-C=Ph_2$. These compounds were stable to 235oC at which temperature rapid loss of 45% of the mass occurs. This corresponds closely to the fission of one of the rings and loss of two



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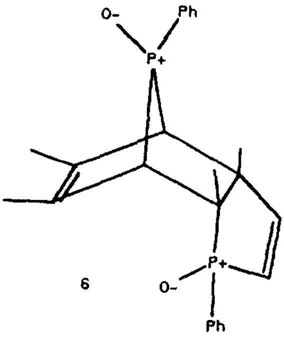

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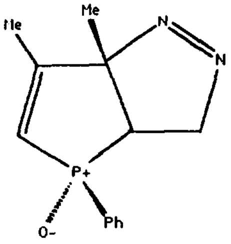

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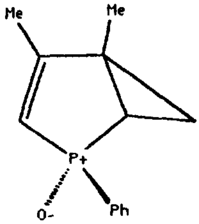

8

molecules of dimethylketen. The same process takes place in the mass spectrometer from which the only molecular ion observed was for the fragment, $C_{34}H_{25}O_2P$, m/e = 496.159.
No dipolar cycloadditions of phospholes were able to be accomplished, reactions tending to take other pathways. Thus, nitrile oxides are readily deoxygenated by phospholes upon mixing to give the phosphole oxides which dimerise. Deoxygenation is a familiar and often preparatively useful reaction of phosphorus-(3) compounds and a few experiments were extended to reactions of ketones using high pressure conditions which would be expected to accelerate reactions. Benzaldehyde was found to react with 1-phenyl-2,3-dimethylphosphole at 9 kbar though not at atmospheric pressure, to give 50% of trans-stilbene. This presumably arises through an intermediate phenylcarbene which dimerises. A similar reaction occurred with triphenylphosphine although a higher temperature was needed than that needed for the deoxygenation by the phosphole. Diazomethane failed to react with phospholes at 10 kbar but, upon oxidation by air, were converted to the more reactive phosphole oxides which in turn gave the dipolar cycloadducts, 7. This reaction is interesting in that it seems to be the only occasion in which the phosphole oxide has been trapped by a different molecule, dimerisation usually being observed whenever these species are generated. Trapping cannot be achieved with added cyclopentadiene, ethyl acrylate or diphenylketen. The same adduct has recently been obtained by Klärner [13] by addition of diazomethene to phosphole under hydrolytic conditions. Irradiation of the cycloadduct then gave the homophosphole oxide,9 , from which by a known route, the homophosphole,10, may be obtained.Thermal decomposition may also lead to the same compound; the ^{31}P-NMR resonance of 8 at +55.4 ppm was found to shift to +83 ppm after the compound had been standing at room temperature for several months.

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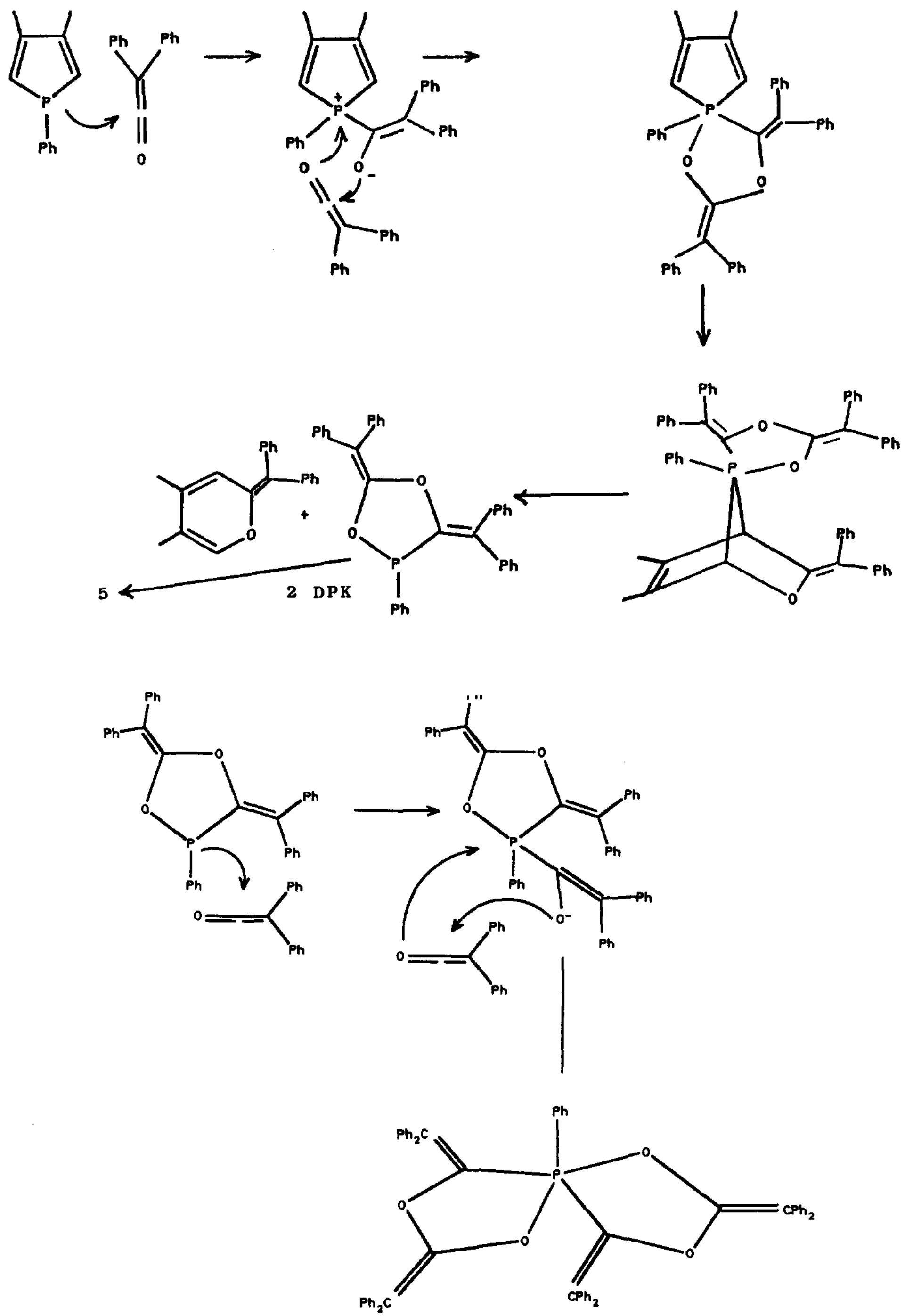
Scheme 2



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