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Phosphinidenes and Related Intermediates. III.[1] Reactions of Phosphinylidenes and Phosphinothioylidenes with Conjugated Dienes

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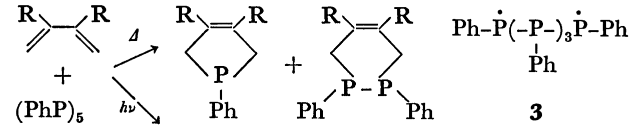
Phenylphosphonic and phenylphosphonothioic dichlorides were dechlorinated with magnesium to generate phenylphosphinylidene and phenylphosphinothioylidene, respectively, in the presence of several 1,3-dienes. Reactions of phenylphosphinothioylidene with 2,3-dimethylbutadiene and 1,3-cyclohexadiene gave Diels-Alder type reaction products, that is, 3,6-dihydro-1,2-thiaphosphorin derivatives (**5** and **6**) and 6-phenyl-5,6-thiaphosphabicyclo[2.2.2]oct-2-ene 6-sulfide (**14**), respectively. Reaction of 2,3-diphenylbutadiene with phenylphosphinothioylidene afforded 1,2,4,5-tetraphenyl-1,2,3,6-tetrahydro-1,2-diphosphorin 1,2-disulfide (**10**), whereas that with phenylphosphinylidene gave 1,3,4-triphenyl-3-phospholene 1-oxide (**12**). The differences of these reactions have been discussed.

Schmidt and Boie[2] reported that thermal decomposition or photolysis of pentaphenylcyclopentaphosphine in the presence of 1,3-dienes gave cyclic compounds such as **1** and **2**, the formation of which can be interpreted by attack of phenylphosphinidene (Ph–P) or a diradical (**3**)[3] upon the 1,3-dienes.

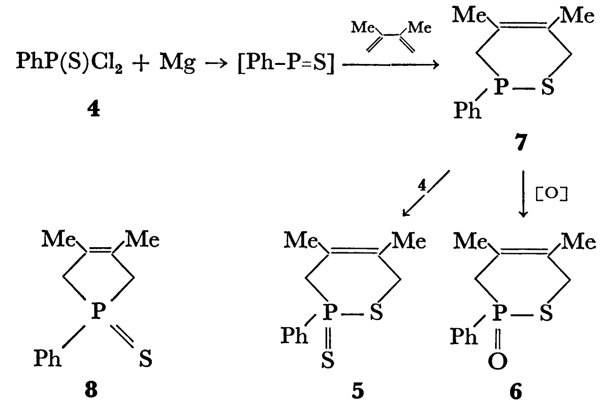


2 **1** **2** **3**

Thus, in the decomposition of the cyclopentaphosphine, phosphinidene is not necessarily the sole reactive intermediate. Furthermore, it is expected that phosphinylidenes (R–P=O) and phosphinothioylidenes (R–P=S) behave not only as analogues of nitrenes and phosphinidenes but also as those of nitroso[4] and thionitroso compounds.[5]

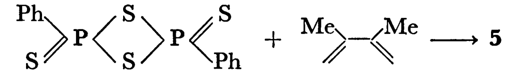
The present paper describes reactions of 1,3-dienes and the related compounds with phosphinylidenes or phosphinothioylidenes[6] generated from magnesium and phosphonic or phosphonothioic dichlorides, respectively.

When phenylphosphonothioic dichloride (**4**) was dechlorinated with magnesium in tetrahydrofuran (THF) in the presence of 2,3-dimethylbutadiene at 50 °C, 4,5-dimethyl-2-phenyl-3,6-dihydro-1,2-thiaphosphorin 2-sulfide (**5**) and the corresponding 2-oxide (**6**) were obtained in 44 and 21% yields, respectively,[7] but another expected product (**8**) could not be isolated.

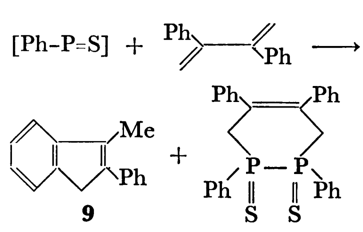


4 **7** **8** **5** **6**

The formation of **5** and **6** is attributable to sulfurization of **7** with **4** and oxidation of **7** during the isolation, respectively. Thus, it is clear that the intermediate (**7**) is formed *via* the Diels-Alder type reaction of the diene with phenylphosphinothioylidene as a 1,2-dipole like thionitroso compounds.[5] The same compound (**5**) has recently been obtained in the following reaction.[8]



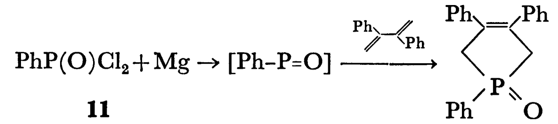
Reaction of **4** with 2,3-diphenylbutadiene and magnesium in THF gave 3-methyl-2-phenylindene (**9**) and 1,2,4,5-tetraphenyl-1,2,3,6-tetrahydro-1,2-diphosphorin 1,2-disulfide (**10**) in 52.5 and 13.5% yields, respectively, after separation by column chromatography.



9 **10**

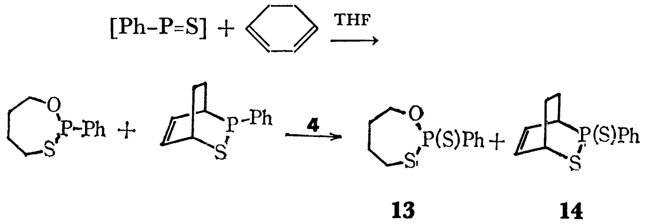
It was proven by a separate experiment that **9** was produced by cyclization of unchanged 2,3-diphenylbutadiene on silica gel (see Experimental).

When phenylphosphonic dichloride (**11**) was used instead of **4**, 1,3,4-triphenyl-3-phospholene 1-oxide (**12**) was obtained in 10% yield.



11 **12**

Dechlorination of **4** with magnesium in the presence of 1,3-cyclohexadiene in THF afforded 2-phenyl-1,3,2-oxathiaphosphepane 2-sulfide (**13**) and 6-phenyl-5,6-thiaphosphabicyclo[2.2.2]oct-2-ene 6-sulfide (**14**) in 6 and 21% yields, respectively.



13 **14**

The compound (**13**) is an insertion product of phenylphosphinothioylidene into the C–O bond of THF. The formation mechanism will be discussed elsewhere.[9] The compound (**14**) is of the same type as **5**.

In the NMR spectrum of **14**, a decoupling experiment showed that two quartets centered at δ 5.98 and 6.58 coupled with two multiplets at δ 2.9—3.4 (–P–CH⟨) and 3.8—4.4 (–S–CH⟨), respectively, indicating that the two quartets are assignable to olefinic protons adjacent to the C–P and C–S bonds, respectively. From the result, the coupling constants may be evaluated as $J_{\mathrm{H-C=C-H}}=J_{\mathrm{HCCH}}=J_{\mathrm{PSCCH}}=8$ Hz. However, since J_{PSCCH} values are generally very small, it would be more reasonable to consider that the quartet centered at δ 6.58 is due to overlapping of two triplets centered at δ 6.52 and 6.64 assignable to each olefinic proton adjacent to the C–S bond of the two isomers on the phosphorus atom, and that the signals of each olefinic proton adjacent to the C–P bond in the two isomers perhaps coincided with each other by chance. Thus, **14** is suggested to be an equimolar mixture of two isomers.

Detectable reaction products could not be isolated in the reactions of phenylphosphinylidene and cyclohexylphosphinothioylidene with 2,3-dimethylbutadiene, the reactions of cyclohexylphosphinylidene and -phosphinothioylidene with 2,3-diphenylbutadiene, and the reactions of phenylphosphinothioylidene with 1,3-cyclooctadiene, *trans,trans*-1,4-diphenylbutadiene, 1,1'-dicyclohexenyl, thiophene, 2,5-diphenylbenzo[*c*]furan, acetophenone azine, and 1,2-bis(*p*-tolylimino)-1,2-diphenylethane. In some reactions with phenylphosphinothioylidene in THF, **13** was also isolated in 3—11% yields.

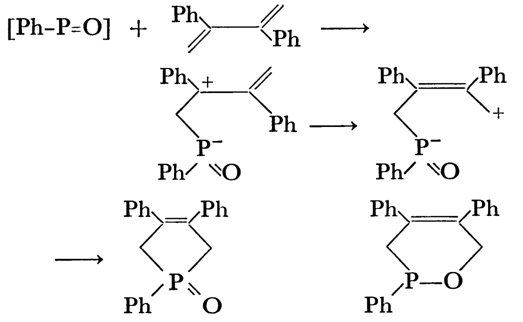
In the reaction of phenylphosphinothioylidene with tetraphenylcyclopentadienone, 2,3,*trans*-4,5-tetraphenylcyclopent-2-en-1-one (**15**) was obtained in 21% yield as the sole product, and may be formed by an analogous mechanism to that reported by Dimroth and Laufenberg[10] or by reduction of tetraphenylcyclopentadienone with magnesium-magnesium(II) chloride system.[1]

Since usually the 1,3-dienes do not react with nucleophiles, participation of Grignard-type intermediate (R–P(X)Cl–MgCl; X=O,S) might be ruled out. Thus, the reactive intermediate is considered to be phosphinylidene and phosphinothioylidene.

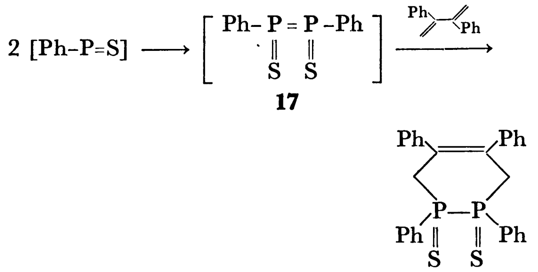
As mentioned above, the types of the products depend on not only the structure of reactive intermediates but also the structure of 1,3-dienes used.

In the reactions of phenylphosphinothioylidene with 1,3-dienes such as 1,3-cyclohexadiene and 2,3-dimethylbutadiene which are fixed in cisoid form or take easily cisoid, phenylphosphinothioylidene behaves as 1,2-dipolar dienophile for 1,3-dienes.

On the contrary, 2,3-diphenylbutadiene takes cisoid form not so easily as 2,3-dimethylbutadiene. Thus the phosphorus atom of phenylphosphinylidene attacks electrophilically on transoid 2,3-diphenylbutadiene and the transoid zwitter ion thus formed converts to the cisoid to form **12**, which is more stable than the isomer (**16**) by a consideration of the bond energies. This difference between the formation of **5**, **6** and **14** and that of **12** may be attributed to the difference in the bond energies of P=O and P=S bonds and to the large nucleophilicity of the sulfur anion.



12 **16**



17

10

In the case of phenylphosphinothioylidene, an analogous transoid zwitter ion is probably less stable because of low electronegativity of the sulfur atom. Then phosphinothioylidene is considered to dimerize competitively to produce a reactive intermediate (**17**) which cyclizes with 2,3-diphenylbutadiene to give **10**.

It is very interesting that phenylphosphinothioylidene shows dual properties in the reactions.

Experimental

All melting and boiling points are uncorrected. IR and mass spectra were measured with Hitachi EPI-G2 and Hitachi RMU-6L spectrometers. ^{1}H-NMR spectra were recorded on Hitachi R-20B, R-24 (60 MHz), R-22 (90 MHz), and JEOL JNM-4H-100 (100 MHz) spectrometers using TMS as an internal standard. ^{31}P-NMR spectra were taken with a Hitachi R-20B-R-204-PB spectrometer using 85% phosphoric acid as an external standard. All reactions were carried out under nitrogen atmosphere.

Materials. The following compounds were prepared by the method described in the literature: 2,3-dimethyl-[11] (mp 68—71 °C), 2,3-diphenylbutadienes[12] (mp 43—46 °C), 1,3-cyclohexadiene[13] (bp 79—82 °C), tetraphenylcyclopentadienone[14] (mp 218—220 °C), phenylphosphonic[15] (**11**) (bp 143 °C/27 mmHg), and phenylphosphonothioic dichlorides[16] (**4**) (bp 134—138 °C/14 mmHg).

Reaction of 4 and Magnesium with 2,3-Dimethylbutadiene. At room temperature, **4** (2.6 g, 12.4 mmol) was added dropwise to a mixture of 2,3-dimethylbutadiene (12 ml, 107 mmol) and magnesium (0.33 g, 13.9 mg-atom) in THF (10 ml) with stirring. A few drops of methyl iodide were added to start the reaction, and the mixture was stirred at 50 °C overnight. After removal of the solvent, the residue was extracted with chloroform. The chloroform extract was washed with water, dried with anhydrous magnesium sulfate, and chromatographed on silica gel to give **5** (0.69 g, 2.7 mmol, 44%) with benzene and **6** (0.62 g, 2.6 mmol, 21%) with dichloromethane and chloroform.

5: mp 61—62 °C (from ether) (lit,[8] 62 °C); IR (KBr): 1650 cm^{-1} (C=C); NMR (CCl_4, 100 MHz): δ 1.68 (s, 3H, 5-Me), 1.93 (d, J_{PCCCH} 5 Hz, 3H, 4-Me), 2.7—3.9 (m, 4H, $2CH_2$), and 7.2—8.0 (m, J_{PH^o} 15 Hz, 5H, Ph).

Found: C, 56.62; H, 5.86; S, 25.34%. Calcd for $C_{12}H_{15}PS_2$: C, 56.66; H, 5.96; S, 25.21%.

6: mp 85.5—86 °C (from ether); IR (KBr): 1660 (C=C) and 1205 cm^{-1} (P=O); NMR (CCl_4, 100 MHz): δ 1.77 (s, 3H, 5-Me), 1.97 (d, J_{PCCCH} 5 Hz, 3H, 4-Me), 2.4—4.0 (m, 4H, $2CH_2$), and 7.4—8.0 (m, 5H, Ph); MS: *m/e* 238 (M$^+$).

Found: C, 60.71; H, 6.49%. Calcd for $C_{12}H_{15}OPS$: C, 60.49; H, 6.35%.

*Reaction of **4** and Magnesium with 2,3-Diphenylbutadiene.* At room temperature, **4** (5.31 g, 25.2 mmol) in THF (5 ml) was added drop by drop with stirring to a mixture of 2,3-diphenylbutadiene (6.08 g, 29.5 mmol), magnesium (0.66 g, 27.5 mg-atom), and THF (20 ml). A small amount of iodine was added to activate magnesium. The mixture was stirred for 1 hr. Unchanged magnesium and produced magnesium chloride were filtered off, and THF was evaporated from the filtrate *in vacuo*. The residue was treated in a similar way. Elution with carbon tetrachloride and carbon tetrachloride-benzene (2 : 1—1 : 1) afforded unchanged **4** (0.02 g, 0.1 mmol) and **9** (3.19 g, 15.5 mmol, 52.5%), mp 76—77 °C (from *n*-hexane) (lit,[17] 76—77 °C), respectively. Elution with benzene and dichloromethane afforded **10** (0.84 g, 1.7 mmol), mp 233—234 °C (from benzene). The yield was 13.5% based on **4** consumed. IR (KBr): 1110 (P-Ph), 625, and 620 cm^{-1} (P=S); NMR ($CDCl_3$): δ 3.3—4.5 (m, 4H, $2CH_2$), and 7.0—8.2 (m, 20H, 4Ph); MS: *m/e* 486 (M$^+$, 21%), 346 (M$^+$−PhPS, 69), 314 (M$^+$−$PhPS_2$, 100), 280 (PhP(S)P(S)Ph, 14), and 206 ($CH_2CPhCPhCH_2$, 32).

Found: C, 69.02; H, 4.66%. Calcd for $C_{23}H_{24}P_2S_2$: C, 69.11; H, 4.98%.

*Reaction of **11** and Magnesium with 2,3-Diphenylbutadiene.* A solution of **11** (4.29 g, 22.0 mmol) in THF (5 ml) was added dropwise to a stirred suspension of magnesium (0.58 g, 24.0 mg-atom) and 2,3-diphenylbutadiene (4.54 g, 22.0 mmol) in THF (20 ml) under occasional cooling with water. The exothermal reaction ceased in about 1 hr. Then the reaction mixture was refluxed for 3 hr, and treated similarly. Elution with carbon tetrachloride and chloroform afforded unchanged diene (3.23 g, 15.7 mmol) and **12** (0.75 g, 2.3 mmol), respectively. The yield of **12** was 37% based on the diene consumed.

12: mp 162.5—163.5 °C (from carbon tetrachloride); IR (KBr): 1190 cm^{-1} (P=O); ^1H-NMR ($CDCl_3$, 90 MHz): δ 3.0—3.75 (m, 4H, $2CH_2$), 6.9—7.3 (m, 10H, 2Ph), 7.4—7.65 (m, 3H, 2H^m and H^p of P-Ph), and 7.65—8.1 (m, 2H, 2H^o of P-Ph); ^{31}P-NMR ($CHCl_3$): δ −48 ppm; MS: *m/e* 330 (M$^+$).

Found: C, 80.10; H, 5.64%. Calcd for $C_{22}H_{19}OP$: C, 77.98; H, 5.80%.

*Conversion of 2,3-Diphenylbutadiene into **9** on Silica Gel Column.* 2,3-Diphenylbutadiene (4.95 g, 23.8 mmol) was adsorbed on silica gel for 6 days. Elution with carbon tetrachloride gave 3.72 g (17.9 mmol, 75%) of **9**, mp 76—77 °C.

*Reaction of **4** and Magnesium with 1,3-Cyclohexadiene.* A solution of **4** (5.24 g, 24.8 mmol) in THF (7 ml) was added drop by drop to a stirred mixture of 1,3-cyclohexadiene (8.0 g, 100 mmol) and magnesium (0.67 g, 27.9 mg-atom) in THF (10 ml). A small amount of iodine was added to initiate the reaction. Exothermal reaction ended in 1 hr. Then the reaction mixture was refluxed for 3 hr and treated similarly. Elution with benzene afforded 0.20 g (0.8 mmol, 6%) of **13** and 0.66 g (2.6 mmol, 21%) of **14**.

13: mp 62—63.5 °C (from *n*-hexane); IR (KBr): 1115 (P-Ph), 1030 (P-O-C), 650, 645, and 545 cm^{-1} (P(S)-S); NMR ($CDCl_3$, 100 MHz): δ 1.7—2.4 (m, 4H, $2CH_2$), 2.72 (dt, J_{PSCH} 22.5, J_{HCCH} 9 Hz, 2H, SCH_2), 4.0—4.5 and 4.5—5.0 (m, 2H, OCH_2), 7.3—7.6 (m, 3H, 2H^m and H^p of P-Ph), and 7.90 (m, J_{PH^o} 15 Hz, 2H, 2H^o of P-Ph); MS: *m/e* 244 (M$^+$).

Found: C, 49.09; H, 5.45; S, 26.44%. Calcd for $C_{10}H_{13}OPS_2$: C, 49.16; H, 5.45; S, 26.25%.

14: mp 92—93.5 °C (from ether); IR (KBr): 1100 (P-Ph), 680, 578, 520, and 488 cm^{-1} (P(S)-S); NMR ($CDCl_3$): δ 1.0—2.9 (m, 4H, $2CH_2$), 2.9—3.4 (m, 1H, P-CH⟨), 3.8—4.4 (m, 1H, S-CH⟨), 5.98 (q, $J_{HC=CH}=J_{HCCH}=J_{PCCH}=8$ Hz, 1H, =CH-), 6.52 and 6.64 (2t, $J_{HC=CH}=J_{=CH-CH}=8$ Hz, 1H, =CH-), 7.2—7.6 (m, 3H, 2H^m and H^p), and 7.65—8.1 (m, J_{PH^o} 13.5 Hz, 2H, 2H^o); MS: *m/e* 252 (M$^+$).

Found: C, 57.28; H, 5.02; S, 25.34%. Calcd for $C_{12}H_{13}PS_2$: C, 57.12; H, 5.19; S, 25.41%.

*Reaction of **4** and Magnesium with Tetraphenylcyclopentadienone.* At room temperature, **4** (0.59 g, 2.8 mmol) was added to a stirring suspension of magnesium (0.17 g, 6.9 mg-atom) and tetraphenylcyclopentadienone (1.16 g, 3.0 mmol) in THF (25 ml), and the mixture was heated at 80 °C for 1 day. After similar treatment, elution with dichloromethane gave 0.23 g (0.6 mmol, 21%) of **15**, mp 165—168 °C (from dichloromethane-ethanol) (lit,[10] 161—163 °C); NMR ($CDCl_3$): δ 3.76 (d, *J* 3 Hz, 1H, CH), 4.56 (d, *J* 3 Hz, 1H, CH), and 7.0—7.5 (m, 20H, 4Ph).

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