Syntheses of 1,2-Thiaphospholes and Their Thermal and Lewis Acid-Promoted Addition Reactions

Ikuo SHINODA, Akihiko TAKAHASHI, Takao SAITO,* and Tokiko UCHIDA†
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
†Department of Industrial and Engineering Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278

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3,5-Di-substituted 1,2-thiaphospholes were efficiently prepared by treating 2,9-dithia-1-phosphabicyclo[4.3.0]-nona-3,7-diene 1-sulfides with *n*-Bu_3P. The thiaphospholes reacted thermally with norbornadiene, norbornene or diethyl azodicarboxylate to produce the 1 : 2 double Diels–Alder cycloadducts. With a mixture of norbornadiene and methyl acrylate or acrylonitrile, the crossed double Diels–Alder cycloadducts were obtained. In the presence of a Lewis acid, the thiaphospholes underwent, at the initial step, the Diels–Alder reaction with acrylic esters, methyl vinyl ketone or acrylonitrile, followed in tandem by the Michael addition of the 1 : 1 cycloadducts to another molecule of the reactant.

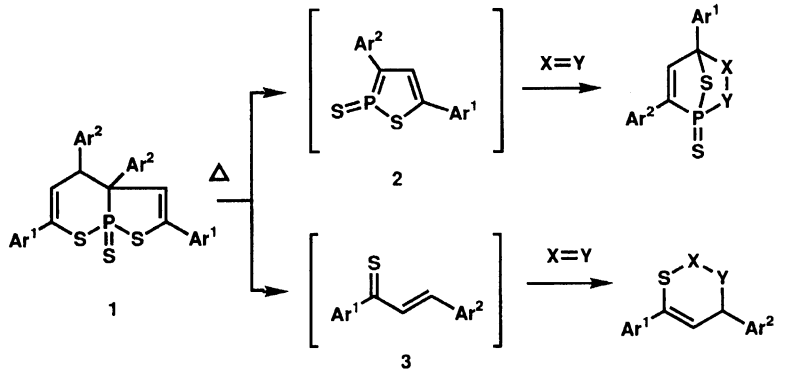
In the previous reports,[1,2] we have demonstrated that thermolysis of 2,9-dithia-1-phosphabicyclo[4.3.0]-nona-3,7-diene 1-sulfides **1** generate 1,2-thiaphosphole 2-sulfides **2** and α,β-unsaturated thioketones **3**, both of which can be trapped with suitable dienophiles (X=Y) as [4+2] cycloadducts (Scheme 1). In our continuing investigation of these bicyclic trithiophosphonates **1**, we have focused our attention on the desulfurization of **1** and found that 3,5-di-substituted 1,2-thiaphospholes **4** could readily be prepared by treating **1** with *n*-Bu_3P and that thiaphospholes **4** underwent both a thermal double Diels–Alder reaction and a Lewis acid-promoted tandem Diels–Alder/Michael addition reaction with suitable dienophiles and Michael acceptors.[3] Here, we report the results in a full account of this line of investigation.

Although the reaction of **1a** with Ph_3P or $(EtO)_3P$ did not proceed under these conditions, the reaction with *n*-Bu_3P in boiling dichloromethane (40 °C) gave **4a** in a 46% yield along with a small amount of **5a** (Table 1, Entry 1, Scheme 2). The use of 3 equiv of *n*-Bu_3P was required for the optimum formation of **4a**. The reaction accelerated gradually as the reaction temperature increased, also giving **4a** in good yields (Entries 3—6). Further treatment of **5a** with *n*-Bu_3P at 40 °C or higher temperatures did not afford **4a**. These results can be reasonably explained by assuming that **4a** is formed from generated **2a** rather than from **1a** and that *n*-Bu_3P-desulfurization from **2a** proceeds more rapidly than that from **1a** giving **5a**. The excess of *n*-Bu_3P would be consumed by the reaction with the other component, **3a**. Similarly, thiaphospholes **4b**—**i** were also obtained (Table 2). It is noteworthy that in contrast to the transient property of the structurally analogous thiaphosphole 2-sulfides **2**, compounds **4** are sufficiently stable.

To our knowledge, 1,2-thiaphospholes are very inaccessible compounds and no useful preparative method is yet known. There are only two reports on their formation in very low yields (8% or below).[4] Accordingly, the present results provide an expedient and useful method for the preparation of these unique heterocycles.

Although compounds **2** readily undergo Diels–Alder reactions with various dienophiles,[1,2] thiaphospholes **4** were relatively stable and did not react with common dienophiles such as methyl acrylate, acrylonitrile, styrene, acrylaldehyde, and dimethyl fumarate in refluxing benzene, xylene, or *o*-dichlorobenzene. With norbornadiene, however, **4a** did react in refluxing *o*-dichlorobenzene to give 1 : 2 double Diels–Alder cycloadduct **8** (70% yield) as separable mixture of two stereoisomers, **8a** and **8b** (Scheme 3). Based on an NMR spectroscopic study,[5] **8a** was assigned to the plane symmetrical *exo-exo* isomer, and **8b** to the *endo-exo* isomer, with respect to both norbornene skeletons.[6] The reaction can be rationalized by the pathway which involves the cleavage of the C–S bond in initially-formed [4+2] cycloadduct **6** to generate cyclic phosphadiene **7** which reacts further with another molecule of norbornadiene to give **8** as the final product. With norbornene, *exo-exo* 1 : 2 cycloadduct **9** was stereoselectively formed.[3]

In the crossover reaction with two component cycloaddends, viz. norbornadiene and methyl acrylate, **4a** gave crossed double Diels–Alder cycloadduct **10**[7] along with **8** whereas methyl acrylate alone did not react with **4a** in refluxing *o*-dichlorobenzene. Intermediary phosphadiene **7** is likely to be more reactive than **4a** in this tandem diene-transmissive Diels–Alder reaction. Similarly, norbornadiene and acrylonitrile afforded crossed cycloadduct **11**.[7] Styrene, methyl methacrylate and methyl crotonate did not take part in the reaction. The reaction with diethyl azodicarboxylate (DAD) proceeded smoothly in refluxing xylene to give 1 : 2 adduct **14**[6] (60% yield) instead of the anticipated cycloadduct **14′** (Scheme 4). In this case, the second cycloaddition of initial adduct **12** was assumed to take place across the phosphadiene moiety involving the P=C bond and the C=C bond in the aromatic ring as a heterodiene rather than that in the diazaphosphorine ring. This result can be attributed to the view that the C=C bond in



Scheme 1.

Table 1. The Reaction of **1a** with *n*-Bu_3P under Various Conditions to Give **4a** and **5a**

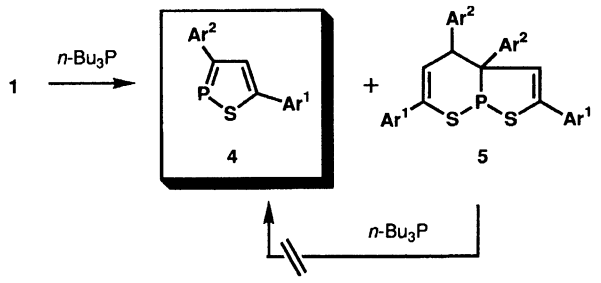
Entry	*n*-Bu_3P	Temp	Solvent	Time	Yield of **4a**	Yield of **5a**
	equiv	°C		h	%	%
1[a]	1	40	CH_2Cl_2	25	46	3
2	2	40	CH_2Cl_2	18	74	18
3	3	40	CH_2Cl_2	7	79	18
4	3	61	$CHCl_3$	3	78	11
5	3	65	THF	2.5	73	17
6	3	80	C_6H_6	0.3	75	15

a) The reaction was incomplete.

Table 2. Preparation of 3,5-Disubstituted 1,2-Thiaphospholes **4**[a]

Reactant	Ar^1	Ar^2	Time/h	Temp/°C	Product	Yield/%	Product	Yield/%
1a	Ph	Ph	7	40	**4a**	79	**5a**	18
1b	*p*-$MeOC_6H_4$	Ph	6.5	40	**4b**	83	**5b**	Trace
1c	*p*-Tol	Ph	9	40	**4c**	84	**5c**	5
1d	2-Thienyl	Ph	4	40	**4d**	86	**5d**	Trace
1e	Styryl	Ph	6	40	**4e**	72	**5e**	Trace
1f	Ph	*p*-$MeOC_6H_4$	6.5	40	**4f**	74	**5f**	Trace
1g	Ph	*p*-Tol	8	40	**4g**	83	**5g**	10
1h	Ph	2-Thienyl	7	40	**4h**	88	**5h**	Trace
1i	Ph	Styryl	2	80[b]	**4i**	44	**5i**	Trace

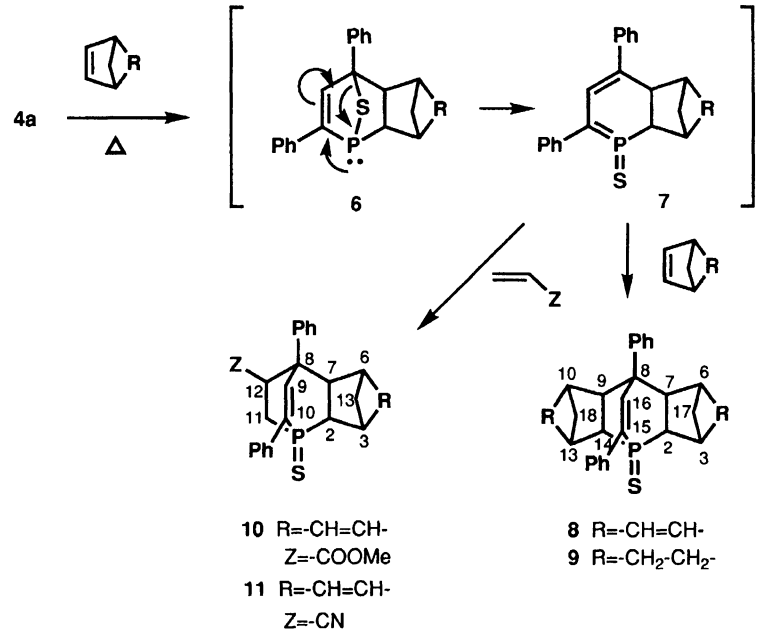
a) The reaction was carried out using 3 equiv *n*-Bu_3P in refluxing dichloromethane. b) In benzene.



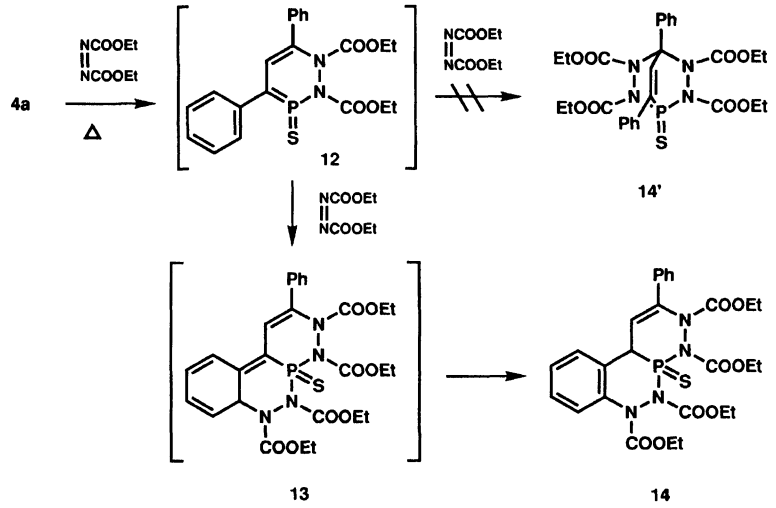
Scheme 2.

the diazaphosphorine ring is deactivated by the strong electron-withdrawing $>$(N–COOEt)$_2$ moiety.

As thiaphospholes **4** were relatively inactive in the thermal reactions with common dienophiles, we next explored the cycloaddition reaction of **4** using a Lewis acid as a catalyst (Schemes 5 and 6). When **4a** was treated with an excess amount of methyl acrylate in the presence of $AlCl_3$ in dichloromethane, the reaction proceeded readily even at room temperature. The mass spectrum suggested that the product was also the 1 : 2 adduct but the X-ray crystallographic analysis proved that the adduct had an unexpected structure (**16a**).[6] The first step of the reaction seems to be the Diels–Alder reaction of **4a** with methyl acrylate to form intermediate **15**, which subsequently undergoes 1,4-addition with another molecule of methyl acrylate, giving the final product, **16a**. It is noteworthy that the formation of **15** is the first example of a Lewis-acid promoted hetero-Diels–Alder reaction in a phosphadiene system. The tandem Diels–Alder/β-addition process would also be interesting. As is shown in Table 3, a reaction us-



Scheme 3.



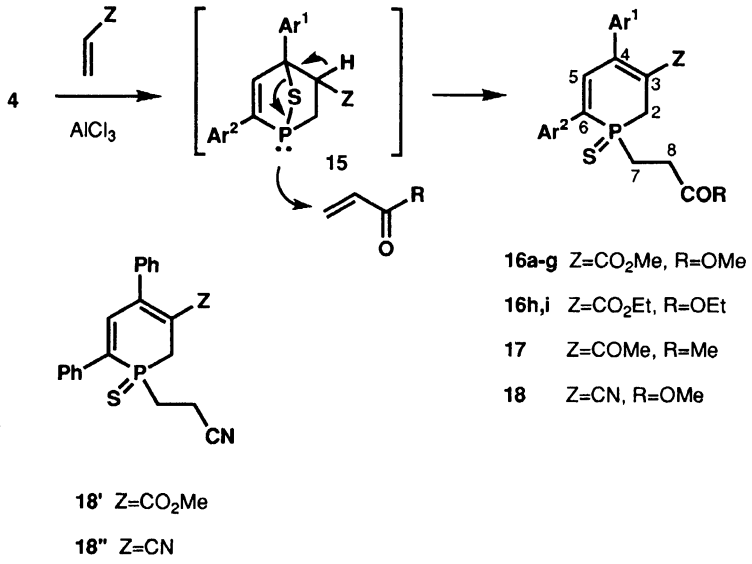
Scheme 4.

Table 3. The Reaction of **4a** with Methyl Acrylate in the Presence of Lewis-Acid to Give **16a**[a)]

Entry	Acrylate/equiv	Lewis-Acid	equiv	Time/h	Yield/%
1	2	$AlCl_3$	2	36	41
2	4	$AlCl_3$	1	8	46
3	6	$AlCl_3$	0.5	94	39
4	6	$AlCl_3$	1	3.5	74
5	6	$AlCl_3$	2	1.5	79
6	6	$AlCl_3$	3	1.1	80
7	6	$AlCl_3$	5	1.1	58
8	6	$AlCl_3$[b)]	3	18	69
9	6	$EtAlCl_2$	1.5	10	58

a) The reaction was carried out in dichloromethane at 25 °C. b) In diethyl ether.

ing excess (6 equiv) methyl acrylate and 1—3 equiv of $AlCl_3$ was found to be the optimum of the conditions examined (Entries 4—6). The use of $AlCl_3$ in Et_2O or $EtAlCl_2$ in CH_2Cl_2 required a longer reaction time to

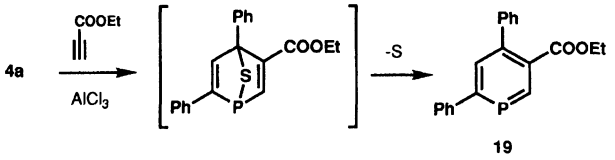


Scheme 5.

Table 4. The Reaction of **4** with the Dienophiles/Michael Acceptors in the Presence of $AlCl_3$[a)]

Entry	Ar^1	Ar^2	Thiaphosphole	Z	R	Time/min	Product	Yield/%
1	Ph	Ph	**4a**	CO_2Me	OMe	70	**16a**	80
2	*p*-$MeOC_6H_4$	Ph	**4b**	CO_2Me	OMe	60	**16b**	71
3	*p*-Tol	Ph	**4c**	CO_2Me	OMe	60	**16c**	61
4	2-Thienyl	Ph	**4d**	CO_2Me	OMe	60	**16d**	41
5	Ph	*p*-$MeOC_6H_4$	**4f**	CO_2Me	OMe	50	**16e**	76
6	Ph	*p*-Tol	**4g**	CO_2Me	OMe	60	**16f**	63
7	Ph	2-Thienyl	**4h**	CO_2Me	OMe	60	**16g**	23
8	Ph	Ph	**4a**	CO_2Et	OEt	120	**16h**	93
9	*p*-$MeOC_6H_4$	Ph	**4b**	CO_2Et	OEt	50	**16i**	59
10[b)]	Ph	Ph	**4a**	COMe	Me	260	**17**	38
11	Ph	Ph	**4a**	CN	OMe	390	**18**	53

a) Conditions, **4**: Acrylic esters: $AlCl_3$ = 1 : 6 : 3 in dichloromethane at 25 °C. b) Conditions, **4**: Methyl vinyl ketone: $AlCl_3$ = 1 : 4 : 2 in dichloromethane at 0→25 °C.



Scheme 6.

give moderate yields. The other adducts, **16b**—**i**, were similarly obtained (Table 4).

The reactions with methyl vinyl ketone in the presence of $AlCl_3$ afforded intractable unidentified decomposition products while moderate catalytic conditions such as $AlCl_3/Et_2O$ or Me_2AlCl/CH_2Cl_2 were not effective for the reaction. However, when the reaction was carried out using $AlCl_3$ at 0 °C to room temperature in a dilute CH_2Cl_2 solution, 1 : 2 adduct **17** (which was rather unstable) was obtained in a 38% yield. Although the reaction with acrylonitrile alone in the presence of $AlCl_3$ resulted in the formation of ill-defined products, the reaction with a mixture of methyl acrylate and excess acrylonitrile produced crossed adduct **18** in a 53% yield along with **16a** (3%) under catalytic conditions ($AlCl_3/CH_2Cl_2$). Neither of the possible adducts, **18'** nor **18"**, were obtained. In this case, the pathway appears to involve the Diels–Alder reaction preferentially with acrylonitrile at the first step, followed by the β-addition of the cycloadduct to methyl acrylate. Reactions with acrylaldehyde, 1,4-naphthoquinone, methyl crotonate, acrylonitrile, and methyl methacrylate under similar conditions resulted in failure.

Finally, the Lewis acid-promoted reaction of **4a** with ethyl propiolate afforded stable 3-ethoxycarbonyl-4,6-diphenylphosphorin (**19**) (27% yield) with the elimination of a sulfur atom (Scheme 6).[8)]

In conclusion, the first efficient synthesis of 1,2-thiaphospholes has been achieved. In addition, the first examples of both the Lewis acid-promoted double Diels–Alder reaction and the tandem Diels–Alder/β-addition reaction of a 1,2-thiaphosphole system have been

demonstrated.

Experimental

All melting points are uncorrected. IR spectra were measured on a Hitachi Model 270-30 spectrometer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL EX-270 spectrometer in $CDCl_3$ solution using TMS as an internal standard. ^{31}P NMR spectra were measured at 109 MHz on a JEOL EX-270 spectrometer in $CDCl_3$ solution using 85% H_3PO_4 as an external standard. Mass spectra were measured on a Hitachi mass spectrometer RMU-7M (70 eV). Elemental analyses were performed using a Yanagimoto Model MT-3 CHN recorder.

General Procedure for the Preparation of 4. To a solution of **1** (2 mmol) in dry dichloromethane (15 ml) was added tributylphosphine (6 mmol) with stirring under a nitrogen atmosphere. The mixture was heated under reflux for 4—9 h until **1** was consumed. Removal of the solvent and excess tributylphosphine followed by chromatography of the residue on silica gel (wakogel C-200) with benzene–hexane (1 : 30) as an eluent gave crude thiaphosphole **4** together with **5**. Compound **4** was recrystallized from ethyl acetate–ethanol and **5** was recrystallized from ethyl acetate–hexane.

3,5-Diphenyl-1,2-thiaphosphole (4a): Colorless needles. UV (Cyclohexane) 335 (ε 11770), 276 (23604), and 236 nm (11141); ^{1}H NMR δ=7.30—7.44 (m, 6H), 7.65—7.73 (m, 4H), and 8.18 (d, H-4, J_{HP}=8.3 Hz); ^{13}C NMR (DEPT) δ=132.6 (d-CH, C-4, J_{CP}=13.5 Hz), 135.8 (d-C, J_{CP}=8.5 Hz), 138.1 (d-C, J_{CP}=19.7 Hz), 159.0 (d-C, C-5, J_{CP}=5.8 Hz), and 183.2 (d-C, C-3, J_{CP}=56.1 Hz); ^{31}P NMR δ=203.8; MS *m/z* 254 (M^+; 100), 191 (M^+-PS; 30), 152 ($PhCPS^+$; 12), 121 ($PhCP^+$; 6), and 63 (PS^+; 10). HRMS Found: *m/z* 254.0319. Calcd for $C_{15}H_{11}PS$: M, 254.0320. Found: C, 70.55; H, 4.27%. Calcd for $C_{15}H_{11}PS$: C, 70.85; H, 4.36%.

5-(*p*-Methoxyphenyl)-3-phenyl-1,2-thiaphosphole (4b): Yellow plates. ^{1}H NMR δ=3.79 (s, CH_3), 6.90 (d, 2H, J_{HH}=8.9 Hz), 7.33—7.68 (m, 7H), and 8.06 (d, H-4, J_{HP}=8.3 Hz); ^{13}C NMR (DEPT) δ=55.3 (CH_3), 128.9 (d-C, J_{CP}=11.0 Hz), 131.6 (d-CH, C-4, J_{CP}=13.4 Hz), 138.2 (d-C, J_{CP}=22.0 Hz), 159.1 (d-C, C-5, J_{CP}=9.8 Hz), and 183.2 (d-C, C-3, J_{CP}=56.2 Hz); MS *m/z* (M^+; 100), 269 (M^+-CH_3; 31), 221 (M^+-PS; 6), 152 ($PhCPS^+$; 7), and 63 (PS^+; 10). Found: C, 67.72; H, 4.81%. Calcd for $C_{16}H_{13}OPS$: C, 67.59; H, 4.61%.

3-Phenyl-5-(*p*-tolyl)-1,2-thiaphosphole (4c): Pale yellow plates. ^{1}H NMR δ=2.34 (s, CH_3), 7.16—7.84 (m, 9H), and 8.12 (d, H-4, J_{HP}=8.3 Hz); ^{13}C NMR (DEPT) δ=21.2 (CH_3), 132.1 (d-CH, C-4, J_{CP}=13.4 Hz), 133.1 (d-C, J_{CP}=8.5 Hz), 138.1 (d-C, J_{CP}=20.7 Hz), 159.3 (d-C, C-5, J_{CP}=8.6 Hz), and 183.2 (d-C, C-3, J_{CP}=56.1 Hz); MS *m/z* 268 (M^+; 100), 205 (M^+-PS; 24), 152 ($PhCPS^+$; 5), and 63 (PS^+; 6). Found: C, 71.89; H, 4.76%. Calcd for $C_{16}H_{13}PS$: C, 71.62; H, 4.88%.

3-Phenyl-5-(2-thienyl)-1,2-thiaphosphole (4d): Pale yellow needles. ^{1}H NMR δ=7.02 (dd, 1H, J_{HH}=3.3 and 5.3 Hz), 7.26 (dd, 1H, J_{HH}=1.0 and 5.3 Hz), 7.32 (dd, 1H, J_{HH}=1.0 and 3.3 Hz), 7.35—7.65 (m, 5H), and 8.08 (d, H-4, J_{HP}=7.9 Hz); ^{13}C NMR (DEPT) δ=132.2 (d-CH, C-4, J_{CP}=13.5 Hz), 137.7 (d-C, J_{CP}=22.0 Hz), 139.1 (d-C, J_{CP}=9.3 Hz), 151.4 (d-C, C-5, J_{CP}=9.7 Hz), and 183.0 (d-C, C-3, J_{CP}=57.4 Hz); MS *m/z* 260 (M^+; 100), 197 (M^+-PS; 36), 152 ($PhCPS^+$; 12), and 63 (PS^+; 12). Found: C, 60.25; H, 3.61 %. Calcd for $C_{13}H_9PS_2$: C, 59.98; H, 3.48%.

3-Phenyl-5-styryl-1,2-thiaphosphole (4e): Orange plates. ^{1}H NMR δ=7.09 (d, 1H, J_{HH}=16.2 Hz), 7.28—7.67 (m, 11H), and 7.91 (d, H-4, J_{HP}=8.6 Hz); ^{13}C NMR (DEPT) δ=123.1 (d-CH, J_{CP}=9.7 Hz), 131.6 (d-CH, J_{CP}=6.2 Hz), 134.8 (d-CH, C-4, J_{CP}=13.5 Hz), 136.5 (C), 137.8 (d-C, J_{CP}=20.8 Hz), 157.1 (d-C, C-5, J_{CP}=9.7 Hz), and 182.6 (d-C, C-3, J_{CP}=57.4 Hz); MS *m/z* 280 (M^+; 100), 215 (30), 152 ($PhCPS^+$; 5), 115 (27), and 63 (PS^+; 15). Found: C, 72.68; H, 4.97%. Calcd for $C_{17}H_{13}PS$: C, 72.84; H, 4.67%.

3-(*p*-Methoxyphenyl)-5-phenyl-1,2-thiaphosphole (4f): Yellow plates. ^{1}H NMR δ=3.80 (s, CH_3), 6.92 (d, 2H, J_{HH}=8.6 Hz), 7.32—7.42 (m, 3H), 7.61 (dd, 2H, J_{HH}=1.7 and 8.6 Hz), 7.70 (dd, 2H, J_{HH}=1.7 and 8.6 Hz), and 8.12 (d, H-4, J_{HP}=8.3 Hz); ^{13}C NMR (DEPT) δ=55.3 (CH_3), 130.9 (d-C, J_{CP}=20.8 Hz), 132.3 (d-CH, C-4, J_{CP}=13.5 Hz), 135.9 (d-C, J_{CP}=7.3 Hz), 158.8 (d-C, C-5, J_{CP}=9.7 Hz), and 183.0 (d-C, C-3, J_{CP}=57.3 Hz); MS *m/z* 284 (M^+; 100), 269 (M^+-CH_3; 31), 221 (M^+-PS; 6), 152 ($PhCPS^+$; 6), and 63 (PS^+; 10). Found: C, 67.64; H, 4.55%. Calcd for $C_{16}H_{13}OPS$: C, 67.59; H, 4.61%.

5-Phenyl-3-(*p*-tolyl)-1,2-thiaphosphole (4g): Colorless needles. ^{1}H NMR δ=2.37 (s, CH_3), 7.19—7.73 (m, 9H), and 8.16 (d, H-4, J_{HP}=8.3 Hz); ^{13}C NMR (DEPT) δ=21.3 (CH_3), 132.5 (d-CH, C-4, J_{CP}=12.2 Hz), 135.3 (d-C, J_{CP}=20.7 Hz), 135.9 (d-C, J_{CP}=7.3 Hz), 158.9 (d-C, C-5, J_{CP}=8.5 Hz), and 183.3 (d-C, C-3, J_{CP}=57.4 Hz); MS *m/z* 268 (M^+; 100), 205 (M^+-PS; 26), 152 ($PhCPS^+$; 6), and 63 (PS^+, 16). Found: C, 71.64; H, 4.91%. Calcd for $C_{16}H_{13}PS$: C, 71.62; H, 4.88%.

5-Phenyl-3-(2-thienyl)-1,2-thiaphosphole (4h): Pale yellow needles. ^{1}H NMR δ=7.03 (dd, 1H, J_{HH}=3.6 and 5.3 Hz), 7.26 (dd, 1H, J_{HH}=1.0 and 5.3 Hz), 7.33—7.42 (m, 4H), 7.68 (dd, 2H, J_{HH}=1.7 and 8.2 Hz), and 8.09 (d, H-4, J_{HP}=7.6 Hz); ^{13}C NMR (DEPT) δ=132.2 (d-CH, C-4, J_{CP}=13.5 Hz), 135.5 (d-C, J_{CP}=7.3 Hz), 140.9 (d-C, J_{CP}=24.4 Hz), 158.8 (d-C, C-5, J_{CP}=9.8 Hz), and 174.1 (d-C, C-3, J_{CP}=56.1 Hz); MS *m/z* 260 (M^+; 100), 197 (M^+-PS; 40), 152 ($PhCPS^+$; 14), 121 ($PhCP^+$; 7), and 63 (PS^+; 21). Found: C, 60.17; H, 3.66%. Calcd for $C_{13}H_9PS_2$: C, 59.98; H, 3.48%.

5-Phenyl-3-styryl-1,2-thiaphosphole (4i): Yellow plates. ^{1}H NMR δ=7.16—7.71 (m, 12H), and 8.16 (d, H-4, J_{HP}=8.6 Hz); ^{13}C NMR (DEPT) δ=124.9 (d-CH, J_{CP}=28.1 Hz), 129.2 (d-CH, J_{CP}=25.6 Hz), 130.7 (d-CH, C-4, J_{CP}=13.5 Hz), 135.7 (d-C, J_{CP}=7.4 Hz), 136.8 (d-C, J_{CP}=2.4 Hz), 158.7 (d-C, C-5, J_{CP}=8.5 Hz), and 179.6 (d-C, C-3, J_{CP}=53.7 Hz); MS *m/z* 280 (M^+; 100), 215 (33), 152 ($PhCPS^+$; 11), 121 ($PhCP^+$; 11), 115 (27), and 63 (PS^+; 15). Found: C, 72.99; H, 4.94%. Calcd for $C_{17}H_{13}PS$: C, 72.84; H, 4.67%.

3,5,6,8-Tetraphenyl-2,9-dithia-1-phosphabicyclo-[4.3.0]nona-3,7-diene (5a): Colorless cubes. ^{1}H NMR δ=4.94 (dd, H-5, $J_{4,5}$=3.0 Hz, J_{HP}=10.9 Hz), 5.96 (dd, H-4, $J_{4,5}$=3.0 Hz, J_{HP}=3.0 Hz), 6.37 (d, H-7, J_{HP}=36.0 Hz), and 7.03—7.67 (m, 20H); ^{13}C NMR (DEPT) δ=47.7 (CH, C-5), 66.5 (d-C, C-6, J_{CP}=56.1 Hz), 108.2 (d-CH, J_{CP}=9.8 Hz), 123.5 (d-CH), J_{CP}=7.4 Hz), 133.4 (d-C, J_{CP}=6.1 Hz), 134.5 (d-C, J_{CP}=3.6 Hz), 135.1 (C), 139.1 (d-C, J_{CP}=13.4 Hz), 141.2 (d-C, J_{CP}=8.5 Hz), and 152.0 (d-C, J_{CP}=12.2 Hz); ^{31}P NMR δ=122.4; MS *m/z* 478 (M^+; very

weak), 414 (M^+-2S; 0.4), 254 (Thiaphosphole$^+$; 100), and 191 (254−PS; 34). HRMS Found: m/z 478.0964. Calcd for $C_{30}H_{23}PS_2$: M, 478.0981.

5,6-Diphenyl-3,8-di-*p*-tolyl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene (5c): Colorless cubes. ^{1}H NMR δ=2.34 (s, CH_3), 2.35 (s, CH_3), 4.92 (dd, H-5, $J_{4,5}$=3.0 Hz, J_{HP}=11.6 Hz), 5.91 (dd, H-4, $J_{4,5}$=3.0 Hz, J_{HP}=3.0 Hz), 6.28 (d, H-7, J_{HP}=36.3 Hz), and 7.03—7.63 (m, 18H); ^{13}C NMR (DEPT) δ=21.3 ($CH_3\times2$), 47.8 (CH, C-5), 66.8 (d-C, C-6, J_{CP}=57.4 Hz), 107.5 (d-CH, J_{CP}=9.7 Hz), 122.5 (d-CH, J_{CP}=8.5 Hz), 130.7 (d-C, J_{CP}=4.9 Hz), 131.8 (d-C, J_{CP}=4.9 Hz), 135.3 (C), 139.2 (C), 139.3 (d-C, J_{CP}=12.2 Hz), 139.8 (C), 141.1 (d-C, J_{CP}=8.6 Hz), and 152.1 (d-C, J_{CP}=12.3 Hz); MS m/z 506 (M^+; very weak), 442 (M^+-2S; 0.3), 268 (Thiaphosphole$^+$; 100), 152 (PhCPS$^+$; 7). HRMS Fouund: m/z 506.1419. Calcd for $C_{32}H_{27}PS_2$: M, 506.1294.

3,8-Diphenyl-5,6-di-*p*-tolyl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene (5g): Colorless cubes. ^{1}H NMR δ=2.27 (s, CH_3), 2.34 (d, CH_3, J_{HP}=2.6 Hz), 4.89 (dd, H-5, $J_{4,5}$=3.0 Hz, J_{HP}=10.9 Hz), 5.93 (dd, H-4, $J_{4,5}$=3.0 Hz, J_{HP}=3.0 Hz), 6.33 (d, H-7, J_{HP}=36.3 Hz), and 6.93—7.66 (m, 18H); ^{13}C NMR (DEPT) δ=21.0 (CH_3), 21.2 (CH_3) 47.1 (CH, C-5), 66.4 (d-C, C-6, J_{CP}=56.2 Hz), 108.5 (d-CH, J_{CP}=9.7 Hz), 124.0 (d-CH, J_{CP}=7.4 Hz), 131.9 (C), 133.5 (d-C, J_{CP}=4.9 Hz), 134.6 (d-C, J_{CP}=3.7 Hz), 136.2 (d-C, J_{CP}=12.2 Hz), 137.1 (C), 138.3 (d-C, J_{CP}=4.9 Hz), 140.4 (d-C, J_{CP}=8.6 Hz), and 151.7 (d-C, J_{CP}=12.2 Hz); MS m/z 506 (M^+; 0.3), 442 (M^+-2S; 0.4), 339 (2.9), and 268 (Thiaphosphole$^+$; 100). HRMS Found: m/z 506.1280. Calcd for $C_{32}H_{27}PS_2$: M, 506.1294.

The Thermal Double Diels–Alder Reaction of 4a with Dienophiles. A solution of **4a** (0.78 mmol) and norbornadiene or norbornene (4.68 mmol) in dry *o*-dichlorobenzene (12 ml) was refluxed under a nitrogen atmosphere for 4 h (18 h for norbornene). After the solvent was removed, the residue was chromatographed on silica gel (Wakogel C-200) with ethyl acetate–hexane (1 : 100) as an eluent to give crude **8** or **9**, which were recrystallized from ethyl acetate–hexane. The reaction of **4a** with diethyl azodicarboxylate was carried out in refluxing xylene for 0.5 h to give adduct **14**.

8, 15- Diphenyl- 1- phosphahexacyclo[6.6.2.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]octadec-4,11,15-triene 1-Sulfide (*exo-exo* 8a): Yield 57%. Colorless cubes. Mp 266—268 °C ^{1}H NMR δ=0.99 (d, 2H, H-17 and 18, J_{HH}=9.2 Hz), 2.01 (d, 2H, H-17′ and 18′, J_{HH}=9.2 Hz), 2.11 (dd, 2H, H-2 and 14, J_{HH}=8.6 Hz, J_{HP}=8.6 Hz), 2.49—2.55 (m, 4H), 3.40 (broad-s, 2H), 6.15 (dd, 2H, J_{HH}=5.3 Hz, J_{HP}=3.0 Hz), 6.29 (dd, 2H, J_{HH}=5.3 Hz, J_{HP}=3.0 Hz), and 7.23—7.66 (m, 11H, H-16 and arom); ^{13}C NMR (DEPT) δ=41.7 ($CH_2\times2$, C-17 and 18), 43.2 (CH×2), 45.6 (CH×2), 46.0 (d-CH×2, C-2 and 14, J_{CP}=47.6 Hz), 48.1 (d-C, C-8, J_{CP}=30.5 Hz), 56.2 (CH×2), 136.4 (d-C, J_{CP}=6.1 Hz), 137.2 (d-C, C-15, J_{CP}=54.9 Hz), 139.7 (CH×2), 140.1 (d-CH×2, J_{CP}=12.2 Hz), 143.2 (C), and 145.3 (CH, C-16); ^{31}P NMR δ=33.2; MS m/z 438 (M^+; 50), 372 ($M^+-C_5H_6$; 12), 280 (372-Norbornadiene; 100), 248 (280-S; 10), and (PhCP$^+$; 30), 115 (7). Found: C, 79.64; H, 6.21%. Calcd for $C_{29}H_{27}PS$: C, 79.42; H, 6.21%.

8, 15- Diphenyl- 1- phosphahexacyclo[6.6.2.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]octadec-4,11,15-triene 1-Sulfide (*endo-exo* 8b): Yield 13%. Colorless cubes. Mp 238—239 °C. ^{1}H NMR δ=0.94 (d, 1H, H-17, J_{HH}=9.2 Hz), 1.26—1.43 (m, 2H, H-18 and 18′), 1.90 (d, 1H, H-17′, J_{HH}=9.2 Hz), 2.10 (dd, 1H, H-2, J_{HH}=8.6 Hz, J_{HP}=8.6 Hz), 2.52—2.66 (m, 3H), 2.78 (ddd, 1H, H-14, J_{HH}=3.3 and 8.9 Hz, J_{HP}=8.9 Hz), 3.10 (ddd, 1H, H-9, J_{HH}=3.3 and 8.9 Hz, J_{HP}=8.9 Hz), 3.28 (broad-s, 1H), 3.40 (broad-s, 1H), 5.74 (dd, 2H, J_{HH}=6.9 Hz, J_{HP}=3.0 Hz), 6.21 (dd, 1H, $J_{HP,HH}$=3.0 and 5.3 Hz), 6.31 (dd, 1H, $J_{HP,HH}$=3.0 and 5.3 Hz), 6.82 (d, 1H, H-16, J_{HP}=29.0 Hz), and 7.25—7.66 (m, 10H); ^{13}C NMR (DEPT) δ=42.1 (CH_2, C-17), 43.1 (CH), 43.6 (d-CH, C-14, J_{CP}=57.4 Hz), 44.5 (CH), 45.5 (CH), 46.2 (CH), 46.7 (d-CH, C-2, J_{CP}=47.6 Hz), 47.7 (d-C, C-8, J_{CP}=29.3 Hz), 51.3 (d-CH_2, C-18, J_{CP}=11.0 Hz), 55.6 (d-CH, C-9, J_{CP}=7.4 Hz), 55.7 (CH), 130.8 (d-CH, J_{CP}=4.8 Hz), 133.2 (d-C, C-15, J_{CP}=58.6 Hz), 134.8 (CH), 136.2 (d-C, J_{CP}=6.1 Hz), 139.8 (CH), 140.0 (d-CH, J_{CP}=12.2 Hz), 143.0 (CH, C-16), and 143.2 (C); ^{31}P NMR δ=32.3; MS m/z 438 (M^+; 57), 372 ($M^+-C_5H_6$; 25), 280 (372-Norbornadiene; 100), 248 (280−S; 12), 217 (248−P; 20), 121 (PhCP$^+$; 57), and 115 (25). Found: C, 79.16; H, 6.18%. Calcd for $C_{29}H_{27}PS$: C, 79.42; H, 6.21%.

8, 15- Diphenyl- 1- phosphahexacyclo[6.6.2.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]octadec-15-ene 1-Sulfide (*exo-exo* 9): Yield 34%. Colorless cubes. Mp 243 °C. ^{1}H NMR δ=0.75 (d, 2H, H-17 and 18, J_{HH}=10.6 Hz), 1.13—1.17 (m, 2H), 1.27—1.44 (m, 4H), 1.51—1.64 (m, 2H), 1.74 (d, 2H, H-17′ and 18′, J_{HH}=10.6 Hz), 1.98 (broad-s, 2H), 2.20 (dd, 2H, H-2 and 14, J_{HH}=9.6 Hz, J_{HP}=9.6 Hz), 2.57 (dd, 2H, H-7 and 9, J_{HH}=9.6 Hz, J_{HP}=9.6 Hz), 2.88 (dd, 2H, J_{HH}=3.3 Hz, J_{HP}=7.9 Hz), and 7.20—7.79 (m, 11H, H-16 and arom); ^{13}C NMR (DEPT) δ=31.5 ($CH_2\times2$), 32.1 (d-$CH_2\times2$, J_{CP}=14.7 Hz), 34.7 ($CH_2\times2$, C-17 and 18), 38.2 (CH×2), 40.4 (CH×2), 47.5 (d-C, C-8, J_{CP}=40.3 Hz), 49.4 (d-CH×2, C-2 and 14, J_{CP}=48.8 Hz), 57.8 (d-CH×2, C-7 and 9, J_{CP}=6.1 Hz), 135.7 (d-C, C-15, J_{CP}=54.9 Hz), 136.5 (d-C, J_{CP}=7.3 Hz), 143.6 (C), and 144.8 (CH, C-16); ^{31}P NMR δ=23.7; MS m/z 442 (M^+; 6), 348 (M^+−Norbornene; 60), 316 (348−S; 4), 254 (Thiaphosphole$^+$; 100), 191 (254−PS; 6), 121 (PhCP$^+$; 7), and 115 (8). HRMS Found: m/z 442.1885. Calcd for $C_{29}H_{31}PS$: M, 442.1886. Found: C, 78.80; H, 7.16%. Calcd for $C_{29}H_{31}PS$: C, 78.70; H, 7.06%.

1,2,9,10-Tetraethoxycarbonyl-3-phenyl-1,2,4a,9,10,10a-hexahydro-1,2,9,10-tetraaza-10a-phosphaphenanthrene 10a-Sulfide (14): Chromatographed with ethyl acetate–hexane (1 : 6) and recrystallized from ethyl acetate–hexane. Yield 60%. Colorless cubes. Mp 149—150 °C. IR (KBr) 1734 and 1756 cm^{-1} (C=O); ^{1}H NMR δ=0.68 (t, CH_3, J_{HH}=7.2 Hz), 1.00 (t, CH_3, J_{HH}=7.2 Hz), 1.32 (t, CH_3, J_{HH}=7.2 Hz, J_{HP}=2.4 Hz), 1.43 (t, CH_3, J_{HH}=7.2 Hz), 4.25—4.54 (m, 8H), 5.37—5.55 (m, 1H, H-4a), and 7.26—7.73 (m, 10H); ^{13}C NMR (DEPT) δ=13.9 (CH_3), 14.2 ($CH_3\times2$), 14.4 (CH_3), 50.0 (d-CH, C-4a, J_{CP}=53.4 Hz), 50.7 (d-CH, C-4a′, J_{CP}=53.5 Hz), 63.3 (CH_2), 63.6 ($CH_2\times2$), 64.0 (CH_2), 119.9 (CH), 126.0 (CH), 126.8 (CH), 128.5 (CH×2), 129.0 (CH), 129.3 (CH×2), 129.6 (CH), 129.9 (CH), 132.1 (C), 132.5 (C), 140.3 (C), 146.8 (C), 152.4 (C=O), 152.6 (C=O), 152.7 (C=O), 153.1 (C=O), ^{31}P NMR δ=−107.8 and −109.5; MS m/z 602 (M^+; 1), 558 (5), 530 (6), and 29 (Et^+; 100). Found: C, 53.64; H, 5.25; N, 9.17%. Calcd for $C_{27}H_{31}N_4O_8PS$: C, 53.82; H, 5.19; N, 9.30%.

The Reaction of 4a with Norbornadiene and

Methyl Acrylate or Acrylonitrile. A solution of **4a** (0.78 mmol), norbornadiene (1.56 mmol), and methyl acrylate (3.90 mmol) in dry *o*-dichlorobenzene (12 ml) was refluxed for 18 h under a nitrogen atmosphere. After the solvent was removed, the residue was chromatographed on silica gel (Wakogel C-200) with ethyl acetate–hexane (1 : 100) as an eluent to give the products. Recrystallization from ethyl acetate–hexane afforded **10a** (14%), **10b** (21%), and **8** (13%). Similarly the reaction of **4a**, norbornadiene, and acrylonitrile afforded **11a** (22%), **11b** (18%), and **8** (24%) under similar conditions.

12- Methoxycarbonyl- 8, 10- diphenyl- 1- phosphatetracyclo[6.2.2.1^{3,6}.0^{2,7}]tridec-4,9-diene 1-Sulfide (10a): Colorless cubes. Mp 191—193 °C. IR (KBr) 1730 cm^{-1} (C=O); ^{1}H NMR δ=1.00 (d, 1H, H-13, J_{HH}=9.6 Hz), 1.97 (d, 1H, H-13, J_{HH}=9.6 Hz), 2.22 (ddd, 1H, H-11, J_{HH}=11.2 and 14.2 Hz, J_{HP}=14.2 Hz), 2.42 (ddd, 1H, H-11, J_{HH}=5.9 and 14.2 Hz, J_{HP}=14.2 Hz), 2.34—2.42 (m, 1H), 2.83 (s, 1H), 2.94 (ddd, 1H, H-12, J_{HH}=5.9 and 11.2 Hz, J_{HP}=5.9 Hz), 3.19 (s, CH_3), 3.21—3.29 (m, 1H), 3.49 (s, 1H), 6.33 (dd, 1H, J_{HH}=3.0 and 5.3 Hz), 6.42 (dd, 1H, J_{HH}=3.0 and 5.3 Hz), 7.22 (d, 1H, H-9, J_{HP}=27.4 Hz), 7.39—7.44 (m, 8H), and 7.63—7.66 (m, 2H); ^{13}C NMR (DEPT) δ=31.7 (d-CH_2, C-11, J_{CP}=50.0 Hz), 41.9 (CH_2, C-13), 43.6 (CH), 44.0 (d-CH, J_{CP}=3.6 Hz), 44.5 (d-CH, C-2, J_{CP}=45.2 Hz), 46.2 (CH), 47.3 (d-C, C-8, J_{CP}=33.0 Hz), 51.8 (CH_3), 54.2 (d-CH, J_{CP}=6.1 Hz), 135.7 (d-C, J_{CP}=6.1 Hz), 138.3 (d-C, C-10, J_{CP}=57.3 Hz), 139.2 (CH), 139.2 (d-CH, J_{CP}=12.2 Hz), 142.8 (C), 147.2 (CH, C-9), and 172.4 (d-C=O, J_{CP}=7.4 Hz); ^{31}P NMR δ=27.6; MS *m/z* 432 (M^+; 5), 346 (M^+ − Methyl acrylate; 8), 280 (346 − C_5H_6; 100), 248 (280 − S; 5), 217 (10), and 121 ($PhCP^+$; 27). HRMS Found: *m/z* 432.1315. Calcd for $C_{26}H_{25}O_2PS$: M, 432.1315.

12- Methoxycarbonyl- 8, 10- diphenyl- 1- phosphatetracyclo[6.2.2.1^{3,6}.0^{2,7}]tridec-4,9-diene 1-Sulfide (10b): White powder. Mp 254—255 °C. IR (KBr) 1732 cm^{-1} (C=O); ^{1}H NMR δ=1.01 (d, 1H, H-13, J_{HH}=9.2 Hz), 2.06—2.21 (m, 3H, H-11 and H-13), 2.39 (dd, 1H, H-2, J_{HH}=9.2 Hz, J_{HP}=9.2 Hz), 2.48—2.61 (m, 2H), 3.37 (s, CH_3), 3.52 (s, 1H), 3.58 (ddd, 1H, H-12, J_{HH}=5.3 and 10.2 Hz, J_{HP}=5.3 Hz), 6.11 (dd, 1H, J_{HH}=3.0 and 5.6 Hz), 6.30 (dd, 1H, J_{HH}=3.0 and 5.6 Hz), 7.26—7.47 (m, 9H, H-9 and arom), and 7.63—7.65 (m, 2H); ^{13}C NMR (DEPT) δ=34.3 (d-CH_2, C-11, J_{CP}=48.9 Hz), 41.5 (CH_2, C-13), 43.6 (CH, C-2, J_{CP}=46.4 Hz), 43.7 (CH), 46.1 (CH), 46.9 (d-C, C-8, J_{CP}=33.0 Hz), 51.9 (CH_3), 52.2 (d-CH, J_{CP}=7.4 Hz), 54.0 (d-CH, J_{CP}=6.1 Hz), 136.0 (d-C, J_{CP}=7.3 Hz), 136.6 (d-C, C-10, J_{CP}=59.8 Hz), 139.5 (CH), 139.6 (d-CH, J_{CP}=9.7 Hz), 141.6 (C) 143.4 (CH, C-9), and 172.8 (d-C=O, J_{CP}=7.3 Hz); ^{31}P NMR δ=27.0; MS *m/z* 432 (M^+; 5), 346 (M^+ − Methyl acrylate; 6), 280 (346 − C_5H_6; 100), 248 (280 − S; 5), 217 (11), and 121 ($PhCP^+$; 22). Found: C, 72.22; H, 5.65%. Calcd for $C_{26}H_{25}O_2PS$: C, 72.20; H, 5.83%.

12-Cyano-8,10-diphenyl-1-phosphatetracyclo[6.2.2.1^{3,6}.0^{2,7}]tridec-4,9-diene 1-Sulfide (11a): Pale yellow cubes. Mp 213—214 °C. IR (KBr) 2236 cm^{-1} (CN); ^{1}H NMR δ=1.07 (d, 1H, H-13, J_{HH}=9.6 Hz), 1.93 (d, 1H, H-13, J_{HH}=9.6 Hz), 2.31 (dd, 1H, H-2, J_{HH}=8.6 Hz, J_{HP}=8.6 Hz), 2.37—2.49 (m, 2H, H-11), 2.97 (s, 1H), 3.06 (ddd, 1H and H-12, J_{HH}=5.6, 11.2 Hz, J_{HP}=5.6 Hz), 3.23 (dd, 1H, H-7, J_{HH}=8.6 Hz, J_{HP}=8.6 Hz), 3.52 (s, 1H), 6.37 (dd, 1H, J_{HH}=3.0 and 5.6 Hz), 6.50 (dd, 1H, J_{HH}=3.0 and 5.6 Hz), 7.11 (d, 1H, H-9, J_{HP}=28.0 Hz), and 7.40—7.62 (m, 10H); ^{13}C NMR (DEPT) δ=32.6 (d-CH_2, C-11, J_{CP}=47.6 Hz), 40.9 (d-CH, C-12, J_{CP}=6.1 Hz), 41.5 (CH_2, C-13), 43.5 (CH), 44.0 (d-CH, C-2, J_{CP}=45.1 Hz), 45.9 (d-CH, C-7, J_{CP}=2.4 Hz), 46.3 (CH), 46.8 (d-C, C-8, J_{CP}=30.5 Hz), 118.8 (d-CN, J_{CP}=4.9 Hz), 135.0 (d-C, J_{CP}=7.3 Hz), 139.3 (CH), 139.4 (d-CH, J_{CP}=13.4 Hz), 139.9 (d-C, C-10, J_{CP}=57.3 Hz), 141.6 (C), and 144.9 (CH, C-9); MS *m/z* 399 (M^+; 7), 346 (M^+ − Acrylonitrile; 8), 280 (346 − C_5H_6; 100), 254 (Thiaphosphole$^+$; 7), 248 (280 − S; 9), and 121 ($PhCP^+$; 22). Found: C, 75.07; H, 5.78; N, 3.38%. Calcd for $C_{25}H_{22}NPS$: C, 75.16; H, 5.55; N, 3.51%.

12-Cyano-8,10-diphenyl-1-phosphatetracyclo[6.2.2.1^{3,6}.0^{2,7}]tridec-4,9-diene 1-Sulfide (11b): Orange solids. Mp 146—148 °C. IR (KBr) 2240 cm^{-1} (CN); ^{1}H NMR δ=1.03 (d, 1H, H-13, J_{HH}=9.6 Hz), 1.99 (d, 1H, H-13, J_{HH}=9.6 Hz), 2.12 (dd, 1H, H-2, J_{HH}=8.9 Hz, J_{HP}=8.9 Hz), 2.30 (ddd, 1H, H-11, J_{HH}=3.6 and 14.5 Hz, J_{HP}=14.5 Hz), 2.36 (dd, 1H, H-7, J_{HH}=8.9 Hz, J_{HP}=8.9 Hz), 2.63 (ddd, 1H, H-11, J_{HH}=11.6 and 14.5 Hz, J_{HP}=11.6 Hz), 2.54 (s, 1H), 3.48 (s, 1H), 3.63 (ddd, 1H, H-12, J_{HH}=3.6 and 11.6 Hz, J_{HP}=6.6 Hz), 6.10 (dd, 1H, J_{HH}=3.3 and 5.3 Hz), 6.30 (dd, 1H, J_{HH}=3.3 and 5.3 Hz), and 7.35—7.64 (m, 11H, H-9 and arom); ^{13}C NMR (DEPT) δ=33.5 (d-CH_2, C-11, J_{CP}=47.6 Hz), 38.0 (d-CH, C-12, J_{CP}=6.1 Hz), 41.3 (CH_2, C-13), 43.6 (CH), 44.2 (d-CH, C-2, J_{CP}=45.2 Hz), 46.5 (CH), 47.2 (d-C, C-8, J_{CP}=31.7 Hz), 53.0 (d-CH, C-7, J_{CP}=2.4 Hz), 119.9 (CN), 135.2 (d-C, J_{CP}=6.2 Hz), 139.1 (CH), 139.8 (d-C, C-10, J_{CP}=58.6 Hz), 140.0 (C), 140.0 (d-CH, J_{CP}=12.2 Hz), and 142.2 (CH, C-9); MS *m/z* 399 (M^+; 6), 346 (M^+ − Acrylonitrile; 6), 280 (346 − C_5H_6; 100), 254 (Thiaphosphole$^+$; 11), 248 (280 − S; 8), and 121 ($PhCP^+$; 30). HRMS Found: *m/z* 399.1211. Calcd for $C_{25}H_{22}NPS$: M, 399.1213.

The Reaction of 4 with Acrylates in the Presence of Aluminum Chloride. Typical Procedure (Table 4, Entry 1). To a solution of aluminum chloride (2.34 mmol) in anhydrous dichloromethane (12 ml) was added methyl acrylate (4.68 mmol) at room temperature. After the solution had cleared with stirring for several minutes, **4a** (0.78 mmol) was added to it and the reaction mixture was stirred at the same temperature for 70 min. The reaction was then quenched with saturated aqueous ammonium chloride, and the organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica gel (Wakogel C-200) with ethyl acetate–hexane (1 : 10) as an eluent and recrystallized from ethyl acetate–hexane to give **16a**.

3- Methoxycarbonyl- 1- [2- (methoxycarbonyl)ethyl]- 4, 6- diphenyl- 1, 2- dihydrophosphorin 1- Sulfide (16a): Pale yellow needles. Mp 138—139 °C. IR (KBr) 1700 and 1736 cm^{-1} (C=O); ^{1}H NMR δ=2.29—2.39 (m, CH_2, H-7), 2.66—2.77 (m, CH_2, H-8), 3.44 (dd, CH_2, H-2, J_{HH}=13.5 Hz, J_{HP}=15.8 Hz), 3.52 (s, CH_3), 3.67 (s, CH_3), 6.76 (d, 1H, H-5, J_{HP}=30.4 Hz), 7.21—7.39 (m, 8H), and 7.66—7.70 (m, 2H); ^{13}C NMR (DEPT) δ=26.8 (CH_2, C-8), 26.9 (d-CH_2, C-7, J_{CP}=57.4 Hz), 33.2 (d-CH_2, C-2, J_{CP}=56.2 Hz), 52.0 (CH_3), 52.1 (CH_3), 121.6 (d-C, C-3, J_{CP}=9.7 Hz), 136.4 (d-C, C-6, J_{CP}=70.8 Hz), 138.8 (CH, C-5), 142.8 (d-C, C-4, J_{CP}=15.9 Hz), 167.8 (d-C=O, J_{CP}=8.6 Hz), and 172.4 (d-C=O, J_{CP}=14.7 Hz); ^{31}P NMR δ=28.2; MS *m/z* 426 (M^+; 75), 393 (M^+ − SH; 100), 339 (M^+ − Meth-

yl acrylate−H; 4), 307 (339−S; 11), 275 (15), 245 (26), 215 (60), 121 ($PhCP^+$; 18), and 115 (36). HRMS Found: m/z 426.1061. Calcd for $C_{23}H_{23}O_4PS$: M, 426.1056. Found: C, 64.77; H, 5.62%. Calcd for $C_{23}H_{23}O_4PS$: C, 64.78; H, 5.44%.

3-Methoxycarbonyl-1-[2-(methoxycarbonyl)ethyl]-4-(*p*-methoxyphenyl)-6-phenyl-1,2-dihydrophosphorin 1-Sulfide (16b): Yellow cubes. Mp 124—125 °C IR (KBr) 1704 and 1732 cm^{-1} (C=O); ^1H NMR δ=2.27—2.38 (m, CH_2, H-7), 2.65—2.76 (m, CH_2, H-8), 3.41 (dd, CH_2, H-2, J_{HH}=14.2 Hz, J_{HP}=15.8 Hz), 3.56 (s, CH_3), 3.67 (s, CH_3), 3.82 (s, CH_3), 6.76 (d, 1H, H-5, J_{HP}=30.3 Hz), 6.86—6.90 (m, 2H), 7.15—7.39 (m, 5H), and 7.66—7.68 (m, 2H); ^{13}C NMR (DEPT) δ=26.9 (CH_2, C-8), 26.9 (d-CH_2, C-7, J_{CP}=57.4 Hz), 33.4 (d-CH_2, C-2, J_{CP}=54.9 Hz), 52.0 (CH_3), 52.1 (CH_3), 55.3 (CH_3), 113.7 (CH×2), 121.0 (d-C, C-3, J_{CP}=11.0 Hz), 136.3 (d-C, C-6, J_{CP}=70.8 Hz), 139.2 (CH, C-5), 142.2 (d-C, C-4, J_{CP}=15.9 Hz), 168.2 (d-C=O, J_{CP}=8.6 Hz), and 172.4 (d-C=O, J_{CP}=17.1 Hz); MS m/z 456 (M^+; 70), 423 (M^+−SH; 100), 369 (M^+−Methyl acrylate−H; 3), 337 (369−S; 8), 275 (20), 215 (18), 121 ($PhCP^+$; 20), and 115 (16). Found: C, 62.92; H, 5.79%. Calcd for $C_{24}H_{25}O_5PS$: C, 63.15; H, 5.52%.

3-Methoxycarbonyl-1-[2-(methoxycarbonyl)ethyl]-6-phenyl-4-(*p*-tolyl)-1,2-dihydrophosphorin 1-Sulfide (16c): Yellow cubes. Mp 84—86 °C. IR (KBr) 1710 and 1738 cm^{-1} (C=O); ^1H NMR δ=2.28—2.38 (m, CH_2, H-7), 2.36 (s, CH_3), 2.65—2.76 (m, CH_2, H-8), 3.43 (dd, CH_2, H-2, J_{HH}=12.5 Hz, J_{HP}=15.8 Hz), 3.55 (s, CH_3), 3.66 (s, CH_3), 6.75 (d, 1H, H-5, J_{HP}=30.7 Hz), 7.09—7.43 (m, 7H), and 7.66—7.69 (m, 2H); ^{13}C NMR (DEPT) δ=21.3 (CH_3), 26.9 (CH_2, C-8), 26.9 (d-CH_2, C-7, J_{CP}=57.4 Hz), 33.3 (d-CH_2, C-2, J_{CP}=56.2 Hz), 52.0 (CH_3), 52.1 (CH_3), 121.3 (d-C, C-3, J_{CP}=9.8 Hz), 136.2 (d-C, C-6 J_{CP}=70.8 Hz), 138.0 (CH, C-5), 142.7 (d-C, C-4, J_{CP}=15.8 Hz), 168.0 (d-C=O, J_{CP}=8.5 Hz), and 172.4 (d-C=O, J_{CP}=14.7 Hz); MS m/z 440 (M^+; 78), 407 (M^+−SH; 100), 353 (M^+−Methyl acrylate−H; 3), 321 (353−S; 7), 259 (15), 215 (22), 121 ($PhCP^+$; 5), and 115 (7). HRMS Found: m/z 440.1217. Calcd for $C_{24}H_{25}O_4PS$: M, 440.1213. Found: C, 65.57; H, 5.90%. Calcd for $C_{24}H_{25}O_4PS$: C, 65.44; H, 5.72%.

3-Methoxycarbonyl-1-[2-(methoxycarbonyl)ethyl]-6-phenyl-4-(2-thienyl)-1,2-dihydrophosphorin 1-Sulfide (16d): Pale green cubes. Mp 78—79 °C. IR (KBr) 1702 and 1738 cm^{-1} (C=O); ^1H NMR δ=2.26—2.37 (m, CH_2, H-7), 2.63—2.75 (m, CH_2, H-8), 3.41 (dd, CH_2, H-2, J_{HH}=15.2 Hz, J_{HP}=15.2 Hz), 3.64 (s, CH_3), 3.66 (s, CH_3), 6.84 (d, 1H, H-5, J_{HP}=30.4 Hz), 7.00—7.04 (m, 2H), 7.34—7.40 (m, 4H), and 7.66—7.69 (m, 2H); ^{13}C NMR (DEPT) δ=26.8 (CH_2, C-8), 26.9 (d-CH_2, C-7, J_{CP}=56.2 Hz), 33.9 (d-CH_2, C-2, J_{CP}=54.9 Hz), 52.2 (CH_3), 52.4 (CH_3), 123.0 (d-C, C-3, J_{CP}=9.8 Hz), 134.1 (d-C, C-4, J_{CP}=17.1 Hz), 136.5 (d-C, C-6, J_{CP}=69.6 Hz), 138.4 (d-CH, C-5, J_{CP}=2.4 Hz), 168.2 (d-C=O, J_{CP}=8.5 Hz), and 172.4 (d-C=O, J_{CP}=14.6 Hz); MS m/z 432 (M^+; 98), 399 (M^+−SH; 100), 345 (M^+−Methyl acrylate−H; 5), 313 (345−S; 8), 121 ($PhCP^+$; 14), and 115 (7). Found: C, 58.47; H, 5.12%. Calcd for $C_{21}H_{21}O_4PS_2$: C, 58.32; H, 4.89%.

3-Methoxycarbonyl-1-[2-(methoxycarbonyl)ethyl]-6-(*p*-methoxyphenyl)-4-phenyl-1,2-dihydrophosphorin 1-Sulfide (16e): Yellow needles. Mp 206—207 °C. IR (KBr) 1698 and 1738 cm^{-1} (C=O); ^1H NMR δ=2.30—2.40 (m, CH_2, H-7), 2.67—2.77 (m, CH_2, H-8), 3.42 (dd, CH_2, H-2, J_{HH}=13.9 Hz, J_{HP}=16.2 Hz), 3.52 (s, CH_3), 3.62 (s, CH_3), 3.82 (s, CH_3), 6.70 (d, 1H, H-5, J_{HP}=30.7 Hz), 6.90 (d, 2H, J_{HH}=8.9 Hz), 7.21—7.41 (m, 5H), and 7.64 (m, 2H, J_{HH}=8.9 Hz); ^{13}C NMR (DEPT) δ=26.9 (CH_2, C-8), 27.0 (d-CH_2, C-7, J_{CP}=56.1 Hz), 33.2 (d-CH_2, C-2, J_{CP}=56.2 Hz), 52.0 (CH_3), 52.2 (CH_3), 55.3 (CH_3), 120.9 (d-C, C-3, J_{CP}=9.7 Hz), 135.9 (d-C, C-6, J_{CP}=69.5 Hz), 137.4 (CH, C-5), 143.1 (d-C, C-4, J_{CP}=15.9 Hz), 167.8 (d-C=O, J_{CP}=9.8 Hz), and 172.4 (d-C=O, J_{CP}=14.6 Hz); MS m/z 456 (M^+; 65), 423 (M^+−SH; 100), 369 (M^+−Methyl acrylate−H; 4), 337 (369−S; 7), 275 (28), 215 (19), and 115 (18). Found: C, 63.11; H, 5.51%. Calcd for $C_{24}H_{25}O_5PS$: C, 63.15; H, 5.52%.

3-Methoxycarbonyl-1-[2-(methoxycarbonyl)ethyl]-4-phenyl-6-(*p*-tolyl)-1,2-dihydrophosphorin 1-Sulfide (16f): Yellow needles. Mp 169—170 °C. IR (KBr) 1702 and 1740 cm^{-1} (C=O); ^1H NMR δ=2.29—2.39 (m, CH_2, H-7), 2.35 (s, CH_3), 2.66—2.77 (m, CH_2, H-8), 3.38 (dd, CH_2, H-2, J_{HH}=13.5 Hz, J_{HP}=15.8 Hz), 3.51 (s, CH_3), 3.67 (s, CH_3), 6.73 (d, 1H, H-5, J_{HP}=30.4 Hz), 7.16—7.40 (m, 7H), and 7.56—7.59 (m, 2H); ^{13}C NMR (DEPT) δ=21.3 (CH_3), 26.9 (CH_2, C-8), 27.0 (d-CH_2, C-7, J_{CP}=56.1 Hz), 33.2 (d-CH_2, C-2, J_{CP}=56.2 Hz), 52.0 (CH_3), 52.1 (CH_3), 121.3 (d-C, C-3, J_{CP}=9.7 Hz), 136.3 (d-C, C-6, J_{CP}=70.8 Hz), 138.1 (d-CH, C-5, J_{CP}=2.4 Hz), 142.9 (d-C, C-4, J_{CP}=15.9 Hz), 167.8 (d-C=O, J_{CP}=9.8 Hz), and 172.4 (d-C=O, J_{CP}=14.7 Hz); MS m/z 440 (M^+; 70), 407 (M^+−SH; 100), 321 (M^+−Methyl acrylate; 6), 259 (7), 215 (20), 135 (p-$TolCP^+$; 5), and 115 (10). Found: C, 65.21; H, 5.94%. Calcd for $C_{24}H_{25}O_4PS$: C, 65.44; H, 5.72%.

3-Methoxycarbonyl-1-[2-(methoxycarbonyl)ethyl]-4-phenyl-6-(2-thienyl)-1,2-dihydrophosphorin 1-Sulfide (16g): Yellow cubes. Mp 81—82 °C. IR (KBr) 1696 and 1738 cm^{-1} (C=O); ^1H NMR δ=2.40—2.51 (m, CH_2, H-7), 2.69—2.82 (m, CH_2, H-8), 3.47 (dd, CH_2, H-2, J_{HH}=14.5 Hz, J_{HP}=17.5 Hz), 3.51 (s, CH_3), 3.67 (s, CH_3), 6.86 (d, 1H, H-5, J_{HP}=30.0 Hz), 7.06 (dd, 1H, J_{HH}=4.0 and 5.3 Hz), 7.19—7.23 (m, 2H), 7.33—7.43 (m, 4H), and 7.88 (d, 1H, J_{HH}=4.0 Hz); ^{13}C NMR (DEPT) δ=26.8 (d-CH_2, C-7, J_{CP}=54.9 Hz), 26.9 (CH_2, C-8), 33.5 (d-CH_2, C-2, J_{CP}=55.9 Hz), 52.0 (CH_3), 52.1 (CH_3), 121.7 (d-C, C-3, J_{CP}=9.7 Hz), 130.0 (d-C, C-6, J_{CP}=68.4 Hz), 136.1 (CH, C-5), 143.0 (d-C, C-4, J_{CP}=15.8 Hz), 167.5 (d-C, J_{CP}=9.8 Hz), and 172.3 (d-C, J_{CP}=14.7 Hz); MS m/z 432 (M^+; 92), 399 (M^+−SH; 100), 345 (M^+−Methyl acrylate−H; 4), and 313 (345−S; 18). HRMS Found: m/z 432.0626. Calcd for $C_{21}H_{21}O_4PS_2$: M, 432.0620. Found: C, 58.29; H, 4.91%. Calcd for $C_{21}H_{21}O_4PS_2$: C, 58.32; H, 4.89%.

3-Ethoxycarbonyl-1-[2-(ethoxycarbonyl)ethyl]-4,6-diphenyl-1,2-dihydrophosphorin 1-Sulfide (16h): Pale yellow cubes. Mp 64—66 °C. IR (KBr) 1704 and 1736 cm^{-1} (C=O); ^1H NMR δ=0.88 (t, CH_3, J_{HH}=7.3 Hz), 1.24 (t, CH_3, J_{HH}=7.3 Hz), 2.29—2.39 (m, CH_2, H-7), 2.64—2.75 (m, CH_2, H-8), 3.43 (dd, CH_2, H-2, J_{HH}=13.5 Hz, J_{HP}=15.8 Hz), 3.96 (q, CH_2, J_{HH}=7.3 Hz), 4.12 (q, CH_2, J_{HH}=7.3 Hz), 6.75 (d, 1H, H-5, J_{HP}=30.7 Hz), 7.21—7.39 (m, 8H), and 7.67—7.70 (m, 2H); ^{13}C NMR (DEPT) δ=13.4 (CH_3), 14.1 (CH_3), 27.0 (d-CH_2, C-7, J_{CP}=57.4 Hz), 27.1 (CH_2, C-8), 33.1 (d-CH_2, C-2, J_{CP}=55.0 Hz), 61.1 (CH×2), 122.1 (d-C, C-3, J_{CP}=8.6 Hz), 136.2 (d-C, C-6, J_{CP}=69.5 Hz), 138.8 (CH, C-5), 142.5 (d-C, C-4, J_{CP}=15.8 Hz), 167.5 (d-C, J_{CP}=8.5 Hz), and 171.9 (d-

C, J_{CP}=14.6 Hz); ^{31}P NMR δ=28.4; MS m/z 454 (M^+; 70), 421 (M^+−SH; 100), 409 (M^+−OEt; 15), 353 (M^+−Ethyl acrylate−H; 3), 321 (353−S; 4), 245 (20), 215 (34), 121 ($PhCP^+$; 17), and 115 (21). Found: C, 65.89; H, 5.96%. Calcd for $C_{25}H_{27}O_4PS$: C, 66.06; H, 5.99%.

3-Ethoxycarbonyl-1-[2-(ethoxycarbonyl)ethyl]-4-(*p*-methoxyphenyl)-6-phenyl-1,2-dihydrophosphorin 1-Sulfide (16i): Pale yellow cubes. Mp 86—87 °C. IR (KBr) 1702 and 1734 cm^{-1} (C=O); ^{1}H NMR δ=0.97 (t, CH_3, J_{HH}=7.3 Hz), 1.24 (t, CH_3, J_{HH}=7.3 Hz), 2.28—2.44 (m, CH_2, H-7), 2.63—2.74 (m, CH_2, H-8), 3.42 (dd, CH_2, H-2, J_{HH}=13.5 Hz, J_{HP}=15.5 Hz), 3.81 (s, CH_3), 4.00 (q, CH_2, J_{HH}=7.26 Hz), 4.11 (q, CH_2, J_{HH}=7.26 Hz), 6.76 (d, 1H, H-5, J_{HP}=30.7 Hz), 6.88 (d, 2H, J_{HH}=8.6 Hz), 7.16 (d, 2H, J_{HH}=8.6 Hz), 7.35—7.39 (m, 3H), and 7.67—7.70 (m, 2H); ^{13}C NMR (DEPT) δ=13.7 (CH_3, 14.1 (CH_3), 27.0 (d-CH_2, C-7, J_{CP}=57.4 Hz), 27.1 (CH_2, C-8), 33.3 (d-CH_2, C-2, J_{CP}=55.0 Hz), 55.3 (CH_3), 61.1 (CH_2×2), 113.7 (CH×2), 121.5 (d-C, C-3, J_{CP}=9.8 Hz), 136.0 (d-C, C-6, J_{CP}=70.8 Hz), 139.3 (CH, C-5), 142.0 (d-C, C-4, J_{CP}=15.8 Hz), 167.8 (d-C=O, J_{CP}=9.8 Hz), and 171.9 (d-C=O, J_{CP}=14.6 Hz); MS m/z 484 (M^+; 55), 451 (M^+−SH; 100), 383 (M^+−Ethyl acrylate−H; 3), 351 (383−S; 5), 275 (16), 215 (11), 121 ($PhCP^+$; 13), and 115 (7). Found: C, 64.69; H, 6.21%. Calcd for $C_{26}H_{29}O_5PS$: C, 64.45; H, 6.03%.

The Reaction of 4a with Methyl Vinyl Ketone in the Presence of Aluminum Chloride. To a solution of aluminum chloride (1.56 mmol) in anhydrous dichloromethane (80 ml) was added **4a** (0.78 mmol) at 0 °C. After the mixture had been stirred for 20 min, methyl vinyl ketone (3.12 mmol) in anhydrous dichloromethane (40 ml) was added dropwise. The reaction mixture was warmed to room temperature on stirring for 4 h. A usual work up and chromatography on silica gel (Wakogel C-200) with ethyl acetate–hexane (1 : 3) as an eluent gave **17** as a yellow oil in a yield of 38%.

3-Acetyl-1-(3-oxobutyl)-4,6-diphenyl-1,2-dihydrophosphorin 1-Sulfide (17): Yellow oil. IR (NaCl) 1668 and 1722 cm^{-1} (C=O); ^{1}H NMR δ=1.79 (s, CH_3), 2.16 (s, CH_3), 2.19—2.38 (m, CH_2, H-7), 2.79—2.91 (m, CH_2, H-8), 3.34 (d, CH_2, H-2, J_{HP}=14.5 Hz), 6.77 (d, 1H, H-5, J_{HP}=30.4 Hz), 7.37—7.47 (m, 8H), and 7.66—7.69 (m, 2H); ^{13}C NMR (DEPT) δ=25.1 (d, CH_2, C-7, J_{CP}=57.4 Hz), 29.7 (CH_3), 30.0 (CH_3), 33.8 (d-CH_2, C-2, J_{CP}=56.1 Hz), 35.9 (CH_2, C-8), 130.9 (d-C, C-3, J_{CP}=9.8 Hz), 137.1 (d-C, C-6, J_{CP}=70.8 Hz), 138.6 (d-CH, C-5, J_{CP}=2.4 Hz), 140.7 (d-C, C-4, J_{CP}=15.9 Hz), 203.4 (d-C, J_{CP}=7.4 Hz), and 205.8 (d-C, J_{CP}=12.0 Hz); ^{31}P NMR δ=29.8; MS m/z 394 (M^+; 100), 361 (M^+−SH; 95), 323 (M^+−Methyl vinyl ketone−H; 11), 291 (323−S; 21), 215 (24), 121 ($PhCP^+$; 5), 115 (12), and 43 ($COMe^+$; 45). HRMS Found: m/z 394.1162. Calcd for $C_{23}H_{23}O_2PS$: M, 394.1158.

The Reaction of 4a with Methyl Acrylate and Acrylonitrile in the Presence of Aluminum Chloride. To a solution of aluminum chloride (2.34 mmol) in anhydrous dichloromethane (12 ml) was added methyl acrylate (1.17 mmol) and acrylonitrile (4.68 mmol) at room temperature with stirring. After the mixture had become a clear solution with stirring for several minutes, **4a** (0.78 mmol) was added to it and the reaction mixture was stirred at the same temperature for 6.5 h. A usual work up and chromatography on silica gel (Wakogel C-200) with ethyl acetate–hexane (1 : 6) as an eluent gave **18** (53%, recrystallized from ethyl acetate–hexane) and **16a** (3%).

3-Cyano-1-[2-(methoxycarbonyl)ethyl]-4,6-diphenyl-1,2-dihydrophosphorin 1-Sulfide (18): Pale yellow needles. Mp 145—146 °C. IR (KBr) 1736 (C=O) and 2208 cm^{-1} (CN); ^{1}H NMR δ=2.18—2.41 (m, CH_2, H-7), 2.56—2.89 (m, CH_2, H-8), 3.31 (dd, 1H, H-2, J_{HH}=17.5 and 16.2 Hz), 3.47 (dd, 1H, H-2, J_{HH}=17.5 Hz, J_{HP}=12.9 Hz), 3.69 (s, CH_3), 6.85 (d, 1H, J_{HP}=29.7 Hz), and 7.39—7.70 (m, 10H); ^{13}C NMR (DEPT) δ=26.7 (CH_2, C-8), 26.7 (d-CH_2, C-7, J_{CP}=57.4 Hz), 34.4 (d-CH_2, C-2, J_{CP}=53.7 Hz), 52.3 (CH_3), 101.5 (d-C, C-3, J_{CP}=9.8 Hz), 118.5 (d-C, CN, J_{CP}=11.0 Hz), 136.4 (d-CH, C-5, J_{CP}=2.4 Hz), 139.4 (d-C, C-6, J_{CP}=69.5 Hz), 149.2 (d-C, C-4, J_{CP}=15.8 Hz), and 172.3 (d-C=O, J_{CP}=12.2 Hz); ^{31}P NMR δ=25.4; MS m/z 393 (M^+; 80), 360 (M^+−SH; 100), 286 (14), 274 (22), 254 (Thiaphosphole$^+$; 5), 243 (47), 215 (22), and 121 ($PhCP^+$; 17). Found: C, 67.16; H, 5.25%. Calcd for $C_{22}H_{20}NO_2PS$: C, 67.16; H, 5.12%.

The Reaction of 4a with Ethyl Propiolate in the Presence of Aluminum Chloride. To a suspension of aluminum chloride (0.86 mmol) in anhydrous dichloromethane (12 ml) was added ethyl propiolate (0.94 mmol) at 0 °C. After the mixture was cooled to −35 °C, **4a** (0.78 mmol) was added to it and the reaction mixture was stirred at the same temperature for 7 h. A usual work up and chromatography on silica gel (Wakogel C-200) with ethyl acetate–hexane (1 : 100) as an eluent gave **19** as a yellow oil in a yield of 27%.

3-Ethoxycarbonyl-4,6-diphenyl-1-phosphorin (19): Yellow oil. IR (NaCl) 1724 cm^{-1} (C=O); ^{1}H NMR δ=0.96 (t, CH_3, J_{HH}=7.3 Hz), 4.08 (q, CH_2, J_{HH}=7.3 Hz), 7.37—7.45 (m, 8H), 7.67 (dt, 2H, J_{HH}=1.7 and 7.9 Hz), 8.05 (d, 1H, H-5, J_{HP}=5.3 Hz), and 9.12 (d, 1H, H-2, J_{HP}=37.6 Hz); ^{13}C NMR (DEPT) δ=13.6 (CH_3), 61.4 (CH_2), 136.0 (d-CH, C-5, J_{CP}=12.2 Hz), 136.3 (d-C, J_{CP}=18.3 Hz), 142.2 (d-C, J_{CP}=2.4 Hz), 142.7 (d-C, J_{CP}=23.2 Hz), 143.3 (d-C, J_{CP}=15.9 Hz), 154.7 (d-CH, C-2, J_{CP}=54.9 Hz), 169.4 (d-C=O, J_{CP}=3.7 Hz), and 172.9 (d-C, C-6, J_{CP}=52.4 Hz); ^{31}P NMR δ=190.1; MS m/z 320 (M^+; 100), 291 (M^+−Et; 10), 275 (M^+−OEt; 20), 244 (30), 215 (29), and 115 (2). HRMS Found: m/z 320.0953. Calcd for $C_{20}H_{17}O_2P$: M, 320.0967.

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References

1) H. Yamaguchi, S. Kametani, T. Karakasa, T. Saito, and S. Motoki, *Tetrahedron Lett.*, **23**, 1263 (1982).

2) H. Tanaka, S. Kametani, T. Saito, and S. Motoki, *Bull. Chem. Soc. Jpn.*, **58**, 667 (1985).

3) S. Motoki, T. Sakai, I. Shinoda, T. Saito, and T. Uchida, *Chem. Lett.*, **1993**, 1563.

4) G. Märkl and W. Hölzl, *Tetrahedron Lett.*, **29**, 4535 (1988); **30**, 4501 (1989).

5) J. B. Stothers, "Carbon-13 NMR Spectroscopy,"

Academic Press, New York (1972), pp. 68 and 414; G. C. Levy, R. L. Lichter, and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley, New York (1972), p. 61.

6) The X-ray crystallographic analysis will be reported elsewhere.

7) These cycloadducts, **10** and **11**, were composed of two separable stereoisomers, respectively. Their stereochemistry remains unclear at present; therefore, they are tentatively assigned as **10a**, **10b**, **11a**, and **11b** where the ^{13}CNMR signals of the C-9 and C-10 carbons in **10a** and **11a** appeared at a lower field than those in **10b** and **11b**.

8) H. Tanaka and S. Motoki, *Bull. Chem. Soc. Jpn.*, **59**, 2047 (1986).