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Generation and Cycloaddition Reactions of 3-Styryl-1,2-thiaphosphole 2-Sulfide and 1,5-Diphenyl-2,4-pentadiene-1-thione

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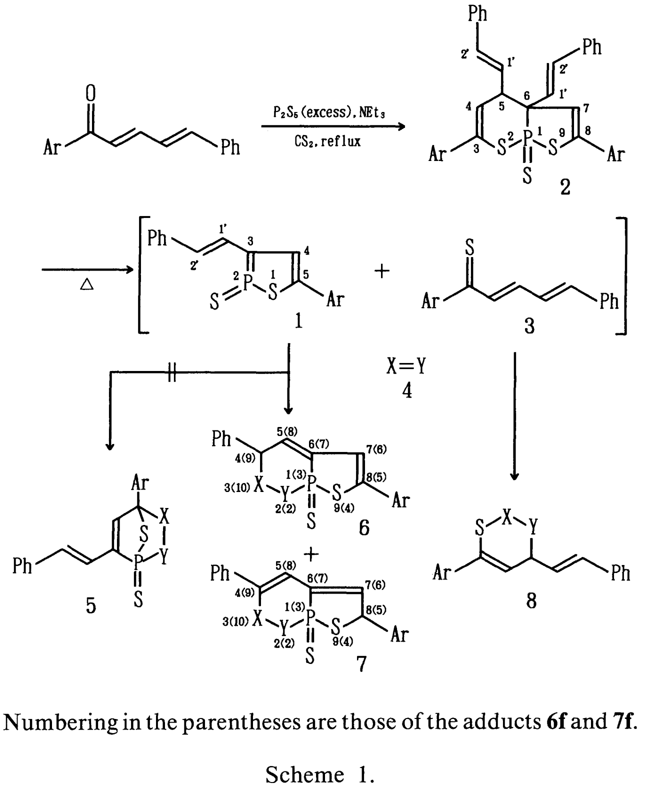
Synopsis. The cycloaddition reaction of 3-styryl-1,2-thia phosphole 2-sulfide and 1,5-diphenyl-2,4-pentadiene-1-thione derivatives generated by the thermolysis of 5,6-distyryl-3,8-diaryl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-sulfides have been described. Methacrylonitrile, methyl methacrylate, α-methylstyrene, norbornene, methyl acrylate, styrene, and methyl vinyl ketone afforded the cycloadducts or their rearranged products with the thiaphosphole 2-sulfides, whereas diethyl azodicarboxylate, dimethyl acetylenedicarboxylate, and *N*-(*p*-methoxyphenyl)maleimide gave the cycloadducts with the thioketone.

In the previous paper, we reported that treatment of α,β:α′,β′-unsaturated ketones with P_2S_5 gave phosphorus-containing compounds which generated α,β:α′,β′-unsaturated thioketones and 3-aryl-5-(2-arylvinyl)-1,2-thiaphosphole 2-sulfides upon heating. The thioketone is a sulfur-containing cross-conjugated heterotriene and underwent diene-transmissive Diels–Alder reaction with dienophiles successively giving bicyclic cycloadducts.[1,2]

In view of the above results, diene-transmissive Diels–Alder reaction of 5-aryl-3-styryl-1,2-thiaphosphole 2-sulfide (**1**) was now attempted. The compound **1** is a new phosphorus-containing cross conjugated heterotriene and we expected that cisoid constrained $C^5{=}C^4{-}C^3{=}P^2$ moiety in the ring would preferentially react with dienophiles to produce the cycloadduct 5 capable of undergoing successive cycloaddition reaction (Scheme 1).



Numbering in the parentheses are those of the adducts **6f** and **7f**.

Scheme 1.

The reaction of 1,5-diphenyl-2,4-pentadien-1-one with large excess of P_2S_5 in the presence of triethylamine gave 5,6-distyryl-3,8-diphenyl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-sulfide **2a** in 34% yield. The mass spectrum of **2a** exhibited fragment peaks of thiaphosphole **1a**-S (280, 100%) and of thioketone **3a** (250, 33%) with a weak parent peak (562, 0.4%). The ^1H NMR spectrum showed six signals of olefinic protons and one methine proton. The ^{13}C NMR spectrum showed signals of one quaternary carbon and one tertiary carbon. The ^{31}P NMR spectrum exhibited a signal at $\delta=120.44$. Similarly, the reaction of 1-*p*-tolyl and 1-(*p*-chlorophenyl)-5-phenyl-2,4-pentadien-1-one with P_2S_5 gave the products **2b** (Ar=*p*-$CH_3C_6H_4$, yield 34%) and **2c** (Ar=*p*-ClC_6H_4, yield 22%).

As expected from the mass spectrum, **1** and **3** were

Table 1. Reaction of **2** with Dieophiles

Compound	Dienophile[a]		Reaction time/h	Product	Yield/%[b]		
2	X	Y			6	7	8
2a	$CH_3OCOC=$ CH_3	$=CH_2$	2.0	**6a**	33	0	0
2b	$CH_3OCOC=$ CH_3	$=CH_2$	2.5	**6b**	32	0	0
2c	$CH_3OCOC=$ CH_3	$=CH_2$	1.0	**6c**	26	0	0
2a	NC–C= CH_3	$=CH_2$	6.0	**6d**	24	0	0
2a	Ph–C= CH_3	$=CH_2$	2.0	**6e**	41	0	0
2a	Norbornene		3.0	**6f+7f**	33	33	0
2a	$CH_3OCOCH=$	$=CH_2$	4.0	**6g+7g**	8	13	8
2a	Ph–CH=	$=CH_2$	10.0	**6h+7h**	12	18	0
2a	$CH_3COCH=$	$=CH_2$	2.0	**6i+7i**	2	18	0
2a	DMAD		2.5	**8j**	0	0	28
2a	DAD		2.0	**8k**	0	0	43
2a	MI		5.0	**8l**	0	0	27

a) Molar ratio of dienophile/compound **2** was 3. b) Yields were based on compound **2**.

generated by the thermolysis of **2** and trapped by dienophiles **4** (Table 1). However, the reactions of **2** with methyl methacrylate, methacrylonitrile and α-methylstyrene gave only the adducts **6a**—**e** which can not be utilized in successive cycloaddition reaction. The ^{13}C NMR (DEPT) spectrum of **6a** exhibited the signals of quaternary (δ=47.5), tertiary (δ=49.8), and secondary (δ=47.1) carbon atoms one by one and the ^{1}H NMR spectrum showed the signals of unequivalent methylene protons (δ=2.80 and 3.29, dd, J_{HH}=13.7, J_{HP}=13.6, 15.8 Hz), one methine proton (δ=4.48, dd, J_{HH}=4.9, J_{HP}=4.8 Hz) and two olefinic protons (δ=6.87, 6.88). On the other hand, the reaction with norbornene afforded the adduct **6f** and its isomer **7f** formed by 1,5-prototropy of **6f**. The signal of H-5 methine proton of **7f** appeared at lower field (δ=5.95) than that of H-9 methine proton of **6f** (δ=4.71). In the 2D ^{1}H NMR (H–H COSY) of **7f**, H-5 was shown to have the coupling only with an olefinic proton (H-6).

The reaction of **2a** with methyl acrylate, styrene and methyl vinyl ketone gave an inseparable mixture of phosphorus-containing adducts in each case. Analysis of the ^{1}H NMR spectra of the mixture referring above mentioned differences in the spectra of **6f** and **7f** proved that these mixtures were composed of the adducts **6g**—**i** and their rearranged products **7g**—**i** respectively. The ratio of **6** to **7** was estimated by the relative intensity of H-4 and H-8 signals.[3] The reaction of **2a** with dimethyl acetylenedicarboxylate (DMAD), diethyl azodicarboxylate (DAD), and *N*-(methoxyphenyl)maleimide (MI) resulted to afford only the cycloadducts with the thioketone (**8j**—**l**).

Preferential formation of **6**(**7**) rather than **5** is recognized by considering that bicyclic compounds **6**(**7**) have less steric strain than bridged compounds **5** and that disubstituted C-5 terminal carbon of **1** is less reactive than its mono substituted C-2′ terminal carbon. It was also found that there is a marked contrast between the formation of the thiaphosphole adducts **6**(**7**) and the thioketone adducts **8**, that is, dienophiles DMAD, DAD, and MI gave **8** while the other dienophiles gave **6**(**7**). For the purpose of obtaining the both adducts **6**(**7**) and **8**, the reaction of **2a** with the mixture of methyl metacrylate and DMAD or methyl metacrylate and DAD were examined but only the adduct **8** was formed even under such conditions. Finally, dienophiles of the type $CH_2=C(CH_3)–Z$ ($Z=CO_2CH_3$, CN, Ph, and $COCH_3$) produced only **6**, while those of the type $CH_2=CH–Z$ and norbornene produced both **6** and **7**. These interesting results are under further investigation.

Experimental

All the melting points are uncorrected. IR spectra were measured on a Hitachi Model 270-30 spectrometer. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ solution using TMS as an internal standard (JEOL JNM-FX 100, JEOL EX-270, JEOL JNM-GSX 500). ^{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 recorded on a Hitachi double-focusing mass spectrometer Model RMU-7M operating at an ionizing potential of 70 eV.

General Procedure for the Preparation of 2. A suspension of conjugated dienone (20 mmol), P_2S_5 powder (6 g) and triethylamine (12 ml) in dry carbon disulfide (80 ml) was gently refluxed under a nitrogen atmosphere for 2—3.5 h. The reaction mixture was filtered and the filtrate was evaporated. The residue was chromatographed on silica gel (Wakogel C-200). The solvent was evaporated and the residue was recrystallized from ethyl acetate–hexane giving the product (**2a**—**c**).

3,8-Diphenyl-5,6-distyryl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfide (2a):[4] Pale yellow crystals; mp 150—151 °C. ^{1}H NMR δ=4.09 (ddd, H-5, $J_{4.5}$=2.81, $J_{5.1'}$=7.26, J_{HP}=12.87 Hz), 5.73 (dd, H-4, $J_{4,5}$=2.81, J_{HP}=2.81 Hz), 6.20 (d, H-7, J_{HP}=35.30 Hz), 6.38 (dd, 5-styryl H-1′, $J_{5.1'}$=7.26, $J_{1'.2'}$=15.84 Hz), 6.44 (dd, 6-styryl H-1′, $J_{1'.2'}$=16.17, J_{HP}=5.94Hz), 6.58 (dd, 6-styryl H-2′, $J_{1'.2'}$=16.17, J_{HP}=6.27 Hz), 6.71 (d, 5-styryl H-2′, $J_{1'.2'}$=15.84 Hz), 7.21—7.64 (m, 20H); ^{13}C NMR (DEPT) δ=42.7 (d-CH, C-5, J_{CP}=3.6 Hz), 63.4 (d-C, C-6, J_{CP}=59.9 Hz); ^{31}P NMR δ=120.4. MS *m*/*z* 562 (M^+; very weak), 280 (M^+—thioketone-S; 100). Found: C, 72.85; H, 4.98%. Calcd for $C_{34}H_{27}PS_3$: C, 72.56; H, 4.84%.

General Procedure for the Generation and Reaction of 1 and 3 with Dienophiles. To a solution of **2a**—**c** (2 mmol) in dry benzene (20 ml) was added the dienophile (6 mmol). The mixture was stirred and refluxed under a nitrogen atmosphere. After the solvent was evaporated, the residue was chromatographed on silica gel (Wakogel C-200) with ethyl acetate–hexane (1 : 10—1 : 45) to give the each product. Benzene–hexane (1 : 1 for **6b**, 1 : 5 for **6e**) was also used as an eluent.

3-Methoxycarbonyl-3-methyl-4,8-diphenyl-9-thia-1-phosphabicyclo[4.3.0]nona-5,7-diene 1-Sulfide (6a):[4] Colorless crystals; mp 158—159 °C. IR (KBr) 1722 cm^{-1} (C=O); ^{1}H NMR δ=1.60 (s, 3H), 2.80 (dd, H-2, $J_{2.2'}$=13.74, J_{HP}=15.75 Hz), 3.29 (dd, H-2′, $J_{2.2'}$=13.74, J_{HP}=13.55 Hz), 3.45 (s, 3H), 4.48 (dd, H-4, $J_{4.5}$=4.94, J_{HP}=4.76 Hz), 6.87 (d, H-7, J_{HP}=31.50 Hz), 6.88 (dd, H-5, $J_{4.5}$=4.94, J_{HP}=38.46 Hz), 7.23—7.57 (m, 10H); ^{13}C NMR (DEPT) δ=25.6 (CH_3), 47.1 (d-CH_2, C-2, J_{CP}=41.5 Hz), 47.5 (C, C-3), 49.8 (d-CH, C-4, J_{CP}=20.8 Hz), 52.1 (CH_3), 118.1 (d-CH, C-7, J_{CP}=15.9 Hz), 134.5 (d-C, C-8, J_{CP}=2.4 Hz), 140.1 (d-CH, C-5, J_{CP}=4.9 Hz), 143.4 (d-C, C-6, J_{CP}=62.3 Hz), 174.5 (d-C, C=O, J_{CP}=13.5 Hz). MS *m*/*z* 412 (M^+; 19), 312 (M^+—Methyl methacrylate; 100), 280 (312-S; 100), 279 (280-H; 80). Found: C, 64.35; H, 5.10%. Calcd for $C_{22}H_{21}O_2PS_2$: C, 64.06; H, 5.13%.

(6d): Colorless needles; mp 168—169 °C. IR (KBr) 2240 cm^{-1} (C≡N); ^{1}H NMR δ=1.43 (d, 3H, J_{HP}=2.57 Hz), 3.08(dd, H-2, $J_{2.2'}$=15.02, J_{HP}=15.02 Hz), 3.59 (dd, H-2′, $J_{2.2'}$=15.02, J_{HP}=12.82 Hz), 4.32 (dd, H-4, $J_{4.5}$=4.58, J_{HP}=4.58 Hz), 6.90 (d, H-7, J_{HP}=31.14 Hz), 6.95 (dd, H-5, $J_{4.5}$=4.58, J_{HP}=38.47 Hz), 7.39—7.59 (m, 10H); ^{13}C NMR δ=27.4 (dq, J_{CP}=6.1 Hz), 40.6 (d, C-3, J_{CP}=6.1 Hz), 48.7 (dd, C-4, J_{CP}=18.3 Hz), 49.3 (dt, C-2, J_{CP}=47.6 Hz), 117.1 (dd, C-7, J_{CP}=15.9 Hz), 122.3 (d, C≡N, J_{CP}=4.9 Hz), 134.1 (d, C-8, J_{CP}=2.4 Hz), 140.2 (dd, C-5, J_{CP}=4.9 Hz), 144.8 (d, C-6, J_{CP}=65.9 Hz). MS *m*/*z* 379 (M^+; 10), 312 (M^+—Methacrylonitrile; 100), 280 (312-S; 93), 67 (Methacrylonitrile; 9). Found: C, 66.23; H, 4.70%. Calcd for $C_{21}H_{18}NPS_2$: C, 66.47; H, 4.78%.

(6e): Colorless Crystals; mp 158—159 °C. MS *m*/*z* 312 (M^+—α-Methylstyrene; 0.4), 280 (312-S; 95), 118 (α-Methylstyrene; 100). Found: C, 72.66; H, 5.16%. Calcd for $C_{26}H_{23}PS_2$: C, 72.52; H, 5.38%. ^{1}H NMR (major adduct) δ=1.77 (s, 3H), 3.35 (dd, H-2, $J_{2.2'}$=14.84, J_{HP}=16.85 Hz), 3.44 (dd, H-2′, $J_{2.2'}$=14.84, J_{HP}=12.49 Hz), 4.77 (dd, H-4, $J_{4.5}$=5.31, J_{HP}=5.31 Hz), 6.68 (d, H-7, J_{HP}=58.98 Hz), 6.80 (dd, H-5, $J_{4.5}$=5.31, J_{HP}=38.47 Hz), 6.88—7.63 (m, 15H).

5,9-Diphenyl-4-thia-3- phosphatetracyclo[9.2.1.0^{2,10}.0^{3,7}]-tetradeca-5,7-diene 3-Sulfide (6f): Colorless crystals; mp 142—143 °C. ^{1}H NMR δ=0.59—3.00 (m, 9H), 3.15 (dd, H-2, $J_{2,10}$=8.41, J_{HP}=14.02 Hz), 4.71 (ddd, H-9, $J_{8,9}$=5.28, $J_{9,10}$=5.28, J_{HP}=5.28 Hz), 6.80 (d, H-6, J_{HP}=31.01 Hz), 7.05 (dd, H-8, $J_{8,9}$=5.28, J_{HP}=35.63 Hz), 7.16—7.61 (m, 10H); ^{13}C NMR (DEPT) δ=35.3 (CH_2, C-14), 42.7 (d-CH, C-9, J_{CP}=26.8 Hz), 51.6 (d-CH, C-10, J_{CP}=7.3 Hz), 55.3 (d-CH, C-2, J_{CP}=40.3 Hz), 117.3 (d-CH, C-6, J_{CP}=14.6 Hz), 140.9 (d-CH, C-8, J_{CP}=3.7 Hz), 144.8 (d-C, C-5, J_{CP}=4.5 Hz), 144.5 (d-C, C-7, J_{CP}=58.6Hz); ^{31}P NMR δ=71.7. MS m/z 406 (M^+; 67), 373 (M^+−S−H; 100), 312 (M^+−Norbornene; 29), 279 (312−S−H; 25). Found: C, 70.77; H, 5.52%. Calcd for $C_{24}H_{23}PS_2$: C, 70.90; H, 5.70%.

5,9-Diphenyl-4-thia-3-phosphatetracyclo[9.2.1.0^{2,10}.0^{3,7}]-tetradeca-6,8-diene 3-Sulfide (7f): Colorless crystals; mp 180—182 °C. ^{1}H NMR δ=1.22—2.78 (m, 8H), 2.86 (dd, H-2, $J_{2,10}$=8.43, J_{HP}=16.12 Hz), 3.52 (dd, H-10, $J_{2,10}$=8.43, J_{HP}=12.82 Hz), 5.95 (m, H-5), 6.39 (broad-d, H-6, J_{HP}=43.00 Hz), 6.73 (d, H-8, J_{HP}=17.22 Hz), 7.28—7.48 (m, 10H); ^{13}C NMR (DEPT) δ=34.8 (CH_2, C-14), 51.6 (d-CH, C-10, J_{CP}=6.1 Hz), 55.9 (d-CH, C-2, J_{CP}=43.9 Hz), 60.3 (d-CH, C-5, J_{CP}=4.9 Hz), 118.7 (d-CH, C-8, J_{CP}=6.1 Hz), 136.0 (d-CH, C-6, J_{CP}=13.5 Hz), 138.4 (d-C, C-7, J_{CP}=61.1 Hz), 149.0 (d-C, C-9, J_{CP}=18.3 Hz); ^{31}P NMR δ=84.3. MS m/z 406 (M^+; 22), 312 (M^+−Norbornene; 100). Found: C, 71.00; H, 5.81%. Calcd for $C_{24}H_{23}PS_2$: C, 70.90; H, 5.70%.

3-Methoxycarbonyl-4,8-diphenyl-9-thia-1-phosphabicyclo[4.3.0]nona-5,7-diene 1-Sulfide (6g) and 3-Methoxycarbonyl-4,8-diphenyl-9-thia-1-phosphabicyclo[4.3.0]nona-4,6-diene 1-Sulfide (7g): Colorless crystals; mp 177—178 °C. IR (KBr) 1738 cm^{-1}. MS m/z 398 (M^+; 100), 366 (M^+−S, 96), 312 (M^+−Methyl acrylate; 35), 280 (312−S, 59). Found: C, 63.04; H, 4.78%. Calcd for $C_{21}H_{19}O_2PS_2$: C, 63.30; H, 4.81%. ^{1}H NMR (**6g**) δ=2.85—2.93 (m, H-2, H-2′), 3.52 (s, 3H), 4.10—4.17 (m, H-3), 4.47 (ddd, H-4, $J_{4,5}$=4.40, $J_{3,4}$=6.23, J_{HP} =4.40 Hz), 6.38 (dd, H-5, $J_{4,5}$=4.40, J_{HP}=39.19 Hz), 6.92 (d, H-7, J_{HP}=26.37 Hz), 7.08—7.62 (m, 10H); (**7g**) δ=3.01 (ddd, H-2, $J_{2,3}$=9.16, $J_{2.2'}$=13.19, J_{HP}=11.72 Hz), 3.10 (ddd, H-2′, $J_{2',3}$=4.76, $J_{2.2'}$=13.19, J_{HP}=16.48 Hz), 3.50 (s, 3H), 4.64—4.69 (m, H-3), 6.04 (m, H-8), 6.46 (broad-d, H-7, J_{HP}=43.95 Hz), 6.72 (d, H-5, J_{HP}=21.61 Hz), 7.08—7.62 (m, 10H).

(6h) and (7h): Colorless crystals; mp 172—173 °C; MS$m/z$ 416 (M^+; 67), 312 (M^+−Styrene; 28), 280 (312−S, 88). Found: C, 72.13; H, 5.15%. Calcd for $C_{25}H_{21}PS_2$: C, 72.09; H, 5.08%. ^{1}H NMR (**6h**) δ=2.78 (ddd, H-2, $J_{2,3}$=2.20, $J_{2.2'}$=13.19, J_{HP}=17.21 Hz), 3.09—3.16 (m, H-2′), 4.19 (ddd, H-4, $J_{3,4}$=4.58, $J_{4,5}$=4.21, J_{HP}=4.40 Hz), 4.44 (dddd, H-3, $J_{2,3}$=2.20, $J_{3,4}$=4.58, $J_{2',3}$=13.19, J_{HP}=15.38 Hz), 6.52 (dd, H-5, $J_{4,5}$=4.21, J_{HP}=39.92 Hz), 7.00 (d, H-7, J_{HP}=26.00 Hz), 7.06—7.67 (m, 15H); (**7h**) δ=2.86 (ddd, H-2, $J_{2.2'}$=13.55, $J_{2,3}$=13.55, J_{HP}=11.35 Hz), 3.09—3.16 (m, H-2′), 4.88—4.91 (m, H-3), 6.06 (m, H-8), 6.48 (broad-d, H-7, J_{HP}=43.59 Hz), 6.80 (d, H-5, J_{HP}=21.98 Hz), 7.06—7.67 (m, 15H).

(6i) and (7i): Colorless crystals; mp 176—177 °C. IR (KBr) 1718 cm^{-1} (C=O); MS m/z 382 (M^+; 48), 312 (M^+−Methyl vinyl ketone; 23), 280 (312−S; 19), 43 ($CH_3C{\equiv}O^+$; 100). Found: C, 65.98; H, 5.19%. Calcd for $C_{21}H_{19}OPS_2$: C, 65.94; H, 5.01%. ^{1}H NMR (**6i**) δ=2.11 (s, 3H), 2.86—2.93 (m, H-2, H-2′), 4.07—4.13 (m, H-3), 4.54 (ddd, H-4, $J_{3,4}$=4.46, $J_{4,5}$=4.46, J_{HP}=6.56 Hz), 6.39 (dd, H-5, $J_{4,5}$=4.46, J_{HP}=39.02 Hz), 6.89 (d, H-7, J_{HP}=27.00 Hz), 7.09—7.61 (m, 10H); (**7i**) δ=2.05 (s, 3H), 2.81 (ddd, H-2, $J_{2,3}$=11.54, $J_{2.2'}$=12.82, J_{HP}=9.52 Hz), 3.00 (ddd, H-2′, $J_{2',3}$=4.95, $J_{2.2'}$=12.82, J_{HP}=16.48 Hz), 4.74 (ddd, H-3, $J_{2',3}$=4.95, $J_{2,3}$=11.54, J_{HP}=5.12 Hz), 6.04 (m, H-8), 6.48 (d, H-7, J_{HP}=45.06 Hz), 6.76 (d, H-5, J_{HP}=21.25 Hz), 7.09—7.61 (m, 10H).

2,3-Bis(methoxycarbonyl)-6-phenyl-4-styryl-4*H*-thiin (8j): Yellow oil; IR (neat) 1734 cm^{-1} (C=O); ^{1}H NMR δ=3.77 (s, 3H), 3.85 (s, 3H), 4.46 (ddd, H-4, $J_{4,5}$=6.7, $J_{4,1'}$=7.3, $J_{4,2'}$=0.5Hz), 6.05 (d, H-5, $J_{4,5}$=6.7Hz), 6.15 (dd, H-1′, $J_{4,1'}$=7.3, $J_{1',2'}$=16.0Hz), 6.52 (dd, H-2′, $J_{4,2'}$=0.5, $J_{1',2'}$=16.0 Hz), 7.01—7.57 (m, 10H); ^{13}C NMR δ=41.8 (d, C-4), 52.6 (q), 53.2 (q), 118.9 (d, C-5), 124.9 (d, C-2′), 128.0 (s, C-6), 131.6 (d, C-1′), 133.2 (s, C-3), 134.8 (s, C-2), 165.1 (s, C=O), 165.8 (s, C=O); MS m/z 392 (M^+, 14), 360 (M^+−S, 45), 333 (M^+−CO_2CH_3, 100), 301 (333−S, 60). Found: m/z 392.1085. Calcd for $C_{23}H_{20}O_4S$; M, 392.1083.

2,3-Bis(ethoxycarbonyl)-6-phenyl-4-styryl-3,4-dihydro-2*H*-1,2,3-thiadiazine (8k): Orange oil. IR (neat) 1728 cm^{-1} (C=O); ^{1}H NMR δ=1.14 (t, 3H, J_{HH}=7.0 Hz), 1.30 (t, 3H, J_{HH}=7.0 Hz), 4.12 (q, 2H, J_{HH}=7.0 Hz), 4.26 (q, 2H, J_{HH}=7.0 Hz), 5.60 (m, H-4), 6.00 (d, H-5, $J_{4,5}$=5.0 Hz), 6.27 (dd, H-1′, $J_{4,1'}$=5.5, $J_{1',2'}$=16.0 Hz), 6.58 (d, H-2′,$J_{1',2'}$=16.0Hz), 7.10—7.54 (m, 10H); ^{13}C NMR δ=14.3 (q, CH_3), 14.5 (q, CH_3), 55.1 (d, C-4), 63.1 (t, CH_2), 63.9 (t, CH_2), 154.6 (s, C=O), 155.0 (s,C=O); MS m/z 424 (M^+; 9), 250 (Thioketone; 92), 29 (CH_2CH_3; 100). Found: m/z 424.1449. Calcd for $C_{23}H_{24}O_4N_2S$: M, 424.1458.

8-(*p*-Methoxyphenyl)-5-styryl-2-thia-8-azabicyclo[4.3.0]-non-3-ene-7,9-dione (8l): Colorless needles; mp 185—187 °C. IR (KBr) 1712 cm^{-1} (C=O); ^{1}H NMR δ=3.56 (ddd, H-5, $J_{4,5}$=5.13, $J_{5,6}$=5.13, $J_{5,1'}$=9.16 Hz), 3.77 (s, 3H), 3.82 (dd, H-6, $J_{5,6}$=5.13, $J_{1,6}$=9.52 Hz), 4.34 (d, H-1, $J_{1,6}$=9.52 Hz), 4.49 (d, H-4, $J_{4,5}$=5.13 Hz), 6.69 (d, H-2′, $J_{1',2'}$=15.94 Hz), 6.86—6.89 (m, 2H), 6.95 (dd, H-1′, $J_{5,1'}$=9.16, $J_{1',2'}$=15.94 Hz), 6.98—7.01 (m, 2H), 7.24—7.60 (m, 10H); ^{13}C NMR (DEPT) δ=44.8 (CH, C-6), 45.1 (CH, C-1), 50.9 (CH, C-5), 55.4 (CH_3), 128.8 (CH, C-4), 128.9 (CH, C-2′), 132.9 (CH, C-1′), 174.9 (C, C=O), 175.2 (C, C=O); MS m/z 453 (M^+; 33), 250 (Thioketone; 100), 203 (MI; 52). Found: C, 73.90; H, 5.05%. Calcd for $C_{28}H_{23}O_3NS$; C, 74.15; H, 5.11%.

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3) In the adduct **6**, stereoisomers with respect to the phenyl group at position 4 and the substituent at position 3 are possible depending on the *endo* and *exo* addition of the dienophiles to the thiaphosphole **1**. However, no stereoisomers were obtained in detectable amount except **6e** (inseparable mixture) and the ^{1}H NMR spectra showed that **6g**—**i** were 3,4-*cis* (*endo*) isomers.

4) (**2b**): Mp 152—153 °C, (**2c**): Mp 152—153 °C, (**6b**): Yellow oil, (**6c**): Mp 151—152 °C. Elementary analyses, IR, NMR, and mass spectra of these compounds gave satisfactory results.