

Chemistry of 1,2-Thiaphosphole 2-Sulfides I. Cycloaddition Reactions of 1,2-Thiaphosphole 2-Sulfides with Some Dienophiles

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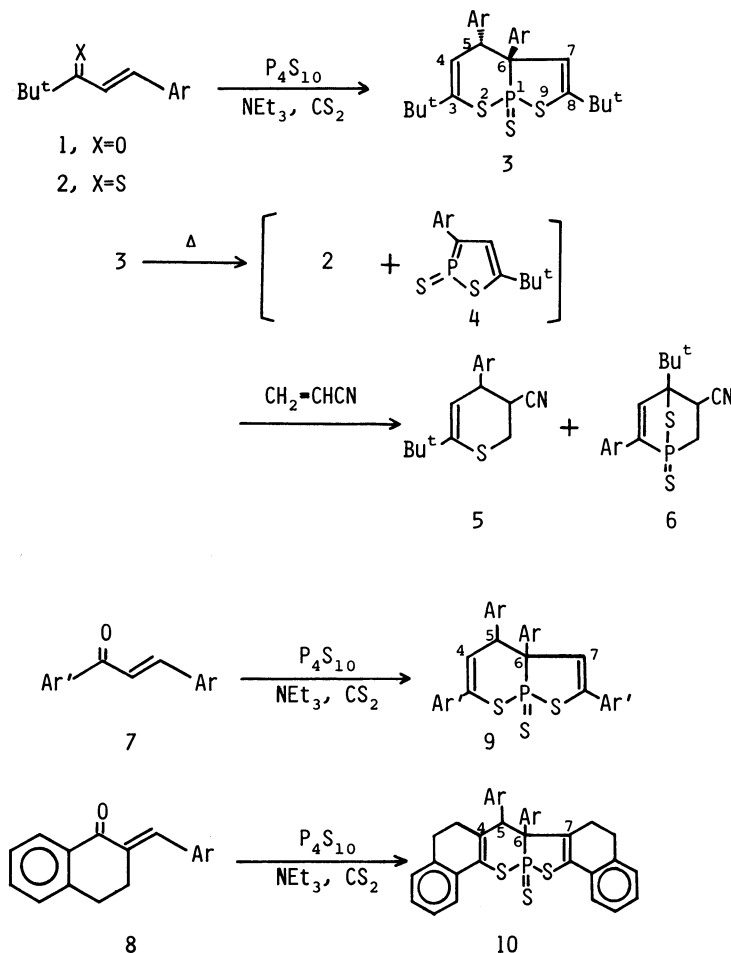
2,9-Dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-sulfides have been prepared by the reaction of α,β -unsaturated ketones with P_4S_{10} in the presence of NEt_3 . 1,2-Thiaphosphole 2-sulfides generated by the thermolysis of the phosphabicyclo compounds underwent cycloaddition reactions with acrylonitrile, styrene, butyl vinyl ether and norbornene to give the [4+2]cycloadducts, respectively.

During the course of the work on the preparation of α,β -unsaturated thione dimers and the cycloaddition reactions of their monomers with various dienophiles,¹⁾ it has been found that attempts to isolate monomeric 1-arylmethylene thiopinacolones **2** resulted in the formation of the unexpected phosphorus-(V)-containing compounds **3**.²⁾ In boiling benzene **3** generated α,β -unsaturated thione monomers **2** and 1,2-thiaphosphole 2-sulfides **4**, both of which could be trapped by acrylonitrile as [4+2]cycloadducts **5** and **6**.³⁾ To our knowledge, the proposed intermediates **4** are the first representatives of five-membered heterocyclic dienes, $S-P(=S)=C-C=C$, though analogous π -bonded phosphorus compounds, $-(S=P=C)<$, have been prepared recently.⁴⁾

In the present paper, we wish to report the detailed study on the cycloaddition reactions of this interesting cyclic heterodienes **4** with a variety of dienophiles leading to P-S-C bridging [4+2]cycloadducts.

Results and Discussion

At first, some additional phosphabicyclo compounds were prepared as starting materials. The results are summarized in Table 1. The yields increased with an increasing electron donating property of the para-substituents of the aromatic rings as in the case of the preparation of the thione dimers.⁵⁾ X-Ray diffraction analysis was performed for **3a**⁶⁾ and the structures of **3b**, **3c**, **9**, and **10** were confirmed by comparison of



Scheme 1.

TABLE 1. PREPARATIONS OF PHOSPHABICYCLO COMPOUNDS **3**, **9**, AND **10**

Compound ^{a)}	Ar	Ar'	Reaction time/h	Mp(dec) $\theta_m/^\circ\text{C}$	Yield/%
3a	Ph	(<i>t</i> -Bu)	20	206—209	20
3b	<i>p</i> -CH ₃ C ₆ H ₄	(<i>t</i> -Bu)	20	210—212	30
3c	<i>p</i> -ClC ₆ H ₄	(<i>t</i> -Bu)	10	220—223	10
9a	Ph	Ph	2	155—159	43
9b	<i>p</i> -CH ₃ OC ₆ H ₄	Ph	2	144—146	57
9c	<i>p</i> -CH ₃ C ₆ H ₄	Ph	2	165—167	45
9d	<i>p</i> -ClC ₆ H ₄	Ph	2	178—180	39
9e	Ph	<i>p</i> -CH ₃ OC ₆ H ₄	2	157—158	70
9f	Ph	<i>p</i> -CH ₃ C ₆ H ₄	2	161—162	41
9g	Ph	<i>p</i> -ClC ₆ H ₄	2	178—179	14
10a	Ph	—	2	172—174	6
10b	<i>p</i> -CH ₃ OC ₆ H ₄	—	2	189—191	22
10c	<i>p</i> -ClC ₆ H ₄	—	2	144—146	8

a) All the compounds are colorless crystals.

TABLE 2. ¹H AND ¹³C NMR SPECTRAL DATA OF **3**, **9**, AND **10** ($\delta(J\text{ Hz})$)

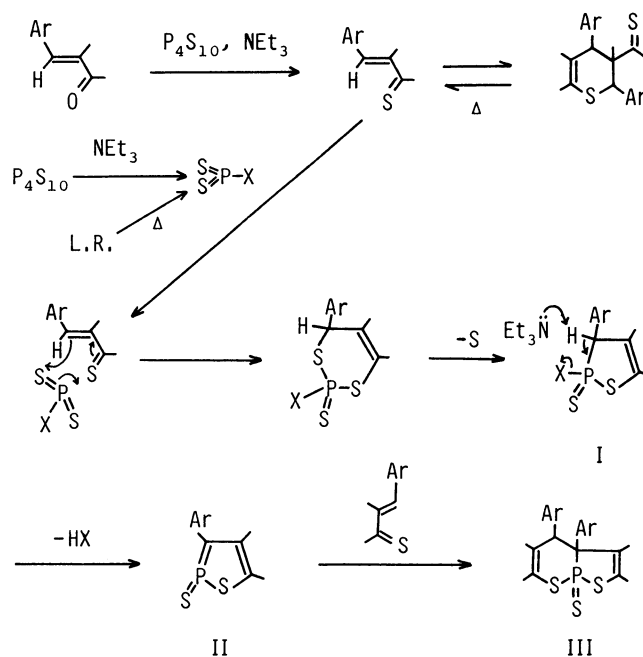
Compound	H(4)	H(5)	H(7)	J_{HH}	$^4J_{\text{H(4)P}}$	$^3J_{\text{H(5)P}}$	$^3J_{\text{H(7)P}}$	C(5)	C(6)	$^2J_{\text{C(5)P}}$	$J_{\text{C(6)P}}$
3a	6.26	4.76	5.76	5.5	5.5	19.5	41.0	55.5	75.5	2.4	42.7
3b	6.24	4.72	5.76	5.5	5.5	20.0	42.0	54.7	75.4	2.4	42.7
3c	6.17	4.67	5.66	5.5	5.5	20.0	42.0	54.9	74.8	2.4	43.9
9a	6.82	5.06	6.35	5.0	5.5	18.0	42.0	56.7	77.2	2.9	42.7
9b	a)	4.96	6.30	5.0	a)	18.0	42.0	55.9	77.0	2.4	41.5
9c	6.82	5.00	6.33	6.0	5.5	20.0	42.0	56.2	77.1	4.0	41.5
9d	6.74	4.96	6.23	6.0	5.5	20.0	42.0	56.2	76.6	2.4	41.5
9e	a)	5.02	6.22	5.0	a)	18.0	42.0	56.7	77.4	2.4	43.9
9f	6.78	5.04	6.29	5.0	5.5	18.0	42.0	56.7	77.2	2.4	41.5
9g	6.82	5.04	6.32	5.0	5.5	18.0	42.0	56.8	77.4	2.4	41.5
10a	—	4.28	—	—	—	28.0	—	56.4	71.9	3.7	41.5
10b	—	4.89	—	—	—	38.0	—	56.5	75.5	≈ 0	41.5
10c	—	4.30	—	—	—	28.0	—	55.5	71.2	2.4	53.7

a) Superimposed on Ar-H. b) Chemical shifts of the signals of C-3, C-4, C-7, and C-8 were not assigned.

their NMR spectral data with those of **3a** (Table 2). The signals of the hydrogen atoms attached to the bicyclic skeleton (H-4, H-5, and H-7) and those of the skeletal saturated carbon atoms (C-5 and C-6) showed characteristic H-P and C-P couplings.⁷⁾

Treatment of the thione dimers with P₄S₁₀ and NEt₃ in refluxing carbon disulfide also produced the phosphabicyclo compounds. P₄S₁₀ is cleaved by liquid NH₃ or NEt₃ to produce diverse complex species containing P, S, and N, *e.g.*, (NH₄)[PS₂(NH₂)₂], (NH₄)₂[PS₃(NH₂)],⁸⁾ Therefore it is assumed that the attack of NEt₃ upon P₄S₁₀ generates the reactive species, X-(S=)P=S (*e.g.*, X=Et₃NH⁺S⁻), which reacts with α,β -unsaturated thiones to form an intermediate **I** in a similar manner to Lawesson's Reagent (L.R.)⁹⁾ (Scheme 2). In the case of L. R. (X=*p*-CH₃OC₆H₄), **I** is actually obtained as a stable compound. But when X is P₄S₁₀ fragment as in the present study, it would be an effective leaving group and can be removed readily under suitable reaction conditions. Accordingly it is rationally considered that by action of a base, NEt₃, H-3 proton is eliminated with X to form 1,2-thiaphosphole 2-sulfide **II** which subsequently undergoes cycloaddition reaction as 2 π system with the thione monomer (4 π) to afford the phosphabicyclo compound **III**.

The reaction of **3a** with acrylonitrile in refluxing



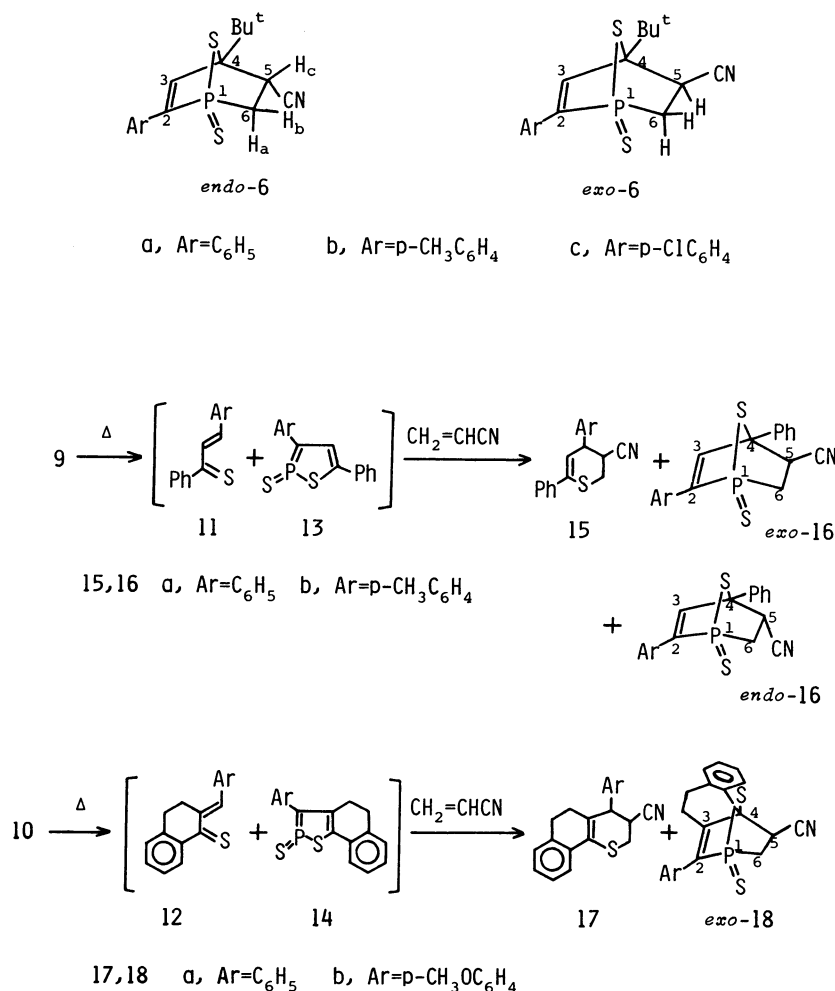
Scheme 2.

benzene gave 1,4-cycloadducts **5a**, *endo*-**6a** and a small amount of *exo*-**6a** without the formation of any regioisomers (Table 3). The cycloadduct **5a** was easily identified by comparison with the authentic compounds reported previously¹⁾ and the structure of *endo*-

TABLE 3. REACTIONS WITH ACRYLONITRILE, STYRENE, BUTYL VINYL ETHER AND NORBORNENE

Material	Dienophile	Reaction time/h	Product					
				Mp $\theta_m/^\circ\text{C}$	Yield/%		Mp (dec) $\theta_m/^\circ\text{C}$	Yield/%
3a		26	5a	137—138	96	endo-6a	142—143	54
						exo-6a	135—136	3
3b	"	18	5b	156—157	37	endo-6b	174—176	15
3c	"	27	5c	149—151	86	endo-6c	145—147	45
9a	"	2	15a	131—132	94	exo-16a	155—156	13
9c	"	2	15b	154—155	86	exo-16b	155—156	14
						endo-16b	164—167	29
10a	"	4	17a	223—225	90	exo-18a	175—177	23
10b	"	1.5	17b	126—128	68	exo-18b	171—172	25
9a		2	19	129—131	69	endo-20	a)	86
10a	"	3	21a	176—178	77	22a	134—135	44
10b	"	1	21b	143—144	72	22b	177—179	56
9a		4.5	23	a)	15	24	a)	7
10a	"	7.5	25	a)	19	26	148—149	36
9a		2	27a	140—142	75	exo-exo-28a	160—161	72
9c	"	4.5	27b	126—127	84	exo-exo-28b	179—181	34
						endo-exo-28b	150—151	39
10a	"	8	29a	99—100	53	exo-30a	229—230	48
10b	"	1.5	29b	124—125	27	exo-30b	211—213	23

a) Oils.



Scheme 3.

6a was confirmed by X-ray analysis.⁶⁾ The cycloadducts *endo*- and *exo*-**6a** showed sharp IR absorptions of ν_{CN} at 2250cm^{-1} , and their mass spectra showed

molecular ion peaks and the fragments due to retro cycloaddition reaction. In the ^{13}C NMR spectra of *endo*- and *exo*-**6a**, the signals of the methylene carbon

TABLE 4. ^{13}C NMR SPECTRAL DATA OF CYCLOADDUCTS (δ (J/Hz))

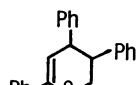
Adduct	C(2)	C(3)	C(4)	C(5)	C(6)	$\underline{\text{C}}\text{N}$	$J_{\text{C}(2)\text{P}}$	$^2J_{\text{C}(3)\text{P}}$	$^2J_{\text{C}(4)\text{P}}$	$^2J_{\text{C}(5)\text{P}}$	$J_{\text{C}(6)\text{P}}$	$^3J_{\text{PCN}}$
<i>endo</i> -6a	146.1	141.1	74.9	33.4	42.4	119.6	59.8	9.8	19.5	3.7	42.7	7.4
<i>exo</i> -6a	146.4	141.4	a)	34.4	42.4	119.8	61.0	12.2	a)	6.1	44.0	3.7
<i>endo</i> -6b	145.9	140.1	75.4	33.6	42.4	119.7	59.8	11.0	19.5	3.7	44.0	8.5
<i>endo</i> -6c	144.9	141.6	75.4	33.4	42.4	119.5	59.8	9.8	19.5	3.7	44.0	7.3
<i>exo</i> -16a	147.0	144.6	68.8	41.0	40.6	118.3	58.6	11.0	24.4	4.9	42.7	3.7
<i>exo</i> -16b	146.6	143.5	68.8	41.0	40.5	118.4	58.6	11.0	24.4	4.9	42.7	3.7
<i>endo</i> -16b	148.2	141.3	66.6	38.7	40.3	118.0	≈ 0	9.8	≈ 0	2.4	42.7	9.8
<i>exo</i> -18a	139.8	155.5	66.2	40.1	41.3	118.2	64.6	11.0	24.4	4.9	41.5	3.7
<i>exo</i> -18b	139.4	154.2	66.2	40.3	41.2	118.3	64.7	12.2	24.4	4.9	42.7	3.7
<i>endo</i> -20	145.3	142.0	69.7	56.3	44.2	—	58.6	9.8	24.4	4.9	42.7	—
22a	137.6	155.7	67.5	56.4	41.8	—	63.5	9.8	25.6	4.9	42.7	—
22b	143.4	154.3	75.1	56.4	41.7	—	60.0	11.0	25.6	4.9	42.7	—
24	138.2	144.0	67.0	84.4	42.1	—	52.5	8.6	22.0	2.4	42.7	—
26	140.3	155.5	70.2	80.8	44.0	—	64.7	13.4	24.4	3.7	41.5	—
<i>exo-exo</i> -28a	147.0	149.7	69.9	58.1	55.4	—	57.4	9.8	29.3	6.1	40.3	—
<i>exo-exo</i> -28b	146.7	148.7	69.9	58.2	55.3	—	58.6	9.8	30.5	6.1	40.3	—
<i>endo-exo</i> -28b	145.1	145.4	68.2	58.7	59.2	—	52.5	9.8	29.3	6.1	40.3	—
<i>exo</i> -30a	139.0	155.7	66.0	62.3	57.4	—	58.6	9.8	29.3	6.1	40.3	—
<i>exo</i> -30b	138.3	154.6	66.0	62.3	57.5	—	52.5	11.0	29.3	6.1	39.0	—

a) Superimposed on CDCl_3 .

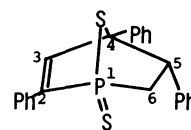
(*endo*-6a; $\delta=42.42$, *exo*-6a; $\delta=42.40$) showed large C-P coupling constants (*endo*-6a; $J_{\text{CP}}=42.7$ Hz, *exo*-6a; $J_{\text{CP}}=44.0$ Hz). This suggests that the methylene carbon is directly bonded to the phosphorus atom.⁷⁾ The ^1H NMR spectrum of *endo*-6a showed double double doublets of three sets of protons at $\delta=2.51$ ($J_{\text{HH}}=3.5$, 14.0 Hz, $J_{\text{HP}}=7.5$ Hz), 3.07 ($J_{\text{HH}}=9.5$, 14.0 Hz, $J_{\text{HP}}=14.0$ Hz) and 3.64 ($J_{\text{HH}}=3.5$, 9.5 Hz, $J_{\text{HP}}=4.5$ Hz), which are assigned to the H_a , H_b , and H_c by spin decoupling experiments, respectively. The coupling constant value of H_c agreed with those of *exo* proton in 2-substituted norbornene ring system.¹⁰⁾ The ^1H NMR of *exo*-6a showed signals of H-5 proton at $\delta=3.08$ –3.32 and of H-6 (*gem*-AB) protons at $\delta=2.70$ –2.86. The coupling pattern was unambiguously different from that of *endo*-6a. *Endo* configuration of cyano group in 6b and 6c was determined by comparing their coupling pattern of $\text{H}_a\sim\text{H}_c$ with that of *endo*-6a. Neither *exo*-6b nor *exo*-6c was obtained.

Similarly, the thermolysis of 9 or 10 in the presence of acrylonitrile yielded 15 and 16, or 17 and 18 (Table 3). The reactions proceeded more rapidly than that of 3. The products 15 and 17 were identified as [4+2]-cycloadducts of 11 and 12 with acrylonitrile, respectively.¹⁾ The structure and configuration of the adduct 16 were determined by comparing their spectral data with those of 6a (*endo*, *exo*) as described above. The ^{13}C NMR spectral data of 18 indicated that the cyano group was linked to the carbon atom at 5-position. It is difficult to determine exactly the configuration of cyano group in 18 by ^1H NMR spectra, however, it was presumed to be *exo* because C-P coupling constants of *endo* cyano carbon were 7.3–9.8 Hz in the adducts 6 and 16, whereas those of the *exo* were 3.7 Hz (Table 4).

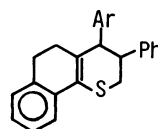
With styrene 9 or 10 produced 19¹⁾ and 20 or 21¹⁾ and 22, respectively. Table 3 shows that the orientation of the 1,4-cycloadducts (20, 22) agrees with that of the



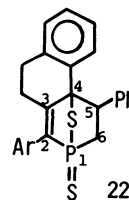
19



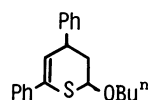
endo-20



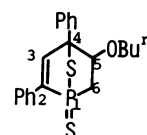
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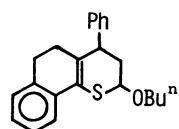
22

21, 22 a, $\text{Ar}=\text{C}_6\text{H}_5$ b, $\text{Ar}=\text{p-CH}_3\text{OC}_6\text{H}_4$ 

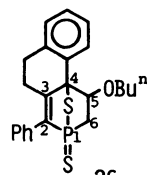
23



24



25



26

acrylonitrile-adducts (16, 18). The ^1H NMR coupling pattern of 20 agreed with that of the *endo*-adduct 6 or 16.

The thermolysis of 9 with butyl vinyl ether gave 23¹⁾ and 24. In the adduct 24, the ^{13}C NMR spectral data proved that butoxyl group was linked to the C-5 carbon. The signal of the C-5 carbon showed small coupling constant $^2J_{\text{C}(5)\text{P}}$ (2.4 Hz) as compared with

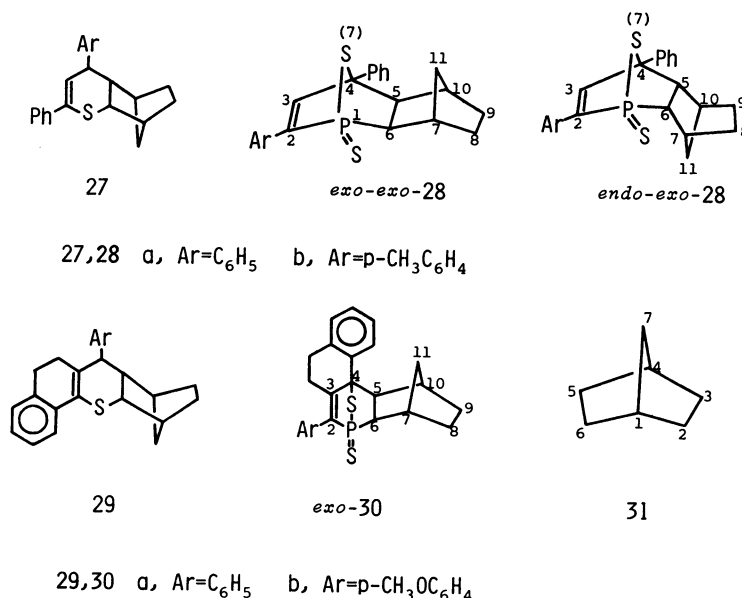


Fig. 1. The configurations of cycloadducts with norbornene. In 2-substituted norbornane, the *exo*-2 group usually shifts the resonance of the C-7 carbon upfield by 1.3–4.4 ppm from the one in norbornane **31** while the *endo*-2 group usually shifts the resonance of C-6 carbon upfield by 4.9–9.7 ppm from one in **31**¹¹⁾ (Table 5).

$J_{C(6)P}$ and shifted downfield owing to the butoxyl group (Table 4). Similarly, the reaction of **10** with butyl vinyl ether afforded **25**¹¹⁾ and **26**. The configurations of **24** and **26** could not be determined.

The reaction of **9** with norbornene gave **27**¹¹⁾ and **28**. In the case of **9c**, two stereo isomers of **28b** were obtained. In general, the chemical shift of the bridged carbon of *exo* substituted norbornane should shift upfield from that of norbornane **31** due to steric repulsion.¹¹⁾ One isomer showed the resonance of the C-11 carbon at $\delta=34.8$ shifted upfield by 4.1 ppm from that of **31**. The other isomer had the resonance at $\delta=30.4$ shifted upfield by 8.0 ppm. The chemical shifts of the C-8 and C-9 carbons of both isomers did not change from those of **31** (Table 5). Therefore, both of the isomers would be *exo* with respect to the norbornyl skeleton. On the other hand, the C-2 and C-3 olefinic carbons¹¹⁾ of the latter isomer resonated upfield by 1.6–3.3 ppm as compared with those of the former, hence the configuration of the latter with respect to 1-phospha-7-thiabicyclo[2.2.1]heptene 1-sulfide ring system would be *endo*; namely the former isomer is *exo-exo-28b* and the latter is *endo-exo-28b*. The reaction of **10** with norbornene gave **29** and **30**. In the ¹³C NMR of **30**, the chemical shifts of the C-8 and C-9 carbons did not change, while the C-11 carbon resonated upfield by 6.3 ppm from that of **31**. Therefore, the configuration should be *exo* with respect to norbornyl ring.

As described above, it has been found that 1,2-thiaphosphole 2-sulfides react as cyclic heterodienes readily and regioselectively with acrylonitrile, styrene or butyl vinyl ether.¹²⁾ Besides the cycloaddition, other varied reactions can be expected for the 1,2-thiaphos-

TABLE 5. ¹³C NMR CHEMICAL SHIFTS OF NORBORNANE **31** AND CYCLOADDUCTS **28b** (J_{CP} /Hz)

Carbons	31	<i>exo-exo-28b</i>		<i>endo-exo-28b</i>	
	δ	δ	J_{CP}	δ	J_{CP}
C-2	—	146.7	58.6	145.1	52.5
C-3	—	148.7	9.8	145.4	9.8
C-7(C-1)	36.8	39.1		38.5	
C-8(C-2)	30.1	30.7	17.1	32.1	15.9
C-9(C-3)	30.1	30.7		32.9	
C-10(C-4)	36.8	36.6	3.7	36.2	2.4
C-11(C-7)	38.7	34.8		30.7	

phole 2-sulfides. The reaction with some nucleophiles are now under investigation.

Experimental

All the melting points are uncorrected. IR spectra were measured on a Hitachi Model 260-10 spectrometer. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer in CDCl₃ solution using Me₄Si as internal standard (¹H; at 100 MHz, ¹³C; at 25 MHz). ¹³C NMR spectral data are shown in Tables 2, 4, and 5. ³¹P NMR spectra were recorded at 40 MHz on a JEOL JNM-FX 100 spectrometer using 85% H₃PO₄ as external standard. Mass spectra were recorded on a Hitachi double focusing mass spectrometer (RMU-7M) operating at an ionizing potential of 70 eV. Elemental analyses of sulfur and phosphorus were performed for some representative compounds. All α,β -unsaturated ketones were prepared by the Aldol condensation of the corresponding ketone with aldehyde.¹³⁾ Acrylonitrile, styrene, butyl vinyl ether and norbornene were obtained commercially.

General Procedure for the Preparation of 2,9-Dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfides. A suspension of α,β -unsaturated ketone (0.04 mol), P₄S₁₀ powder (12 g) and NEt₃ (24 cm³) in dry carbon disulfide (320 cm³) was gent-

ly refluxed (50—55°C) under a nitrogen atmosphere (Reaction times are shown in Table 1). 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 chloroform-ethanol giving the product as colorless crystals.

3,8-Di-*t*-butyl-5,6-diphenyl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfide (3a). Chromatographed by eluting with benzene-hexane (2:3); ^1H NMR (CDCl_3) δ =1.22 (s, 9H), 1.27 (s, 9H), 4.76 (dd, 1H, $J_{\text{HH}}=5.5$ Hz, $J_{\text{HP}}=19.5$ Hz), 5.76 (d, 1H, $J_{\text{HP}}=41.0$ Hz), 6.26 (dd, 1H, $J_{\text{HH}}=5.5$ Hz, $J_{\text{HP}}=5.5$ Hz), and 7.00—7.30 (m, 10H); ^{31}P NMR (CDCl_3) δ =117.1 (dd, $J_{\text{PH}}=41.0$, 19.5 Hz); MS m/z (rel intensity) 470 (M^+ ; 3), 266 (19), 234 (47), 204 (34), 203 (32), and 147 (100). Found: C, 66.33; H, 6.48; S, 20.46; P, 6.43%. Calcd for $\text{C}_{26}\text{H}_{31}\text{S}_3\text{P}$: C, 66.35; H, 6.64; S, 20.43; P, 6.58%.

3,8-Di-*t*-butyl-5,6-bis(*p*-methylphenyl)-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfide (3b). Chromatographed by eluting with benzene-hexane (2:3); ^1H NMR (CDCl_3) δ =1.21 (s, 9H), 1.27 (s, 9H), 2.23 (s, 3H), 2.29 (s, 3H), 4.72 (dd, 1H, $J_{\text{HH}}=5.5$ Hz, $J_{\text{HP}}=20.0$ Hz), 5.76 (d, 1H, $J_{\text{HP}}=42.0$ Hz), 6.24 (dd, 1H, $J_{\text{HH}}=5.5$ Hz, $J_{\text{HP}}=5.5$ Hz), and 6.90—7.30 (m, 8H); MS m/z (rel intensity) 498 (M^+), 280 (8), 248 (65), 218 (22), 203 (41), and 161 (75). Found: C, 67.50; H, 7.12; S, 19.39; P, 6.31%. Calcd for $\text{C}_{28}\text{H}_{35}\text{S}_3\text{P}$: C, 67.43; H, 7.07; S, 19.28; P, 6.21%.

3,8-Di-*t*-butyl-5,6-bis(*p*-chlorophenyl)-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfide (3c). Chromatographed by eluting with benzene-hexane (2:3); ^1H NMR (CDCl_3) δ =1.22 (s, 9H), 1.27 (s, 9H), 4.67 (dd, 1H, $J_{\text{HH}}=5.5$ Hz, $J_{\text{HP}}=20.0$ Hz), 5.66 (d, 1H, $J_{\text{HP}}=42.0$ Hz), 6.17 (dd, 1H, $J_{\text{HH}}=5.5$ Hz, $J_{\text{HP}}=5.5$ Hz), and 6.90—7.30 (m, 8H); MS m/z (rel intensity) 538 (M^+), 300 (20), 268 (54), 238 (27), 233 (94), and 181 (100). Found: C, 57.90; H, 5.43; S, 18.16; P, 5.80%. Calcd for $\text{C}_{26}\text{H}_{29}\text{Cl}_2\text{S}_3\text{P}$: C, 57.88; H, 5.42; S, 17.83; P, 5.74%.

3,5,6,8-Tetraphenyl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfide (9a). Chromatographed by eluting with benzene-hexane (1:1); ^1H NMR (CDCl_3) δ =5.06 (dd, 1H, $J_{\text{HH}}=5.0$ Hz, $J_{\text{HP}}=18.0$ Hz), 6.35 (d, 1H, $J_{\text{HP}}=42.0$ Hz), 6.82 (dd, 1H, $J_{\text{HH}}=5.0$ Hz, $J_{\text{HP}}=5.5$ Hz), and 7.18—7.58 (m, 20H); ^{31}P NMR (CDCl_3) δ =116.8; MS m/z (rel intensity) 254 (100), 224 (15), 223 (30), and 191 (60). Found: C, 70.61; H, 4.78; S, 19.12; P, 5.56%. Calcd for $\text{C}_{30}\text{H}_{23}\text{S}_3\text{P}$: C, 70.56; H, 4.54; S, 18.83; P, 6.07%.

5,6-Bis(*p*-methoxyphenyl)-3,8-diphenyl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfide (9b). Chromatographed by eluting with benzene-hexane (1:1); ^1H NMR (CDCl_3) δ =3.70 (s, 3H), 3.74 (s, 3H), 4.96 (dd, 1H, $J_{\text{HH}}=5.0$ Hz, $J_{\text{HP}}=18.0$ Hz), 6.30 (d, 1H, $J_{\text{HP}}=42.0$ Hz), and 6.66—7.54 (m, 19H); ^{31}P NMR (CDCl_3) δ =116.6; MS m/z (rel intensity) 284 (100), 269 (25), 254 (18), and 253 (19). Found: C, 67.18; H, 4.83%. Calcd for $\text{C}_{32}\text{H}_{27}\text{O}_2\text{S}_3\text{P}$: C, 67.35; H, 4.83%.

5,6-Bis(*p*-methylphenyl)-3,8-diphenyl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfide (9c). Chromatographed by eluting with benzene-hexane (1:1); ^1H NMR (CDCl_3) δ =2.26 (s, 3H), 2.30 (s, 3H), 5.00 (d, 1H, $J_{\text{HH}}=6.0$ Hz, $J_{\text{HP}}=20.0$ Hz), 6.33 (d, 1H, $J_{\text{HP}}=42.0$ Hz), 6.82 (dd, 1H, $J_{\text{HH}}=6.0$ Hz, $J_{\text{HP}}=5.5$ Hz), and 6.92—7.56 (m, 18H); MS m/z (rel intensity) 300, 268 (100), 238 (13), 237 (18), and 205 (29). Found: C, 71.27; H, 5.20%. Calcd for $\text{C}_{32}\text{H}_{27}\text{S}_3\text{P}$: C, 71.34; H, 5.05%.

5,6-Bis(*p*-chlorophenyl)-3,8-diphenyl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfide (9d). Chromatographed by eluting with benzene-hexane (1:1); ^1H NMR (CDCl_3) δ =4.96 (dd, 1H, $J_{\text{HH}}=6.0$ Hz, $J_{\text{HP}}=20.0$ Hz), 6.23 (d, 1H, $J_{\text{HP}}=42.0$ Hz),

6.74 (dd, 1H, $J_{\text{HH}}=6.0$ Hz, $J_{\text{HP}}=5.5$ Hz), and 6.96—7.54 (m, 18H); MS m/z (rel intensity) 288 (100), 258 (24), 257 (28), and 225 (36). Found: C, 62.32; H, 3.81%. Calcd for $\text{C}_{30}\text{H}_{21}\text{Cl}_2\text{S}_3\text{P}$: C, 62.71; H, 3.65%.

3,8-Bis(*p*-methoxyphenyl)-5,6-diphenyl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfide (9e). Chromatographed by eluting with benzene-hexane (1:1); ^1H NMR (CDCl_3) δ =3.77 (s, 3H), 3.78 (s, 3H), 5.02 (dd, 1H, $J_{\text{HH}}=5.0$ Hz, $J_{\text{HP}}=18.0$ Hz), 6.22 (d, 1H, $J_{\text{HP}}=42.0$ Hz), and 6.66—7.50 (m, 19H); ^{31}P NMR (CDCl_3) δ =117.0; MS m/z (rel intensity) 284 (100), 253 (25), and 221 (9). Found: C, 67.58; H, 4.97%. Calcd for $\text{C}_{32}\text{H}_{27}\text{O}_2\text{S}_3\text{P}$: C, 67.35; H, 4.77%.

3,8-Bis(*p*-methylphenyl)-5,6-diphenyl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfide (9f). Chromatographed by eluting with benzene-hexane (1:1); ^1H NMR (CDCl_3) δ =2.33 (s, 6H), 5.04 (dd, 1H, $J_{\text{HH}}=5.0$ Hz, $J_{\text{HP}}=18.0$ Hz), 6.29 (d, 1H, $J_{\text{HP}}=42.0$ Hz), 6.78 (dd, 1H, $J_{\text{HH}}=5.0$ Hz, $J_{\text{HP}}=5.5$ Hz), and 7.06—7.44 (m, 18H); MS m/z (rel intensity) 268 (100), 238 (27), 237 (49), and 205 (29). Found: C, 71.35; H, 5.34%. Calcd for $\text{C}_{32}\text{H}_{27}\text{S}_3\text{P}$: C, 71.34; H, 5.05%.

3,8-Bis(*p*-chlorophenyl)-5,6-diphenyl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfide (9g). Chromatographed by eluting with benzene-hexane (1:1); ^1H NMR (CDCl_3) δ =5.04 (dd, 1H, $J_{\text{HH}}=5.0$ Hz, $J_{\text{HP}}=18.0$ Hz), 6.32 (d, 1H, $J_{\text{HP}}=42.0$ Hz), 6.82 (dd, 1H, $J_{\text{HH}}=5.0$ Hz, $J_{\text{HP}}=5.5$ Hz), and 7.16—7.56 (m, 18H); MS m/z (rel intensity) 288 (100), 258 (1), 257 (2), and 225 (29). Found: C, 62.38; H, 3.74%. Calcd for $\text{C}_{30}\text{H}_{21}\text{Cl}_2\text{S}_3\text{P}$: C, 62.17; H, 3.65%.

6b,7-Diphenyl-5,6,6b,7,8,9-hexahydro-14,15-dithia-14a-phosphabenz[4,5]indeno[1,2-b]phenanthrene 14a-Sulfide (10a). Chromatographed by eluting with benzene-hexane (2:3); ^1H NMR (CDCl_3) δ =1.24—2.98 (m, 8H), 4.28 (d, 1H, $J_{\text{HP}}=28.0$ Hz), and 6.86—7.60 (m, 18H); ^{31}P NMR (CDCl_3) δ =123.7; MS m/z (rel intensity) 530, 312 (30), 280 (100), 250 (9), and 249 (17). Found: C, 72.70; H, 4.70; S, 17.62; P, 5.12%. Calcd for $\text{C}_{34}\text{H}_{27}\text{S}_3\text{P}$: C, 72.44; H, 5.01; S, 17.06; P, 5.49%.

6b,7-Bis(*p*-methoxyphenyl)-5,6,6b,7,8,9-hexahydro-14,15-dithia-14a-phosphabenz[4,5]indeno[1,2-b]phenanthrene 14a-Sulfide (10b). Chromatographed by eluting with benzene-hexane (2:3); ^1H NMR (CDCl_3) δ =1.54—2.74 (m, 8H), 3.75 (s, 6H), 4.89 (d, 1H, $J_{\text{HP}}=38.0$ Hz), and 6.66—7.52 (m, 16H); ^{31}P NMR (CDCl_3) δ =109.4; MS m/z (rel intensity) 310 (100), 279 (25). Found: C, 69.43; H, 5.32%. Calcd for $\text{C}_{36}\text{H}_{31}\text{O}_2\text{S}_3\text{P}$: C, 69.32; H, 5.17%.

6b,7-Bis(*p*-chlorophenyl)-5,6,6b,7,8,9-hexahydro-14,15-dithia-14a-phosphabenz[4,5]indeno[1,2-b]phenanthrene 14a-Sulfide (10c). Chromatographed by eluting with benzene-hexane (2:3); ^1H NMR (CDCl_3) δ =1.57—1.84 (m, 8H), 4.30 (d, 1H, $J_{\text{HP}}=28.0$ Hz), and 7.00—7.58 (m, 16H); MS m/z (rel intensity) 314 (100), 285 (22), and 283 (22). Found: C, 64.63; H, 3.97%. Calcd for $\text{C}_{34}\text{H}_{27}\text{Cl}_2\text{S}_3\text{P}$: C, 64.65; H, 3.99%.

General Procedure for the Cycloaddition Reactions of the 2,9-Dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-Sulfides with Dienophiles. A solution of the 2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-sulfide (2 mmol) and dienophile (6 mmol) in dry benzene (5 cm^3) was refluxed under a nitrogen atmosphere until all the phosphabicyclo compound had been consumed as indicated by TLC. The solvent was evaporated and the residue was chromatographed on silica gel (Wakogel C-200). The solvent was evaporated and the residue was recrystallized from ethanol to give the cycloadduct.

6-*t*-Butyl-3-cyano-4-phenyl-3,4-dihydro-2H-thiopyran (5a). Chromatographed by eluting with benzene-ligroin (1:1); IR

(KBr) 2250 cm^{-1} (CN); ^1H NMR (CDCl_3) δ = 1.22 (s, 9H), 3.00–3.40 (m, 3H), 3.78 (dd, 1H, $J_{\text{HH}}=4.8$ Hz), 5.66 (d, 1H, $J_{\text{HH}}=4.8$ Hz), and 7.20–7.30 (m, 5H); MS m/z (rel intensity) 257 (M^+ ; 30), 203 (63), and 147 (100). Found: C, 74.68; H, 7.47; N, 5.37; S, 12.74%. Calcd for $\text{C}_{16}\text{H}_{19}\text{NS}$: C, 74.66; H, 7.44; N, 5.44; S, 12.46%.

6-*t*-Butyl-3-cyano-4-(*p*-methylphenyl)-3,4-dihydro-2H-thiopyran (5b). Chromatographed by eluting with benzene–hexane (2:1); IR (KBr) 2250 cm^{-1} (CN); ^1H NMR (CDCl_3) δ =1.21 (s, 9H), 2.34 (s, 3H), 2.90–3.40 (m, 3H), 3.60–3.80 (m, 1H), 5.63 (d, 1H, $J_{\text{HH}}=5.0$ Hz), and 7.00–7.20 (m, 4H); MS m/z (rel intensity) 271 (M^+ ; 29), 218 (22), 203 (100), and 161 (70). Found: C, 75.39; H, 7.85; N, 5.17%. Calcd for $\text{C}_{17}\text{H}_{21}\text{NS}$: C, 75.23; H, 7.80; N, 5.16%.

6-*t*-Butyl-3-cyano-4-(*p*-chlorophenyl)-3,4-dihydro-2H-thiopyran (5c). Chromatographed by eluting with benzene–hexane (1:1); IR (KBr) 2250 cm^{-1} (CN); ^1H NMR (CDCl_3) δ =1.22 (s, 9H), 2.98–3.36 (m, 3H), 3.78 (dd, 1H, $J_{\text{HH}}=4.6$ Hz), 5.60 (d, 1H, $J_{\text{HH}}=4.6$ Hz), and 7.06–7.36 (m, 4H); MS m/z (rel intensity) 291 (M^+ ; 25), 238 (41), 203 (40), and 181 (100). Found: C, 65.79; H, 6.02; N, 4.77%. Calcd for $\text{C}_{16}\text{H}_{18}\text{NClS}$: C, 65.85; H, 6.22; N, 4.80%.

4-*t*-Butyl-endo-5-cyano-2-phenyl-7-thia-1-phosphabicyclo[2.2.1]hept-2-ene 1-Sulfide (endo-6a). IR (KBr) 2250 cm^{-1} (CN); ^1H NMR (CDCl_3) δ =1.34 (s, 9H), 2.51 (ddd, 1H, $J_{\text{HH}}=3.5$, 14.0 Hz, $J_{\text{HP}}=7.5$ Hz), 3.07 (ddd, 1H, $J_{\text{HH}}=9.5$, 14.0 Hz, $J_{\text{HP}}=14.0$ Hz), 3.64 (ddd, 1H, $J_{\text{HH}}=3.5$, 9.5 Hz, $J_{\text{HP}}=4.5$ Hz), and 7.05–7.72 (m, 6H); ^{31}P NMR (CDCl_3) δ =–28.9; MS m/z (rel intensity) 319 (M^+ ; 2), 266 (100), 251 (22), 234 (52), 219 (85), and 203 (18). Found: C, 60.18; H, 5.77; N, 4.41; S, 20.02; P, 9.78%. Calcd for $\text{C}_{16}\text{H}_{18}\text{NS}_2\text{P}$: C, 60.16; H, 5.68; N, 4.39; S, 20.07; P, 9.70%.

exo-6a: IR (KBr) 2250 cm^{-1} (CN); ^1H NMR (CDCl_3) δ =1.39 (s, 9H), 2.70–2.86 (m, 2H), 3.08–3.32 (m, 1H), and 6.72–7.70 (m, 6H); MS m/z (rel intensity) 319 (M^+ ; 2), 266 (100), 251 (22), 234 (29), 219 (22), and 203 (17). Found: C, 60.32; H, 5.60; N, 4.35%. Calcd for $\text{C}_{16}\text{H}_{18}\text{NS}_2\text{P}$: C, 60.16; H, 5.68; N, 4.39%.

4-*t*-Butyl-endo-5-cyano-2-(*p*-methylphenyl)-7-thia-1-phosphabicyclo[2.2.1]hept-2-ene 1-Sulfide (endo-6b). IR (KBr) 2250 cm^{-1} (CN); ^1H NMR (CDCl_3) δ =1.32 (s, 9H), 2.36 (s, 3H), 2.48 (ddd, 1H, $J_{\text{HH}}=3.0$, 13.0 Hz, $J_{\text{HP}}=7.5$ Hz), 3.04 (ddd, 1H, $J_{\text{HH}}=10.0$, 13.0 Hz, $J_{\text{HP}}=13.0$ Hz), 3.60 (ddd, 1H, $J_{\text{HH}}=3.0$, 10.0 Hz, $J_{\text{HP}}=4.0$ Hz), and 6.92–7.64 (m, 5H); MS m/z (rel intensity) 333 (M^+ ; 2), 280 (100), 265 (21), and 248 (39). Found: C, 61.56; H, 5.97; N, 4.18%. Calcd for $\text{C}_{17}\text{H}_{20}\text{NS}_2\text{P}$: C, 61.24; H, 6.05; N, 4.20%.

4-*t*-Butyl-endo-5-cyano-2-(*p*-chlorophenyl)-7-thia-1-phosphabicyclo[2.2.1]hept-2-ene 1-Sulfide (endo-6c). IR (KBr) 2250 cm^{-1} (CN); ^1H NMR (CDCl_3) δ =1.34 (s, 9H), 2.50 (ddd, 1H, $J_{\text{HH}}=3.0$, 14.0 Hz, $J_{\text{HP}}=7.5$ Hz), 3.08 (ddd, 1H, $J_{\text{HH}}=10.0$, 14.0 Hz, $J_{\text{HP}}=14.0$ Hz), 3.64 (ddd, 1H, $J_{\text{HH}}=3.0$, 10.0 Hz, $J_{\text{HP}}=4.5$ Hz), and 7.04–7.68 (m, 5H); MS m/z (rel intensity) 355 (M^+ ; 1), 302 (44), 287 (11), 270 (23), and 255 (37). Found: C, 54.25; H, 5.00; N, 3.94%. Calcd for $\text{C}_{16}\text{H}_{17}\text{NClS}_2\text{P}$: C, 54.31; H, 4.84; N, 3.96%.

exo-5-Cyano-2,4-diphenyl-7-thia-1-phosphabicyclo[2.2.1]hept-2-ene 1-Sulfide (exo-16a). Chromatographed by eluting with benzene–ligroin (1:1); IR (KBr) 2250 cm^{-1} (CN); ^1H NMR (CDCl_3) δ =2.82–3.04 (m, 2H), 3.54–3.80 (m, 1H), and 6.82–7.68 (m, 11H); ^{31}P NMR (CDCl_3) δ =–52.6; MS m/z (rel intensity) 286 (15), 254 (100). Found: C, 63.90; H, 4.35; S, 19.35; P, 8.88%. Calcd for $\text{C}_{18}\text{H}_{14}\text{NS}_2\text{P}$: C, 63.70; H, 4.16; S, 18.89; P,

9.13%.

exo-5-Cyano-2-(*p*-methylphenyl)-4-phenyl-7-thia-1-phosphabicyclo[2.2.1]hept-2-ene 1-Sulfide (exo-16b). Chromatographed by eluting with benzene–ligroin (1:1); IR (KBr) 2250 cm^{-1} (CN); ^1H NMR (CDCl_3) δ =2.36 (s, 3H), 2.64–3.12 (m, 2H), 3.50–3.80 (m, 1H), and 7.04–7.60 (m, 10H); MS m/z (rel intensity) 353 (M^+ ; 1), 300 (30), and 268 (100). Found: C, 64.44; H, 4.32%. Calcd for $\text{C}_{19}\text{H}_{16}\text{NS}_2\text{P}$: C, 64.57; H, 4.56%.

endo-16b: IR (KBr) 2250 cm^{-1} (CN); ^1H NMR (CDCl_3) δ =2.38 (s, 3H), 2.58 (ddd, 1H, $J_{\text{HH}}=4.0$, 13.0 Hz, $J_{\text{HP}}=8.0$ Hz), 3.12 (ddd, 1H, $J_{\text{HH}}=9.0$, 13.0 Hz, $J_{\text{HP}}=13.0$ Hz), 4.06 (ddd, 1H, $J_{\text{HH}}=4.0$, 10.0 Hz, $J_{\text{HP}}=3.0$ Hz), and 7.12–7.70 (m, 10H); MS m/z (rel intensity) 353 (M^+ ; 300 (24), and 268 (100). Found: C, 64.38; H, 4.28%. Calcd for $\text{C}_{19}\text{H}_{16}\text{NS}_2\text{P}$: C, 64.57; H, 4.56%.

exo-10-Cyano-7-phenyl-2,3-benzo-11-thia-8-phosphatricyclo[6.2.1.0^{1,6}]undec-6-ene 8-Sulfide (exo-18a). Chromatographed by eluting with benzene–hexane (3:2); IR (KBr) 2250 cm^{-1} (CN); ^1H NMR (CDCl_3) δ =2.58–3.52 (m, 7H) and 7.14–7.67 (m, 9H); ^{31}P NMR (CDCl_3) δ =–52.1; MS m/z (rel intensity) 365 (M^+ ; 312 (34), and 280 (100). Found: C, 65.75; H, 4.71; S, 17.96; P, 8.28%. Calcd for $\text{C}_{20}\text{H}_{16}\text{NS}_2\text{P}$: C, 65.73; H, 4.41; S, 17.55; P, 8.48%.

exo-10-Cyano-7-(*p*-methoxyphenyl)-2,3-benzo-11-thia-8-phosphatricyclo[6.2.1.0^{1,6}]undec-6-ene 8-Sulfide (exo-18b). Chromatographed by eluting with benzene–hexane (1:2); IR (KBr) 2250 cm^{-1} (CN); ^1H NMR (CDCl_3) δ =2.40–3.56 (m, 7H), 3.82 (s, 3H), and 6.80–7.72 (m, 8H); MS m/z (rel intensity) 395 (M^+ ; 342 (3), and 310 (100). Found: C, 63.87; H, 4.89%. Calcd for $\text{C}_{21}\text{H}_{18}\text{ONS}_2\text{P}$: C, 63.87; H, 4.58%.

endo-5-Phenyl-2,4-diphenyl-7-thia-1-phosphabicyclo[2.2.1]hept-2-ene 1-Sulfide (endo-20). Chromatographed by eluting with benzene–hexane (1:2); ^1H NMR (CDCl_3) δ =2.48–4.20 (m, 3H), 6.60–6.76 (m, 1H), and 6.80–7.92 (m, 15H); MS m/z (rel intensity) 390 (M^+ ; 1), 287 (2), and 254 (100).

7,10-Diphenyl-2,3-benzo-11-thia-8-phosphatricyclo[6.2.1.0^{1,6}]undec-6-ene 8-Sulfide (22a). Chromatographed by eluting with benzene; ^1H NMR (CDCl_3) δ =1.42–3.80 (m, 6H), 4.42–4.60 (m, 1H), and 6.34–7.79 (m, 14H); ^{31}P NMR (CDCl_3) δ =–49.6; MS m/z (rel intensity) 416 (M^+ ; 312 (6), 280 (100), and 249 (10). Found: C, 71.83; H, 5.34; S, 15.47; P, 7.26%. Calcd for $\text{C}_{25}\text{H}_{21}\text{S}_2\text{P}$: C, 72.09; H, 5.08; S, 15.39; P, 7.44%.

7-(*p*-Methoxyphenyl)-10-phenyl-2,3-benzo-11-thia-8-phosphatricyclo[6.2.1.0^{1,6}]undec-6-ene 8-Sulfide (22b). Chromatographed by eluting with benzene–hexane (1:1); ^1H NMR (CDCl_3) δ =1.40–3.60 (m, 5H), 3.86 (s, 3H), 4.40–4.64 (m, 1H), and 6.75–7.82 (m, 13H); MS m/z (rel intensity) 446 (M^+ ; 342 (6), and 310 (100). Found: C, 69.82; H, 5.41%. Calcd for $\text{C}_{26}\text{H}_{23}\text{OS}_2\text{P}$: C, 69.93; H, 5.19%.

5-Butoxy-2,4-diphenyl-7-thia-1-phosphabicyclo[2.2.1]hept-2-ene 1-Sulfide (24). Chromatographed by eluting with benzene–hexane (1:1); ^1H NMR (CDCl_3) δ =0.60–1.48 (m, 9H), 2.00–2.32 (m, 1H), 2.76–3.00 (m, 1H), 3.12–3.40 (m, 1H), and 7.00–7.76 (m, 11H).

10-Butoxy-7-phenyl-2,3-benzo-11-thia-8-phosphatricyclo[6.2.1.0^{1,6}]undec-6-ene 8-Sulfide (26). Chromatographed by eluting with benzene–hexane (3:4); ^1H NMR (CDCl_3) δ =0.39–1.56 (m, 7H), 2.34–3.00 (m, 7H), 3.12–3.36 (m, 1H), 3.80–4.16 (m, 1H), and 7.00–7.60 (m, 9H); MS m/z (rel intensity) 412 (M^+ ; 378 (1), 346 (1), 312 (13), 280 (100), and 215 (31). Found: C, 66.84; H, 6.20%. Calcd for $\text{C}_{23}\text{H}_{25}\text{OS}_2\text{P}$: C, 66.96; H, 6.11%.

8,10-Diphenyl-11-thia-1-phosphatetetracyclo[6.2.1^{3,6}.0^{2,7}]dec-9-ene 1-Sulfide (exo-exo-28a). Chromatographed by eluting

with benzene-hexane (3:2); ^1H NMR (CDCl_3) $\delta=0.94\text{--}3.10$ (m, 10H), 7.03—7.67 (m, 11H); ^{31}P NMR (CDCl_3) $\delta=-44.4$; MS m/z (rel intensity) 380 (M^+ ; 2), 286 (100), 254 (8), 223 (10), and 121 (14). Found: C, 69.71; H, 5.82; S, 17.18; P, 7.88%. Calcd for $\text{C}_{22}\text{H}_{21}\text{S}_2\text{P}$: C, 69.45; H, 5.56; S, 16.85; P, 8.14%.

10-(p-Methylphenyl)-8-phenyl-11-thia-1-phosphatetracyclo[6.2.1^{3,6}.0^{2,7}]dec-9-ene 1-Sulfide (**exo-exo-28b**). Chromatographed by eluting with benzene-hexane (1:2); ^1H NMR (CDCl_3) $\delta=0.92\text{--}3.07$ (m, 10H), 2.36 (s, 3H), and 6.97—7.66 (m, 10H); MS m/z (rel intensity) 394 (M^+ ; 3), 300 (100), and 268 (19). Found: C, 70.33; H, 5.92%. Calcd for $\text{C}_{23}\text{H}_{23}\text{S}_2\text{P}$: C, 70.02; H, 5.88%.

endo-exo-28b: ^1H NMR (CDCl_3) $\delta=0.68\text{--}3.40$ (m, 10H), 2.36 (s, 3H), and 6.90—7.68 (m, 10H); MS m/z (rel intensity) 394 (M^+ ; 5), 300 (100), and 268 (15). Found: C, 70.30; H, 5.82%. Calcd for $\text{C}_{23}\text{H}_{23}\text{S}_2\text{P}$: C, 70.02; H, 5.88%.

9-Phenyl-13,14-benzo-15-thia-8-phosphapentacyclo[6.6.1.1^{3,6}.0^{1,10}.0^{2,7}]hexadeca-9,13-diene 8-Sulfide (**exo-30a**). Chromatographed by eluting with benzene; ^1H NMR (CDCl_3) $\delta=0.82\text{--}3.32$ (m, 14H) and 7.16—7.58 (m, 9H); ^{31}P NMR (CDCl_3) $\delta=-41.3$; MS m/z (rel intensity) 406 (M^+ ; 3), 312 (100), 280 (9), and 249 (10). Found: C, 70.94; H, 5.75; S, 15.55; P, 7.80%. Calcd for $\text{C}_{24}\text{H}_{23}\text{S}_2\text{P}$: C, 70.91; H, 5.70; S, 15.77; P, 7.62%.

9-(p-Methoxyphenyl)-13,14-benzo-15-thia-8-phosphapentacyclo[6.6.1.1^{3,6}.0^{1,10}.0^{2,7}]hexadeca-9,13-diene 8-Sulfide (**exo-30b**). Chromatographed by eluting with benzene-hexane (1:1); ^1H NMR (CDCl_3) $\delta=1.78\text{--}3.32$ (m, 14H), 3.80 (s, 3H), and 6.80—7.64 (m, 8H); MS m/z (rel intensity) 436 (M^+ ; 1), 342 (100), and 310 (10). Found: C, 69.01; H, 6.01%. Calcd for $\text{C}_{25}\text{H}_{25}\text{O}\text{S}_2\text{P}$: C, 68.78; H, 5.77%.

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arylmethylenepinacolones **1** was carried out under the same reaction conditions, no reaction took place. Treatment of these ketones (0.1 mol) with large amount of P_4S_{10} (30 g) and NEt_3 (60 cm^3) in refluxing carbon disulfide is suitable for the preparation of phosphabicyclo compounds **3**, **9**, and **10**.

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