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

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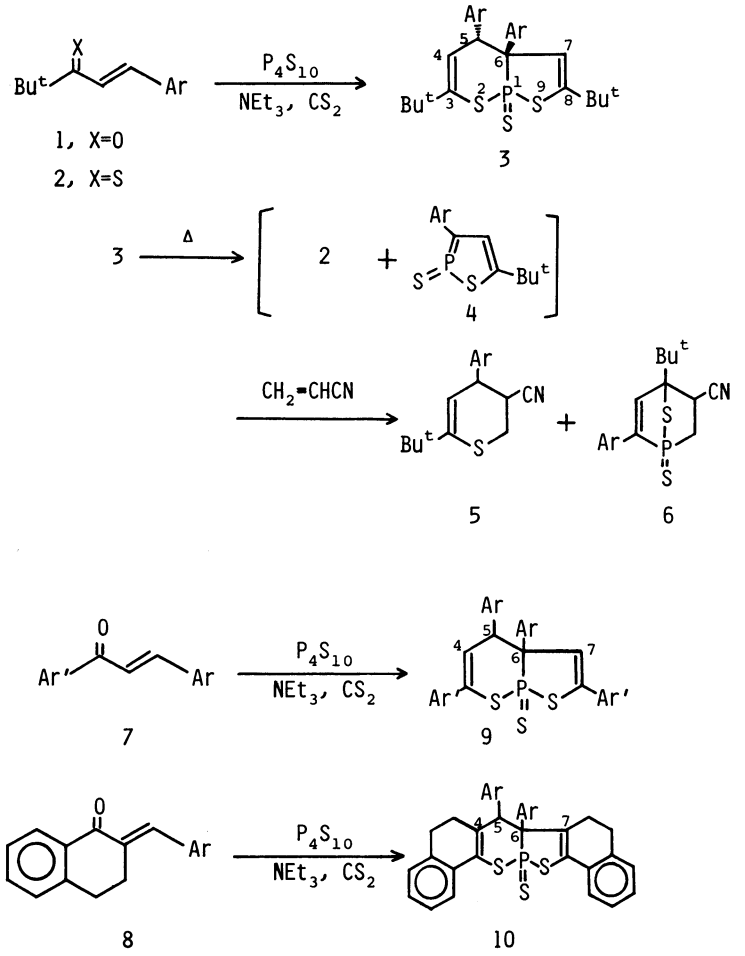
2,9-Dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-sulfides have been prepared by the reaction of α,β-unsaturated ketones with P_4S_{10} in the presence of NEt_3. 1,2-Thiaphosphole 2-sulfides generated by the thermolysis of the phosphabicyclo compounds underwent cycloaddition reactions with acrylonitrile, 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 difraction 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) θ_m/°C	Yield/%
3a	Ph	(*t*-Bu)	20	206—209	20
3b	*p*-$CH_3C_6H_4$	(*t*-Bu)	20	210—212	30
3c	*p*-ClC_6H_4	(*t*-Bu)	10	220—223	10
9a	Ph	Ph	2	155—159	43
9b	*p*-$CH_3OC_6H_4$	Ph	2	144—146	57
9c	*p*-$CH_3C_6H_4$	Ph	2	165—167	45
9d	*p*-ClC_6H_4	Ph	2	178—180	39
9e	Ph	*p*-$CH_3OC_6H_4$	2	157—158	70
9f	Ph	*p*-$CH_3C_6H_4$	2	161—162	41
9g	Ph	*p*-ClC_6H_4	2	178—179	14
10a	Ph	—	2	172—174	6
10b	*p*-$CH_3OC_6H_4$	—	2	189—191	22
10c	*p*-ClC_6H_4	—	2	144—146	8

a) All the compounds are colorless crystals.

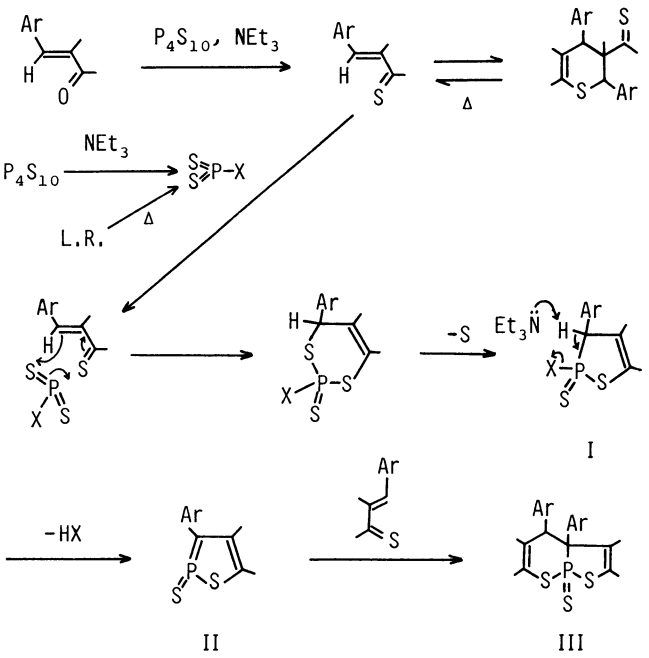
Table 2. ^1H and ^{13}C NMR spectral data of **3**, **9**, and **10** (δ(J Hz))

Compound	H(4)	H(5)	H(7)	J_{HH}	$^4J_{H(4)P}$	$^3J_{H(5)P}$	$^3J_{H(7)P}$	C(5)	C(6)	$^2J_{C(5)P}$	$J_{C(6)P}$
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 P_4S_{10} and NEt_3 in refluxing carbon disulfide also produced the phosphabicyclo compounds. P_4S_{10} is cleaved by liquid NH_3 or NEt_3 to produce diverse complex species containing P, S, and N, *e.g.*, $(NH_4)[PS_2(NH_2)_2]$, $(NH_4)_2[PS_3(NH_2)]$.[8)] Therefore it is assumed that the attack of NEt_3 upon P_4S_{10} generates the reactive species, X-(S=)P=S (*e.g.*, $X=Et_3NH^+S^-$), 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*-$CH_3OC_6H_4$), **I** is actually obtained as a stable compound. But when X is P_4S_{10} 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, NEt_3, H-3 proton is eliminated with X to form 1,2-thiaphosphole 2-sulfide **II** which subsequently undergoes cycloaddition reaction as 2π system with the thione monomer (4π) to afford the phosphabicyclo compound **III**.



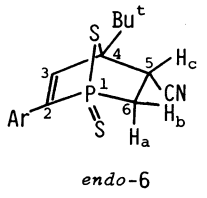
Scheme 2.

The reaction of **3a** with acrylonitrile in refluxing 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 previously[1)] and the structure of ***endo***-

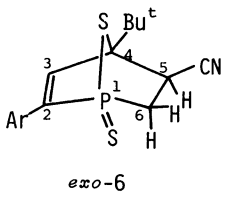
Table 3. Reactions with acrylonitrile, styrene, butyl vinyl ether and norbornene

Material	Dienophile	Reaction time/h	Product					
				Mp θ_m/°C	Yield/%		Mp (dec) θ_m/°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.

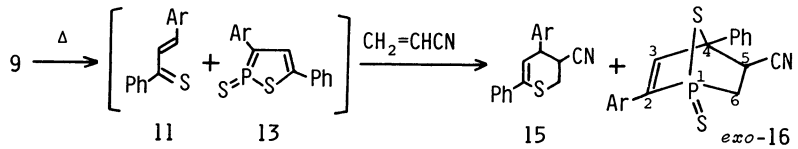


endo-6



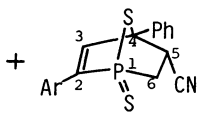
exo-6

a, Ar=C_6H_5 b, Ar=p-$CH_3C_6H_4$ c, Ar=p-ClC_6H_4

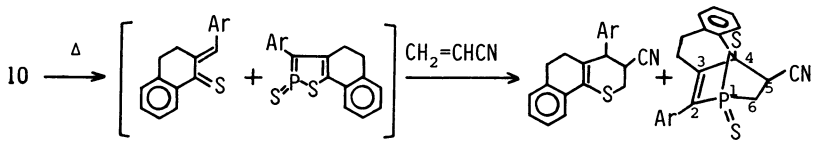


11 13 15 *exo*-16

15,16 a, Ar=C_6H_5 b, Ar=p-$CH_3C_6H_4$



endo-16



12 14 17 *exo*-18

17,18 a, Ar=C_6H_5 b, Ar=p-$CH_3OC_6H_4$

Scheme 3.

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

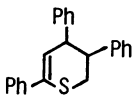
Adduct	C(2)	C(3)	C(4)	C(5)	C(6)	CN	$J_{C(2)P}$	$^2J_{C(3)P}$	$^2J_{C(4)P}$	$^2J_{C(5)P}$	$J_{C(6)P}$	$^3J_{PCN}$
***endo*-6a**	146.1	141.1	74.9	33.4	42.4	119.6	59.8	9.8	19.5	3.7	42.7	7.4
***exo*-6a**	146.4	141.4	a)	34.4	42.4	119.8	61.0	12.2	a)	6.1	44.0	3.7
***endo*-6b**	145.9	140.1	75.4	33.6	42.4	119.7	59.8	11.0	19.5	3.7	44.0	8.5
***endo*-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
***exo*-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
***exo*-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
***endo*-16b**	148.2	141.3	66.6	38.7	40.3	118.0	≃0	9.8	≃0	2.4	42.7	9.8
***exo*-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
***exo*-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
***endo*-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	—
***exo-exo*-28a**	147.0	149.7	69.9	58.1	55.4	—	57.4	9.8	29.3	6.1	40.3	—
***exo-exo*-28b**	146.7	148.7	69.9	58.2	55.3	—	58.6	9.8	30.5	6.1	40.3	—
***endo-exo*-28b**	145.1	145.4	68.2	58.7	59.2	—	52.5	9.8	29.3	6.1	40.3	—
***exo*-30a**	139.0	155.7	66.0	62.3	57.4	—	58.6	9.8	29.3	6.1	40.3	—
***exo*-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**; δ=42.42, ***exo*-6a**; δ=42.40) showed large C-P coupling constants (***endo*-6a**; J_{CP}=42.7 Hz, ***exo*-6a**; J_{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 δ=2.51 (J_{HH}=3.5, 14.0 Hz, J_{HP}=7.5 Hz), 3.07 (J_{HH}=9.5, 14.0 Hz, J_{HP}=14.0 Hz) and 3.64 (J_{HH}=3.5, 9.5 Hz, J_{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 δ=3.08—3.32 and of H-6 (*gem*-AB) protons at δ=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 H_a~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 identfied 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 **19**[1] and **20** or **21**[1] and **22**, respectively. Table 3 shows that the orientation of the 1,4-cycloadducts (**20**, **22**) agrees with that of the



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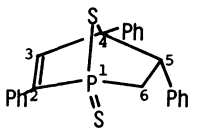
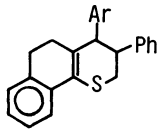


endo-20



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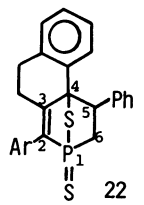
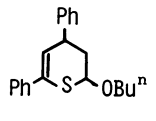


22

21,22 a, Ar=C_6H_5 b, Ar=p-$CH_3OC_6H_4$



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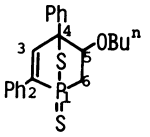

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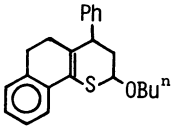

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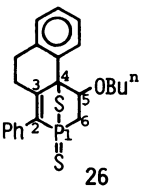

26

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 **23**[1] 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 $^2J_{C(5)P}$(2.4 Hz) as compared with

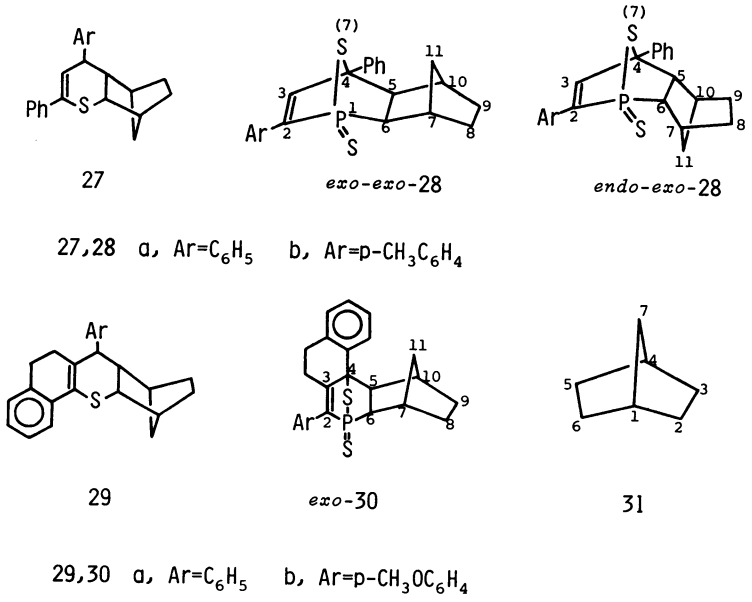

Fig. 1. The configurations of cycloadducts with norbornene. In 2-substituted norbornane, the *exo*-2 group usually shifts the resonance of the C-7 carbon upfield by 1.3—4.4 ppm from the one in norbornane **31** while the *endo*-2 group usually shifts the resonamce of C-6 carbon upfield by 4.9—9.7 ppm 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**[1] and **26**. The configurations of **24** and **26** could not be determined.

The reaction of **9** with norbornene gave **27**[1] 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 δ=34.8 shifted upfield by 4.1 ppm from that of **31**. The other isomer had the resonance at δ=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 carbons[11] 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 ^{13}C 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-thiaphosphole 2-sulfides. The reaction with some nucleophiles are now under investigation.

Table 5. ^{13}C NMR Chemical shifts of norbornane **31** and cycloadducts **28b** (J_{CP}/Hz)

Carbons	**31**	***exo-exo*-28b**		***endo-exo*-28b**	
	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	

Experimental

All the melting points are uncorrected. IR spectra were measured on a Hitachi Model 260-10 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer in $CDCl_3$ solution using Me_4Si as internal standard (^1H; at 100 MHz, ^{13}C; at 25 MHz). ^{13}C NMR spectral data are shown in Tables 2, 4, and 5. ^{31}P NMR spectra were recorded at 40 MHz on a JEOL JNM-FX 100 spectrometer using 85% H_3PO_4 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), P_4S_{10} powder (12 g) and NEt_3 (24 cm^3) in dry carbon disulfide (320 cm^3) 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); ^{1}H NMR ($CDCl_3$) δ=1.22 (s, 9H), 1.27 (s, 9H), 4.76 (dd, 1H, J_{HH}=5.5 Hz, J_{HP}=19.5 Hz), 5.76 (d, 1H, J_{HP}=41.0 Hz), 6.26 (dd, 1H, J_{HH}=5.5 Hz, J_{HP}=5.5 Hz), and 7.00—7.30 (m, 10H); ^{31}P NMR ($CDCl_3$) δ=117.1 (dd, J_{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 $C_{26}H_{31}S_3P$: 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); ^{1}H 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_{HH}=5.5 Hz, J_{HP}=20.0 Hz), 5.76 (d, 1H, J_{HP}=42.0 Hz), 6.24 (dd, 1H, J_{HH}=5.5 Hz, J_{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 $C_{28}H_{35}S_3P$: 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); ^{1}H NMR ($CDCl_3$) δ= 1.22 (s, 9H), 1.27 (s, 9H), 4.67 (dd, 1H, J_{HH}=5.5 Hz, J_{HP}=20.0 Hz), 5.66 (d, 1H, J_{HP}=42.0 Hz), 6.17 (dd, 1H, J_{HH}=5.5 Hz, J_{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 $C_{26}H_{29}Cl_2S_3P$: 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); ^{1}H NMR ($CDCl_3$) δ=5.06 (dd, 1H, J_{HH}=5.0 Hz, J_{HP}=18.0 Hz), 6.35 (d, 1H, J_{HP}=42.0 Hz), 6.82 (dd, 1H, J_{HH}=5.0 Hz, J_{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 $C_{30}H_{23}S_3P$: 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); ^{1}H NMR ($CDCl_3$) δ=3.70 (s, 3H), 3.74 (s, 3H), 4.96 (dd, 1H, J_{HH}=5.0 Hz, J_{HP}=18.0 Hz), 6.30 (d, 1H, J_{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 $C_{32}H_{27}O_2S_3P$: 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); ^{1}H NMR ($CDCl_3$) δ= 2.26 (s, 3H), 2.30 (s, 3H), 5.00 (d, 1H, J_{HH}=6.0 Hz, J_{HP}=20.0 Hz), 6.33 (d, 1H, J_{HP}=42.0 Hz), 6.82 (dd, 1H, J_{HH}=6.0 Hz, J_{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 $C_{32}H_{27}S_3P$: 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); ^{1}H NMR ($CDCl_3$) δ= 4.96 (dd, 1H, J_{HH}=6.0 Hz, J_{HP}=20.0 Hz), 6.23 (d, 1H, J_{HP}=42.0 Hz), 6.74 (dd, 1H, J_{HH}=6.0 Hz, J_{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 $C_{30}H_{21}Cl_2S_3P$: 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); ^{1}H NMR ($CDCl_3$) δ= 3.77 (s, 3H), 3.78 (s, 3H), 5.02 (dd, 1H, J_{HH}=5.0 Hz, J_{HP}=18.0 Hz), 6.22 (d, 1H, J_{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 $C_{32}H_{27}O_2S_3P$: 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); ^{1}H NMR ($CDCl_3$) δ= 2.33 (s, 6H), 5.04 (dd, 1H, J_{HH}=5.0 Hz, J_{HP}=18.0 Hz), 6.29 (d, 1H, J_{HP}=42.0 Hz), 6.78 (dd, 1H, J_{HH}=5.0 Hz, J_{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 $C_{32}H_{27}S_3P$: 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); ^{1}H NMR ($CDCl_3$) δ=5.04 (dd, 1H, J_{HH}=5.0 Hz, J_{HP}=18.0 Hz), 6.32 (d, 1H, J_{HP}=42.0 Hz), 6.82 (dd, 1H, J_{HH}=5.0 Hz, J_{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 $C_{30}H_{21}Cl_2S_3$ 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); ^{1}H NMR ($CDCl_3$) δ=1.24—2.98 (m, 8H), 4.28 (d, 1H, J_{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 $C_{34}H_{27}S_3P$: 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); ^{1}H NMR ($CDCl_3$) δ=1.54—2.74 (m, 8H), 3.75 (s, 6H), 4.89 (d, 1H, J_{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 $C_{36}H_{31}O_2S_3P$: 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); ^{1}H NMR ($CDCl_3$) δ=1.57—1.84 (m, 8H),4.30 (d, 1H, J_{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 $C_{34}H_{27}Cl_2S_3P$: 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_{HH}=4.8 Hz), 5.66 (d, 1H, J_{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 $C_{16}H_{19}NS$: 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_{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 $C_{17}H_{21}NS$: 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_{HH}=4.6 Hz), 5.60 (d, 1H, J_{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 $C_{16}H_{18}NClS$: 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_{HH}=3.5, 14.0 Hz, J_{HP}=7.5 Hz), 3.07 (ddd, 1H, J_{HH}=9.5, 14.0 Hz, J_{HP}= 14.0 Hz), 3.64 (ddd, 1H, J_{HH}=3.5, 9.5 Hz, J_{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 $C_{16}H_{18}NS_2P$: 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 $C_{16}H_{18}NS_2P$: 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_{HH}=3.0, 13.0 Hz, J_{HP}=7.5 Hz), 3.04 (ddd, 1H, J_{HH}=10.0, 13.0 Hz, J_{HP}=13.0 Hz), 3.60 (ddd, 1H, J_{HH}=3.0, 10.0 Hz, J_{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 $C_{17}H_{20}NS_2P$: 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_{HH}=3.0, 14.0 Hz, J_{HP}=7.5 Hz), 3.08 (ddd, 1H, J_{HH}=10.0, 14.0 Hz, J_{HP}=14.0 Hz), 3.64 (ddd, 1H, J_{HH}=3.0, 10.0 Hz, J_{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 $C_{16}H_{17}NClS_2P$: 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 $C_{18}H_{14}NS_2P$: 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 $C_{19}H_{16}NS_2P$: 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_{HH}=4.0, 13.0 Hz, J_{HP}=8.0 Hz), 3.12 (ddd, 1H, J_{HH}=9.0, 13.0 Hz, J_{HP}=13.0 Hz), 4.06 (ddd, 1H, J_{HH}=4.0, 10.0 Hz, J_{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 $C_{19}H_{16}NS_2P$: 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 $C_{20}H_{16}NS_2P$: 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 $C_{21}H_{18}ONS_2P$: 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 $C_{25}H_{21}S_2P$: 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 $C_{26}H_{23}OS_2P$: 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 $C_{23}H_{25}OS_2P$: C, 66.96; H, 6.11%.

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

with benzene–hexane (3:2); ^{1}H NMR ($CDCl_3$) δ=0.94—3.10 (m, 10H), 7.03—7.67 (m, 11H); ^{31}P NMR ($CDCl_3$) δ=—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 $C_{22}H_{21}S_2P$: 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); ^{1}H NMR ($CDCl_3$) δ=0.92—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 $C_{23}H_{23}S_2P$: C, 70.02; H, 5.88%.

endo-exo-28b: ^{1}H NMR ($CDCl_3$) δ=0.68—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 $C_{23}H_{23}S_2P$: 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; ^{1}H NMR ($CDCl_3$) δ=0.82—3.32 (m, 14H) and 7.16—7.58 (m, 9H); ^{31}P NMR ($CDCl_3$) δ=—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 $C_{24}H_{23}S_2P$: 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); ^{1}H NMR ($CDCl_3$) δ=1.78—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 $C_{25}H_{25}OS_2P$: C, 68.78; H, 5.77%.

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