Chemistry of 1,2-Thiaphosphole 2-Sulfides. III.[1] Cycloaddition Reactions with Some Acetylenic Dienophiles and Generation of Phosphorin 1-Sulfides

Hideyuki TANAKA and Shinichi MOTOKI*
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
(Received December 20, 1985)

Synopsis. 1,2-Thiaphosphole 2-sulfides reacted with dimethyl acetylenedicarboxylate or phenylacetylene to afford 1-phosphabarrelene 1-sulfides (1-phosphabicyclo[2.2.2]octa-2,5,7-triene 1-sulfides) via phosphorin 1-sulfides.

Previously, we reported that 1,2-thiaphosphole 2-sulfides **2** generated by the thermolysis of 2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-sulfides **1** underwent cycloaddition reactions with various olefins to afford the stable 1:1 adducts **4**.[1]

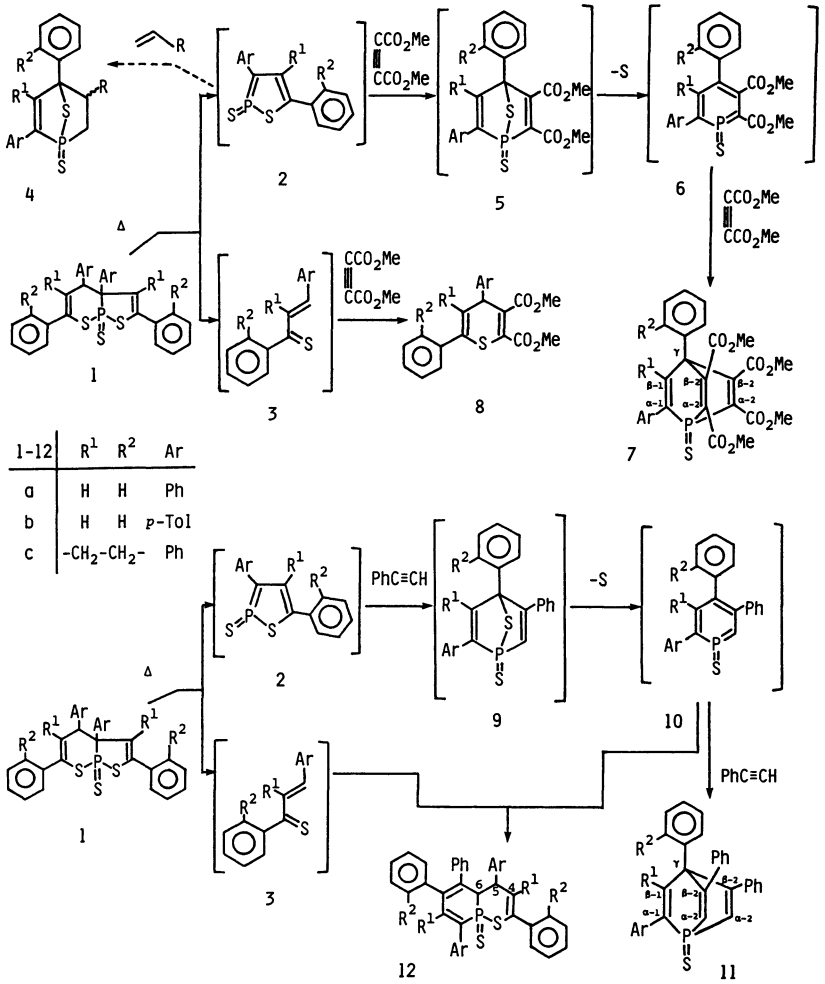
Meanwhile, numerous studies have been devoted to the chemistry of phosphorin derivatives,[2] however, phosphorin 1-sulfides are little known because of their instability. Only one example was reported by Mathey et al. very recently. They treated 4,5-dimethyl-2-phenylphosphorin with an excess of sulfur in the presence of 2,3-dimethylbutadiene or dimethyl acetylenedicarboxylate (DMAD), and transiently formed phosphorin 1-sulfide was trapped as cycloadducts.[3,4]

In view of the recent investigation, we attempted the cycloaddition reactions of **1** (**2**) with acetylenic dienophiles and also expected the formation of the phosphorin 1-sulfides **6** from the adducts **5** by elimination of the bridged sulfur atom.

Results and Discussion

When the reaction of **1a—c** with DMAD was carried out in refluxing benzene, 1-phosphabarrelene 1-sulfides **7a—c** were obtained along with the other products **8a—c** (Table 1). This interesting results are explained as follows. Initially formed cycloadducts **5** are unstable under the reaction conditions and produce intermediary phosphorin 1-sulfides **6** by the elimination of the bridged sulfur atom. Subsequently, **6** react with DMAD to afford **7a—c** as reported by Mathey et al.[3] (Scheme 1).

The elementary analyses and the mass spectra indi-



Scheme 1.

Table 1. Reactions of **1** with Acetylenic Dienophiles

Material	Dienophile	Reaction time/h	Product					
				Mp θ_m/°C[a]	Yield/%[b]		Mp θ_m/°C[a]	Yield/%[b]
1a	DMAD	1	**7a**	237—239	72	**8a**	c)	82
1b	DMAD	1	**7b**	202—204	59	**8b**	c)	70
1c	DMAD	1.5	**7c**	199—201	74	**8c**	103—105	61
1a	PhC≡CH	2	**11a**	218—220	38	**12a**	203—205	36
1b	PhC≡CH	2	**11b**	224—226	28	**12b**	180—182	54
1c	PhC≡CH	2	**11c**	228—230	86	**12c**	258—260	13

a) All the products decomposed at the melting points. b) The yield of products was based on **1**. c) Oil.

Table 2. ^{13}C NMR Spectral Data of **7** and **11** (δ(J_{CP}/Hz))

Compd	C(α-1)	C(α-2)	C(β-1)	C(β-2)	C(γ)	$J_{C(\alpha\text{-}1)P}$	$J_{C(\alpha\text{-}2)P}$	$J_{C(\beta\text{-}2)P}$	$J_{C(\gamma)P}$
7a	147.3	139.9	145.7	161.1	59.9	64.7	57.4	2.4	29.3
7b	147.1	139.9	144.8	161.0	59.5	64.7	57.4	2.4	29.3
7c	138.5	139.7	160.2	160.4	58.9	67.1	57.4	9.8	30.5
11a	148.9	134.1	145.0	170.9	66.3	61.0	67.1	3.7	30.5
11b	148.8	134.1	144.8	170.9	66.3	61.0	67.1	3.7	30.5
11c	140.7	134.4	157.9	170.5	65.6	63.5	65.9	3.7	31.7

a) **7** and **11**: $J_{C(\beta\text{-}1)P} \simeq 0$

Table 3. ^{1}H and ^{13}C NMR Spectral Data of **12** (δ(J/Hz))

Compd	H(4)	H(5)	H(6)	$J_{H(4)H(5)}$	$J_{H(5)H(6)}$	$J_{H(4)P}$	$J_{H(5)P}$	$J_{H(6)P}$	C(5)	C(6)	$J_{C(5)P}$	$J_{C(6)P}$
12a	6.41	4.28	3.75	4.5	10.0	2.5	14.5	14.0	50.7	53.6	2.5	48.8
12b	6.41	4.23	3.73	4.5	10.0	2.5	15.5	14.0	49.8	54.1	2.4	47.6
12c	—	4.16	3.78	—	8.0	—	22.0	14.5	47.0	52.0	4.9	48.8

cated that **7a—c** were 1:1 adducts of **6** with DMAD and the structures were confirmed by the ^{1}H and ^{13}C NMR spectral data. In the ^{1}H NMR spectrum of **7a**, the methoxycarbonyl groups resonated at δ=3.43 (s, 6H) and 3.89 (s, 6H). The doublet at δ=8.26 (1H, J_{HP}=30.0 Hz) was assigned to the olefinic H(β-1) proton. The ^{13}C NMR spectrum of **7a** showed signals of the C(α-1) and C(α-2) olefinic carbons at δ=147.3 (J_{CP}=64.7 Hz) and 139.9 (2×C, J_{CP}=57.4 Hz), respectively. The large C–P coupling constants suggest that these carbons are directly bonded to the phosphorus atom. The signals of the C(β-1) and C(β-2) carbons showed small C–P coupling constants ($J_{C(\beta\text{-}1)P} \simeq 0$ Hz, $J_{C(\beta\text{-}2)P}$=2.4 Hz). The signal of C(γ) carbon appeared at δ=59.9 and showed unusual large coupling constant (J_{CP}=29.3 Hz). These spectral data are closely similar to those of the 1-phosphabarrelene 1-sulfide reported previously.[3,5] The structures of **7b, c** were determined similarly (Table 2).

On the other hand, the mass spectra indicated that **8a—c** were 1:1 adducts of **3** with DMAD and their ^{1}H NMR spectral data suggested that they would be 4*H*-thiin derivatives. However, rearranged 2*H*-thiin structures can not be excluded strictly.[6]

The reaction of **1** with an excess of phenylacetylene gave the corresponding phosphabarrelene sulfides **11a—c** regioselectively. The orientation of phenyl group was determined by the ^{1}H NMR spectrum of **11b**. In this spectrum, signals of one proton (δ=8.45, J_{HP}=30.0 Hz), three protons (CH_3), two sets of two protons (*p*-Tol-H), and seventeen protons were observed. The first signal was assigned to the H(β-1) and the remaining two protons attached to the barrelene skeleton should be linked to the C(α-2) carbon atom. Signals of the H(α-2) couldn't be distinguished from those of other aromatic protons. Similarly, the structures of **11a** and **11c** were determined.

Cycloadducts of the thiones **3** with phenylacetylene were not obtained in this case, however, the analytical and the mass spectral data of the other products **12a—c** indicated that the compounds were 1:1 adducts of **10** and the thiones **3**. The ^{13}C NMR spectrum of **12a** showed a signal of the C(6) carbon at δ=53.6 with a large C–P coupling constant (J_{CP}=48.8 Hz), suggesting a direct bonding of the C(6)–P (Table 3).[1] In the ^{1}H NMR spectra, H(4), H(5), and H(6) protons resonated at δ=6.41 (dd, J_{HH}=4.5 Hz, J_{HP}=2.5 Hz), 4.28 (ddd, J_{HH}=4.5, 10.0 Hz, J_{HP}=14.5 Hz), and 3.75 (dd, J_{HH}=10.0 Hz, J_{HP}=14.0 Hz), respectively. These spectral data are in accord with the proposed structures. The structures of **12b, c** were determined similarly (Table 3). In these cycloaddition reactions, phosphorin sulfides **10** and α,β-unsaturated thiones **3** act as 2π- and 4π-electron components, respectively. Cycloadducts of this type did not form in the reaction of **1** and DMAD. From these results, it has been found that the sulfides **2** react with phenylacetylene more rapidly than the thiones **3**, and **3** are trapped by the generating **10** rather than phenylacetylene.

The mass spectra of **12** show fragments of thiones **3** and the phosphorin 1-sulfides **10**. So the preparation of the corresponding phosphorins[4] by the thermolysis of **12** in the presence of desulfurizing agent is now under investigation.

Experimental

All melting points are uncorrected. IR spectra were measured on a Hitachi Model 260-10 spectrometer. ^{1}H and

^{13}C NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer in $CDCl_3$ solution using Me_4Si as an internal standard (^1H; at 100 MHz, ^{13}C; 25.05 MHz). ^{31}P NMR spectra were recorded at 36.21 MHz on a JEOL FX-90A 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 (RMU-7M), operating at an ionizing potential of 70 eV. Elemental analyses were performed using a Yanaco Model MT-3 CHN corder. 2,9-Dithia-1-phosphabicyclo-[4.3.0]nona-3,7-diene 1-sulfides **1** were prepared according to the previously described method.[1)]

General Procedure for the Reaction of the Phosphabicyclo Compounds 1 with Acetylenic Dienophiles: A solution of **1** (2 mmol) and DMAD (7 mmol) or phenylacetylene (18 mmol) in 5 cm^3 of dry benzene was refluxed under a nitrogen atmosphere until **1** was consumed, as indicated by TLC. After evaporation of the solvent the residue was chromatographed on silica gel (Wakogel C-200) with benzene-ethyl acetate (10:1) or benzene-hexane (1:1) as an eluent to afford the products and were recrystallized from ethanol.

4,7-Diphenyl-2,3,5,6-tetrakis(methoxycarbonyl)-1-phosphabicyclo[2.2.2]octa-2,5,7-triene 1-Sulfide (7a): IR (KBr) 2970, 1740 (C=O), 1300, and 1260 cm^{-1}; ^1H NMR δ=3.43 (s, 6H, OCH_3), 3.89 (s, 6H, OCH_3), 7.22—7.62 (m, 8H, Ar-H), and 8.26 [d, 1H, J_{HP}=30.0 Hz, H(β-1)]; ^{31}P NMR δ=9.33 (d, J_{PH}=30.2 Hz); MS *m/z* 538 (M^+, 52), 506 (M^+—S, 35), 474 (15), 447 (506-$COOCH_3$, 14), 418 (11), 302 (M^+—4$COOCH_3$, 37), 271 (34), and 93 (100). Found: C,60.38; H, 4.27; S, 6.09%. Calcd for $C_{27}H_{23}O_8PS$: C, 60.22; H, 4.30; S, 5.95%.

4-Phenyl-2,3,5,6-tetrakis(methoxycarbonyl)-7-*p*-tolyl-1-phosphabicyclo[2.2.2]octa-2,5,7-triene 1-Sulfide (7b): IR (KBr) 2960, 1740 (C=O), 1280, and 1240 cm^{-1}; ^1H NMR δ=2.39 (s, 3H, CH_3), 3.42 (s, 6H, OCH_3), 3.88 (s, 6H, OCH_3), 7.08—7.56 (m, 9H, Ar-H), and 8.22 [d, 1H, J_{HP}=30.0 Hz, H(β-1)]; MS *m/z* 552 (M^+, 33), 520 (M^+—S, 21), 488 (7), 461 (520-$COOCH_3$, 9), 432 (10), 316 (M^+—4$COOCH_3$, 39), 285 (19), and 93 (100). Found: C, 60.80; H, 4.45%. Calcd for $C_{28}H_{25}O_8PS$: C, 60.87; H, 4.56%.

2,3-Benzo-7-phenyl-9,10,11,12-tetrakis(methoxycarbonyl)-8-phosphatricyclo[6.2.2.0^{1,6}]dodeca-6,10,11-triene 8-Sulfide (7c): IR (KBr) 2970, 1730 (C=O), 1285, and 1250 cm^{-1}; ^1H NMR δ=2.86 (s, 4H, $-CH_2CH_2-$), 3.44 (s, 6H, OCH_3), 3.88 (s, 6H, OCH_3), and 6.96—7.60 (m, 9H, Ar-H); MS *m/z* 564 (M^+, 70), 532 (M^+—S, 7), 500 (17), 473 (532-$COOCH_3$, 21), 444 (1), 328 (M^+—4$COOCH_3$, 48), 297 (21), 239 (54), and 93 (100). Found: C, 61.41; H, 4.56%. Calcd for $C_{29}H_{25}O_8PS$: C, 61.70; H, 4.46%.

2,3-Bis(methoxycarbonyl)-4,6-diphenyl-4*H*-thiin (8a): IR (neat) 2975, 1740 (C=O), 1260, and 1230 cm^{-1}; ^1H NMR δ= 3.58 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 4.87 (d, 1H, J_{HH}= 6.0 Hz), 6.08 (d, 1H, J_{HH}=6.0 Hz), and 7.00—7.60 (m, 10H, Ar-H); MS *m/z* 366 (M^+, 29), 334 (M^+—S, 13), 307 (M^+—$COOCH_3$, 100), and 289 (M^+—Ph, 53).

2,3-Bis(methoxycarbonyl)-6-phenyl-4-*p*-tolyl-4*H*-thiin (8b): IR (neat) 2950, 1720 (C=O), 1250, and 1220 cm^{-1}; ^1H NMR δ=2.26 (s, 3H, CH_3), 3.62 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 4.83 (d, 1H, J_{HH}=6.0 Hz), 6.08 (d, 1H, J_{HH}=6.0 Hz), and 6.83—7.60 (m, 9H, Ar-H); MS *m/z* 380 (M^+, 17), 348 (M^+—S, 19), 321 (M^+—$COOCH_3$, 100), and 289 (M^+-*p*-Tol, 35).

2,3-Bis(methoxycarbonyl)-1-phenyl-9,10-dihydro-1*H*-4-thiaphenanthrene (8c): IR (KBr) 2950, 1740 (C=O), 1260, and 1240 cm^{-1}; ^1H NMR δ=2.18—2.92 (m, 4H, $-CH_2CH_2-$), 3.68 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.77 (s, 1H), and 7.12—7.48 (m, 9H, Ar-H); MS *m/z* 392 (M^+, 30), 360 (M^+—S, 13), 333 (M^+—$COOCH_3$, 82), and 315 (M^+—Ph, 100).

3,4,5,7-Tetraphenyl-1-phosphabicyclo[2.2.2]octa-2,5,7-triene 1-Sulfide (11a): ^1H NMR δ=6.48—7.78 [m, 22H, H(α-2) and Ar-H] and 8.49 [d, 1H, J_{HP}=30.0 Hz, H(β-1)]; MS *m/z* 458 (M^+, 1), 395 (M^+—PS, 5), 356 (**10a**, 75), 324 (**10a**-S, 70), 254 (**10a**-PhC≡CH, 100), and 102 (PhC≡CH, 72). Found: C, 81.08; H, 5.08%. Calcd for $C_{31}H_{23}PS$: C, 81.20; H, 5.06%.

7-*p*-Tolyl-3,4,5-triphenyl-1-phosphabicyclo[2.2.2]octa-2,5,7-triene 1-Sulfide (11b): ^1H NMR δ=2.42 (s, 3H, CH_3), 6.56—7.40 [m, 17H, H(α-2) and Ar-H], 7.28 (d, 2H, J_{HH}=8.0 Hz, *p*-Tol-H), 7.62 (dd, 2H, J_{HH}=8.0 Hz, J_{HP}=1.5 Hz, *p*-Tol-H), and 8.45 [d, 1H, J_{HP}=30.0 Hz, H(β-1)]; MS *m/z* 472 (M^+, 10), 438 (M^+—H_2S, 4), 409 (M^+—PS, 12), 370 (**10b**, 100), 338 (**10b**-S, 98), 268 (**10b**-PhC≡CH, 83), and 102 (PhC≡CH, 98). Found: C, 81.20; H, 5.23%. Calcd for $C_{32}H_{25}PS$: C, 81.33; H, 5.33%.

2,3-Benzo-7,10,11-triphenyl-8-phosphatricyclo[6.2.2.0^{1,6}]-dodeca-6,10,11-triene 8-Sulfide (11c): ^1H NMR δ=2.98 (s, 4H, $-CH_2CH_2-$), 5.88—6.40 (m, 2H, Ar-H), and 6.60—7.60 [m, 19H, H(α-2) and Ar-H]; ^{31}P NMR δ=8.43 (t, J_{PH}= 20.3 Hz); MS *m/z* 484 (M^+, 11), 450 (M^+—H_2S, 9), 421 (M^+—PS, 21), 382 (**10c**, 25), 350 (**10c**-S, 27), 280 (**10c**-PhC≡CH, 50), and 102 (PhC≡CH, 100). Found: C, 81.83; H, 5.18; S, 6.26%. Calcd for $C_{33}H_{25}PS$: C, 81.79; H, 5.20; S, 6.62%.

3,5,7,8,10-Pentaphenyl-1-phospha-2-thiabicyclo[4.4.0]deca-3,7,9-triene 1-Sulfide (12a): ^1H NMR δ=3.75 [dd, 1H, J_{HH}= 10.0 Hz, J_{HP}=14.0 Hz, H(6)], 4.28 [ddd, 1H, J_{HH}=4.5, 10.0 Hz, J_{HP}=14.5 Hz, H(5)], 6.32—6.60 (m, 2H), 6.41 [dd, 1H, J_{HH}= 4.5 Hz, J_{HP}=2.5 Hz, H(4)], 6.72—7.52 (m, 22H), and 7.72—7.94 (m, 2H); ^{31}P NMR δ=49.39 (dddd, J_{PH}=2.5, 14.0, 14.5, 36.0 Hz); MS *m/z* 580 (M^+, 1), 356 (**10a**, 31), 324 (**10a**-S, 76), 254 (**10a**-PhC≡CH, 43), and 223 (**3a**-H, 100). Found: C, 78.52; H, 5.04; S, 11.03%. Calcd for $C_{38}H_{29}PS_2$: C, 78.59; H, 5.03; S, 11.04%.

5,10-Di-*p*-tolyl-3,7,8-triphenyl-1-phospha-2-thiabicyclo[4.4.0]-deca-3,7,9-triene 1-Sulfide (12b): ^1H NMR δ=2.26 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 3.73 [dd, 1H, J_{HH}=10.0 Hz, J_{HP}=14.0 Hz, H(6)], 4.23 [ddd, 1H, J_{HH}=4.5, 10.0 Hz, J_{HP}=15.5 Hz, H(5)], 6.32—7.44 [m, 22H, H(9) and Ar-H], 6.41 [dd, 1H, J_{HH}=4.5 Hz, J_{HP}=2.5 Hz, H(4)], and 7.75 (dd, 2H, J_{HH}= 8.0 Hz, J_{HP}=2.5 Hz, *p*-Tol-H); MS *m/z* 608 (M^+, 1), 370 (**10b**, 29), 338 (**10b**-S, 100), 268 (**10b**-PhC≡CH, 34), and 237 (**3b**-H, 56). Found: C, 78.84; H, 5.51%. Calcd for $C_{40}H_{33}PS_2$: C, 78.91; H, 5.46%.

7,15,16-Triphenyl-5,6,13,14,15,15a-hexahydro-7a-phospha-8-thiadibenzo[*a*,*j*]naphthacene 7a-Sulfide (12c): ^1H NMR δ=2.04—2.20 (m, 4H, $-CH_2-$), 2.48—2.92 (m, 4H, $-CH_2-$), 3.78 [dd, 1H, J_{HH}=8.0 Hz, J_{HP}=14.5 Hz, H(6)], 4.16 [dd, 1H, J_{HH}=8.0 Hz, J_{HP}=22.0 Hz, H(5)], and 6.50—7.70 (m, 23H, Ar-H); MS *m/z* 632 (M^+, 1), 382 (**10c**, 98), 350 (**10c**-S, 100), 280 (**10c**-PhC≡CH, 91), and 249 (**3c**-H, 51). Found: C, 79.68; H, 5.18%. Calcd for $C_{42}H_{33}PS_2$: C, 79.72; H, 5.26%.

The authors wish to thank JEOL LTD. for measuring the ^{31}P NMR spectra and also Mr. Yasuhiro Terauchi for technical assistance.

References

1) H. Yamaguchi, S. Kametani, T. Karakasa, T. Saito, and S. Motoki, *Tetrahedron Lett.*, **23**, 1263 (1982); T. Uchida, K. Kozawa, T. Saito, and S. Motoki, *Bull. Chem. Soc. Jpn.*, **57**, 1985; 1990 (1984); H. Tanaka, S. Kametani, T. Saito, and S. Motoki, *ibid.*, **58**, 667 (1985); H. Tanaka, T. Saito, and S. Motoki, *ibid.*, **59**, 59 (1986).

2) G. Märkl, *Angew. Chem., Int. Ed. Engl.*, **5**, 846 (1966) and later papers.

3) J.-M. Alcaraz and F. Mathey, *J. Chem. Soc., Chem. Commun.*, **1984**, 508.

4) J.-M. Alcaraz and F. Mathey, *Tetrahedron Lett.*, **25**, 4659 (1984).

5) G. Märkl and F. Lieb, *Angew. Chem., Int. Ed. Engl.*, **7**, 733 (1968).

6) E. T. Østensen, A. A.-A. Abdallah, S. H. Skaare, and M. M. Mishrikey, *Acta Chem. Scand., Ser. B*, **31**, 496 (1977).