Generation and Reactions of Phosphorin 1-Sulfides

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(Received September 26, 1986)

Synopsis. Phosphorin 1-sulfides generated by the thermolysis of 1-phospha-2-thiabicyclo[4.4.0]deca-3,7,9-triene 1-sulfides reacted with triphenylphosphine, dienophiles, or nucleophiles to give the corresponding phosphorins, 1-phosphabicyclo[2.2.0]octa-2,5-diene 1-sulfide, or 1,2-dihydrophosphorin 1-sulfide derivatives, respectively.

Previously, we reported that 2,9-dithia-1-phosphabicyclo-[4.3.0]nona-3,7-diene 1-sulfides (**2**)[1] derived from α,β-unsaturated ketones **1** reacted with phenylacetylene to afford 1-phospha-2-thiabicyclo[4.4.0]deca-3,7,9-triene 1-sulfides (**3**).[2] From the mass spectral fragments, it is expected that thermolysis of **3** generates phosphorin 1-sulfides (**4**) along with α,β-unsaturated thiones (**5**)[3] in the manner of the retro-Diels-Alder reaction.

Recently, Mathey et al. reported that 4,5-dimethyl-2-phenylphosphorin 1-sulfide formed by the treatment of the corresponding phosphorin with sulfur in boiling xylene was trapped by 2,3-dimethylbutadiene or dimethyl acetylenedicarboxylate.[4] However, no other papers on the synthesis or reactions of phosphorin 1-sulfides have been presented.

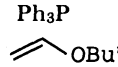
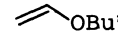
In this paper, we wish to describe some reactions of phosphorin 1-sulfides **4** generated by the thermolysis of the precursors **3**.

Results and Discussion

Treatment of **3** with triphenylphosphine in refluxing toluene produced phosphorins **6** and triphenylphosphine sulfide (Table 1). Another component, thiones **5** were decomposed by triphenylphosphine. The phosphorins **6** were easily identified by comparison of the ^{1}H NMR spectral data with those of **6a** in the literature.[5] The ^{13}C NMR spectra of **6** were assigned as shown in Table 2.[6]

Phosphorins were synthesized by Märkl et al. by the

Table 1. Reaction of **3** with Various Reagents

Material	Reagent	Reaction time/h	Product from **4**			Product from **5**	
				Mp θ_m/°C	Yield/%[a]	Yield/%[a]	
3a	Ph_3P	3	**6a**	170—172[b]	60	—	
3b	Ph_3P	3	**6b**	173—175	59	—	
3a		5	**7a**	134—136	13	**8a**	56
3b		5	**7b**	113—116	31	**8b**	77
3a		2	**9a** **10a**	187—189 186—188	47 48	**11a**	94
3b		2	**9b** **10b**	128—130 171—173	45 46	**11b**	95
3a	$PhCH_2OH$	1	**12a**[c]	113—115	96	**14a**	98
3b	$PhCH_2OH$	1	**12b**[c]	152—154	95	**14b**	95
3a	PhSH	2.5	**13a**[c]	210—212	48	**14a**	60
3b	PhSH	2.5	**13b**[c]	196—198	44	**14b**	56

a) The yield of the products was based on **3**. b) Lit,[5] 164—166°C. c) Yellow crystals.

Table 2. ^{13}C NMR Spectral Data of the Products [$\delta(J_{CP}$/Hz)]

Product	C(2)	C(3)	C(4)	C(5)	C(6)	$J_{C(2)P}$	$^2J_{C(3)P}$	$^3J_{C(4)P}$	$^2J_{C(5)P}$	$J_{C(6)P}$
6a	169.5	136.6	142.7	141.1	156.4	48.8	11.0	3.7	17.1	52.5
6b	169.4	136.3	142.7	141.1	156.4	48.8	12.2	3.7	17.1	53.7
7a	141.4	147.0	59.6	164.7	127.0	61.0	2.4	31.7	2.4	69.6
7b	141.5	147.0	59.8	165.0	127.0	61.0	2.4	31.7	2.5	69.6
9a	140.5	151.7	57.4	164.2	128.3	61.0	0	36.6	2.4	67.1
9b	140.3	150.9	57.3	164.2	128.3	61.0	0	36.6	2.4	67.1
10a	139.4	148.4	57.6	166.9	128.0	58.6	0	36.6	3.7	69.6
10b	139.2	147.5	57.5	166.9	128.1	58.6	0	35.4	2.4	67.1
12a	135.5	141.1	a)	a)	42.2	61.0	6.1	a)	a)	73.2
12b	134.3	140.5	a)	a)	42.1	61.0	6.1	a)	a)	72.0
13a	139.6	141.4	a)	a)	44.2	56.2	3.7	a)	a)	53.7
13b	139.6	141.1	a)	a)	44.0	56.2	3.7	a)	a)	52.5

a) These signals were not confirmed.

reaction of the corresponding pyrylium salts with $P(CH_2OH)_3$ or $P(SiMe_3)_3$.[7] By our method, **6** can be readily obtained from α,β-unsaturated ketones **1** by three step reactions.

Phosphorin sulfides **4** reacted as heterodienes at their 1, 4 positions with some dienophiles to give the corresponding cycloadducts.[1,4] When the reaction of **3** with butyl vinyl ether was carried out in refluxing toluene, the cycloadducts **7** were obtained along with **8** (Table 1). The cycloadducts **8** were easily identified by comparison with the authentic compounds reported previously.[3] In the ^{13}C NMR spectra of the cycloadducts **7**, the signals for the methine carbons [δ=77.6 (J_{CP}=8.5 Hz)] and the methylene carbons [δ=37.5 (J_{CP}=47.6 Hz)] indicated that butoxyl groups were linked to C(β) carbons,[1] but the cofiguration of the C(β) carbons could not be determined. The signals for the C(2)-(6) carbons in **7** were assigned as shown in Table 2.[2,4]

The reaction of **3** with norbornene gave the cycloadducts **9**, **10**, and **11** in high yields (Table 1). The thione(**5**)-norbornene cycloadducts (**11**) were identified by comparing the spectral data with those for the authentic compounds.[3] The elemental analyses and mass spectra indicated that both **9** and **10** were 1 : 1 adducts of **4** with norbornene. In the ^{13}C NMR spectra of these adducts, seven signals due to the norbornane ring system were observed and the C(α), C(β) methine carbons showed C-P coupling [C(α), δ=52.2—53.2 (J_{CP}=46.4 Hz); C(β), δ=51.1—53.7 ($^2J_{CP}$=8.5—9.8 Hz)]. The signals for the C(2)-C(6) carbons in 1,4-dihydrophosphorin 1-sulfide ring system were assigned by comparison with those for phosphabarrelene derivatives[2,4] (Table 2). The chemical shifts for the C(2), C(3), and C(5) carbons gave the information on the configuration of **9** and **10**. The cycloadducts **10** showed the resonance for C(2) and C(3) carbons shifted upfield by 1.1 and 3.4 ppm, respectively, compared with those for **9**, whereas **9** showed that the resonance for C(5) carbon shifted upfield by 2.7 ppm compared with that for **10**. On the basis of these shifts, the norbornyl skeleton is considered to be situated on the side of the C(5) and C(6) carbons in **9** and on the side of the C(2) and C(3) carbons in **10**.[1,8] The signals for the bridged methylene carbons (C*) in **9** and **10** shifted upfield by 4.8—4.6 ppm compared with that in unsubstituted norbornane and appeared at δ=33.9 and 34.1, respectively. This suggested that the configuration of these isomers would be *exo* with respect to the norbornyl ring.[1,8]

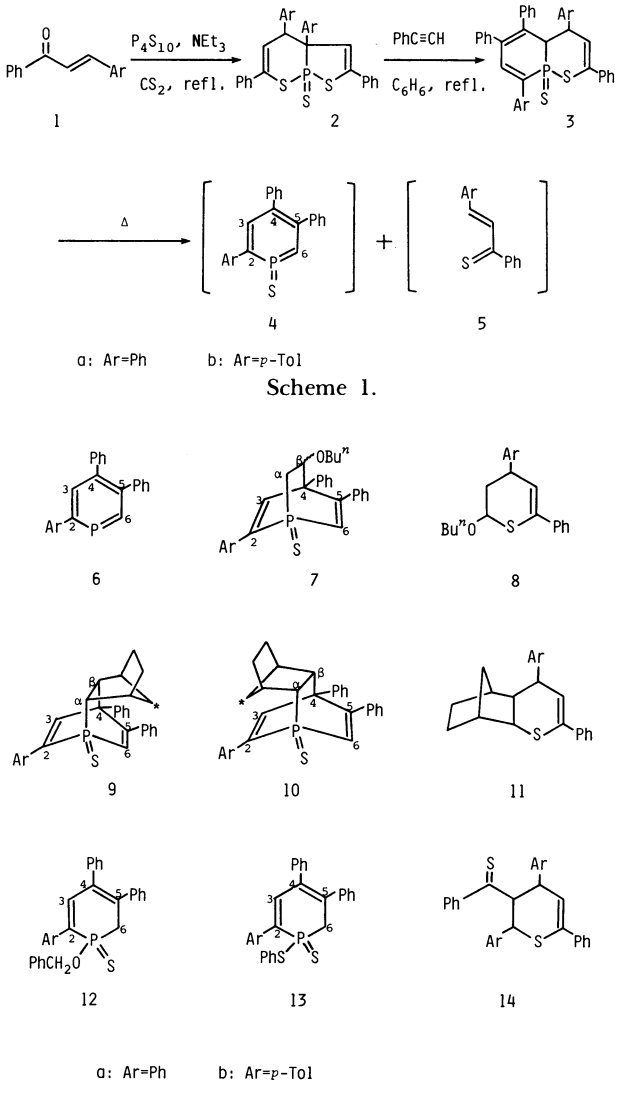
The reactions of **3** with styrene or acrylonitrile were unsuccessful.

Finally, we examined the reaction of **3** with nucleophiles.[9] Treatment of **3** with benzyl alcohol in boiling toluene gave **12** in high yields. The products showed strong IR absorptions due to the P-O bonding at about 1000 cm^{-1}. In the ^1H NMR spectra, the multiplets of two protons at δ=3.33—3.67 were assigned to the H(6) AB protons. The signals for the C(6) methylene carbon showed large C-P coupling constant (Table 2).

Similarly, the reaction of **3** with benzenethiol gave the expected adducts **13**. The structure of **13** was confirmed by comparison of the spectral data with those for **12**.

In these reactions, addition of the hydrogen of the nucleophiles Nu-H to the C(6) carbons took place preferentially. These adducts **12** and **13** seem to be more stable than their isomeric 1,2- or 1,4-dihydrophosphorin 1-sulfides due to the effective conjugation of the double bond in dihydrophosphorin ring with three aryl groups at the 2-, 4-, and 5-positions. In both cases thiones **5** did not react with the nucleophiles, and were recovered as their dimers **14**.[3]

Reaction of **3** with amines was complicated and no identified product was isolated.



Scheme 1.

Experimental

All melting points are uncorrected. IR spectra were recorded on a Hitachi Model 260-10 spectrometer. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ solution using Me_4Si as an internal standard [spectrometer: ^1H; JEOL JNM-PMX60SI (60 MHz), ^{13}C; JEOL JNM-FX 100 (25.05 MHz)]. Mass spectra were recorded on a Hitachi M-80 spectrometer or a JEOL JMS-D300 spectrometer, operating at an ionizing potential of 70 eV. Elemental analyses were performed using a Yanaco Model MT-3 CHN corder. 1-Phospha-2-thiabicyclo[4.4.0]deca-3,7,9-triene 1-sulfides

(**3**) were prepared according to the method previously described.[1)]

General Procedure for the Reaction of 3 with Triphenylphosphine: A solution of **3** (1.0 mmol) and triphenylphosphine (1.2 mmol) in dry toluene (5.0 cm^3) was refluxed under a nitrogen atmosphere for 3 h. The toluene was removed, and the residue was chromatographed on Wakogel C-200 with benzene-hexane (1 : 3) as an eluent. The solvent was evaporated, and the residue was recrystallized from hexane to give **6**.

2,4,5-Triphenylphosphorin (6a): ^{1}H NMR δ=6.93—7.87 (m, 15H, Ar-H), 8.08 [d, 1H, J_{HP}=6.0 Hz, H(3)], and 8.73 [d, 1H, J_{HP}=38.0 Hz, H(6)]; MS *m/z* 324 (M^+, 100). Found: C, 84.99; H, 5.23%. Calcd for $C_{23}H_{17}P$: C, 85.17; H, 5.28%. The ^{1}H NMR spectrum is identical with that reported by Märkl et al.[5)]

4,5-Diphenyl-2-*p*-tolylphosphorin (6b): ^{1}H NMR δ=2.43 (s, 3H, CH_3), 6.97—7.90 (m, 14H, Ar-H), 8.08 [d, 1H, J_{HP}=6.0 Hz, H(3)], and 8.73 [d, 1H, J_{HP}=38.0 Hz, H(6)]; MS *m/z* 338 (M^+, 100). Found: C, 85.14; H, 5.62%. Calcd for $C_{24}H_{19}P$: C, 85.19; H, 5.66%.

General Procedure for the Reaction of 3 with Dienophiles or Nucleophiles: A solution of **3** (1.0 mmol) and large excess of dienophile or nucleophile (10.0 mmol) in dry toluene (2.5 cm^3) was refluxed under a nitrogen atmosphere until **3** was consumed, as indicated by TLC. After evaporation of the solvent, the residue was chromatographed on Wakogel C-200 with benzene-hexane (2 : 1—3 : 1) as an eluent. The products were recrystallized from ethanol or ligroine.

8-Butoxy-2,4,5-triphenyl-1-phosphabicyclo[2.2.2]octa-2,5-diene 1-Sulfide (7a): IR(KBr) 1085 cm^{-1} (C-O); ^{1}H NMR δ=0.67—2.67 (m, 9H), 3.33—4.83 (m, 3H), 6.53 [d, 1H, J_{HP}=20.0 Hz, H(3)], and 6.83—7.67 (m, 16H); MS *m/z* 456 (M^+, 1), 356 (**4a**, 72), 324 (**6a**, 50), 254 (**4a**-PhC≡CH, 100), and 100(CH_2=CHOBu^n, 75). Found: C, 76.37; H, 6.45%. Calcd for $C_{29}H_{29}OPS$: C,76.29; H, 6.40%.

8-Butoxy-4,5-diphenyl-2-*p*-tolyl-1-phosphabicyclo[2.2.2]-octa-2,5-diene 1-Sulfide (7b): IR(KBr) 1085 cm^{-1}(C-O); ^{1}H NMR δ=0.67—2.27 (m, 9H), 2.33 (s, 3H, *p*-Tol-CH_3), 3.33—4.00(m, 3H), 6.52 [d, 1H, J_{HP}=20.0 Hz, H(3)], and 6.93—7.67 (m, 15H); MS *m/z* 470 (M^+, 1), 370 (**4b**, 94), 338 (**6b**, 100), 268 (**4b**-PhC≡CH, 82), and 100 (CH_2=CHOBu^n, 76). Found: C, 76.50; H, 6.66%. Calcd for $C_{30}H_{31}OPS$: C, 76.57; H, 6.64%.

8,10,12-Triphenyl-1-phosphatetracyclo[6.2.2.1^{3,6}.0^{2,7}]trideca-9,11-diene 1-Sulfide (9a): ^{1}H NMR δ=0.75—3.17 (m, 9H), 3.67—3.83 (m, 1H), 6.45 [d, 1H, J_{HP}=20.0 Hz, H(3)], and 6.67—7.75 (m, 16H); MS *m/z* 450 (M^+, 3), 356 (**4a**, 100), 324 (**6a**, 65), 254 (**4a**-PhC≡CH, 68), 121 (39), 94 (13), and 66 (81). Found: C, 79.99; H,5.92%. Calcd for $C_{30}H_{27}PS$: C, 79.97; H, 6.04%.

10a: ^{1}H NMR δ=0.67—3.17 (m, 10H), 6.37 [d, 1H, J_{HP}=19.0 Hz, H(3)], and 6.50—7.67 (m, 16H); MS *m/z* 450 (M^+, 2), 356 (**4a**, 100), 324 (**6a**, 42), 254 (**4a**-PhC≡CH, 69), 121 (22), 94 (4), and 66 (31). Found: C, 79.74; H, 6.04%. Calcd for $C_{30}H_{27}PS$: C, 79.97; H, 6.04%.

8,12-Diphenyl-10-*p*-tolyl-1-phosphatetracyclo[6.2.2.1^{3,6}.0^{2,7}]-trideca-9,11-diene 1-Sulfide (9b): ^{1}H NMR δ=0.75—3.17 (m, 9H), 2.35 (s, 3H, CH_3), 3.67—3.83 (m, 1H), 6.45 [d, 1H, J_{HP}=18.0 Hz, H(3)], 6.67—7.50 (m, 13H), and 7.50 (d, 2H, J_{HH}=8.0 Hz, *p*-Tol-H); MS *m/z* 464(M^+, 1), 370 (**4b**, 100), 338 (**6b**, 36), 268 (**4b**-PhC≡CH, 80), 135 (38), 94 (10), and 66 (69). Found: C, 79.81; H, 5.99%. Calcd for $C_{31}H_{29}PS$: C, 80.14; H, 6.29%.

10b: ^{1}H NMR δ=0.67—3.17 (m, 10H), 2.40 (s, 3H, CH_3), 6.35 [d, 1H, J_{HP}=20.0 Hz, H(3)], 6.50—7.50 (m, 13H), and 7.62 (d, 2H, J_{HH}=8.0 Hz, *p*-Tol-H); MS *m/z* 464 (M^+, 2), 370 (**4b**, 100), 338 (**6b**, 63), 268 (**4b**-PhC≡CH, 80), 135 (28), 94 (7), and 66 (47). Found: C, 80.28; H, 6.17; S, 6.96%. Calcd for $C_{31}H_{29}PS$: C, 80.14; H, 6.29; S, 6.90%.

1-Benzyloxy-3,4,6-triphenyl-1,2-dihydrophosphorin 1-Sulfide (12a): IR(KBr) 1000, 970 cm^{-1} (P-O); ^{1}H NMR δ=3.33—3.67 [m, 2H, H(6)], 4.75—5.50 (m, 2H, $PhCH_2O$), 6.82 [d, 1H, J_{HP}=22.0 Hz, H(3)], and 6.67—7.83 (m, 20H, Ar-H); MS *m/z* 464 (M^+, 72), 356 (**4a**, 22), 340 (75), 324 (**6a**, 10), 293 (66), 254 (**4a**-PhC≡CH, 23), 215 (44), and 91 (100). Found: C, 77.58; H, 5.44%. Calcd for $C_{30}H_{25}PS$: 77.56; H, 5.42%.

1-Benzyloxy-3,4-diphenyl-6-*p*-tolyl-1,2-dihydrophosphorin 1-Sulfide (12b): IR(KBr) 980, 960 cm^{-1} (P-O); ^{1}H NMR δ=2.38 (s, 3H, CH_3), 3.33—3.67 [m, 2H, H(6)], 4.75—5.50(m, 2H, $PhCH_2O$), 6.77 [d, 1H, J_{HP}=20.0 Hz, H(3)], 6.60—7.57 (m, 17H, Ar-H), and 7.57 (d, 2H, J_{HH}=8.0 Hz, *p*-Tol-H); MS *m/z* 478 (M^+, 67), 370 (**4b**, 11), 354 (59), 338 (**6b**, 22), 307 (100), 268 (**4b**-PhC≡CH, 15), 215 (33), and 91 (74). Found: C, 77.54; H, 5.57; S, 6.66%. Calcd for $C_{31}H_{27}OPS$: C, 77.80; H, 5.69; S, 6.70%.

1-(Phenylthio)-3,4,6-triphenyl-1,2-dihydrophosphorin 1-Sulfide (13a): ^{1}H NMR δ=3.50—4.00 [m, 2H, H(6)], 6.68 [d, 1H, J_{HP}=18.0 Hz, H(3)], and 6.68—7.83 (m, 20H, Ar-H); MS *m/z* 466 (M^+, 10), 356 (**4a**, 100), 324 (**6a**, 69), 254 (**4a**-PhC≡CH, 87), 121 (36), and 110 (46). Found: C, 74.40; H, 4.88%. Calcd for $C_{29}H_{23}S_2P$: C, 74.65; H, 4.97%.

3,4-Diphenyl-1-(phenylthio)-6-*p*-tolyl-1,2-dihydrophosphorin 1-Sulfide (13b): ^{1}H NMR δ=2.37 (s, 3H, CH_3), 3.50—4.00 [m, 2H, H(6)], 6.68 [d, 1H, J_{HP}=19.0 Hz, H(3)], 6.67—7.50 (m, 17H, Ar-H), and 7.65 (d, 2H, J_{HH}=8.0 Hz, *p*-Tol-H); MS *m/z* 480 (M^+, 3), 370 (**4b**, 87), 338 (**6b**, 100), 268 (**4b**-PhC≡CH, 80), 135 (40), 110 (78), and 66 (17). Found: C, 75.03; H, 5.21%. Calcd for $C_{30}H_{25}S_2P$: C, 74.97; H, 5.24%.

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