

Preparation and Reactions of 1,2-Thiaphospholes

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Treatment of 2,9-dithia-1-phosphabicyclo[4.3.0]-nona-3,7-diene 1-sulfides with *n*-Bu₃P afforded 1,2-thiaphospholes in good yields. The thiaphospholes reacted thermally with norbornene to produce 1:2 double Diels-Alder cycloadducts, whereas they reacted with acrylic esters in the presence of Lewis acid to give tandem Diels-Alder / β -addition adducts.

We previously reported that 2,9-dithia-1-phosphabicyclo[4.3.0]-nona-3,7-diene 1-sulfides **1** prepared by the reaction of α,β -unsaturated ketone with excess P₄S₁₀ in the presence of triethylamine,¹⁾ generated 1,2-thiaphosphole 2-sulfides **2** and the corresponding α,β -unsaturated thioketones **3** by thermolysis and that both of these heterodienes could be trapped with dienophiles (X=Y) as [4+2] cycloadducts.²⁾

This paper deals with new and efficient preparation of 1,2-thiaphospholes **4** via desulfurization of **1** and with their novel reactions with norbornene or acrylic esters.

A solution of **1a** (Ar¹=Ar²=Ph, 2 mmol) and *n*-Bu₃P (6 mmol) in dichloromethane (12 ml) was refluxed for 7 h. The reaction mixture was chromatographed on silica gel using benzene-hexane (1:30) as an eluent to give 3,5-diphenyl-1,2-thiaphosphole **4a**³⁾ in a 79% yield along with **5a**⁴⁾ (18% yield). In contrast to the transient property of **2**, **4a** was found to be sufficiently stable for isolation. In a similar way, some other thiaphospholes **4b-e** were obtained in 74-84% yields. The results are shown in Table 1.⁵⁾ To our knowledge, 1,2-thiaphospholes are very inaccessible compounds and there are only two reports on their preparation in very low yields (8% or below).⁶⁾ Accordingly, the present results provide a useful and convenient method for the preparation of these heterocycles.

The thiaphosphole **4a** (0.78 mmol) was allowed to react with norbornene (4.68 mmol) at 180 °C for 18 h in *o*-dichlorobenzene (12 ml) to afford the 1:2 Diels-Alder adduct **8**⁷⁾ in 34% yield. Cleavage of the C-S bond in the initially formed [4+2] cycloadduct **6**, generates 2,3-dihydrophosphorin 1-sulfide **7**, which reacts further with another molecule of norbornene to give **8** as the final product.

Because **4** is reluctant for the thermal reaction with dienophiles,⁸⁾ we next examined the reaction of **4** with methyl acrylate using AlCl₃ as a catalyst. When **4a** (0.78 mmol) was treated with an excess amount of methyl acrylate (4.68 mmol) in dichloromethane (12 ml) in the presence of AlCl₃ (2.34 mmol), the reaction proceeded readily even at room temperature. Usual work up and chromatography on silica gel with ethyl

acetate-hexane (1:10) as an eluent gave the product. The mass spectra indicated a 1:2 adduct but the X-ray analysis proved that the adduct had an unexpected structure **10a**.⁹⁾ It seems that the first step is cycloaddition reaction of **4a** with methyl acrylate to form the intermediate **9** which subsequently undergoes the 1,4-addition with another molecule of methyl acrylate, giving the final product **10a**. 1-[2-(Alkoxy carbonyl)ethyl]-1,2-dihydrophosphorin 1-sulfides **10b-d** were similarly obtained in 61-93% yields. The results are shown in Table 2.

Table 1. Yield and Mp's of Products from the Reaction of **1** with *n*-Bu₃P a)

Ar ¹	Ar ²	Product	Yield / %	Mp / °C	Product	Yield / %	Mp / °C
Ph	Ph	4a	79	92-93	5a	18	151-153
<i>p</i> -MeOC ₆ H ₄	Ph	4b	83	112-113	5b	trace	-
<i>p</i> -Tol	Ph	4c	84	100-102	5c	5	163-164
Ph	<i>p</i> -MeOC ₆ H ₄	4d	74	112-114	5d	trace	-
Ph	<i>p</i> -Tol	4e	83	75-76	5e	10	155-156

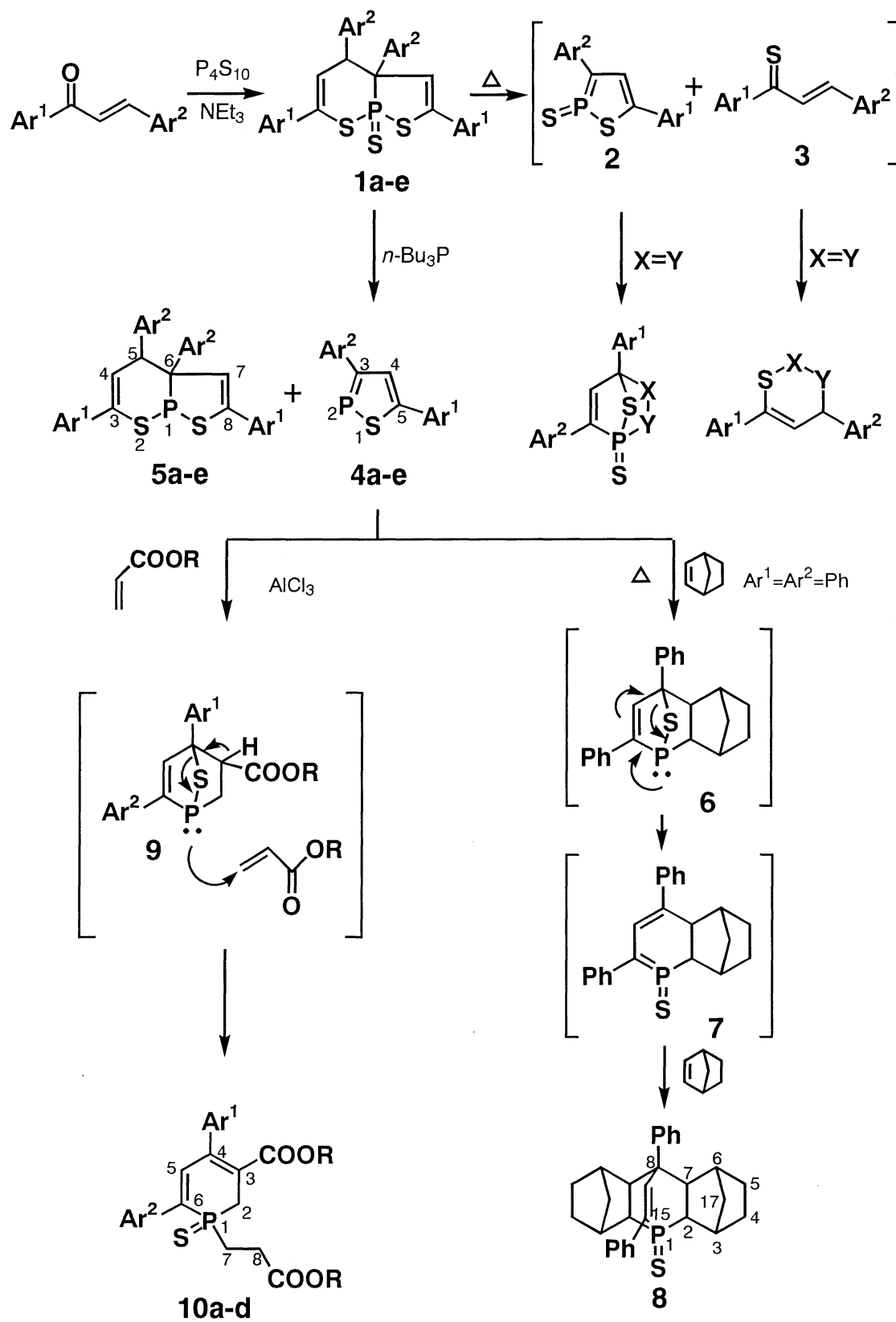
a) The reaction required 7-9 h in refluxing dichloromethane.

Table 2. The Reaction of **4** with Acrylic Esters

Ar ¹	Ar ²	R	Thiaphosphole	Time / h	Product	Yield / %	Mp / °C
Ph	Ph	Me	4a	1	10a	80	138-139
<i>p</i> -MeOC ₆ H ₄	Ph	Me	4b	1	10b	71	124-125
<i>p</i> -Tol	Ph	Me	4c	1	10c	61	84-86
Ph	Ph	Et	4a	2	10d	93	64-66

It is noteworthy that the formation of **9** is the first example of Lewis acid-promoted hetero Diels-Alder reaction of a phosphadiene system. Tandem Diels-Alder / β -addition process to form phosphorus compound **10** would be also interesting. Remarkable difference of the reactivity toward dienophiles between **2** and **4** may be due to the valence states of the phosphorus in **2** (pentavalent) and **4** (trivalent).

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References

- 1) H. Yamaguchi, S. Kametani, T. Karakasa, T. Saito, and S. Motoki, *Tetrahedron Lett.*, **23**, 1263 (1982).
- 2) H. Tanaka, S. Kametani, T. Saito, and S. Motoki, *Bull. Chem. Soc. Jpn.*, **58**, 667 (1985).
- 3) **4a**: Colorless needles. $^1\text{H-NMR}$ (CDCl_3): $\delta=8.18$ (d, H-4, $J_{\text{HP}} = 8.25$ Hz). $^{13}\text{C-NMR}$ (CDCl_3 , DEPT): $\delta=132.6$ (d-CH, C-4, $J_{\text{CP}} = 13.5$ Hz), 159.0 (d-C, C-5, $J_{\text{CP}} = 5.80$ Hz), 183.2 (d-C, C-3, $J_{\text{CP}} = 56.1$ Hz). $^{31}\text{P-NMR}$ (CDCl_3): $\delta=203.8$. MS m/z 254 (M^+ , 100), 191 ($\text{M}^+ - \text{PS}$, 30), 121 (PhCP^+ , 6). HRMS Found: m/z 254.0319. Calcd for $\text{C}_{15}\text{H}_{11}\text{PS}_2\text{:M}^+$, 254.0320. UV (Cyclohexane): 335 nm (11770), 276 (23604), 235 (11141).
- 4) **5a**: Colorless cubes. $^1\text{H-NMR}$ (CDCl_3): $\delta=4.94$ (dd, H-5, $J_{4,5} = 2.97$, $J_{\text{HP}} = 10.88$ Hz), 5.96 (dd, H-4, $J_{4,5} = 2.97$, $J_{\text{HP}} = 2.97$ Hz), 6.37 (d, H-7, $J_{\text{HP}} = 35.96$ Hz). $^{13}\text{C-NMR}$ (CDCl_3 , DEPT): $\delta=47.7$ (CH, C-5), 66.5 (d-C, C-6, $J_{\text{CP}} = 56.1$ Hz), 108.2 (d-CH, C-4, $J_{\text{CP}} = 9.8$ Hz), 123.5 (d-CH, C-7, $J_{\text{CP}} = 7.4$ Hz). $^{31}\text{P-NMR}$ (CDCl_3): $\delta=122.4$. MS m/z (rel. intensity.): 478 (M^+ , very weak), 414 ($\text{M}^+ - 2\text{S}$, 0.4), 254 (**4a** $^+$, 100). HRMS Found: m/z 478.0964. Calcd for $\text{C}_{30}\text{H}_{23}\text{PS}_2\text{:M}^+$, 478.0981. mp 151-153 °C.
- 5) It seems that another component **3** was decomposed by *n*-Bu₃P. Any identified product other than **4** and **5** was not obtained.
- 6) G. Märkl and W. Hölzl, *Tetrahedron Lett.*, **29**, 4535 (1988); *ibid.*, **30**, 4501 (1989).
- 7) **8**: Colorless cubes. $^{13}\text{C-NMR}$ (CDCl_3 , DEPT): $\delta=34.7$ (CH_2 , C-17), 47.5 (d-C, C-8, $J_{\text{CP}} = 40.3$ Hz), 49.4 (d-CH, C-2, $J_{\text{CP}} = 48.8$ Hz), 57.8 (d-CH, C-3 or C-7, $J_{\text{CP}} = 6.1$ Hz), 135.7 (d-C, C-15, $J_{\text{CP}} = 54.9$ Hz). $^{31}\text{P-NMR}$ (CDCl_3): $\delta=23.7$. MS m/z (rel. int.): 442 (M^+ , 6), 348 ($\text{M}^+ - \text{norbornene}$, 60), 316 ($\text{M}^+ - \text{norbornene-S}$, 4), 254 (**4a** $^+$, 100). HRMS Found: m/z 442.1885. Calcd for $\text{C}_{29}\text{H}_{31}\text{PS}$: M^+ , 442.1886. mp 243 °C.
- 8) The reaction of **1** with the other dienophiles such as methyl acrylate, acrolein and acrylonitrile did not proceed in boiling benzene or xylene and only decomposition reaction of the material took place in boiling *o*-dichlorobenzene.
- 9) **10a**: Pale yellow needles. $^1\text{H-NMR}$ (CDCl_3): $\delta=2.34$ (m, 2H), 2.71 (m, 2H), 3.44 (dd, 2H, H-2,2', $J_{2,2'} = 13.52$, $J_{\text{HP}} = 15.83$ Hz), 3.52 (s, 3H), 3.67 (s, 3H), 6.76 (d, H-5, $J_{\text{HP}} = 30.35$ Hz). $^{13}\text{C-NMR}$ (CDCl_3 , DEPT): $\delta=26.8$ (CH_2 , C-8), 26.9 (d- CH_2 , C-7, $J_{\text{CP}} = 57.4$ Hz), 33.2 (d- CH_2 , C-2, $J_{\text{CP}} = 56.2$ Hz), 52.0 (CH_3), 52.1 (CH_3), 121.6 (d-C, C-3, $J_{\text{CP}} = 9.7$ Hz), 136.4 (d-C, C-6, $J_{\text{CP}} = 70.8$ Hz), 167.8 (C=O), 172.4 (C=O). $^{31}\text{P-NMR}$ (CDCl_3): $\delta=28.2$. MS m/z (rel. int.): 426 (M^+ , 75), 393 ($\text{M}^+ - \text{SH}$, 100), 307 ($\text{M}^+ - 2\text{COOCH}_3$, 11). HRMS Found: m/z 426.1061. Calcd for $\text{C}_{23}\text{H}_{23}\text{PSO}_4\text{:M}^+$, 426.1056. mp 138-139 °C. IR (KBr): 1736 cm^{-1} (C=O), 1700 (C=O). The X-ray data of **10a** will be published elsewhere.

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