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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*-Bu_3P 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 P_4S_{10} 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 preparaion of 1,2-thiaphospholes **4** via desulfurization of **1** and with their novel reactions with norbornene or acrylic esters.

A solution of **1a** (Ar^1=Ar^2=Ph , 2 mmol) and *n*-Bu_3P (6 mmol) in dichlorometane (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 $AlCl_3$ 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 $AlCl_3$ (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-(Alkoxycarbonyl)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*-Bu_3P $^{a)}$

Ar^1	Ar^2	Product	Yield / %	Mp / °C	Product	Yield / %	Mp / °C
Ph	Ph	**4a**	79	92-93	**5a**	18	151-153
p-$MeOC_6H_4$	Ph	**4b**	83	112-113	**5b**	trace	-
p-Tol	Ph	**4c**	84	100-102	**5c**	5	163-164
Ph	*p*-$MeOC_6H_4$	**4d**	74	112-114	**5d**	trace	-
Ph	*p*-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
p-$MeOC_6H_4$	Ph	Me	**4b**	1	**10b**	71	124-125
p-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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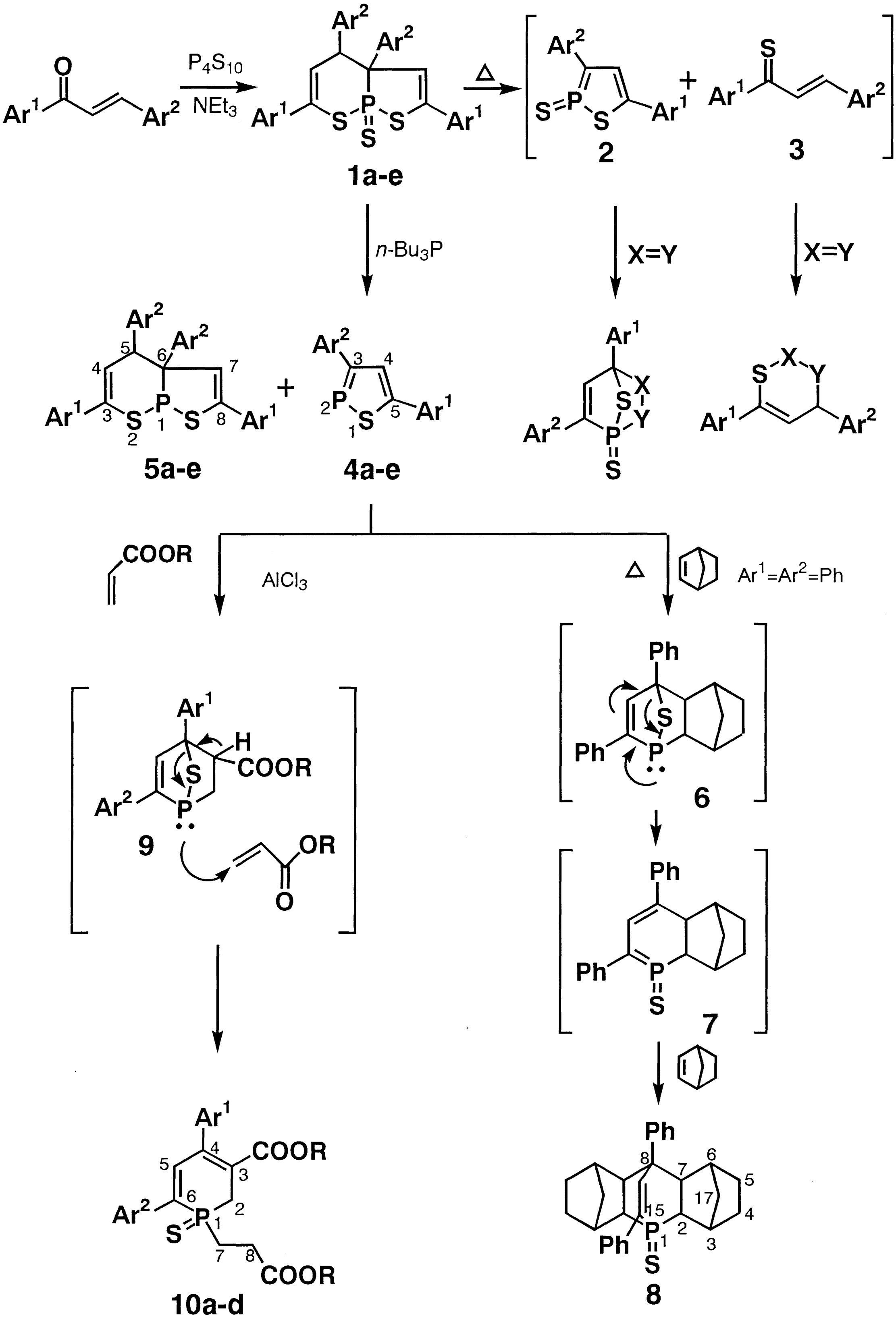
P4S10
NEt3
1a-e
Δ
2
3
n-Bu3P
X=Y
X=Y
5a-e
4a-e
COOR
AlCl3
Δ
Ar1=Ar2=Ph
9
6
7
10a-d
8

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}H-NMR (CDCl$_3$): δ=8.18 (d, H-4, J_{HP} = 8.25 Hz). ^{13}C-NMR (CDCl$_3$, DEPT): δ=132.6 (d-CH, C-4, J_{CP} = 13.5 Hz), 159.0 (d-C, C-5, J_{CP} = 5.80 Hz), 183.2 (d-C, C-3, J_{CP} = 56.1 Hz). ^{31}P-NMR (CDCl$_3$): δ=203.8. MS *m/z* 254 (M$^+$, 100) , 191 (M$^+$-PS , 30) , 121 (PhCP$^+$, 6). HRMS Found: *m/z* 254.0319. Calcd for $C_{15}H_{11}PS_2$:M$^+$,254.0320. UV (Cyclohexane): 335 nm (11770), 276 (23604), 235 (11141).

4) **5a**: Colorless cubes. ^{1}H-NMR (CDCl$_3$): δ=4.94 (dd, H-5, $J_{4,5}$ = 2.97, J_{HP} = 10.88 Hz), 5.96 (dd, H-4, $J_{4,5}$ = 2.97, J_{HP} = 2.97 Hz), 6.37 (d, H-7, J_{HP} = 35.96 Hz). ^{13}C-NMR (CDCl$_3$, DEPT): δ=47.7 (CH, C-5), 66.5 (d-C, C-6, J_{CP} = 56.1 Hz), 108.2 (d-CH, C-4, J_{CP} = 9.8 Hz), 123.5 (d-CH, C-7, J_{CP} = 7.4 Hz). ^{31}P-NMR(CDCl$_3$): δ=122.4. MS *m/z* (rel. intensity.): 478 (M$^+$, very weak), 414 (M$^+$-2S, 0.4), 254 (**4a**$^+$, 100). HRMS Found: *m/z* 478.0964. Calcd for $C_{30}H_{23}PS_2$:M$^+$,478.0981. mp 151-153 °C.

5) It seems that another component **3** was decomposed by *n*-Bu$_3$P. 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}C-NMR (CDCl$_3$,DEPT): δ=34.7 (CH$_2$, C-17), 47.5 (d-C, C-8, J_{CP} = 40.3 Hz), 49.4 (d-CH, C-2, J_{CP} = 48.8 Hz), 57.8 (d-CH, C-3 or C-7, J_{CP} = 6.1 Hz), 135.7 (d-C, C-15, J_{CP} = 54.9 Hz). ^{31}P-NMR (CDCl$_3$): δ= 23.7. MS *m/z* (rel. int.): 442 (M$^+$, 6), 348 (M$^+$-norbornene, 60), 316 (M$^+$-norbornene-S, 4), 254 (**4a**$^+$, 100). HRMS Found: *m/z* 442.1885. Calcd for $C_{29}H_{31}PS$: 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}H-NMR (CDCl$_3$): δ=2.34 (m, 2H), 2.71 (m, 2H), 3.44 (dd, 2H, H-2,2', $J_{2,2'}$ = 13.52, J_{HP} = 15.83 Hz), 3.52 (s, 3H), 3.67 (s, 3H), 6.76 (d, H-5, J_{HP} = 30.35 Hz). ^{13}C-NMR (CDCl$_3$,DEPT): δ=26.8 (CH$_2$, C-8), 26.9 (d-CH$_2$, C-7, J_{CP} = 57.4 Hz), 33.2 (d-CH$_2$, C-2, J_{CP} = 56.2 Hz), 52.0 (CH$_3$), 52.1 (CH$_3$), 121.6 (d-C, C-3, J_{CP} = 9.7 Hz), 136.4 (d-C, C-6, J_{CP} = 70.8 Hz), 167.8 (C=O), 172.4 (C=O). ^{31}P-NMR (CDCl$_3$): δ=28.2. MS *m/z* (rel. int.): 426 (M$^+$, 75), 393 (M$^+$-SH, 100), 307 (M$^+$-2COOCH$_3$, 11). HRMS Found: *m/z* 426.1061. Calcd for $C_{23}H_{23}PSO_4$: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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