

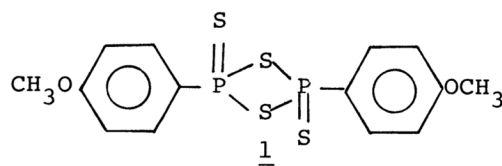
REACTION OF CHALCONES WITH 2,4-BIS(4-METHOXYPHENYL)-  
1,3,2,4-DITHIADIPHOSPHETANE-2,4-DISULFIDEShunichi KAMETANI, Haruo OHMURA, Hideyuki TANAKA,  
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Though the reaction of chalcones 2 with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide 1 in refluxing benzene gave the corresponding thiochalcone dimers 3, the reaction in refluxing xylene gave new phosphorus-containing compounds, 2-(4-methoxyphenyl)-3,5-diaryl- $\Delta^4$ -1,2-thiaphospholene-2-sulfides 4.

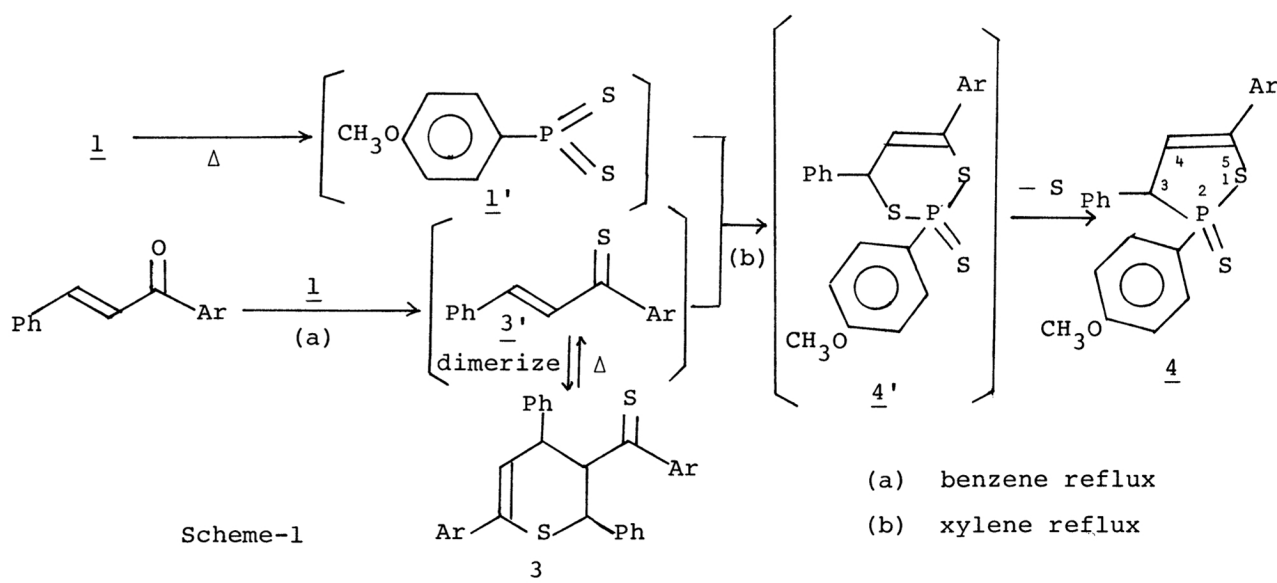
We have previously reported that thiochalcone dimers and 2-arylmethylene-1-tetralinthione dimers are readily prepared by treatment of chalcones and 2-arylmethylene-1-tetralones with tetraphosphorus decasulfide ( $P_4S_{10}$ ) in the presence of triethylamine.<sup>1,2)</sup>

In recent years, 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide 1 was found to be an effective thionation reagent for ketones and many reports referring to the utilization of this reagent were presented by Lawesson and his co-workers.<sup>3)</sup> Accordingly the reaction of 1 with chalcones and 2-arylmethylene-1-tetralones has been studied in the present paper.

Treatment of chalcone 2 (0.01 mol) with 1 (2.4 g, 0.006 mol) in refluxing benzene (30 cm<sup>3</sup>) gave the corresponding thione dimer 3 as in the case of the reaction with  $P_4S_{10}$  and  $Et_3N$  (Table-1).

Table-1 Preparation of thiochalcone dimers 3 with 1

Product	Ar	Reaction time	Yield(%)
<u>3a</u>	C <sub>6</sub> H <sub>5</sub>	2 h	20
<u>3b</u>	p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	15 min	16
<u>3c</u>	p-ClC <sub>6</sub> H <sub>4</sub>	3 h	27



However, when the reaction of 2a with twice amount of 1 was carried out in refluxing xylene, new phosphorus-containing compound 4a was obtained in relatively good yield.

A mixture of 2a (2.1 g, 0.01 mol) and 1 (4.8 g, 0.012 mol) in xylene (20 cm<sup>3</sup>) was refluxed for 30 min. After cooling, the reaction mixture was filtered and the filtrate was evaporated. The residue was chromatographed on Wakogel C-200 using benzene as an eluent. The solvent was evaporated and the residue was recrystallized from ethanol to give colorless crystals of 2-(4-methoxyphenyl)-3,5-diphenyl- $\Delta^4$ -1,2-thiaphospholene-2-sulfide 4a (2.22 g, 56% yield, mp 204-205 °C dec).

Found: C, 67.08; H, 4.88; S, 16.34; P, 7.90%; Calcd for C<sub>22</sub>H<sub>19</sub>OS<sub>2</sub>P: C, 66.98; H, 4.85; S, 16.25; P, 7.85%. The mass spectral fragmentation pattern and the NMR

( $^1\text{H}$ , and  $^{13}\text{C}$ ) spectral data gave strong substantiation for the structure 4a. Namely, the mass spectrum exhibited the molecular ion peak (394, 64%) and a fragment from the thione monomer 5a (223, 99%,  $\text{5a}^+ - \text{H}$ )<sup>1)</sup> which would be formed by the cleavage of 4a. The  $^1\text{H}$ -NMR spectrum showed the signals of one olefinic proton ( $\delta$  6.32, dd,  $J_{\text{PH}}=32$  Hz,  $J_{\text{HH}}=4$  Hz, H(4)) and one methine proton ( $\delta$  5.17, dd,  $J_{\text{PH}}=18$  Hz,  $J_{\text{HH}}=4$  Hz, H(3)). In the  $^{13}\text{C}$ -NMR spectrum, a signal with a large coupling constant at  $\delta$  67.76 ( $J_{\text{PC}}=42.73$  Hz) was easily assigned to the carbon atom [C(3)] directly attached to the phosphorus atom.<sup>4)</sup>

The  $^{31}\text{P}$ -NMR spectrum showed the presence of one kind of phosphorus atom (85%  $\text{H}_3\text{PO}_4$ ,  $\text{CDCl}_3$ ;  $\delta$  95.1).

5-p-Methoxyphenyl and 5-p-chlorophenyl analogues (4b and 4c) were prepared similarly (Tables-2 and 3).

The reaction would proceed by the way similar to that of 1,3-diene and 1<sup>5)</sup> as illustrated in Scheme-1.

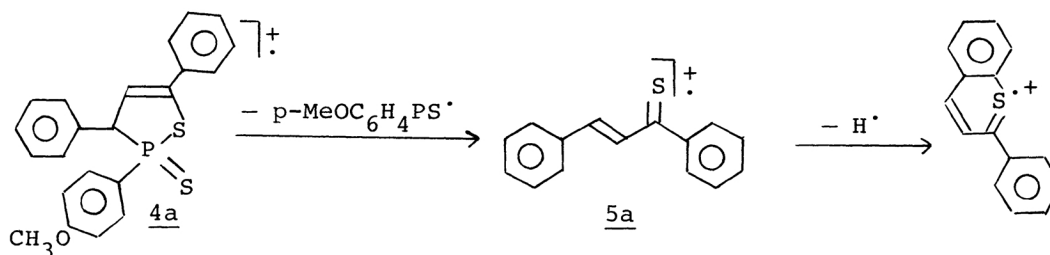


Table-2 Preparation of 2-(4-methoxyphenyl)-3,5-diaryl- $\Delta^4$ -1,2-thiaphospholene-2-sulfides 4

Product	Ar	Reaction time	Yield(%)	Mp(°C)
<u>4a</u>	$\text{C}_6\text{H}_5$	30 min	56	204-205
<u>4b</u>	p- $\text{CH}_3\text{OC}_6\text{H}_4$	30 min	56	137-138
<u>4c</u>	p- $\text{ClC}_6\text{H}_4$	30 min	21	169-171

Table-3  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectral data of 4

	$\delta$ H(3)	$\delta$ H(4)	$J_{\text{HH}}$	$J_{\text{PH}}(3)$	$J_{\text{PH}}(4)$	$\delta$ C(3)	$J_{\text{PC}}(3)$
<u>4a</u>	5.17	6.32	4 Hz	18 Hz	32 Hz	67.76	42.73 Hz
<u>4b</u>	5.14	6.18	4 Hz	20 Hz	32 Hz	67.66	42.73 Hz
<u>4c</u>	5.14	6.31	4 Hz	20 Hz	32 Hz	67.86	42.73 Hz

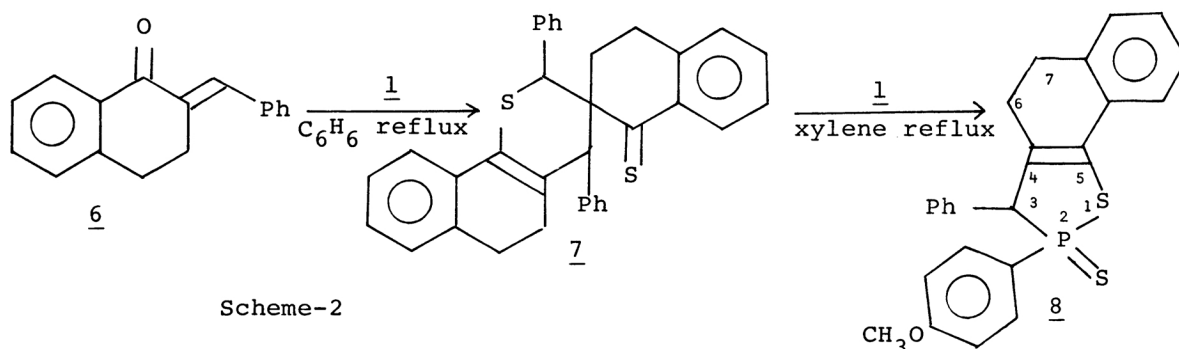
When thiochalcone dimer 3a (2.3 g, 0.01 mol as the monomer) was allowed to react with 1 (4.8 g, 0.012 mol) in refluxing xylene (10 cm<sup>3</sup>) for 2h, 4a was obtained in 36% yield.

The result also indicates that the reaction of 2 with 1 proceed via thione monomer 3'.

The reaction of 2-phenylmethylene-1-tetralone 6 with 1 in refluxing benzene also gave the corresponding thione dimer 7.

In refluxing xylene, the reaction of 6 with 1 did not afford any identified product, however, 7 reacted with 1 to give the corresponding phosphorus compound 8 (0.26 g, 31% yield, mp 156-157 °C dec).

The assignment were as follows: MS(70eV); 420(54%,M<sup>+</sup>), 387(100), 250(17, M<sup>+</sup>- p-MeOC<sub>6</sub>H<sub>4</sub>PS), 249(77), 215(25); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 2.22-2.39 (m, -CH<sub>2</sub>CH<sub>2</sub>-), δ 3.81 (s, OCH<sub>3</sub>), δ 4.42 (d, J<sub>PH</sub>=8 Hz, 1H, H(3)), δ 6.84-8.05 (m, 13H, Ar-H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 26.58 [d, J<sub>PC</sub>=13.21 Hz, C(6)], δ 28.17, δ 55.46 [OCH<sub>3</sub>], δ 66.30 [d, J<sub>PC</sub>=49.97 Hz, C(3)].



#### References

- 1) T. Karakasa and S. Motoki, *J. Org. Chem.*, **43**, 4147 (1978).
- 2) T. Karakasa and S. Motoki, *J. Org. Chem.*, **44**, 4151 (1979).
- 3) B. S. Perderson, S. Scheibye, N. H. Nilsson, and S. O. Lawesson, *Bull. Soc. Chim. Belg.*, **87**, 223 (1978) and later papers.
- 4) E. F. Moony, "ANNUAL REPORTS ON NMR SPECTROSCOPY," Vol. 5B, Academic Press, New York (1973), P. 12.
- 5) A. Ecker, I. Boie, and U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **10**, 191 (1971).

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