CHEMISTRY LETTERS, pp. 793-796, 1982.

REACTION OF CHALCONES WITH 2,4-BIS(4-METHOXYPHENYL)-1,3,2,4-DITHIADIPHOSPHETANE-2,4-DISULFIDE

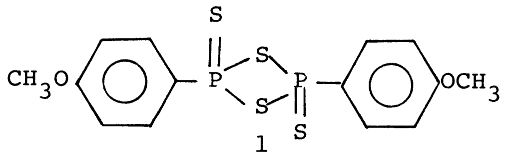
Shunichi KAMETANI, Haruo OHMURA, Hideyuki TANAKA,
and Shinichi MOTOKI*
Department of Chemistry, Faculty of Science,
Science University of Tokyo, Kagurazaka, Shinjuku-ku,
Tokyo 162

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-Δ^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.[1,2]

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.[3] Accordingly the reaction of 1 with chalcones and 2-arylmethylene-1-tetralones has been studied in the present paper.

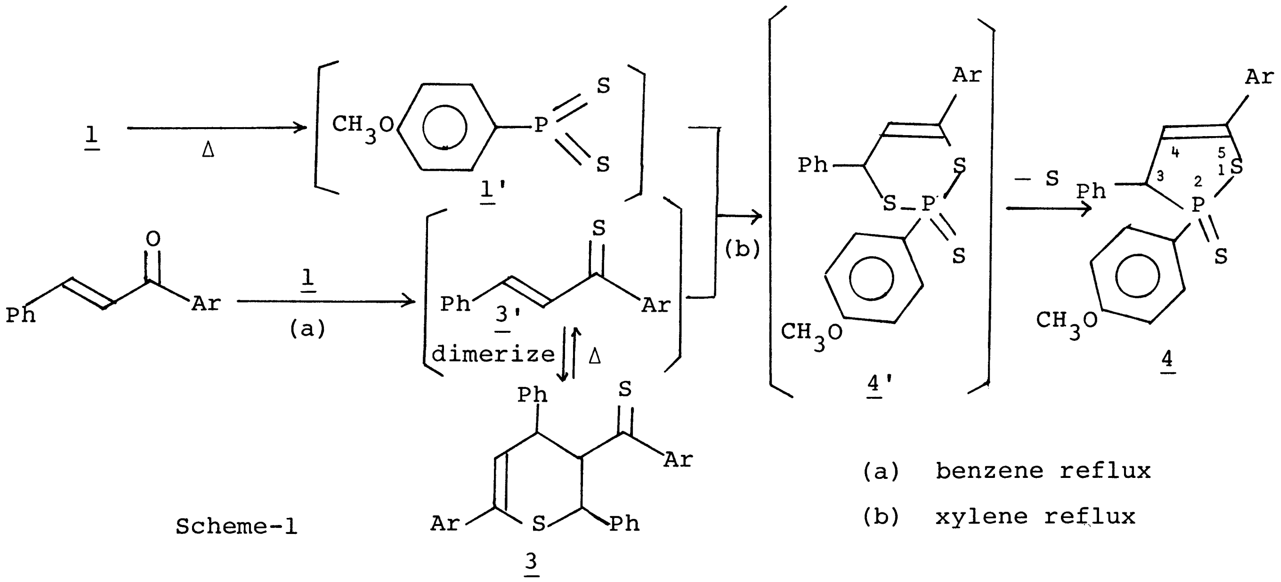
Treatment of chalcone 2 (0.01 mol) with 1 (2.4 g, 0.006 mol) in refluxing benzene (30 cm^3) gave the corresponding thione dimer 3 as in the case of the reaction with P_4S_{10} and Et_3N (Table-1).



1

Table-1 Prepapration of thiochalcone dimers 3 with 1

Product	Ar	Reaction time	Yield(%)
3a	C_6H_5	2 h	20
3b	p-$CH_3OC_6H_4$	15 min	16
3c	p-ClC_6H_4	3 h	27



Scheme-1

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^3) 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-Δ^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 $C_{22}H_{19}OS_2P$: C, 66.98; H, 4.85; S, 16.25; P, 7.85%. The mass spectral fragmentation pattern and the NMR

(^{1}H, and ^{13}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%, $5a^+ - H$)[1] which would be formed by the cleavage of 4a. The ^{1}H-NMR spectrum showed the signals of one olefinic proton (δ 6.32, dd, J_{PH}=32 Hz, J_{HH}=4 Hz, H(4)) and one methine proton (δ 5.17, dd, J_{PH}=18 Hz, J_{HH}=4 Hz, H(3)). In the ^{13}C-NMR spectrum, a signal with a large coupling constant at δ 67.76 (J_{PC}=42.73 Hz) was easily assigned to the carbon atom [C(3)] directly attached to the phosphorus atom.[4]

The ^{31}P-NMR spectrum showed the presence of one kind of phosphorus atom (85% H_3PO_4, $CDCl_3$; δ 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[5] as illustrated in Scheme-1.

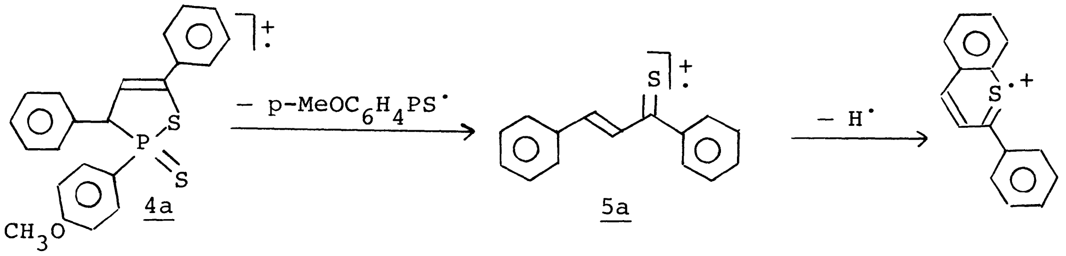


Table-2 Preparation of 2-(4-methoxyphenyl)-3,5-diaryl-Δ⁴-1,2-thiaphospholene-2-sulfides 4

Product	Ar	Reaction time	Yield(%)	Mp(°C)
4a	C_6H_5	30 min	56	204-205
4b	p-$CH_3OC_6H_4$	30 min	56	137-138
4c	p-ClC_6H_4	30 min	21	169-171

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

	δ H(3)	δ H(4)	J_{HH}	$J_{PH(3)}$	$J_{PH(4)}$	δ C(3)	$J_{PC(3)}$
4a	5.17	6.32	4 Hz	18 Hz	32 Hz	67.76	42.73 Hz
4b	5.14	6.18	4 Hz	20 Hz	32 Hz	67.66	42.73 Hz
4c	5.14	6.31	4 Hz	20 Hz	32 Hz	67.86	42.73 Hz

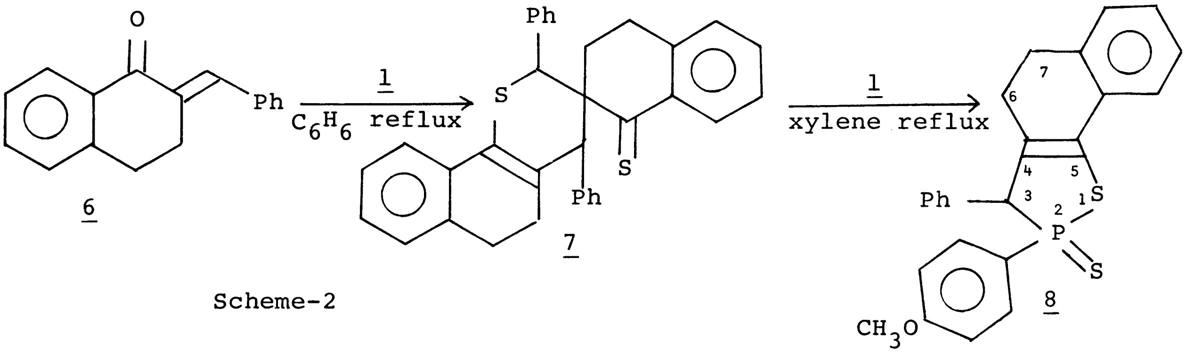
When thiochalcone dimer 3a (2.3 g, 0.01 mol as the monomer) was allowed to react with 1 (4.8 g, 0.012 mol) in refluxing xylene (10 cm^3) for 2h, 4a was obtained in 36% yield.

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^+), 387(100), 250(17, M^+– p-$MeOC_6H_4PS$), 249(77), 215(25); ^{1}H-NMR ($CDCl_3$) δ 2.22-2.39 (m, $-CH_2CH_2-$), δ 3.81 (s, OCH_3), δ 4.42 (d, J_{PH}=8 Hz, 1H, H(3)), δ 6.84-8.05 (m, 13H, Ar-H); ^{13}C-NMR ($CDCl_3$) δ 26.58 [d, J_{PC}=13.21 Hz, C(6)], δ 28.17, δ 55.46 [$O\underline{C}H_3$], δ 66.30 [d, J_{PC}=49.97 Hz, C(3)].



Scheme-2

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. Perdersen, 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).

(Received February 19, 1982)