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Generation and Reactions of Bis(arylmethylene)propanethione

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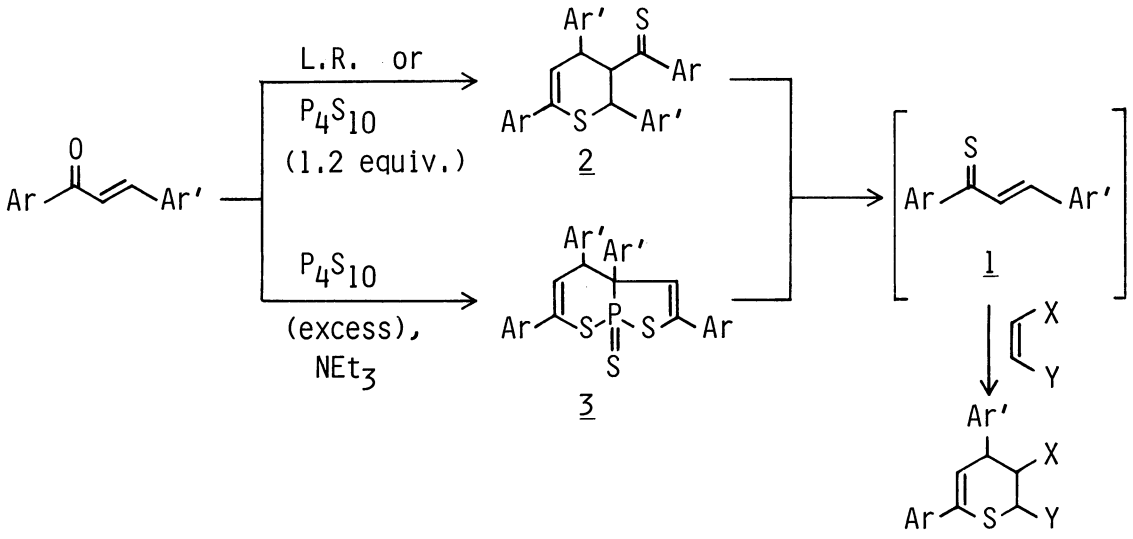
The reaction of bis(arylmethylene)propanone and P_4S_{10} gave 3,8-bis(2-arylvinyl)-5,6-diaryl-2,9-dithia-1-phosphabicyclo[4.3.0]-nona-3,7-diene 1-sulfide. Upon heating, the sulfide generated the title compound which was trapped by various dienophiles as [4+2]-cycloadducts.

α,β-Unsaturated ketones react with Lawesson's Reagent (L.R.) or tetraphosphorus decasulfide (P_4S_{10}) to give the dimer (2) of corresponding thioketones (1),[1,2] whereas, the ketones give phosphorus-containing compounds (3) by treatment with large amount of P_4S_{10} in the presence of triethylamine.[3,4] Upon heating 2 or 3, α,β-unsaturated thioketone monomers 1 are generated and react as heterodienes with a variety of dienophiles to give [4+2]cycloadducts.[3,4]



In the present paper, we wish to report the generation and reactions of more highly unsaturated thioketone, bis(arylmethylene)propanethione (5).

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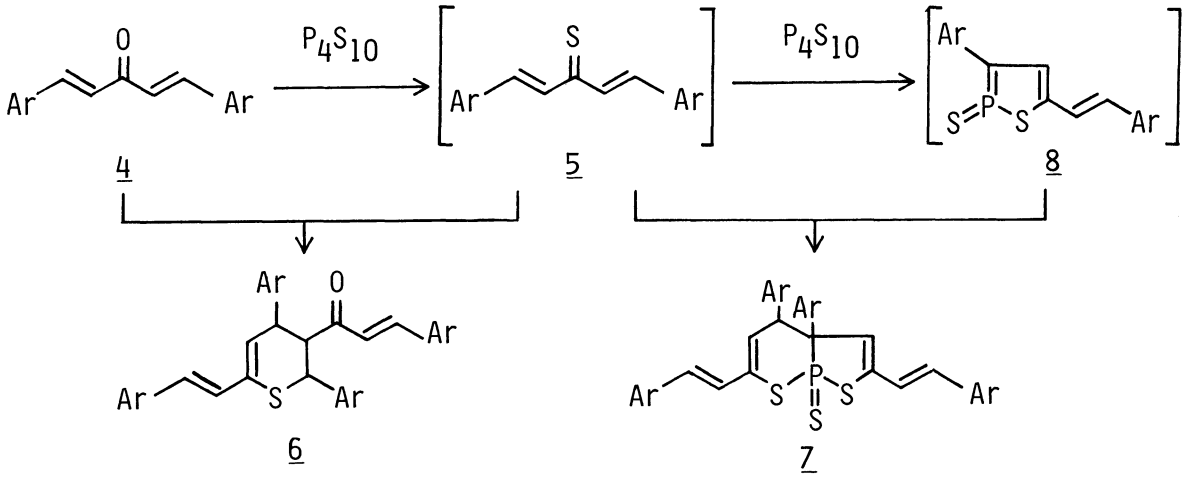
The reaction of bis(arylmethylene)propanone (4) and L.R. gave the product 6. Although this was the cycloadduct of 4 and 5, it was stable and did not generate 5 on heating.

On the other hand, 3,8-bis(2-arylvinyl)-5,6-diaryl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-sulfide (7) was obtained by use of a large excess of P_4S_{10} in the presence of triethylamine as follows: A suspension of 4a (2.62 g), P_4S_{10} (3 g), and NEt_3 (6 ml) in CS_2 (80 ml) was refluxed for 1 h. The reaction mixture was filtered and the filtrate was evaporated. The residue was chromatographed on Wakogel C-200 by eluting with benzene-hexane (1:2). The solvent was evaporated and the residue was recrystallized from hexane to give pale yellow crystals of 7a. The results are shown in Table 1.

Table 1. Synthesis of 3,8-bis(2-arylvinyl)-5,6-diaryl-2,9-dithia-1-phosphabicyclo[4.3.0]nona-3,7-diene 1-sulfide 7

	Ar	Reaction time /h	Yield %	Mp[a] °C	MS thione	MS thiaphosphole
a	*p*-Tol.	1	56	196-8	278(7)	308(100)
b	Ph	4	7	166-8	250(5)	280(100)
c	*p*-ClC_6H_4	3	23	172-5	318(8)	348(100)

a) All the products decomposed at the melting point.



It is considered that 7 was formed by the cycloaddition of thioketone 5 and thiaphosphole 8 as in the case of the formation of 3.[4)]

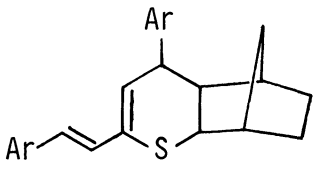
The structure of 7 was determined by the elemental analysis, the mass spectral fragmentation pattern, and the NMR spectral data (Table 2). The mass spectrum exhibited fragments of thioketone 5 and of thiaphosphole (8). The 100 MHz ^{1}H-NMR spectrum showed three signals of protons at 4-, 5-, and 7-positions with hydrogen-phosphorus coupling.

In the ^{13}C-NMR spectrum, two signals of saturated carbon atoms at 5- and 6-positions also showed carbon-phosphorus coupling.
Signals of the other unsaturated hydrogen or carbon atoms could not be assigned.

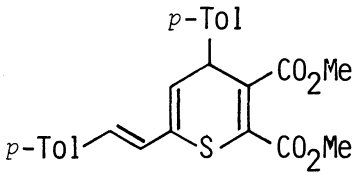
Table 2. ^{1}H- and ^{13}C-NMR Spectral data of the product 7

	H(4)			H(5)			H(7)		C(5)		C(6)	
	δ	J_{HP}	J_{HH}	δ	J_{HP}	J_{HH}	δ	J_{HP}	δ	J_{CP}	δ	J_{CP}
a	6.86	5.5	6	4.98	16	6	6.08	42	55.55	2.44	76.07	43.95
b	6.88	5.5	6	5.04	16	6	6.14	42	56.19	2.44	75.64	42.72
c	6.88	5.5	6	4.95	16	6	6.03	42	55.71	2.44	75.52	42.73

As expected from the mass spectral fragment, 5 was generated by thermolysis of 7 and trapped by 2-norbornene, dimethyl acetylenedicarboxylate (DMAD), diethyl azodicarboxylate (DAD) and acrylonitrile as [4+2]cycloadducts 9,10, 11, and 12 respectively.[5-7] To our knowledge, this is the first example of generation of α,β,α',β'-unsaturated thioketones.
Another component 8 could be trapped only by norbornene.



9a; Ar=*p*-Tol
9b; Ar=Ph



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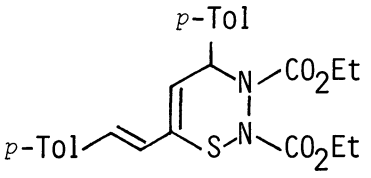

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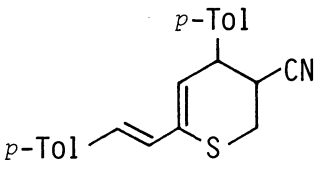

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Table 3. The reaction of 5 with dienophiles

	Reaction time/min[a)]	Yield %	
9a	120	77	colorless oil
9b	120	70	mp: 113-115 °C
10	30	78	orange oil
11	10	77	yellow oil
12[b)]	30	17	mp: 179-182 °C

a) All the reaction was carried out in refluxing benzene.
b) Formation of the regioisomer could not be confirmed.

It seems to be of interest that the diene moiety in the adducts 9-12 would be capable of undergoing successive cycloaddition reaction.
So, it is expected that the unsaturated thioketones 5 are available heterodienes for "diene-transmissive Diels-Alder reaction".[8]

References

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4) H. Tanaka, S. Kametani, T. Saito, and S. Motoki, Bull. Chem. Soc. Jpn., 58, 667 (1985).
5) All adducts were fully characterized by spectral and analytical data. (δ/ Hz) 9a: ^{1}H-NMR ($CDCl_3$) 1.03-2.40(9H,m), 2.03(3H,s), 2.34(3H,s), 3.02-3.20(2H,m), 6.20(1H,d,J=4.0), 6.60-6.85(2H,m), 7.02-7.32(8H,m); ^{13}C-NMR ($CDCl_3$) 21.06(q), 21.24(q), 29.19(t), 29.89(t), 34.05(t), 41.30(d), 43.76(d), 48.62(d), 50.79(d), 58.68(d). 9b: ^{1}H-NMR ($CDCl_3$) 1.00-2.30(9H,m), 3.01-3.22(2H,m), 6.21(1H,d, J=4.0), 6.62-7.02(2H,m), 7.08-7.40(10H,m); ^{13}C-NMR ($CDCl_3$) 29.14(t), 29.82(t), 34.01(t), 41.23(d), 43.66(d), 49.02(d), 50.73(d), 58.62(d). 10: ^{1}H-NMR ($CDCl_3$) 2.27(6H,S), 3.61(3H,s), 3.82(3H,s), 4.72(1H,d,J=6.0), 5.96(1H,d,J=6.0), 6.67 (2H,s), 7.02-7.28(8H,m); ^{13}C-NMR ($CDCl_3$) 21.06(q), 21.18(q), 52.30(q), 53.06 (q), 165.15(s), 165.97(s). 11: ^{1}H-NMR ($CDCl_3$) 0.81(3H,t,J=7.0), 1.29(3H,t, J=7.0), 2.32(3H,s), 2.33(3H,s), 3.81(2H,q,J=7.0), 4.27(2H,q,J=7.0), 5.96(2H,S), 6.54(1H,d,J=16.5), 6.76(1H,d,J=16.5), 7.04-7.33(8H,m); ^{13}C-NMR ($CDCl_3$) 13.79 (q), 14.57(q), 21.10(q), 21.30(q), 63.02(t), 63.46(t), 154.64(s). 12: ^{1}H-NMR ($CDCl_3$) 2.33(6H,s), 3.08(2H,d,J=6.0), 3.22-3.42(1H,m), 3.85(1H,dd,J=5.0, 5.0), 5.90(1H,d,J=5.0), 6.72(2H,s), 7.04-7.33(8H,m); ^{13}C-NMR ($CDCl_3$) 21.10(q), 21.25 (q), 25.54(t), 32.51(d), 41.96(d), 118.72(s).
6) In the ^{13}C-NMR spectra of 9a and 9b, the C-7 resonances are shifted upfield 4.02 and 4.06 ppm respectively in comparison with those of norbornane (=38.07). This indicates that 9a and 9b have exo configuration.
7) The cis-trans relationship between tolyl and cyano group in 12 could not be determined by the NMR spectra.
8) O. Tsuge, S. Kanemasa, E. Wada, and H. Sakoh, Yuki Gosei Kagaku Kyokai Shi, 44, 756 (1986).

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