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 (P₄S₁₀) to give the dimer (<u>2</u>) of corresponding thicketones (<u>1</u>),^{1,2}) whereas, the ketones give phosphorus-containing compounds (<u>3</u>) by treatment with large amount of P₄S₁₀ in the presence of triethylamine.^{3,4}) Upon heating <u>2</u> or <u>3</u>, α , β -unsaturated thicketone monomers <u>1</u> 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 thicketone, bis(arylmethylene) propanethione (5).

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The reaction of bis(arylmethylene)propanone ($\underline{4}$) and L.R. gave the product $\underline{6}$. Although this was the cycloadduct of $\underline{4}$ and $\underline{5}$, it was stable and did not generate $\underline{5}$ 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 ($\underline{7}$) was obtained by use of a large excess of P₄S₁₀ in the presence of triethylamine as follows: A suspension of <u>4a</u> (2.62 g), P₄S₁₀ (3 g), and NEt₃ (6 ml) in CS₂ (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 <u>7a</u>. 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	Yield	Mp ^a)	MS	
-		time /h	સ્ટ	°C	thione	thiaphosphole
a	p-Tol.	1	56	196-8	278(7)	308(100)
b	Ph	4	7	166-8	250(5)	280(100)
с	$p-ClC_6H_4$	3	23	172-5	318(8)	348(100)

a) All the products decomposed at the melting point.



It is considered that $\underline{7}$ was formed by the cycloaddition of thicketone $\underline{5}$ and thiaphosphole $\underline{8}$ as in the case of the formation of $\underline{3}$.⁴⁾

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

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

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



As expected from the mass spectral fragment, <u>5</u> was generated by thermolysis of <u>7</u> and trapped by 2-norbornene, dimethyl acetylenedicarboxylate (DMAD), diethyl azodicarboxylate (DAD) and acrylonitrile as [4+2]cycloadducts <u>9,10</u>, <u>11</u>, and <u>12</u> respectively.⁵⁻⁷⁾ To our knowledge, this is the first example of generation of $\alpha, \beta, \alpha', \beta'$ -unsaturated thioketones.

Another component $\underline{8}$ could be trapped only by norbornene.



Table 3. The reaction of 5 with	dienophiles
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	Reaction time/min ^{a)}	Yield %	
<u>9a</u>	120	77	colorless oil
<u>9b</u>	120	70	mp: 113-115 °C
<u>10</u>	30	78	orange oil
11	10	77	yellow oil
<u>12</u> 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 thicketones 5 are available heterodienes for "diene-transmissive Diels-Alder reaction".⁸)

References

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- 5) All adducts were fully characterized by spectral and analytical data. (δ / Hz) <u>9a</u>: ¹H-NMR (CDCl₃) 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); ¹³C-NMR (CDCl₃) 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). <u>9b</u>: ¹H-NMR (CDCl₃) 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); ¹³C-NMR (CDCl₃) 29.14(t), 29.82(t), 34.01(t), 41.23(d), 43.66(d), 49.02(d), 50.73(d), 58.62(d). <u>10</u>: ¹H-NMR (CDCl₃) 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); ¹³C-NMR (CDCl₃) 21.06(q), 21.18(q), 52.30(q), 53.06 (q), 165.15(s), 165.97(s). <u>11</u>: ¹H-NMR (CDCl₃) 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); ¹³C-NMR (CDCl₃) 13.79 (q), 14.57(q), 21.10(q), 21.30(q), 63.02(t), 63.46(t), 154.64(s). <u>12</u>: ¹H-NMR (CDCl₃) 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); ¹³C-NMR (CDCl₃) 21.10(q), 21.25 (g), 25.54(t), 32.51(d), 41.96(d), 118.72(s).
- 6) In the ¹³C-NMR spectra of <u>9a</u> and <u>9b</u>, 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 $\underline{12}$ could not be determined by the NMR spectra.
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