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2,9-DITHIA-1-THIOXOPHOSPHABICYCLO[4.3.0]NONA-3,7-DIENES. PRECURSORS OF NEW TYPE HETERODIENES, 2-THIOXO-1,2-THIAPHOSPHOLES

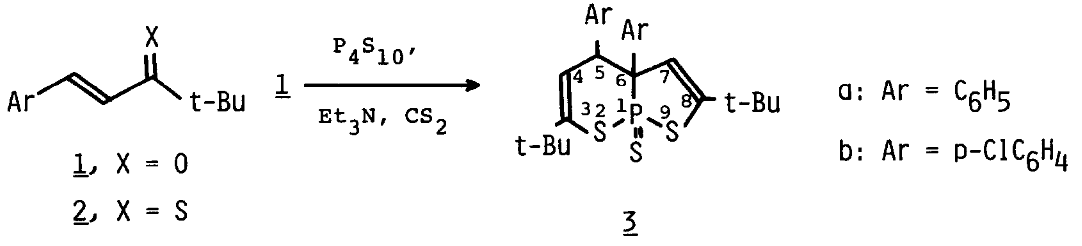
Hiroshi Yamaguchi, Shunichi Kametani, Takayuki Karakasa,
Takao Saito, and Shinichi Motoki*

Department of Chemistry, Faculty of Science, Science University of Tokyo,
Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

Summary: The reaction of arylmethylenepinacolones, chalcones and 2-arylmethylene-1-tetralones with P_4S_{10} in the presence of triethylamine gave the title compounds, from which 2-thioxo-1,2-thiaphospholes (phosphathiophenes) were generated by the thermolysis and reacted with acrylonitrile to give [4+2]cycloadducts.

Recently, we found that α,β-unsaturated thiones derived from thiochalcone and 2-arylmethylene-1-tetralinthione dimers readily underwent cycloaddition reaction with various dienophiles.[1-3)]

As a continuation of the work, we now attempted the thionation of arylmethylenepinacolone 1, anticipating isolation of monomeric thiopinacolone 2. However, the unexpected product, bicyclic thiophosphonic acid derivative 3 was obtained as follows: A suspension of 1a (18,8g), P_4S_{10} (30g), and triethylamine (60 ml) in carbon disulfide (200 ml) was refluxed for 10 hr. The reaction mixture was filtered and the filtrate was evaporated. The residue was recrystallized from ethanol to give colorless crystals (4.60g, 20% yield; mp 205-209 °C dec). The product had the molecular formula $C_{26}H_{31}S_3P$ and its X-ray analysis[4)] proved the structure 3a:[5)] Bond lengths; P-S 2.097(6) Å (5-, 6-rings); P=S 1.933(7); P-C (bridge) 1.90(2); C-S 1.78(1) (5-ring), 1.80(1) (6-ring); C=C 1.30(2) (5-ring), 1.38(2) (6-ring); C-C 1.50(2) (5-ring), 1.49(2) (6-ring, C-4-a), 1.63(3) (6-ring, C-5-a).



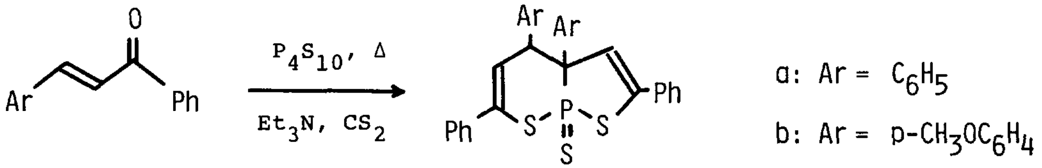
1, X = O
2, X = S

3

a: Ar = C_6H_5
b: Ar = p-ClC_6H_4

Scheme 1

The mass spectral fragmentation pattern and the ^{1}H-NMR and ^{13}C-NMR spectral data also gave a strong substantiation for the structure 3a. The assignments were as follows: MS (70 eV) m/e 470 (3, M^+), 266 (19, $8a^+$), 234 (47), 219 (79), 204 (34, $2a^+$), 203 (32), 147 (100, $2a^+$ -t-Bu); ^{1}H-NMR ($CDCl_3$) δ 1.22 (s, 9H, t-Bu), 1.27 (s, 9H, t-Bu), 4.76 (dd, J_{PH}= 19.5 Hz, J_{HH}= 5.5 Hz, H(5)), 5.76 (d, J_{PH}= 41 Hz, H(7)), 6.26 (dd, J_{PH}= 5.5 Hz, J_{HH}= 5.5 Hz, H(4)), 7.0-7.3 (m, 10H, Ar-H); ^{13}C-NMR δ 29.1 [$C(\underline{C}H_3)_3$], 29.9 [$C(\underline{C}H_3)_3$], 37.4 [d, J_{PC}= 2.4 Hz, $\underline{C}(CH_3)_3$], 37.8 [$\underline{C}(CH_3)_3$], 55.5 [C(5)], 75.5 [d, J_{PC}= 42.7 Hz, C(6)], 117.8, 118.2, 127.0-130.8 (m), 135.9, 138.9, 139.5, 147.8, 148.1, 153.9, 154.1; ^{31}P-NMR ($CDCl_3$, 85% H_3PO_4) δ 117.13 (dd, J_{PH}= 41 Hz, J_{PH}= 19.5 Hz). Similarly, treatment of 1b with P_4S_{10} and triethylamine afforded the product 3b: colorless crystals (10% yield), mp 220-223 °C dec; MS m/e 538 (M^+), 300 (20, $8b^+$), 268 (54), 233 (94), 238 (27, $2b^+$), 181 (100, $2b^+$ -t-Bu); ^{1}H-NMR ($CDCl_3$) δ 1.22, 1.27 (s, 9H, t-Bu), 4.67 (dd, J_{PH}= 20 Hz, J_{HH}= 5.5 Hz, H(5)), 5.66 (d, J_{PH}= 42 Hz, H(7)), 6.17 (dd, J_{PH}= 5.5 Hz, J_{HH}= 5.5 Hz, H(4)), 6.9-7.3 (m, 8H, Ar-H); ^{13}C-NMR δ 29.1, 29.9 [$C(\underline{C}H_3)_3$], 37.5 [d, J_{PC}= 3.7 Hz, $\underline{C}(CH_3)_3$], 37.8 [$\underline{C}(CH_3)_3$], 54.9 [d, J_{PC}= 2.4 Hz, C(5)], 74.8 [d, J_{PC}= 43.9 Hz, C(6)], 116.7, 117.1, 127.9-134.3 (m), 137.2, 137.7, 148.5, 155.1, 155.4.

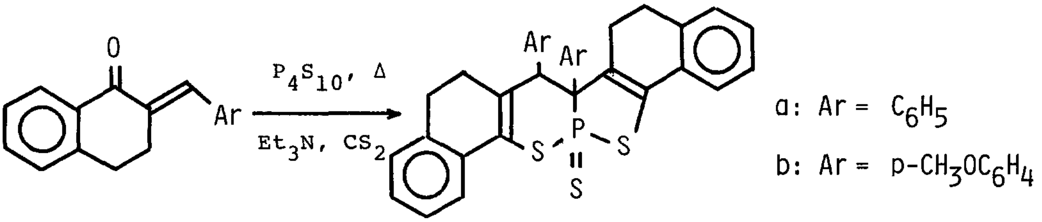


4

5 a: 43% yield

b: 57% yield

Scheme 2



6

7 a: 6% yield

b: 22% yield

Scheme 3

Though the reaction of 4 and 6 with P_4S_{10} exclusively gave the correaponding thione dimers, refluxing of the CS_2 solution (2 hr) and use of a large amount of P_4S_{10} and Et_3N also produced 5 and 7, respectively (Schemes 2 and 3). The structures of 5 and 7 were proved by elemental analyses and ^{1}H-NMR and ^{13}C-NMR spectral determinations compared with those of 3 (Tables 1 and 2).5) Mass spectral fragmentation pattern also supported the proposed structure.

Table 1. ^{13}C-NMR Spectral Data of 5 and 7.

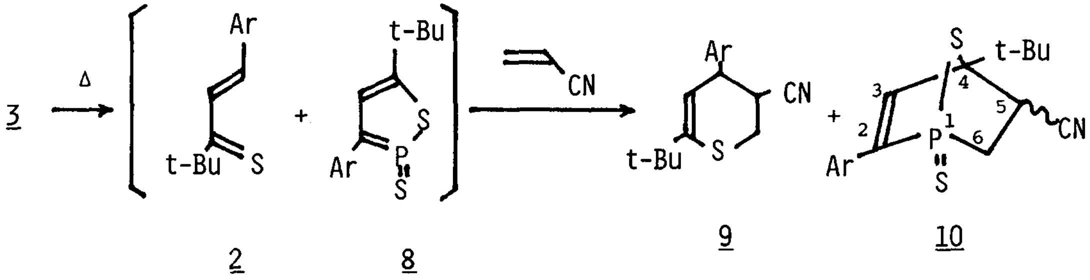
	δ C(5)	δ C(6)	$J_{PC(5)}$	$J_{PC(6)}$
5a	56.7	77.2	2.9 Hz	42.7 Hz
5b	55.9	77.0	2.4 Hz	41.5 Hz
7a	56.4	71.9	3.7 Hz	41.5 Hz
7b	56.5	75.5	~ 0 Hz	41.5 Hz

Table 2. ^{1}H-NMR Spectral Data of 5 and 7.

	δ H(4)	δ H(5)	δ H(7)	J_{HH}	$J_{PH(4)}$	$J_{PH(5)}$	$J_{PH(7)}$
5a	6.82	5.06	6.35	5 Hz	5.5 Hz	18 Hz	42 Hz
5b	*	4.96	6.30	5 Hz	*	18 Hz	42 Hz
7a	-	4.28	-	-	-	28 Hz	-
7b	-	4.89	-	-	-	38 Hz	-

* superimposed on Ar-H.

As expected from the mass spectral fragments, thermolysis of 3 in benzene generated thione monomer 2 and 2-thioxo-1,2-thiaphosphole 8, both of which were trapped by acrylonitrile to give 9 (a: 96% yield, mp 137-138 °C, b: 78% yield, mp 149-151 °C) and 10 (a: 54% yield, mp 142-143 °C, b: 40% yield, mp 145-147 °C), respectively (Scheme 4).5)



Scheme 4

The products $\underline{9}$ were readily identified as [4+2]cycloadducts of $\underline{2}$ and acrylonitrile by comparison with the related compounds.$^{1)}$ The product $\underline{10a}$ showed a ν_{CN} absorption at 2250 cm^{-1} in the IR spectrum, and the signals of one olefinic proton (δ 7.25, d, J_{PH}= 16 Hz) and complex ABX-type three protons ($-CH_2CH-$, 2.39-2.64, 2.88-3.25, 3.56-3.72, m) in addition to single t-butyl and phenyl group in the ^{1}H-NMR spectrum. In the ^{13}C-NMR spectrum, each carbon signal of >C(2)=, -HC(3)=, C(4), HC(5), and $H_2C(6)$ was observed at δ 146.1, 141.1, 74.9, 33.4, and 42.4, respectively, in which two sets of signals with large coupling constants (δ 146.1, J_{PC}= 60 Hz; δ 42.4, J_{PC}= 43 Hz) were easily attributable to the carbon atom at 2- and 6-positions directly attached to the phosphorus atom.$^{6)}$ The ^{31}P-NMR spectrum showed the presence of one kind of phosphorus atom (δ 70.26, d of m). The mass spectrum exhibited the molecular ion peak (319, 2%) and a fragment assignable to $\underline{8a}$ (266, M^+ -53, 100%) which would be formed by retro-Diels-Alder cleavage of $\underline{10a}$. The structure of $\underline{10b}$ was similarly confirmed.$^{5)}$

It seems to be interesting that $\underline{3}$, $\underline{5}$, and $\underline{7}$ have novel structures and generate 2-thioxo-1,2-thiaphospholes, which react as dienes in cycloaddition reaction with acrylonitrile.

References and Notes

1) T. Karakasa and S. Motoki, J. Org. Chem., 43, 4147 (1978).
2) Idem, ibid., 44, 4151 (1979).
3) T. Karakasa, H. Yamaguchi, and S. Motoki, ibid., 45, 927 (1980).
4) The authors thank Prof. Dr. Uchida for performing the X-ray analysis. Detailed data will be published elsewhere.
5) All the new compounds obtained gave satisfactory elemental analyses.
6) E. F. Moony "ANNUAL REPORTS ON NMR SPECTROSCOPY VOL. 5B", Academic Press, New York, 1973, p. 12.

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