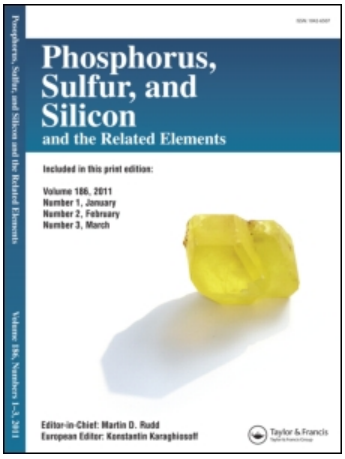

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Synthesis of New Heterocyclic Compounds Using Lawesson Reagent

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*Lawesson reagent **1** reacts with Mannich bases of β-naphthol **2** and 8-hydroxyquinoline **4** to give oxthiaphosphinine-3-sulfide derivatives **3** and **5**, respectively. Reaction of **1** with benzaldehyde in the presence of trialkyl phosphite yields 1,3,5,2-trithiaphosphinane-2-sulfide derivative **8** and, in the presence of ethyl acrylate, affords 2,4,6-triphenyl-1,3,5-trithiane **9**. A mechanism is proposed to explain the formation of adduct **3**.*

Keywords Mannich bases; Lawesson reagent; benzaldehyde; trialkyl phosphite; ethyl acrylate

INTRODUCTION

In previous articles[1–3] we reported on the reactions of 2,4-bis-(4-methoxy-phenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulphide (Lawesson reagent) **1** with certain active centers. Extending this work, we have now investigated the reactions of reagent **1** with some Mannich bases and benzaldehyde.

RESULTS AND DISCUSSION

We have found that compound **1** reacts with 1-dimethylaminomethyl-2-naphthol **2** in refluxing dry toluene to give 3-(4-methoxyphenyl)-1H-naphtho [1,2-e]-1,3,2-oxathiaphosphinine-2-sulfide **3**. Structure **3** is deduced from correct microanalyses, MS, IR, ^{1}H-NMR, and ^{31}P-NMR. (a) Elemental analyses and the molecular weight determination of adduct **3** correspond to $C_{18}H_{15}O_2PS_2$.

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(b) The MS of 3 showed a prominent peak at m/e 358 (M^+, 50%); the loss of the S atom from the M^+ affords the positive ion radical at m/e 326 (49%); the further loss of the S atom from the latter gives rise to the positive radical ion at m/e 294 (30%); the ejection of the CH_3O-C_6H_4-PO radical from the latter gives a radical at 140 (75%). Also there is a peak at 156 (25%), which originates from the expulsion of the CH_3O-C_6H_4-PS_2 radical from the parent ion.

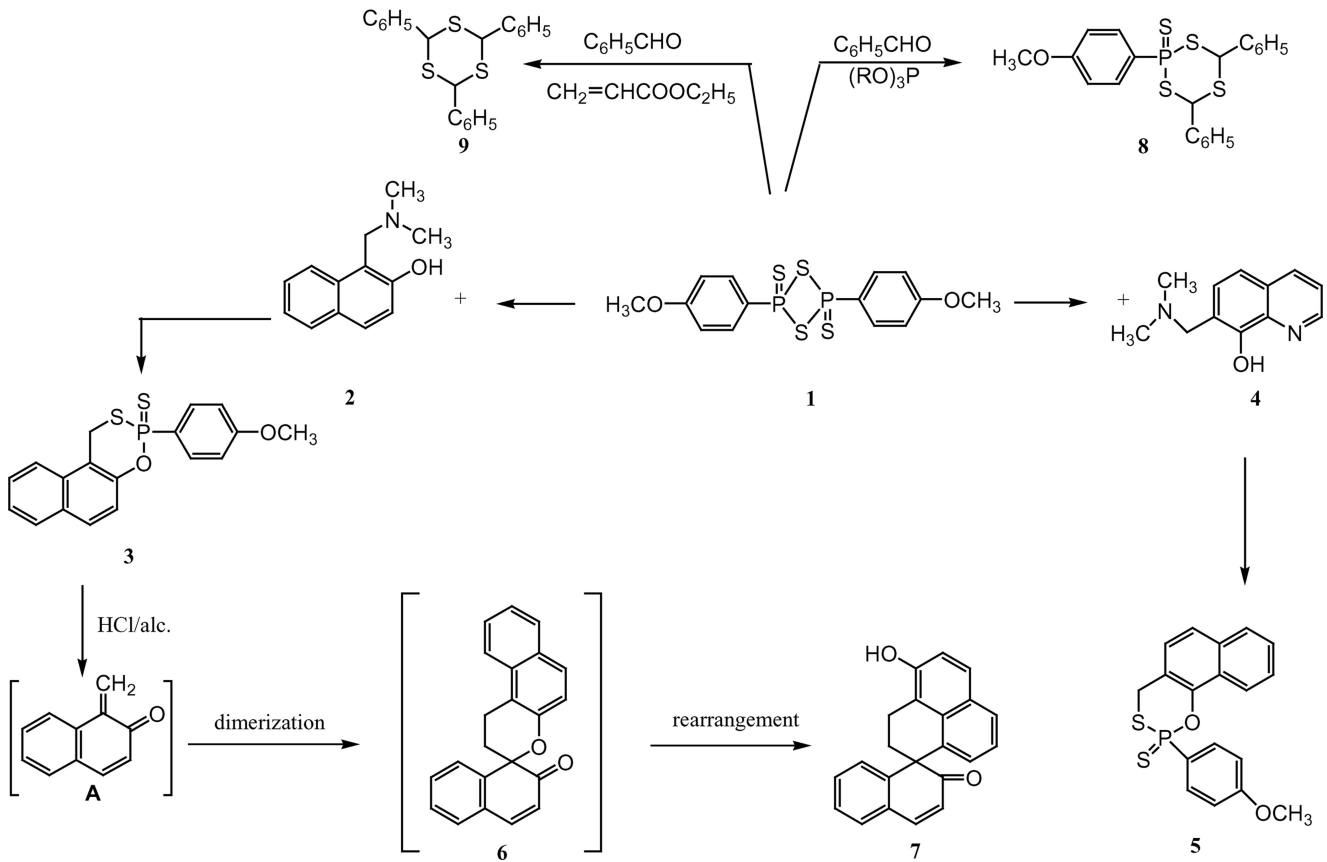
(c) The IR spectrum of adduct 3 (in KBr) reveals the absence of the OH group of the Mannich base; it gives an absorption band at 1445 (P-C-aryl),[4] and 1595 (C=C aromatic). (d) The ^{1}H-NMR showed a singlet at $\delta = 3.9$(3H, OCH_3), two triplets at $\delta = 4.7$ and 4.11 with a coupling constant $J_{HH} = 16.50$ Hz (for the two unequivalent hydrogen atoms of the CH_2 group), and a multiplet at $\delta = 7.25 - 8.10$ (10 H, aromatic protons). (e) The ^{31}P-NMR gave a positive chemical shift (vs. 85% H_3PO_4) at $\delta = 90.95$ ppm.[5]

Adduct **3** can be hydrolyzed by the action of alcoholic hydrochloric acid on refluxing to give 1′,2,2′,3-tetrahydro-4-hydroxyphenalene-1-spiro-1′-naph-thalene-2′-one **7** through the dimerization of A to give 6 and the rearrangement of **6**. Compound **7** was identified from m.p., mixed m.p. 239°C, IR, and MS with an authentic sample (cf. Scheme 1).[6]

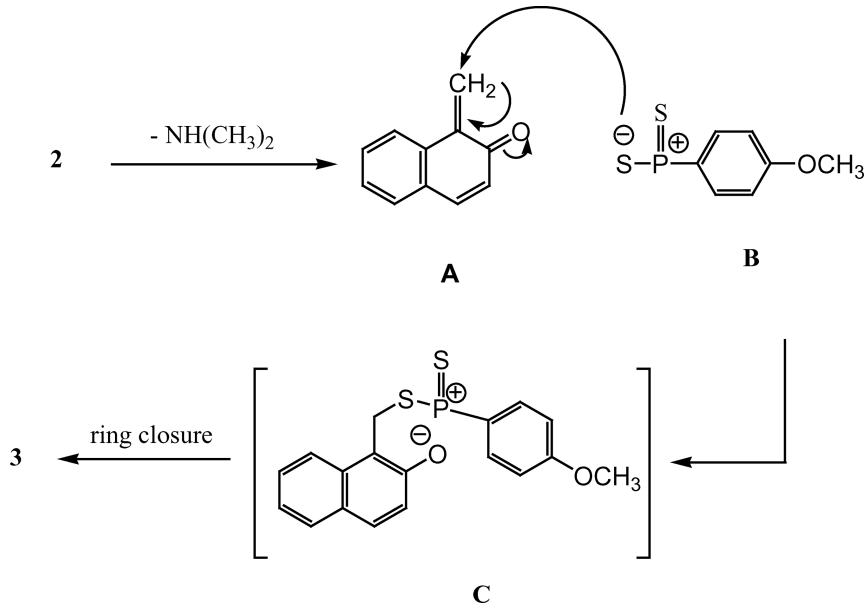
A mechanism accounting for the formation of structure **3** is depicted in Scheme 2. The Mannich base **2** loses a molecule of dimethylamine to give the o-quinonemethide **A**; a nucleophilic attack on the methine group of **A** by the sulfur anion of the monomeric species **B** existing probably in equilibrium with reagent[7–9] **1** can produce the dipolar form **C**. The latter undergoes ring closure to give the end product **3**.

In a similar manner, reagent **1** reacts with 7-dimethylaminomethyl-8-hydroxyquinoline **4** in refluxing toluene to yield 2-(4-methoxyphenyl)-4H-[1,3,2]-oxathiaphosphinino[5,6-H]quinoline-2-sulfide **5**, which is verified by spectral data and correct combustion values, which correspond to $C_{17}H_{14}NO_2PS_2$ (cf. Experimental).

Next, when reagent **1** is allowed to react with benzaldehyde in refluxing toluene, a polymerized product is formed, which could not be isolated, but when the same reaction is repeated in the presence of trimethyl or triethyl phosphite, 2-(4-methoxyphenyl)-4,6-diphenyl-1,3,5,2-trithiaphosphinane-2-sulfide **8** is produced. Structure **8** is based on the correct microanalyses, which correspond to $C_{21}H_{19}OPS_4$ and on ^{1}H-NMR, MS, and ^{31}P-NMR. The ^{1}H-NMR gave a singlet at $\delta = 3.95$ (3H, OCH_3), a doublet at $\delta = 6.82$ with coupling constant $J_{HP} = 12.50$ Hz(2H, $2\,C_6\,H_5\,CH$), and a multiplet at $\delta = 7.40 - 8.20$ (14 aromatic protons). The ^{31}P-NMR gave a chemical shift at around $\delta = 89.05$.[10] The same adduct **8** is obtained when we used triethylamine



SCHEME 1



SCHEME 2

instead of trialkyl phosphite. This may explain that trialkyl phosphite acts as a base in this reaction.

When we use ethyl acrylate in the reaction of **1** with benzaldehyde in refluxing toluene, 2, 4, 6-triphenyl-1,3,5-trithiane **9** is isolated. The formation of the adduct **9** arises from the thiation of benzaldehyde by reagent **1** to give thiobenzaldehyde which polymerized under the experimental condition to give the trimer **9**. Structure **9** is based on the correct analytical and spectroscopic evidence (cf. Experimental).

This finding gives us the idea that using L.R. represents a novel route for the synthesis of heterocyclic systems containing a phosphorus and/or sulfur moiety; these heterocyclic systems are interesting in the field of pesticidal chemistry.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were measured in KBr on a Perkin-Elmer Infracord spectrometer Model 157G (Grating). The ^{1}H-NMR spectra were done on a JEOL JNM-EX 270 FTNMR system. The ^{31}P-NMR spectra were run on a Varian FT-80 spectrometer (vs. 85% H_3PO_4). The MS spectra were performed at 70 eV on a

Finnigan MAT SSQ 7000 spectrometer. The microanalyses were carried out at the Microanalytical Centre, Cairo University, Cairo, Egypt.

Reaction of Mannich Base 2 or 4 With Lawesson Reagent 1

A mixture of the Mannich base **2** or **4** (0.001 mole) and reagent **1** (0.001 mole) in 40 mL of dry toluene was refluxed for 12 h. After cooling to r.t., the reaction mixture was evaporated on silica gel under reduced pressure and applied to a silica-gel column using the suitable solvent stated in the following section.

3-(4-Methoxyphenyl)-1H-naphtho-[1,2-e][1,3,2]-oxathiaphosphinine-2-sulfide (3)

Eluent, methylene chloride/petroleum ether 40/60 (2:3), yield 62%, pale yellow crystals m.p. 220°C; $C_{18}H_{15}O_2PS_2$(358), Calcd: C, 60.32; H, 4.22; P, 8.64; S, 17.98. Found: C, 60.30; H, 4.30; P, 8.69; S = 18.00.

2-(4-Methoxyphenyl)-4H-[1,3,2]oxathiaphosphinino[5,6-h]-quinoline-2-sulfide (5)

Eluent, acetone/petroleum ether (1:3), yield 51%, straw yellow crystals m.p. 198°C. IR, 1445 (P-C-aryl), 1570–1580 (C=C aromatic). ^{1}H-NMR, $\delta = 3.8$(3H, OCH_3), $\delta = 7.15 - 7.85$ (9 aromatic protons, m), $\delta = 4.8$ (2H, CH_2, d, $J_{HP} = 13.00$ Hz). $C_{17}H_{14}NO_2PS_2$ (359.4), Calcd: C, 56.81; H, 3.93; N, 3.90; P, 8.62; S, 17.84. Found: C, 56.79; H, 3.90; N, 3.92; P, 8.68; S, 17.92. MS, 359 (M^+), 327 (M^+-S), 295 (327-S), 141 (295-CH_3O-C_6H_4PO).

Action of Alcoholic Hydrochloric Acid on 3

Adduct 3 (0.001 mole) in 7 mL of HCl (20%) and 3 mL of ethanol were refluxed on a water bath for 2 h; the mixture was concentrated on a water bath and neutralized with 5% NaOH. The precipitate formed was collected and extracted with ethyl acetate to give **7**; m.p. and mixed m.p. 239°C, MS, 312 (100%); IR and NMR are identical with that of the authentic sample.[6]

Reaction of Reagent 1 With Benzaldehyde in the Presence of Trialkyl Phosphite

A mixture of **1** (0.005 mole), benzaldehyde (0.005 mole), and trimethyl or triethyl phosphite (0.005 mole) was refluxed in dry toluene (40 mL) for 15 h, the volatile materials were removed under reduced pressure, then the residue was placed on a column of silica gel and eluted with

a mixture of chloroform/petroleum ether (3:1) to give **8** in a 55% yield; m.p. 188°C, MS, 446 (M^+ 30%), 324 (M^+-C_6H_5CHS, 202 (324-C_6H_5S), 138 (202-2S).

Reaction of 1 with Benzaldehyde in the Presence of Ethyl Acrylate

In a similar manner, **1** reacted with benzaldehyde in the presence of ethyl acrylate (0.005 mole) eluted with acetone/petroleum ether (1:2), and gave **9** as pale yellow crystals, m.p. 150°C in a 45% yield. The ^{1}H-NMR of **9** showed a singlet at $\delta = 5.85$ (3H, 3 C_6H_5CH), $\delta = 7.30 - 7.50$ (15 aromatic protons multiplet). $C_{21}H_{18}S_3$ (363.5), Calcd: C, 68.81; H, 4.95; S, 26.24. Found: C, 68.83; H, 4.93; S, 26.22. MS, 366 (M^+ 100%), 244 (M^+-C_6H_5CHS 80%), 122 (244-C_6H_5CHS 70%) and 90 (122-S, 20%).

REFERENCES AND NOTES

[1] A. A. El-Kateb, I. T. Hennawy, R. Shabana, and H. A. Abdel-Maleck, *Phosphorus, Sulfur, and Silicon*, **63,** 13 (1991).
[2] A. A. El-Kateb, R. Shabana, and F. H. Osman, *Z. Naturforsch*, **39,** 1614 (1984).
[3] A. A. El-Kateb, I. T. Hennawy, R. Shabana, and F. H. Osman, *Phosphorus and Sulfur*, **20,** 329 (1984).
[4] M. Hesse, H. Meier, and B. Zech, Spectroskopische Methoden in der Organischen Chemie (G. Thiem Verlag, Stuttgart), 1979.
[5] A. A. El-Barbary and S. O. Lawesson, *Tetrahedron*, **37,** 2641 (1981).
[6] G. Catterall, *J. Chem. Soc. Chem. Comm.*, 41 (1974).
[7] M. Yoshifuji, K. Toyta, K. Ando and N. Inamoto, *Chem. Lett.*, 317 (1984).
[8] R. Appel, F. Knoch, and H. Kunze, *Angew. Chem.*, **95,** 1008 (1983).
[9] S. Bracher. J. I. G. Cadogan, I. Gosney, and S. Yaslak, *J. Chem. Soc. Comm*., 857 (1983).
[10] S. Scheiby, R. Shabana, S. O. Lawesson, and C. Roemming, *Tetrahedron*, **38,** 993 (1982).