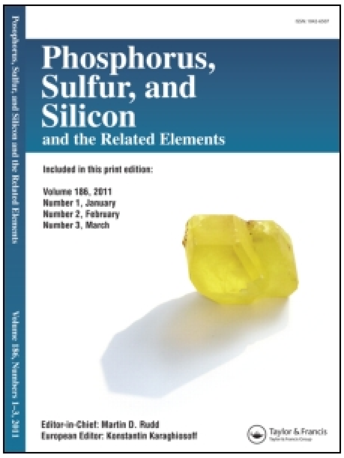

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

NEW ORGANOPHOSPHORUS COMPOUNDS FROM 2-HYDROXY-4-AMINO BENZOIC ACID

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To cite this Article Fahmy, Afaf A.(1991) 'NEW ORGANOPHOSPHORUS COMPOUNDS FROM 2-HYDROXY-4-AMINO BENZOIC ACID', Phosphorus, Sulfur, and Silicon and the Related Elements, 63: 1, 81 — 86

To link to this Article: DOI: 10.1080/10426509108029430

URL: http://dx.doi.org/10.1080/10426509108029430

Phosphorus, Sulfur, and Silicon, 1991, Vol. 63, pp. 81–86
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NEW ORGANOPHOSPHORUS COMPOUNDS FROM 2-HYDROXY-4-AMINO BENZOIC ACID

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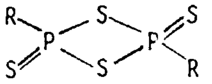
(Received January 28, 1991; in final form May 28, 1991)

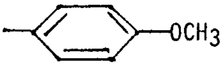
Dimethyl and diethyl phosphite add to carbon-nitrogen double bond in compound 2-hydroxy-4-(2-thenylidene) amino benzoic acid **III**$_b$ to give the corresponding phosphonates **IV**$_a$ and **IV**$_b$. 1,3,2,4-Dithiadiphosphetane-2,4-disulfides **I**$_a$ and **I**$_b$ react with 2-hydroxy-4-amino benzoic acid **II** and **III**$_b$ to give cyclic compounds **V**$_{a,b,c}$ and **V**$_d$, respectively. The given structures were based upon analytical, chemical and spectroscopic results.

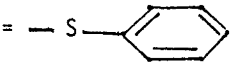
Key words: Schiff base; alkyl phosphite; 2-hydroxy-4-amino benzoic acid; Lawesson and Japanese reagents.

It has been found that 2,4-bis (4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, Lawesson reagent (LR), **I**$_a$ and 2,4-bis (phenyl thio)-1,3,2,4-dithiadiphosphetane, 2,4-disulfide Japanese reagent (JR), **I**$_b$ are potent thiating agents for diverse carbonyl compounds e.g. ketones,[1] esters[2] and lactans.[3] The reagents LR and JR easily available and undergo also ring-closure reactions with substrates containing two functional groups.[4–7]



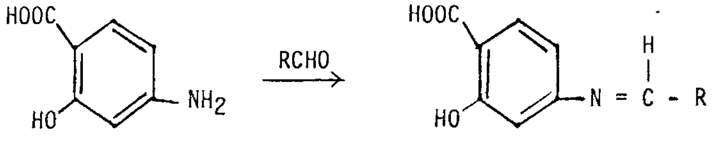
I

a, R = 

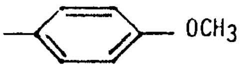
b, R = 

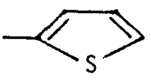
To extend the use of **I**$_{a,b}$ to the other bifunctional substrates, its reactions with 2-hydroxy-4(2-thenylidene) aminobenzoic acid **III**$_b$, have been investigated and found to give new phosphorus heterocycles. Our results are reported in this paper.

II reacted with aromatic aldehydes, namely, 4-methoxy benzaldehyde and 2-thiophen aldehyde to yield **III**$_a$ and **III**$_b$.



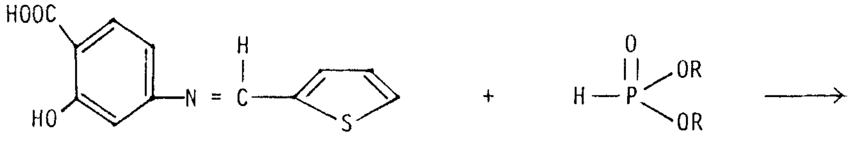
II

III a, R = 

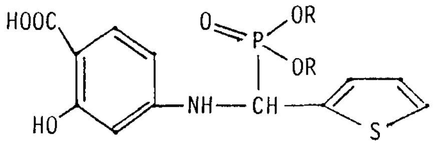
b, R = 

The IR spectrum of compound **III$_a$** (using KBr), as an example, showed the characteristic bands 1650 cm^{-1} ($>$C=N—), 1600 cm^{-1} (aromatic band) and 2840–2820 cm^{-1} (—OCH$_3$).[8] The ^{1}H NMR showed aromatic protons in the region δ 7.8–8.8 ppm (7H, multiplet), at δ 3.3 ppm (O—CH$_3$, s) and the methine proton at δ 4.1 ppm.[9]

Compound **III$_b$** was allowed to react with dimethyl phosphite (DMP) and diethyl phosphite (DEP) in absence of solvent at 100°C to give the phosphonates adducts **IV$_a$** and **IV$_b$**,[10,11] which were confirmed by elemental analyses (Table I), molecular weight determination (MS), IR and ^{1}H-NMR spectra.



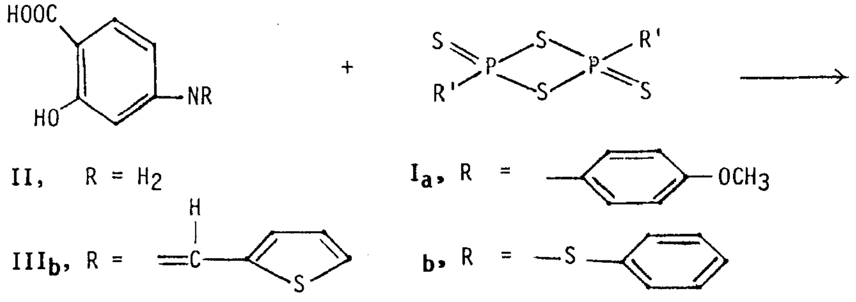
III$_b$

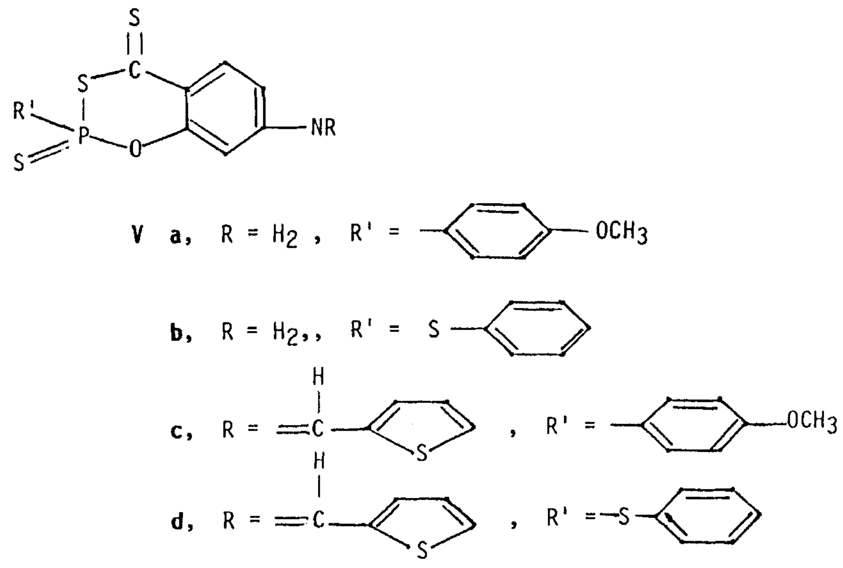


IV a, R = CH$_3$
b, R = C$_2$H$_5$

The mechanism for the addition of HP(O)(OR)$_2$ to the C=N bond is probably nucleophilic attack on the C=N bond on the phosphite. The IR spectrum of **IV$_b$** (using KBr) as an example was quite consistent with the assigned structure. It showed bands at 3400 cm^{-1} (—NH), 1600 cm^{-1} (aromatic band), 1250 cm^{-1} (P=O) and at 1050 cm^{-1} (P—O—C$_2$H$_5$). Its NMR spectrum showed aromatic protons in the region δ 8.0–9.0 ppm (6H), methine proton at δ 4.3 ppm, signals at δ 3.6 ppm (4H, ethoxy CH$_2$, q), δ 1.6 ppm (6H, ethoxy CH$_3$, t) and the NH proton appears as a doublex of doublets in the region δ 12.0–12.5 ppm.

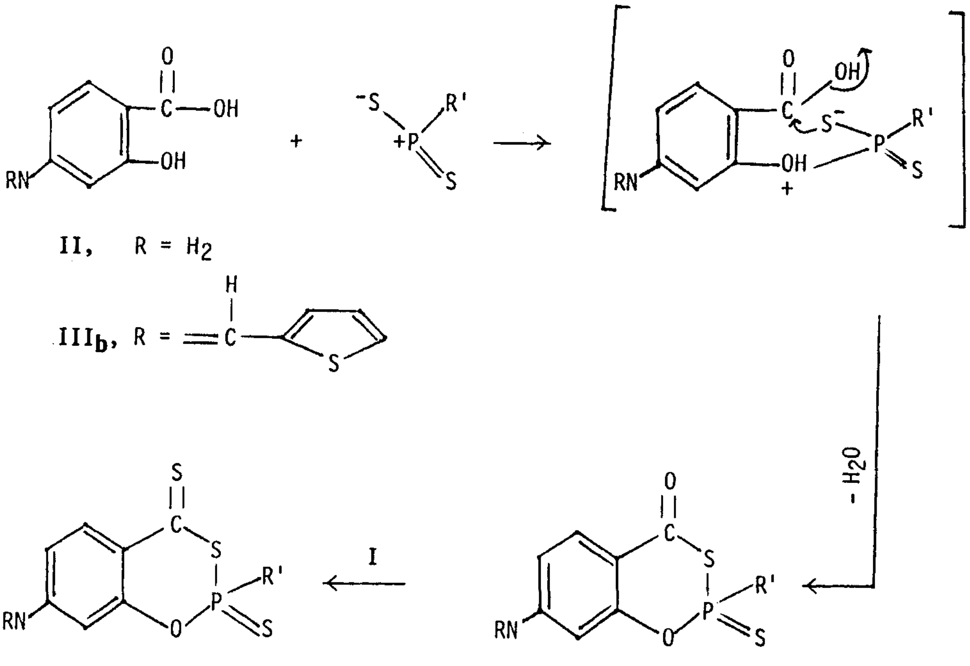
By refluxing **II** and **III$_b$** in boiling dry toluene with LR, **I$_a$** and JR, **I$_b$** new phosphorus heterocycles **V$_a$**, **V$_b$**, **V$_c$** and **V$_d$** are formed respectively.



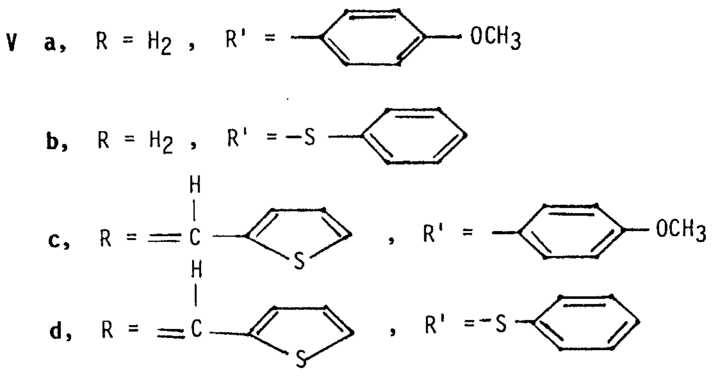


The structures of the aforementioned compounds were confirmed by elemental analyses (Table I), molecular weight determination MS, IR, ^{1}H-NMR and ^{31}P NMR spectra.

A possible explanation[7] of the reaction of **II** and **III**$_b$ with **I**$_a$ and **I**$_b$ can be illustrated in "Scheme A".



Scheme A



Scheme A (*Continued*)

Taking **V**$_a$ and **V**$_d$ as examples, the elemental analyses of **V**$_a$ corresponded to $C_{14}H_{12}NS_3PO_2$, the IR spectrum (using KBr) revealed the OH and COOH absorption bands and showed absorption bands at 3400 cm^{-1} due to NH_2, at 650 cm^{-1} due to $\mathrm{S}\diagdown\mathrm{P{=}S}$ and showed strong absorption bands in the region 1600–1500 cm^{-1} due to aromatic C=C stretching vibrations. The NMR spectrum of **V**$_a$ in Demso showed signals at δ 3.8 ppm (3H, OCH_3), at δ 11.4 ppm (2H, NH_2) and the aromatic protons gave multiplet at δ 6.0–7.6 ppm region (7H, multiplet). The MS spectrum showed m/e 353 (M^+).

The elemental analyses of **V**$_d$ corresponded to $C_{18}H_{12}NS_5PO$, the IR spectrum (using KBr) was identical to the proposed structure, it showed absorption bands at 2900 cm^{-1} due to —CH, at 650 cm^{-1} due to $\mathrm{S}\diagdown\mathrm{P{=}S}$ and 1600–1500 cm^{-1} due to the aromatic C=C vibrations. The NMR spectrum showed signals at δ 1.2 ppm due to (1H, CH, singlet) and at δ 6.4–7.8 ppm due to the aromatic protons (8H, multiplet). The MS spectrum showed m/e 449 (M^+). In the ^{31}P NMR spectrum the chemical shift of **V**$_d$ was found at 24 ppm.

EXPERIMENTAL

All melting points were uncorrected. Toluene and petroleum ether were dried over sodium. Dialkyl phosphites were prepared according to established procedure[12] and twice distilled before use. The reagents **I**$_a$ and **I**$_b$ were freshly prepared according to established procedure and twice crystallized before use.[13,14]

The IR spectra (run in KBr and expressed in cm^{-1}) were recorded with a Beckman 4220 Infracord Model and the ^1H-NMR spectra were measured (in $CDCl_3$ or DMSO-d_6 and expressed in the δ scale) at 60 MHz or 90 MHz on a Varian instrument using TMS as an internal standard. The mass spectra were performed at 70 eV using a Varian MAT 112 Mass Spectrometer.

Action of aldehydes on 2-hydroxy-4-amino benzoic acid **II**. To a solution of 2-hydroxy-4-amino benzoic acid (0.1 mol) **II** in absolute ethanol (20 ml), 2 drops of triethylamine and (0.1 mol) aldehyde were added. The reaction mixture was refluxed for 6 hrs, cooled and the precipitate that formed was filtered and crystallized from the proper solvent to give **III**$_a$ and **III**$_b$.

TABLE I

Physical constants of analytical data of new compounds

Compound	M.P. °C	Solvent of crystallization	Yield %	Formula mol. wt.	C	Analysis calc./found			
						H	N	S	P
III$_a$	195	Ethanol	85	$C_{15}H_{13}NO_4$ 271	66.42 66.44	4.80 4.81	5.17 5.16	— —	— —
III$_b$	158	Ethanol + water	80	$C_{12}H_9NSO_3$ 247	58.30 58.32	3.64 3.65	5.67 5.69	12.96 12.95	— —
IV$_a$	over 290	Ethyl acetate + pet. ether	65	$C_{14}H_{16}NSPO_6$ 357	47.06 47.03	4.48 4.47	3.92 3.91	8.96 8.93	8.68 8.66
IV$_b$	over 290	Ethanol + pet. ether	70	$C_{16}H_{20}NSPO_6$ 385	49.87 49.90	5.20 5.21	3.64 3.63	8.31 8.33	8.05 8.02
V$_a$	140	Ethanol	75	$C_{14}H_{12}NS_3PO_2$ 353	47.59 47.60	3.40 3.42	3.97 3.98	27.20 27.21	8.78 8.80
V$_b$	150	Ethanol	70	$C_{13}H_{10}NS_4PO$ 355	43.94 43.92	2.82 2.81	3.94 3.93	36.06 36.03	8.73 8.74
V$_c$	195	Ethanol + water	60	$C_{19}H_{14}NS_4PO_2$ 447	51.01 50.99	3.13 3.12	3.13 3.10	28.64 28.65	6.94 6.92
V$_d$	169	Ethyl acetate + pet. ether	70	$C_{18}H_{12}NS_5PO$ 449	48.11 48.09	2.67 2.66	3.12 3.09	35.64 35.63	6.90 6.92

General procedure for the reactions of **III**$_b$ *with DMP and DEP.* A mixture of **III**$_b$ (0.005 mol) and DMP or DEP (0.05 ml) was heated at 100°C for 12 hrs. After removal of the volatile materials in vacuo, the residual substances were collected and recrystallized from the proper solvent to give the adducts **IV**$_a$ and **IV**$_b$ respectively.

General procedure for the reactions of **II** *and* **III**$_b$ *with* **I**$_a$ *and* **I**$_b$. 0.01 mole of the starting compound and 0.01 mole of **I**$_a$ (or **I**$_b$) was refluxed in 10 ml of dry toluene at 110°C with stirring until no more of the starting material could be detected (TLC). After cooling to room temperature the excess of **I**$_a$ (or **I**$_b$) was filtered off. Then the reaction mixture was evaporated on silica gel column arising ether/light petroleum as eluant. The physical data are summarized in Table I.

REFERENCES

1. B. S. Pedersen, S. Scheibye, N. H. Nilsson and S.-O. Lawesson, *Bull. Soc. Chem. Belg.*, **87**, 223 (1978).
2. B. S. Pedersen, S. Scheibye, K. Clausen and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, **87**, 293 (1978).
3. R. Shabana, S. Scheibye, K. Clausen, S. O. Olesen and S.-O. Lawesson, *Nouv. J. Chim.*, **4**, 47 (1980).
4. B. S. Pedersen and S.-O. Lawesson, *Tetrahedron*, **35**, 2433 (1979).
5. R. Shabana, J. B. Rasmussen, S. O. Olesen and S.-D. Lawesson, *Tetrahedron*, **36**, 3047 (1980).
6. A. A. El-Barbary, S. Scheibye, S.-O. Lawesson and H. Fritz, *Acta. Chem. Scand. B.*, **34**, 597 (1980).
7. A. A. El-Barbary and S.-O. Lawesson, *Tetrahedron*, Vol. 37, No. 15, pp. 2641–2646 (1981).
8. L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Willy, New York, p. 311 (1964).
9. F. Ramirez, O. P. Madan and S. Heller, *J. Am. Chem. Soc.*, **87**, 731 (1965).
10. A. R. Stiles, W. E. Vaughan and F. F. Rust, *J. Am. Chem. Soc.*, **80**, 714 (1958).
11. T. S. Hafez and A. A. Fahmy, *Phosphorus and Sulfur*, Vol. 37, pp. 129–132 (1988).
12. A. H. Ford Moore and J. Perry, *Organic Syntheses*, **31**, 111 (1951).
13. K. A. Jorgensen, A. B. G. Gnattas and S.-O. Lawesson, *Tetrahedron*, Vol. 38, No. 9, pp. 1163–1168 (1982).
14. M. Yokoyama, Y. Hasegawa, H. Hatanaka, Y. Kawrazoe and T. Imamoto, *Synthesis*, 827 (1984).