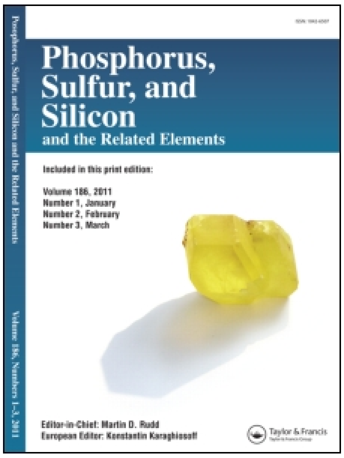


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STUDIES ON ORGANOPHOSPHORUS COMPOUNDS PART XVII. THE REACTION OF LAWESSON'S REAGENT WITH 1,2-PHENYLENEDIAMINE DERIVATIVES, 2-AMINOPHENOL AND 2-AMINO-2-METHYL-1-PROPANOL, A NEW ROUTE TO 1,3,2-DIAZAPHOSPHOLE-2-SULFIDE

R. Shabana[a]; S. S. Atrees[a]
[a] National Research Centre, Cairo, Egypt

To cite this Article Shabana, R. and Atrees, S. S.(1995) 'STUDIES ON ORGANOPHOSPHORUS COMPOUNDS PART XVII. THE REACTION OF LAWESSON'S REAGENT WITH 1,2-PHENYLENEDIAMINE DERIVATIVES, 2-AMINOPHENOL AND 2-AMINO-2-METHYL-1-PROPANOL, A NEW ROUTE TO 1,3,2-DIAZAPHOSPHOLE-2-SULFIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 105: 1, 57 — 62

To link to this Article: DOI: 10.1080/10426509508042046

URL: http://dx.doi.org/10.1080/10426509508042046

Phosphorus, Sulfur, and Silicon, 1995, Vol. 105, pp. 57–62
Reprints available directly from the publisher
Photocopying permitted by license only

STUDIES ON ORGANOPHOSPHORUS COMPOUNDS PART XVII.† THE REACTION OF LAWESSON'S REAGENT WITH 1,2-PHENYLENEDIAMINE DERIVATIVES, 2-AMINOPHENOL AND 2-AMINO-2-METHYL-1-PROPANOL, A NEW ROUTE TO 1,3,2-DIAZAPHOSPHOLE-2-SULFIDE

R. SHABANA‡ and S. S. ATREES
National Research Centre, Dokki, Cairo, 12622, Egypt

(Received January 5, 1995; in final form April 8, 1995)

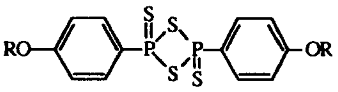
Lawesson's reagent (LR) reacts with 1,2-phenylenediamine derivatives (**2a–c**) to give 1,3-dihydro-1,3,2-diazaphosphole-2-sulfide (**3a–e**). Also it reacts with 2-aminophenol (**4**) and 2-amino-2-methyl-1-propanol (**6**) to give 1,3,2-oxazaphospholes **5**, **7** respectively.

Key words: Lawesson's reagent, 1,2-phenylenediamine, 1,3,2-diazaphosphole, 1,3,2-oxazaphosphole.

INTRODUCTION

2,4-Bis(4-methoxyphenyl)-1,3,2,4 dithiadiphosphetane-2,4-disulfide (**1**) is not only the reagent of choice for thiating different types of carbonyl compounds,[1–8] but also it reacts with certain substrates to give phosphorus heterocycles[9–16] which contain the (4-methoxyphenyl) phosphinothioylidene $\left\{CH_3O—C_6H_4—P(S)\Big<\right\}$ moiety. These heterocyclic compounds are of potential interest as fungicides, insecticides, and herbicides.

In our recent papers, we succeeded in preparing these compounds by reacting LR with Visnaginone, Khellinone, *o*-hydroxyacetophenone,[17] aliphatic dihydric alcohols,[18] aromatic dihydroxy compounds[19] and benzil dianil.[20] This paper reports the reaction of LR (**1a**) and its *p*-phenoxy derivative (**1b**), with 1,2-phenylenediamine derivatives, 2-aminophenol and, 2-amino-2-methyl-1-propanol.

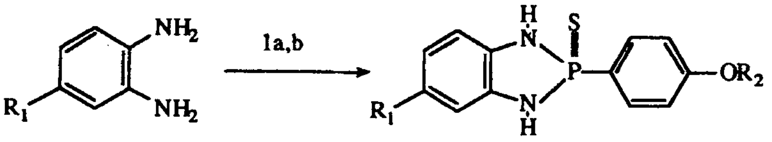


1a, R = CH_3 (Lawesson's Reagent, LR)
b, R = C_6H_5

[†] For part XVI see *Phosphorus, Sulfur,* and *Silicon*, **102**, 9 (1995).
[‡] To whom all correspondence should be addressed.

RESULTS AND DISCUSSION

1,2-Phenylenediamine derivatives (**2a–c**) react with LR in toluene or xylene at reflux temperature to give the corresponding 1,3-dihydro-1,3,2-benzodiazaphosphole-2-sulfide-2-*p*-alkoxy (phenoxy) phenyl (**3a–e**) in moderate to good yield (Scheme I). In the reaction of LR with the diamine **2**, 0.5 mole of LR is sufficient for the conversion of 1 mole of the substrate to the phosphorus heterocyclic **3a–e**. In one case when reacting 1,2-phenylenediamine (**2a**) one mole LR has been used to effect total conversion, this is because LR starts to decompose at higher temperature 140°C.[21,22]

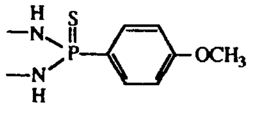


2a, R_1 = H
b, R_1 = CH_3
c, R_1 = Cl

3a, R_1 = H R_2 = CH_3
b, R_1 = CH_3 R_2 = CH_3
c, R_1 = Cl R_2 = CH_3
d, R_1 = H R_2 = C_6H_5
e, R_1 = CH_3 R_2 = C_6H_5

SCHEME I

The structure of **3a**, taken as representative example, was established by elemental analysis, IR, ^{1}H, ^{31}p NMR, and MS (Table I, experimental). In the ^{1}H NMR compound **3a** ($CDCl_3$) shows signals at $\delta = 3.8$ (3H, s, OCH_3, para to the phosphorus atom), 5.25–5.40 (2H, d, 2 similar NH splitted by phosphorus atom), 6.75 (4H, m, of the ring benzene), 6.9 (2H, dd with $^4J_{\mathrm{PH}} = 3$ Hz and $^2J_{\mathrm{HH}} = 9$ Hz meta proton to phosphorus), 7.8–7.95 (2H, dd, $^3J_{\mathrm{PH}} = 15$ Hz and $J_{\mathrm{H..H}} = 9$ Hz ortho-protons to phosphorus in the anisole ring). Compound **3a** gave ^{31}P NMR chemical shifts at 74.02 which is in accordance with other compounds containing the following structure.[23]

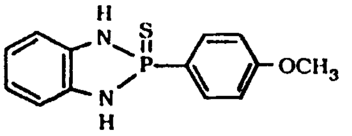
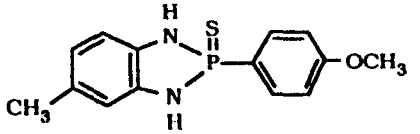
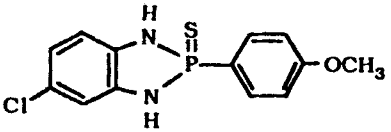
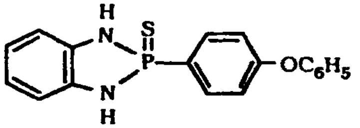
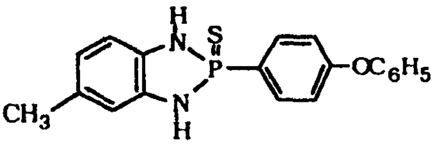
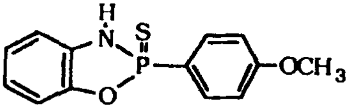
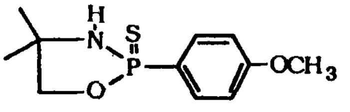


Compound **3a** under electron impact gives the molecular ion peak m/z 276. The first conspicuous peak, however, corresponds to fragment **c** at m/z 243, probably is due to the rearrangement of **3a** to **b** followed by extrusion of SH. The second peak corresponds to fragment **d** with m/z 200 after losing a benzyne radical. The third peak (m/z 137) originates through a rearrangement of **3a** to **e** followed by fission along the P—S axis (Scheme II).

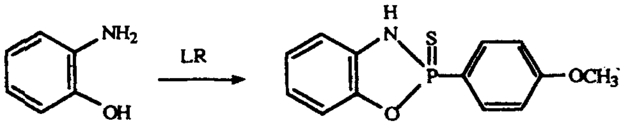
As to the formation of **3a–e**, the electrophilic center of phosphorus of the monomeric part of LR can attack any of the two nucleophilic centers of **2a** to give **2a′** and/or **2a″** which loose H_2S to give **3a** (Scheme III).

TABLE 1

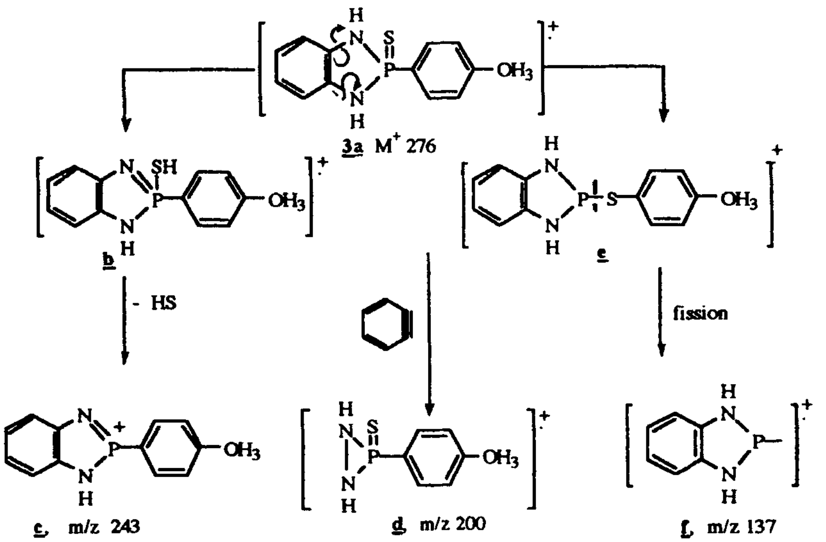
^1H NMR and available ^{31}P NMR for compounds **3a–e** and **5** and **7**

Compd.	Formula	^{31}P	^1H NMR ($CDCl_3$), δ (ppm)
3a		74.02	3.80 (s, 3H, OCH_3), 5.25–5.40 (d, 2H2 similar NH split by P), 6.75 (m, 4H, benzene ring), 6.9 (dd, 2H, $^4J_{P..H}$ = 3 Hz and $J_{H..H}$ = 9 Hz, meta proton to P), 7.80–7.95 (dd, 2H, $3J_{P..H}$ = 15 Hz and $J_{H..H}$ = 9 Hz, ortho protons to P).
3b		74.69	2.25 (s, 3H, CH_3 in the benzene ring), 3.85 (s, 3H, OCH_3), 5.25 (2d, 2 NH split by P) 6.6 (m, 3H, benzene ring), 6.9 (dd, 2H meta proton to P), 7.95 (dd, 2H, ortho protons to P in the anisyl part).
3c		75.64	3.80 (s, 3H, OCH_3), 5.65 (d, NH para to Cl atom), 5.80 (d, NH meta to Cl atom) 6.65 (m, 3H, benzene ring) 6.90 (dd, 2H, meta proton to P), 7.90 (dd, 2H, ortho protons to P in the anisyl part.
3d		—	5.20 (d, 2H, 2 similar NH splitted by P), 6.70–7.40 (m, 11H, aromatics), 7.85–8.00 (dd, 2H, ortho protons to P).
3e		—	2.25 (s, 3H, CH_3), 5.00 (2d, 2 NH), 6.50–7.40 (m, 10H, aromatics), 7.90–8.00 (dd, 2H, ortho protons to P in the ether part).
5		94.04	3.85 (s, 3H, OCH_3), 5.20 (d, 1H, NH) 6.90-7.10 (m, 6H, aromatics), 7.95 (dd, 2H, ortho protons to P in the anisyl part).
7		97.10	1.40 – 1.60 (two singlets, 2 CH_3 groups), 3.90 (s, 3H, OCH_3), 4.00–4.30 (m, 2 H, OCH_2), 6.95–7.00 (dd, 2H, meta protons to P) in the anisyl part), 7.90–8.00 (dd, 2 H, ortho protons to P in the anisyl part).

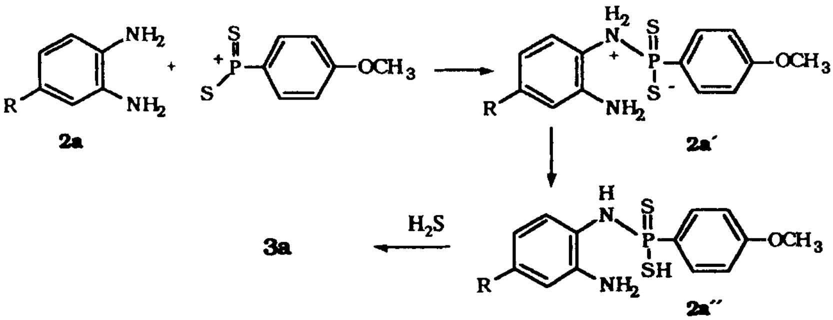
The reaction of LR with 2-aminophenol (**4**) gives rise to the corresponding 1,3,2-oxazaphosphole (**5**) in good yield.



4 **5**

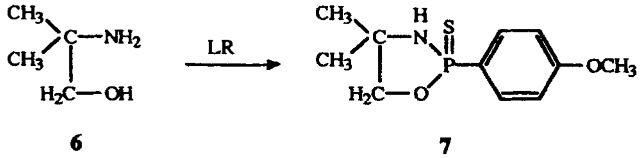


SCHEME II

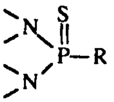


SCHEME III

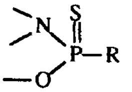
Also, the 4,4-dimethyl-1,3,2-oxazaphosphole-2-sufide-2-(*p*-methoxyphenyl) (**7**) has been prepared by reacting 2-amino-2-methyl-1-propanol (**6**) with LR. The structures of **5** and **7** have been proven by elemental analysis and spectroscopic methods (Table I). The results of the ^{31}P chemical shifts of the oxazaphosphole **5** and **7** enable us to show that the diazaphosphole with structure **3** exhibits a downfield ^{31}P chemical shift (δ = 74) as compared with oxazaphosphole (δ = 94) and also relative to the dioxaphosphole 7 (δ = 108).[19]



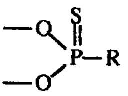
In conclusion, the reaction of LR with 1,2-phenylenediamine derivatives, 2-aminophenol and 2-amino-2-methyl-1-propanol affords an easy entry to the synthesis of 1,3,2-diazaphosphole and oxazaphosphole derivatives as the sole products.



3 $\delta\,^{31}P = 74$



5 $\delta\,^{31}P = 94$



7 $\delta\,^{31}P = 108$

EXPERIMENTAL

Melting points were determined with a Mel Temp apparatus and are uncorrected as are the boiling points. IR spectra were recorded by using a Unicam SP, 1100, or PU 9712 infrared spectrometer. The ^1H NMR spectra were recorded on a Varian Gemini 200 (200 MHz) or Bruker 250 MHz spectrometer in $CDCl_3$ as solvent. ^1H and ^{31}P chemical shifts are reported relative to TMS as an internal standard and to external 35% H_3PO_4, respectively. MS data were obtained on gas chromatography/mass spectrometer (GC/MS) Ex 1000, QP Schimadzu Japan. The reported yields are of pure isolated materials obtained by column chromatography using silica gel 60 (Merck).

Lawesson's reagent (**1a**) is commercially available and can also be prepared as described earlier.[24] Also, the p-phenoxy derivative (**1b**) is prepared from diphenyl ether and P_4S_{10} (following the same procedure as in **1a**). The starting materials 1,2-phenylenediamine, 2-aminophenol and 2-amino-2-methyl-1-propanol derivatives, are commercially available. ^1H NMR and ^{31}P chemical shifts are given in Table I.

Reaction of Lawesson's Reagent with 1,2-Phenylenediamine, preparation of 1,3-Dihydro-1,3,2-benzodiazaphosphole-2-sulfide (**3a**): An amount of 1.08 g (5 mmol) of 1,2-phenylenediamine and 2.02 g (5 mmol) of LR in 25 ml dry xylene were stirred magnetically at reflux temperature (140°C) until no more of the starting material could be detected by TLC (2 hours). The solvent was evaporated under reduced pressure and applied to silica gel column using ethyl acetate/petroleum ether mixtures as eluent (starting from 2% up 20%) to give 0.68 g (24%) of **3a**, mp 192°C, Anal. Calcd. for $C_{13}H_{13}N_2OPS$ (276.2): C, 56.53; H, 4.71; P, 11.21; S, 11.61% Found: C, 56.40; H, 4.66; P, 11.00; S, 11.42% IR (u, cm-1, group), 625 (P=S), 1600 (>c=c<), 3400 and 3296 (2NH). MS; m/z (% rel. int), 276 (M^+, 90), 243 (M^+-SH, 85); 229 (M^+-SCH_3,25); 200 (M^+-C_6H_4,10) 137 (M^+-C_7H_7O,7O).

Reaction of LR with 4-methyl-1,2-phenylenediamine, preparation of 1,3-dihydro-1,3,2-benzodiazaphosphole-2-sulfide-5-methyl (**3b**): The same method for **3a** was used to give 0.24 g of 3b, (8.3%) mp 193°C. Anal. Calcd. for $C_{14}H_{15}N_2OPS$ (290.2), C, 57.94; H, 5.17; P, 10.67; S, 11.05% Found: C, 57.72; H, 5.05; P, 10.60; S. 10.90% IR (u, cm^{-1} group) 640 (P=S), 1600 (>c=c<), 3404 and 3288 (2NH) MS: 290 (M^+,100), 257 (M^+-SH, 98), 151 (M^+-C_7H_7OS).

Reaction of LR with 4-chloro-1,2-phenylenediamine, preparation of 1,3-dihydro-1,3,2-benzodiazaphosphole-2 sulfide-5-chloro (**3c**): As described for **3b**, 1 g (7 mmol) of **2c** and 1.41 g (3.5 mmol) of LR were used to give 1.57 g (72.4%) of 3c. mp 161°C, Anal. Calcd. for $C_{13}H_{12}N_2$ OPSCl, (310.6) C, 50.26; H, 3.87. P 9.97; S, 10.32% Found: C, 49.94; H, 3.79; P, 9.85; S, 10.30% IR (u, cm-1, group): 650 (P=S) 1594 (C=C), 3356 and 3264 (2NH) MS: 310 (M^+, 100, base peak) 277 (M^+-SH, 90), 171 (M^+-C_7H_7OS).

Reaction of **Ib** *with 1,2-phenylenediamine, preparation of 1,3-dihydro-1,3,2-benzodiazaphosphole-2-sulfide-2-p-phenoxyphenyl* (**3d**): As described for **3a**; 0.54 g (5 mmol) of **3d** and 1.32 g (2.5 mmol) of **Ib** were used to give 0.06 g (3.5%) of **3d**; mp 60°C. Anal. Calcd. for $C_{18}H_{15}N_2OPS$ (338.2): C, 63.92, H, 4.44; P, 9.16; S, 9.48%, Found: C, 63.84; H, 4.40; P, 9.05; S, 9.35; MS: 338 (M^+, 93), 306 (M^+-SH, 100) 137 (M^+-$C_{12}H_9OS$, 61), 77, 51.

Reaction of **Ib** *with 4-methyl-1,2-phenylenediamine, preparation of 1,3-dihydro-1,3,2-benzodiazaphosphole-2-sulfide-2 (p-phenoxyphenyl) 5-methyl* (**3e**): The same method as for **3b** was applied. Thus 1.22 g (10 mmol) and 2.64 g (5 mmol) of **Ib** yielded 1.5 g (42.8%) of **3e** mp 56°C. Anal. Calcd. for $C_{19}H_{17}N_2OPS$ (352.27), C, 64.78; H, 4.83; P 8.79; S, 9.10 Found: C, 64.69; H, 4.79; P, 8.70; S, 9.02; MS: 352 (M^+, 88), 319 (M^+-SH, 100, base peak), 151 ($C_7H_8N_2P$, 36), 77, 51.

Reaction of LR with 2-aminophenol, preparation of benzo-1,3,2-oxazaphosphole-2-sulfide-2-p-methoxyphenyl (**5**): A mixture of 0.76 g (7 mmol) of 2-aminophenol and 2.83 g (7 mmol) of LR in 25 ml toluene was stirred at reflux temperature for 3 hr until no more of the starting material could be detected (TLC). Evaporation of the solvent under reduced pressure followed by purifying the residue on a silica gel column using 5% up to 20% ethyl acetate-pet. ether mixtures to give 0.12 g (6.2%) of **5**, mp 126°C. Anal. Calcd. for $C_{13}H_{12}NO_2PS$ (277.2), C, 56.33; H, 4.33; P; 11.17; S. 11.57 Found: C, 56.20; H, 4.20; P, 11.00; S, 11.49%. IR (u cm^{-1}, group) 646 (P=S), 1597 (>c=c< aromatic), 3316 (NH), MS: 277 (M^+, 100, basic peak), 244 (M^+-SH, 28) 138 (C_6H_5NOP, 84), 108 (C_6H_6NO, 31), 91, 63.

Reaction of LR with 2-amino-2-methyl-l-propanol, preparation of 4,4-dimethyl-1,3,2-oxazaphosphole-2-sulfide-2-(p-methoxyphenyl) (**7**): A mixture of 0.8 g (10 mmol) of 2-amino-2-methyl-1-propanol and 2.02 g (5 mmol) of LR in 25 ml dry toluene was stirred at reflux temperature for 1 hr. Evaporation of the solvent and purification of the product on a silica gel column using 5% up to 20% ethyl acetate pet. ether (60–80) to give 0.09 g (3.5%) of **7**, mp 95°C, MS: 257 (M^+, 100, base peak), 224 (M^+-SH, 10), 170 (29), 134 (20), 70 (38).

REFERENCES

1. B. S. Pedersen, S. Scheibye, N. H. Nilsson and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, **87**, 223 (1978).
2. S. Scheibye, B. S. Pedersen and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, **87**, 229 (1978).
3. R. Shabana and A. A. El-Kateb, *Polish J. of Chem.*, **57**, 647 (1983).
4. R. Shabana, J. B. Rasmussen, S. O. Olesen and S.-O. Lawesson, *Tetrahedron*, **36**, 3047 (1980).
5. A. A. El-kateb, R. Shabana and F. H. Osman, *Z. Naturforsch*, **39b**, 1614 (1984).
6. B. S. Pedersen, S. Scheibye, K. Clausen and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, **87**, 293 (1978).
7. B. S. Pedersen and S.-O. Lawesson, *Tetrahedron*, **35**, 2433 (1979).
8. S. Scheibye, J. Kristensen and S.-O. Lawesson, *Tetrahedron*, **35**, 1339 (1979).
9. R. Shabana, S. Scheibye, K. Clausen, S. O. Olesen and S.-O. Lawesson, *Nouv. J. Chim.*, **4**, 47 (1980).
10. R. Shabana, A. A. El-barbary, A.-B. A. G. Ghattas and S.-O. Lawesson, *Sulfur Letter*, **2**, 223 (1984).
11. N. M. Yousif, R. Shabana and S.-O. Lawesson, *Bull. Soc. Chim. France*, **2**, 283 (1986).
12. R. Shabana, M. R. Mahran and T. S. Hafez, *Phosphorus and Sulfur*, **31**, 1 (1987).
13. K. A. Jorgensen, R. Shabana, S. Scheibye and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, **89**, 247 (1980).
14. R. Shabana, J. B. Rasmussen and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, **90**, 75 (1981).
15. R. Shabana, J. B. Rasmussen and S.-O. Lawesson, *Bull. Soc. Chim. Belg.*, **90**, 103 (1981).
16. S. Scheibye, R. Shabana, S.-O. Lawesson and C. Romming, *Tetrahedron*, **38**, 993 (1982).
17. R. Shabana, E. M. Yakout and S. S. Atress, *Hetroatom Chem.*, **4**, 491 (1993).
18. R. Shabana, F. H. Osman and S. S. Atrees, *Tetrahedron*, **49**, 1271 (1993).
19. R. Shabana, F. H. Osman and S. S. Atrees, *Tetrahedron*, **50**, 6975 (1994).
20. R. Shabana and S. S. Atrees, *Phosphorus, Sulfur and Silicon*, accepted for publication, 1994.
21. S.-O. Lawesson, J. Perregaard, S. Scheibye, H. J. Meyer and I. Thomsen, *Bull. Soc. Chim. Belg.*, **86**, 679 (1977).
22. H. Z. Lecher, R. A. Greenwood, K. C. Whitehouse and T. H. Chao, *J. Am. Chem. Soc.*, **78**, 5018 (1956).
23. K. Clausen, A. A. El Barbary and S.-O. Lawesson, *Tetrahedron*, **37**, 1019 (1981).
24. I. Thomsen, K. Clausen, S. Scheibye and S.-O. Lawesson, *Org. Synth.*, **62**, 158 (1984).