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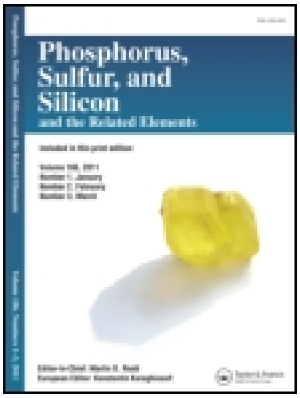

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

ORGANOPHOSPHORUS CHEMISTRY, 29[l]. THE ACTION OF 2,4-BIS-(4-METHOXY-PHENYL)-1,3,2,4-DITHIAPHOSPHETANE-2,4-DIS-ULFIDE (LAWESSON'S REAGENT) ON α, β-UNSATURATED NITRILES

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Published online: 24 Sep 2006.

To cite this article: Maha D. Khidre , El-Sayed M. A. Yakout & Mohamed Refat H. Mahran (1998) ORGANOPHOSPHORUS CHEMISTRY, 29[l]. THE ACTION OF 2,4-BIS-(4-METHOXY-PHENYL)-1,3,2,4-DITHIAPHOSPHETANE-2,4-DIS-ULFIDE (LAWESSON'S REAGENT) ON α, β-UNSATURATED NITRILES, Phosphorus, Sulfur, and Silicon and the Related Elements, 133:1, 119-125, DOI: 10.1080/10426509808032459

To link to this article: http://dx.doi.org/10.1080/10426509808032459

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Phosphorus, Sulfur and Silicon, Vol. 133, pp. 119-125
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ORGANOPHOSPHORUS CHEMISTRY, 29[1]. THE ACTION OF 2,4-BIS-(4-METHOXY-PHENYL)-1,3,2,4-DITHIAPHOSPHETANE-2,4-DISULFIDE (LAWESSON'S REAGENT) ON α, β-UNSATURATED NITRILES*

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(Received 17 November, 1997; In final form 23 March, 1998)

The reaction of 2,4-bis-(4-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide (Lawesson's reagent. LR, **1**) with ylidenemalononitriles (**5a-f**) was studied. Partial hydrolysis of 5a-f followed by thiation with LR yields the respective thioamides **7a-f.** Nucleophilic attack by the monomeric form **1a** of LR on **5**, on the other hand, affords the respective 1,2-thiaphosphole-2-sulfides (cf. **9**).

Compatible elementary and spectroscopic measurements were gained for the new products (**7a-f** and **9a-d**).

Keywords: Lawesson's reagent; α, β-unsaturated nitriles; thiation; 1, 2-thiaphosphole-2-sulfide

INTRODUCTION

The activity of 2,4-bis-(4-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide (Lawesson's reagent, LR, **1**) as a thiating agent, has been experienced among diverse classes of carbonyl compounds.(2–4) At elevated temperature, LR, **1** exists in equilibrium with the monomeric species **1a**,(5)which allows it to undergo [2+4] cycloaddition with acyclic α,β-unsaturated ketones **2** to give heterocyclic structures of types **3** and/or **4**.(2,3,6).

To the best of our knowledge, however, the reaction of LR, **1,** with α,β-unsaturated nitriles has not been explored. In the line with our growing interest in the chemistry of both LR, **1**(7–9) and α,β-unsaturated nitriles,(10–15) we have now

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* Dedicated to Professor Sidky on the occasion of his 69th birthday.

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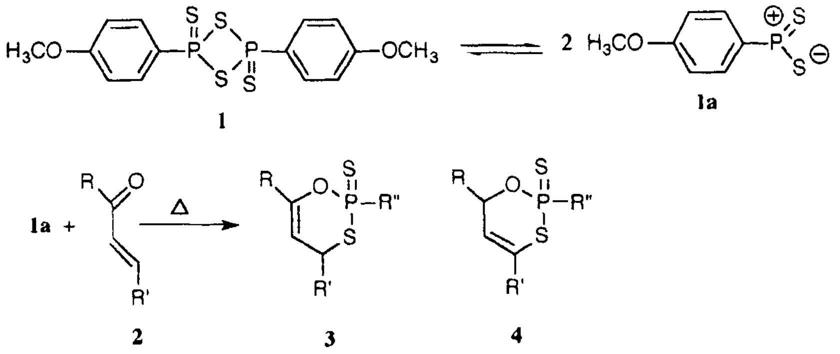
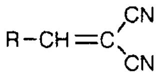


R and R'=alkyl or aryl ; R, R' as in **2**; $R''=C_6H_4\text{-}OCH_3\text{-}p$

studied the reaction of **1** with arylidene malononitriles **5a-d**, 2-furfurylidenemalononitrile (**5e**) and 2-thienylidenemalononitrile (**5f**).



$R\text{-}CH{=}C(CN)_2$

5a, $R=C_6H_5$
b, $R=C_6H_4\text{-}OH\text{-}o$
c, $R=C_6H_4\text{-}OCH_3\text{-}p$
d, $R=C_6H_4\text{-}NO_2\text{-}p$
e, R=2-furyl
f, R=2-thienyl

RESULTS AND DISCUSSION

We have found that benzylidenemalononitrile **5a** reacts with LR, **1** in boiling toluene to give mainly a yellow crystalline product. It was formulated as α-cyano-β-phenylthioacrylamide (**7a**) for the following reasons : (a) Its microanalysis and molecular weight determination (MS) corresponded to $C_{10}H_8N_2S$. (b) Its IR spectrum (KBr, cm^{-1}) showed two bands at 3410, 3430 due to the stretching vibration of the NH_2 group and a band at 2220 for the CN-group. (c) The ^1H-NMR spectrum of **7a** ($CDCl_3$, δ ppm) revealed the presence of signals at 8.05 (2H, NH_2, bs., exchangeable with D_2O) and at 8.80–7.55 (6H, aromatics and exocyclic vinyl proton, m).

Under similar conditions, the reaction of o-hydroxybenzylidenemalononitrile (**5b**) with LR, **1** yielded a mixture of two products (A+B) which could be separated in pure forms by column chromatography. The first (A, 70%) was formulated as α-cyano-β-(2-hydroxyphenyl)thioacrylamide (**7b**)based upon analytical and spectroscopic arguments similar to those mentioned in the case of **7a.** The second product (B, 20%) was formulated as 3,3-dicyano-2-(4′-methoxyphenyl)-4-(2-hydroxyphenyl)- 1,2-thiaphosphole-2-sulfide (**9a**) for the following reasons : (a) Its microanalysis and molecular weight determination (MS) agreed with the molecular formula $C_{17}H_{13}N_2O_2PS_2$. (b) Its ^{31}P-NMR spectrum (in $CDCl_3$, *vs* 85% H_3PO_4) recorded a positive shift at δ 48.39 ppm which matches a cyclic structure incorporating a 1,2-thiaphosphole-2-sulfide moiety.(7,16) (c) The IR spectrum of **9a** revealed the absence of absorption bands around 3300 cm^{-1} (NH_2). However, it showed strong absorption bands at 2320 cm^{-1} (CN), 1580 cm^{-1}(C=C, aromatic). Moreover, the strong ethylenic $>C=C<$ band present in the spectrum of **5b** at 1640 cm^{-1} was absent in the spectrum of **9a.** (d) The ^{1}H-NMR spectrum of **9a** (in $CDCl_3$, δ ppm) revealed the presence of a signal at 4.2 ppm (1H, S-*CH*-C, d, $^3J_{HP}$=12 Hz). This signal is partially obscured by the signal (singlet) due to the OCH_3 protons present at 3.8 ppm. The aromatics (8H) gave a multiplet in the δ 6.9–7.9 ppm region wherein the AB-system due to the 1,4-disubstituted benzene ring was well-characterized by two doublets (each with J_{HH}=8 Hz) at 7.53 and 7.70 ppm. The reaction of ylidenemalononitriles **5c-f**with LR, **1** resulted likewisely in production of 4-ylidene-1,2-thiaphospholene-2-sulfides (cf. **9b-d**) and/or thioamides (**7c-f**) depending upon the nature of the reacting substrate. For physical, analytical and spectroscopic data of compounds **7** and **9,** cf. Table I.

Apparently, formation of compounds **7** can be interpreted in terms of partial hydrolysis of **5** to yield the respective α-cyano-β-substituted acrylamides (*cf.* **6**) which undergo ketone-to-thioketone conversion under the thiating effect of LR, **1**(2–4) (Scheme 1). The proposed mechanism(3,7) for formation of **9a-d** involves a nucleophilic attack by **1** on **5** to give the transient intermediate **8.** This process is followed by ring closure to yield **9** or both may exist in equilibrium with each other : 8 $\rightleftharpoons$ **9.**

It is worthy to report that, in all the above mentioned reactions, a colorless crystalline phosphorus-containing product was isolated (or detected by TLC) and proved to be trimer **10** by comparing its m.p. as well as IR and ^{1}H-NMR spectra with those of an authentic specimen.(17–19) Formation of **10** is frequently observed during the thiation processes initiated by LR, **1.**

TABLE I Physical, Analytical and Infrared Data of Compounds 7a-f and 9a-d

Compd.	*M.P. °C*	*Yield* %*	*Molecular formula (Mol. wt.)*	*MS (M+, rel. int.)*	*Analysis (Calcd./found)*					*IR (cm^{-1})*
					C	*H*	*N*	*P*	*S*	
7a	145	70	$C_{10}H_8N_2S$	188 (39%)	63.80	4.28	14.88	-	17.03	3410, 3310 (NH$_2$), 2220 (CN), 1627 (C=C), 1250 (C=S), 1580 (C=C, aromatic).
			(188.25)		63.52	3.89	14.57		16.75	
b	215	70	$C_{10}H_8N_2OS$	204 (15%)	58.80	3.94	13.71	-	15.69	3280, 3000 (NH$_2$), 2250 (CN), 1600 (C=C, ethylenic), 1260 (C=S), 1570 (C=C, aromatic).
			(204.25)		58.44	3.68	13.40		15.28	
c	196	50	$C_{11}H_{10}N_2OS$	218 (100%)	60.53	4.62	12.83	-	14.69	3400, 3320 (NH$_2$), 2200 (CN), 1640 (C=C, ethylenic), 1250 (C=S), 1580 (C=C, aromatic).
			(218.28)		60.11	4.32	12.50		14.35	
d	210	70	$C_{10}H_7N_3O_2S$	178 (100%)	51.49	3.02	18.01	-	13.74	3420, 3390 (NH$_2$), 2180 (CN), 1620 (C=C, ethylenic), 1250 (C=S), 1580 (C=C, aromatic).
			(233.25)		51.07	2.80	17.76		13.51	
7e	170	70	$C_8H_6N_2OS$	178 (100%)	53.91	3.39	15.71	-	17.99	3320, 3280 (NH$_2$), 2200 (CN), 1625 (C=C, ethylenic), 1240 (C=S), 1600 (C=C, aromatic).
			(178)		53.62	3.02	15.39		17.64	
f	178	52	$C_8H_6N_2S_2$	194 (100%)	49.45	3.11	14.41	-	33.00	3360, 3260 (NH$_2$), 2160 (CN), 1640 (C=C, ethylenic), 1240 (C=S), 1560 (C=C, aromatic).
			(194.27)		49.11	2.85	14.20		32.73	
9a	156	20	$C_{17}H_{13}N_2O_2PS_2$	372 (100%)	54.82	3.51	7.52	8.31	17.21	2300 (CN), 1580 (C=C, aromatic).
			(372.40)		54.50	3.22	7.19	8.01	16.87	
b	140	25	$C_{18}H_{15}N_2O_2PS_2$	386 (5%)	55.94	3.91	7.24	8.01	16.59	2200 (CN), 1600 (C=C, aromatic).
			(386.43)		55.68	3.60	6.92	7.77	16.27	
c	178	30	$C_{17}H_{12}N_3O_3PS_2$	401 (5%)	50.86	3.01	10.46	7.71	15.97	2250 (CN), 1580 (C=C, aromatic).
			(401.40)		50.49	2.88	10.12	7.50	15.71	
d	153	20	$C_{15}H_{11}N_2OPS_3$	362 (5%)	49.70	3.05	7.72	8.54	26.54	2200 (CN), 1620 (C=C, aromatic).
			(362.43)		49.34	2.69	7.55	8.27	26.30	

*Approximated.

TABLE II ^{1}H-NMR Spectral data for compounds 7a-f and 9a-d

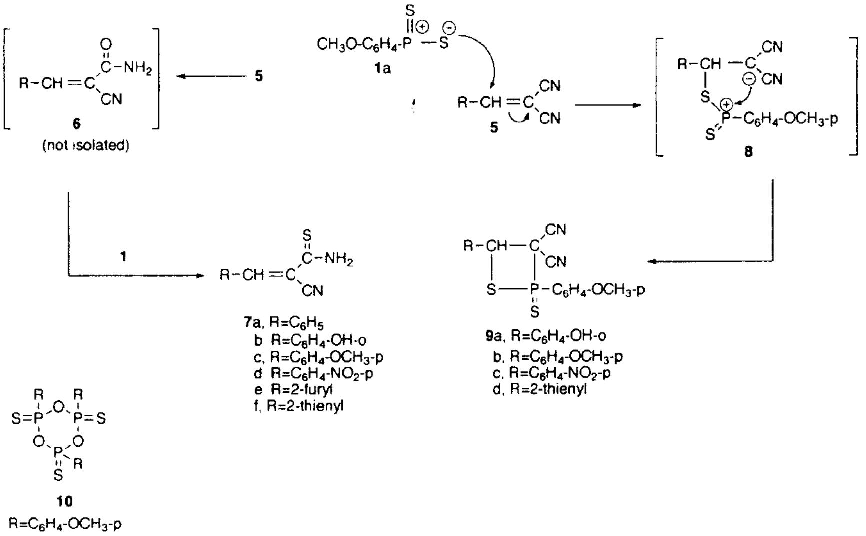
Compd.	*^{1}H-NMR (in $CDCl_3$, δ, ppm)*
7a	7.55–8.80 (m, 6H, aromatics and exocyclic proton); 8.05 (bs, 2H, NH_2, exchangeable with D_2O).
b	7.10–8.10 (m, 6H, aromatics and exocyclic proton); 9.40 (s, 1H, OH); 12.35 (bs., 2H, NH_2, exchangeable with D_2O).
c	3.90 (s, 3H, $OC\underline{H}_3$); 6.85–8.75 (m, 5H, 4 aromatics and exocyclic proton); 7.55 (bs., 2H, NH_2, exchangeable with D_2O).
d	7.00–7.95 (m, 5H, 4 aromatics and exocyclic proton); 8.15 (bs., 2H, NH_2, exchangeable with D_2O).
e	6.80 (dd, 1H, furan); 7.50 (d, 1H, furan); 8.00 (d, 1H, furan); 8.35 (s, 1H, exocyclic proton); 8.60, 9.35 (br, 2H, NH_2, exchangeable with D_2O).
f	7.35 (dd, 1H, thiophene); 8.00 (d, 1H, thiophene), 8.10 (d, 1H, thiophene); 8.70 (s, 1H, exocyclic proton); 9.25 (bs., 2H, NH_2, exchangeable with D_2O).
9a	3.8 (s, 3H, $OC\underline{H}_3$); 4.2 (d, 1H, S-C$\underline{H}$-C, $^3J_{HP}$=12 Hz); 6.9–7.9 (m, 8H, aromatics); 9.25 (s, 1H, OH, exchangeable with D_2O).
b	3.85 (s, 3H, $OC\underline{H}_3$) ; 3.95 (s, 3H, $OC\underline{H}_3$) ; 4.00 (d, 1H, S-C$\underline{H}$-C); 6.95-8.15 (m, 8H, aromatics).
c	3.55 (s, 3H, $OC\underline{H}_3$); 4.00 (d, 1H, S-C$\underline{H}$-C, $^3J_{HP}$=12 Hz); 6.55–7.60 (m, 8H, aromatics).
d	3.9 (s, 3H, $OC\underline{H}_3$) ; 4.00 (d, 1H, S-C$\underline{H}$-C, $^3J_{Hp}$=12 Hz); 7.25–8.20 (m, 7H, 4 aromatics and 3 thiophene protons).

CONCLUSION

Lawesson reagent LR, **1** reacts with the α,β-unsaturated nitriles **5a-f** both in the dimeric form **1** to produce thioamides **7a-f** as well as in the monomeric dipolar form **1a** to yield 1,2-thiaphosphole-2-sulfides **(9a-d)**. The ability of LR to produce 5- and 6-membered P-S-heterocycles from bifunctional systems is well-established.(3) However, to the best of our knowledge, utilizing LR for producing 4-membered P-S-heterocycles (cf. **9a-d**) is now reported for the first time.

Experimental

Melting points are uncorrected. IR spectra were recorded by using Unicam SP 1100 or PU 9712 infracords. The ^{1}H-NMR spectra were recorded on Jeol GLM EX 270 MHz Spectrometer (super conducting magnet) in $CDCl_3$ using TMS as an internal standard. ^{31}P-NMR spectra were recorded with Jeol GLM EX 270 MHz Spectrometer in $CDCl_3$ (vs 85% H_3PO_4). Mass spectra were obtained with Finnigan MAT-SSQ 7000 Spectrometer (70 eV). Columm chromatography (on Silica gel G, E. Merck) was adopted for isolation and purification of the products using appropriate acetone/pet. ether mixture as eluents. LR, **1** was commercially available (from Aldrich Chem. Co.) or prepared as described.(2–4) The α,β-unsaturated nitriles **5a,**$^{(20)}$ **5b,**$^{(21)}$ **5c,**$^{(20)}$ **5d,**$^{(22)}$ **5e,**$^{(20)}$ and **5f** $^{(23)}$ were prepared according to known procedures.



SCHEME 3

GENERAL PROCEDURE

5 Mmol of the dicyanomethylene compound **(5a-f)** was dissolved in dry toluene (25 ml) and Lawesson's reagent **1** (5 mmol, 2.02 gm) was added to the solution. The reaction mixture was refluxed and the starting materials were traced by TLC until the reaction was finished. The reaction mixture was evaporated under reduced pressure and applied to silica gel column using acetone/pet. ether (60–80 °C b.r.) mixture as eluent (starting from 5% up to 25% acetone) to give the new products **7a-f** and **9a-d.**

References

[1] For part 28 of this series, cf. M.R.H. Mahran, T.S. Hafez and M.M. Henary, Phosphorus, Sulfur and Silicon, (1996) in press.

[2] S. Scheibye, R. Shabana, S.-O. Lawesson and C. Römming, Tetrahedron, **38,** 993 (1982).

[3] M.P. Cava and M.I. Levinson (Tetrahedron report Number 192), Tetrahedron, **41** (22), pp 5061–5087 (1985).

[4] D. Brillon, Sulfur Reports, **12**, 297 (1992).

[5] R. Apple, F. Knoch and H. Kunze, Angew. Chem., **95,** 1008 (1983).

[6] A. Ecker, I. Boie and U. Schmidt, Monatsh. Chem., **104,** 503 (1973).

[7] R. Shabana, M.R. Mahran and T.S. Hafez, Phosphorus, Sulfur and Silicon, **31,** 1 (1987).

[8] T.S. Hafez, Y.O. El-Khoshnieh, M.R. Mahran and S.M.S. Atta, Phosphorus, Sulfur and Silicon, **56,** 165 (1991).

[9] T.S. Hafez, S.M.S. Atta, A.A. Fahmy and M.R. Mahran, Sulfur Letters, **16,** (5&6), 227 (1993).

[10] M.R. Mahran, W.M. Abdou, N.M. Abdel-Rahman and M.M. Sidky, Phosphorus, Sulfur and Silicon, **45,** 47 (1989).

[11] W.M. Abdou, N.A.F. Ganoub and M.R. Mahran, Bull. Chem. Soc. (Japan), **64**, 747 (1991).

[12] W.M. Abdou, M.D. Khidre and M.R. Mahran, J. Für prakt. Chem., **332** (6)**,** 1029 (1990).

[13] M.R. Mahran, W.M. Abdou and N.A.F. Ganoub, Bull NRC (Egypt), **16** (2), 91 (1991).

[14] M.R. Mahran, W.M. Abdou, N.A.F. Ganoub, and H.A. Abdallah, Phosphorus, Sulfur and Silicon, **57,** 217 (1991).

[15] M.R. Mahran, W.M. Abdou, N.M. Abdel Rahman and M.D. Khidre, Heteroatom Chem., **3** (2), 93 (1992).

[16] M.M. Crutchfield, O.H. Dungan, J.H. Letches, V. Mark and J.R. van Wazer, "Topics in phosphorus Chem.; Vol. 5, ^{31}P-Nuclear Magnetic Resonance, Chapter 4 (Compilation of ^{31}P-NMR Data)", Interscience Publishers, a Division of John Wiley and Sons (1967).

[17] P.S. Pedersen, S. Scheibye, N.H. Nilson and S.O. Lawesson, Bull. Chem. Soc. Belg., **87**, 223 (1978); C.A., **89,** 128559 (1978).

[18] S. Scheibye, P.S. Pedersen, and S.O. Lawesson, Bull. Chem. Belg., **87**, 229 (1978).

[19] P.S. Pedersen, S. Scheibye, K. Clausen and S.O. Lawesson, Bull. Soc. Chem. Belg., **87**, 293 (1978).

[20] B.B. Corson and R.W. Stoughton, J. Amer. Chem. Soc., **50**, 2825 (1928).

[21] W. Baker and C.S. Howes, J. Chem. Soc., 119 (1953).

[22] D.T. Mowry, J. Amer. Chem. Soc., **67**, 1050 (1945).

[23] W.S. Emerson and T.M. Patrick, Jr., J. Org. Chem., **14**, 790 (1949).