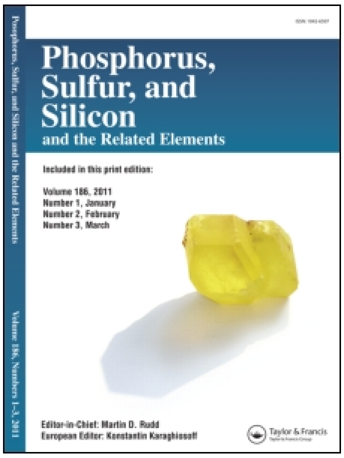

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Shabana, R. , Mahran, M. R. and Hafez, T. S.(1987) 'STUDIES ON ORGANOPHOSPHORUS COMPOUNDS PART VIII.[1] THE ACTION OF 1,3,2,4-DITHIADIPHOSPHETANE-2,4-DISULFIDES ON BENZILMONOANILS. NOVEL SYNTHESIS OF 4,5-DIPHENYL δ^4-1,3,2-THIAZAPHOSPHOLINE-2-SULFIDE DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 31: 1, 1 — 6

To link to this Article: DOI: 10.1080/03086648708079334

URL: http://dx.doi.org/10.1080/03086648708079334

Phosphorus and Sulfur, 1987, Vol. 31, pp. 1-6
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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS PART VIII.[1] THE ACTION OF 1,3,2,4-DITHIADIPHOSPHETANE-2,4-DISULFIDES ON BENZILMONOANILS. NOVEL SYNTHESIS OF 4,5-DIPHENYL Δ^4-1,3,2-THIAZAPHOSPHOLINE-2-SULFIDE DERIVATIVES

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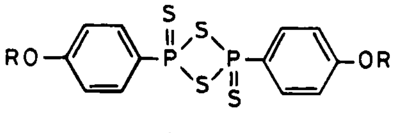
(Received July 10, 1986; in final form August 12, 1986)

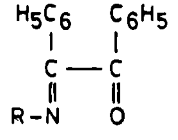
1,3,2,4-Dithiadiphosphetane 2,4-disulfides **1a,b** react with benzilmonoanils **2a–d** to give 4,5-diphenyl Δ^4-1,3,2-thiazaphospholine-2-sulfide derivatives of type **3**. Compatible analytical and spectroscoptic results were obtained for all the new compounds. A mechanism is proposed to explain the formation of compounds **3**.

INTRODUCTION

It is widely realized that 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, LR, (**1a**) is potent thiating agent for diverse carbonyl compounds, e.g., ketones,[2] carboxamides,[3–7] esters,[8,9] enaminones,[10] lactams,[11] as well as β and γ-lactones.[12] To the best of our knowledge, however thiation of α-diketonemonoanils with the same reagents has not been explored. We report in this paper the reaction of benzilmonoanils **2a–d** with compounds **1**.



1 a, R = CH_3 (Lawesson reagent)
b, R = C_6H_5



2 a, R = C_6H_5
b, R = C_6H_4-CH_3-o
c, R = C_6H_4-CH_3-m
d, R = C_6H_4-CH_3-p

RESULTS AND DISCUSSION

We have now found that the reaction of 2,4–bis(4-methoxyphenyl) 1,3,2,4-dithiadiphosphetane 2,4-disulfide (Lawesson Reagent, LR), **1a**, with benzil-

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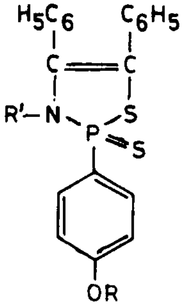
monoanils **2a–d**, proceeds in boiling toluene to give chromatographically pure products encorporating both sulfur and phosphorus (elementary analysis). These products assigned the Δ^4-1,3,2-thiazaphospholine-2-sulfide structure **3a–d**, respectively for the following reasons;

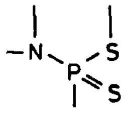
(a) correct elementary analysis and molecular weight determination (ms) were obtained for each product.

(b) The ^{31}P NMR shifts for **3a**, taken as example were 91.37; 86.14 ppm, (6:1),



3 a, R= CH_3 ; R'= C_6H_5
b, R= CH_3 ; R'= C_6H_4-CH_3-o
c, R =CH_3 ; R'= C_6H_4-CH_3-m
d, R = CH_3 ; R'= C_6H_4-CH_3-p
e, R = R'= C_6H_5
f, R = C_6H_5 ; R'= C_6H_4-CH_3-o
g, R = C_6H_5 ; R = C_6H_4-CH_3-p

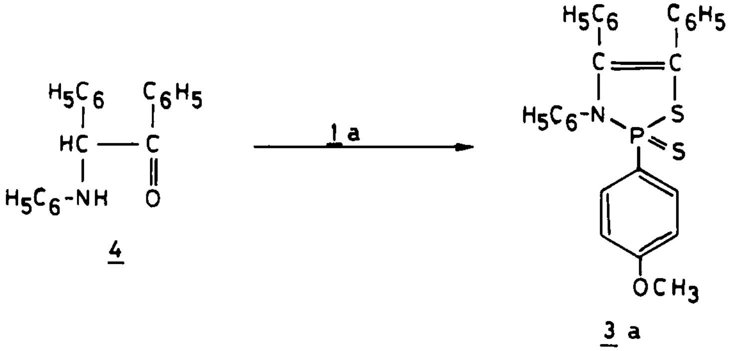
which are in complete accordance with shifts recorded for structures encorporating moiety "A"[13,14]



(A)

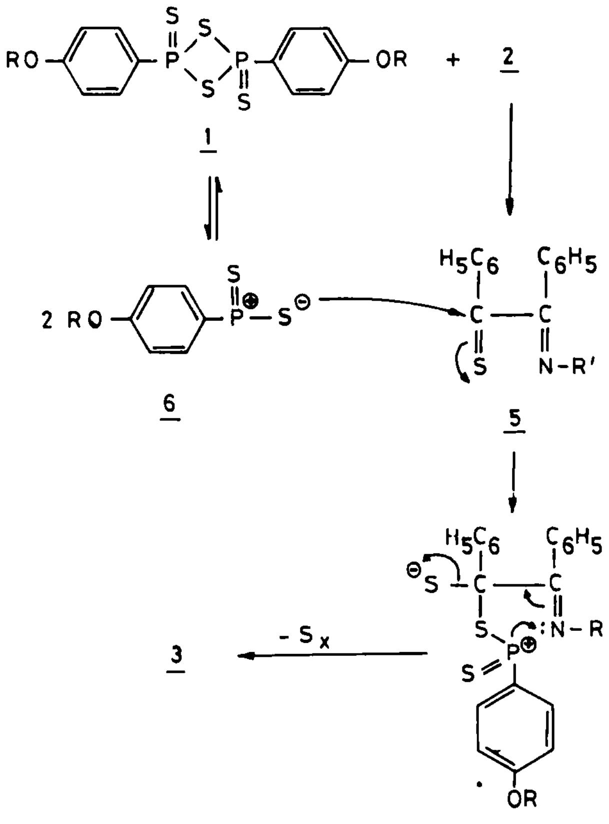
(c) The ^{1}H NMR spectra of **3a** showed a singlet due to the —OCH_3 protons at $\delta = 3.8$ ppm, a multiplet due to 17 ^{1}H (aromatic) in the region 7.70–7.30 ppm, while the other two aromatic protons appear as a double of doublets in the area 7.65–8.15 ppm with $^3J_{pH} = 15$ Hz and $J_{HH} = 9$ Hz (ortho protons to P).

(d) Moreover, compound **3a** has been proved to be identical (m.p., mixed m.p. and comparative IR, ^{1}H, ^{31}P NMR as well as mass spectra) with a sample unequivocally prepared[15] by reacting Lawesson reagent **1a** with α-anilino-α-phenyl acetophenone, **4**.



In the same way, monoanils **2a**, **2b** and **2d** reacted with the diphosphetane-2,4-disulfide reagent **1b** and yielded the new thiazaphospholines **3e**, **3f** and **3g** respectively. Compatible analytical and spectral data (IR, ^{1}H NMR, ^{31}P NMR and ms) were equally obtained for the new compounds (cf. experimental and Table I).

A mechanism accounting for the formation of the ring structure **3a–g** is depicted in Scheme 1. It is based on the assumption of initial thiation of benzil



Scheme 1

TABLE I

NMR (^{1}H, ^{31}P), mass spectra, m.p.s and yields of compounds **3a–g***

Compound	M.P. (°C)	^{1}H NMR (ppm) ($CDCl_3$)	$^{31}P^+$	MS	Yield
3a	170–1	3.8 (s, 3H, OCH_3), 6.70–7.30 (complex pattern, 17 H, aromatic), 7.65–8.15 (dd, 2H, $^3J_{PH}$ = 15 Hz, J_{HH} = 9 Hz (protons o to P.	91.37 86.14	471 (M^+), 456 (M^+—CH_3), 439 (M^+—S) 332 ($C_{20}H_{15}NPS$), 316, 269 (M^+—1/2 LR) 180 (C_6H_5—C=N—C_6H_5).	51
3b	78–80	two signals at 1.65 and 2.25 with intergrals corresponds to 3H (CH_3); 3.80 (s, 3H, OCH_3); 6.80–7.25 (complex pattern, 16 H, aromatic); 7.60–8.10 (dd, 2H, $^3J_{PH}$ = 15 Hz, J_{HH} = 9 Hz) ortho protons to P.	91.06 88.89	485 (M^+) 469 194 (C_6H_5—C=N—$C_6H_4 \cdot CH_3$)	58
3c	oil	2.10 two signals for CH_3, 3.80 (s, OCH_3) 6.60–7.40 (complex pattern, 16^{1}H, aromatics), 7.70–8.25 (dd, 2H with $^3J_{PH}$ = 15 Hz and J_{HH} = 9 Hz for aromatic protons o to P.	91.16 86.11	468, 315, 300, 210	41
3d	75–77	2.20 (singlet, CH_3), 3.85 (s, OCH_3) 6.75–7.50 (complex pattern, 16 H, aromatic), 7.70–8.15, the same two aromatic protons o to p.	91.14 85.95	485, 469, 330, 284, 195	54
3e	145–7	6.70–7.40 (complex pattern, 22 H, aromatics), 7.60–8.20 (dd, 2H, o to P.	90.38	533 (M^+), 518 (M^+—CH_3), 501 (M^+—S), 440 (M^+—Oph), 269 (M^+—1/2 LR), 181 (ph—C=N—ph) 77 (C_6H_5)	38
3f	183–5	two signals at 1.70 and 2.30 with integrals corresponds to 3H (CH_3), 6.70–7.40 (complex pattern, 21 H, aromatics), 7.60–8.15 (dd, 2^{1}H o to P.	90.13 88.05	547 (M^+), 531, 194, 105	18
3g	85–7	broad signals at 2.10 for CH_3, 6.60–7.50 (complex pattern, 21 ^{1}H, aromatics), 7.60–8.20 the same 2^{1}H o to P.	90.30 85.15	547 (M^+), 531 194, 105, 91	44

* Sufficiently correct microanalyses or precise mass measurements have been obtained for all the new products. Ratio of isomer: **3a** (6:1); **3b** (1:1); **3c** (10:6); **3d** (9:1); **3e** (only one isomer); **3f** (9:10); **3g** (9:1).

monoanils **2** by reagents **1** in the conventional manner [2–7] to yield the thioketones **5**. Nucleophilic attack on the thiocarbonyl carbon of **5** by the sulfur anion of the monomeric species **6**—existing probably in equilibrium with reagent **1**[16–18]—can afford the transient dipolar form **7**. The latter undergoes ring-closure via elimination of sulfur, to give the final products **3**.

This finding, which represents a novel route to **3**, supplements to the expanded utility of reagents **1** for production of unique heterocyclic systems.

EXPERIMENTAL

^{1}H NMR spectra were recorded at 60 MHz on a Varian A-60 Spectrometer. ^{13}C and ^{31}P NMR spectra were obtained on a Varian EM 360 instrument at 20.14 MHz and 32.19 MHz respectively. $CDCl_3$ was used as solvent and TMS as internal reference standard. Chemical shifts are expressed as δ values. Also ^{31}P chemical shifts are reported positive low field to (external) H_3PO_4. Mass spectra were recorded on a micromass 7070 ev using direct inlet. Elementary analyses were carried by Lovens Kemiske Fabrik, DK-2750 Ballerup (Microanalytical Laboratory), Denmark. Silica gel 60 (Merck) was used for column chromatography. The light petroleum used boiled below 45° M.P. are uncorrected.

Starting materials

Compound 1 (now available from Fluka AG, CH—9470, Buchs SG) was prepared as described earlier.[19]

General procedure for the reaction of benzilmonoanils with 1,3,2,4-dithiadiphosphetane 2,4-disulfide: A mixture of 0.005 mole of benzilmonoanils and 0.0025 mole of 1,3,2,4-dithiadiphosphetane 2,4-disulfide was heated in 25 ml dry toluene under reflux with stirring until no more of the starting materials could be detected (TLC). After cooling to room temperature, the reaction mixture was evaporated on silica gel under reduced pressure and applied to silica gel column using the eluent stated below. The reaction conditions and yields are also given. The spectroscopic data (^{1}H, ^{13}C, ^{31}P and Ms are cited in Table I.

Compound **3a**: 2-(*P*-methoxyphenyl)-3,4,5-triphenyl-Δ^4-1,3,2-thiazaphospholine-2-sulfide, reaction temperature, 110°, reaction time, 3 hrs, eluent, ether/light petroleum (1:2, V:V) yield 1.2 g. (51%) mp. 170–1°.

Compound **3b**: 2-(*p*-methoxyphenyl)-4,5-diphenyl-3-*o*-tolyl-Δ^4-1,3,2-thiazaphospholine-2-sulfide. 110°, 3 hrs, ether/light petroleum 1:4 V:V yield 1.7 g (58%).

Compound **3c**: 2-*p*-methoxyphenyl)-4,5-diphenyl-3-*m*-tolyl-Δ^4-1,3,2-thiazaphospholine-2-sulfide, 110°, $3\frac{3}{4}$ hrs, eluent, ether/light petroleum 15:100 V:V followed by 25:100 V:V, yield (41%).

Compound **3d**: 2-(*p*-methoxyphenyl)-4,5-diphenyl-3-*p*-tolyl-Δ^4-1,3,4-thiazaphospholine-2-sulfide, 100°, 2 hrs, eluent ether/light petroleum 10:90 followed by 25:75 V:V yield 1.3 g (54%).

Compound **3e**: 2-(*p*-phenoxyphenyl)-3,4,5-triphenyl-Δ^4-1,3,2-thiazaphospholine-2-sulfide, 110°, 4 hrs, eluent CH_2Cl_2/light petroleum 1:1 V:V 1.0 g (38%).

Compound **3f**: 2-(*p*-phenoxyphenyl)-4,5-diphenyl-3-*o*-tolyl-Δ^4-1,3,2-thiazaphospholine-2-sulfide. 110°, $3\frac{1}{2}$ hrs, eluent ether/light petroluem 1:4 V/V followed by 1:2 V:V yield 0.5 g (18%).

Compound **3g**: 2-(*p*-phenoxyphenyl)-4,5-diphenyl-3-*p*-tolyl-Δ^4-1,3,2-thiazaphospholine-2-sulfide, yield (44%).

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