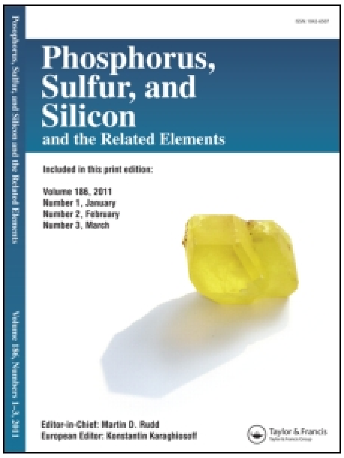

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ORGANOPHOSPHORUS COMPOUNDS REACTION OF THIOPHENOLS AND THIOL ACIDS WITH BENZILMONOANILS

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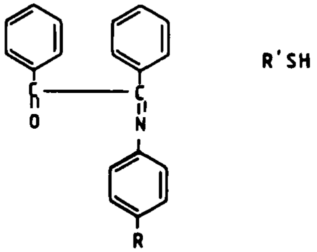
Thiophenols and diphenylphosphinodithioic acid add to carbonyl-carbon double bound in benzilmonoanil $\mathbf{I}_a$, benzilmonoanil p-toluidine I_b and benzilmonoanil p-chloro $\mathbf{I}_c$ to give the corresponding diphenylethyl thiophenol $\mathbf{III}_{a,d,g}$, diphenylethyl thiophenol 2-amino $\mathbf{III}_{b,e,h}$ and diphenylethyl diphenylphosphinodithioates $\mathbf{III}_{c,f,i}$ respectively. The given structures were based upon analytical, chemical and spectroscopic results.

Key words: Monoanils; thiophenols; diphenylphosphinodithioates, phosphorothiolates.

RESULTS AND DISCUSSION

In contribution to our studies on benzilmonoanils with alkyl phosphites[1,2] and with Lawesson reagents,[3] we reported here the reaction of benzilmonoanils with thiophenols and thiol acids.

We have found that the reagent adds preferentially at the carbonyl-carbon double bond in benzilmonoanils. The IR spectrum of the new products shows a strong absorption band of the hydroxyl group and the absence of the band of the carbonyl group.



Ia , R = H
b , R = CH_3-P
c , R = Cl - P

IIa , R' = C_6H_5
b , R' = C_6H_4-NH_2-O
c , R' = $(C_6H_5)_2$ PS

Benzilmonoanils I_{a-c} reacted with thiophenol II_a, o-aminothiophenol II_b and diphenylphosphinodithioic acid II_c in boiling solvent to yield:

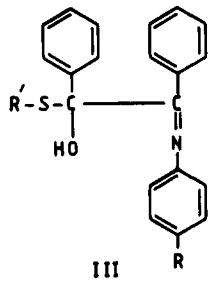
a) 1-Hydroxy-2-[phenyl imino]-1,2-diphenylethyl thiophenol III_a, 1-hydroxy-2-[phenyl imino]-1,2-diphenylethyl thiophenol-2-amino III_b and 1-hydroxy-2-[phenyl imino]-1,2-diphenylethyl diphenylphosphinodithioates III_c.

b) 1-Hydroxy-2-[(4-methylphenyl)imino]-1,2-diphenylethyl thiophenol III_d; 1-hydroxy-2-[(4-methylphenyl)imino]-1,2-diphenylethyl thiophenol-2-amino III_e and 1-hydroxy-2-[(4-methylphenyl)imino]-1,2-diphenylethyl diphenyl-phosphinodithioates III_f.

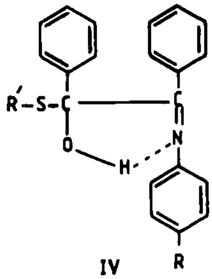
c) 1-Hydroxy-2-[(4-chlorophenyl)imino]-1,2-diphenylethyl thiophenol III_g, 1-hydroxy-2-[(4-chlorophenyl)imino]-1,2-diphenylethyl thiophenol-2-amino III_h and 1-hydroxy-2-[(4-chlorophenyl)imino]-1,2-diphenylethyl diphenyl-phosphinodithioates III_i.

Benzilmonoanils I_{a-c} were allowed to react with reagents $II_{a,b}$ in boiling toluene and with reagent II_c in boiling benzene to give products of structures III_{a-i}.

The mechanism involved the addition of the thiol radical to the carbonyl-carbon double bond followed by hydrogen abstraction from thiophenols and thiol acid.[4]



III



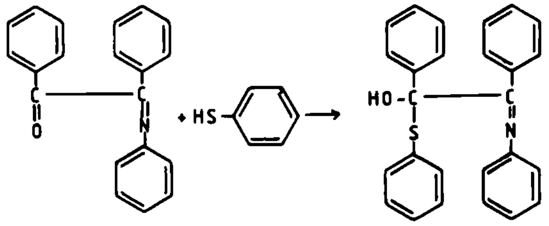
IV

III a , R = H ; $R' = C_6H_5$
b , R = H ; $R' = C_6H_4\text{-}NH_2\text{-}O$
c , R = H ; $R' = (C_6H_5)_2PS$
d , R = CH_3 ; $R' = C_6H_5$
e , R = CH_3 ; $R' = C_6H_4\text{-}NH_2\text{-}O$
f , R = CH_3 ; $R' = (C_6H_5)_2PS$
g , R = Cl ; $R' = C_6H_5$
h , R = Cl ; $R' = C_6H_4 - NH_2 - O$
i , R = Cl ; $R' = (C_6H_5)_2PS$

The addition of phosphorothiolate nucleophiles II_c to compounds I_{a-c} was found to occur in a manner analogus to phosphorus nucleophiles at the more electrophilic carbonyl-carbon atom,[5,6] in agreement with the spectral data.

The I.R. spectra of compounds III_{a-i} in KBr (Table II) showed bands around 3500 cm^{-1} (—OH, free). When the IR spectra of compounds III_{a-i} was measured in $CHCl_3$, the —OH bands appeared in the spectra of these compounds at nearly the same positions. This finding agrees with the absence of chelation between the —OH and —C=N groups in these compounds (cf. IV).

The IR spectrum of compound III_a (using KBr) was consistent with the assigned structure. It showed bands at 3400 cm^{-1} (—OH), 1500 cm^{-1} (aromatic band),



I_a II_a III_a

1620 cm^{-1} (—C=N) and (—C=O) was absent.[7] Its NMR showed aromatic protons (19 H) in the region δ 7.0–8.8 ppm and at δ 1.5 ppm a signal due to the —OH proton which disappeared when deuterated.[8] The mass spectrum of the compound showed a molecular ion peak at 395.

This compound **III$_a$** regenerated the parent benzil when oxidized with lead tetraacetate, also when heated with alcoholic hydrochloric acid.

The adduct **III$_a$** is chromatographically pure, possesses a sharp melting point and dissolves in dilute aqueous alkali, also exhibits no colour reaction with ferric chloride solution. On the other hand, compound **III$_c$** regenerated benzilmonoanil **I$_a$** upon mild alkali hydrolysis and upon heating over its melting point.

Table I indicates the physical constants and analytical data of the new compounds. Table II shows the spectral data IR and ^{1}H-NMR.

EXPERIMENTAL

All melting points were uncorrected. Benzene (thiophene free), toluene and petroleum ether (60–80°C) were dried over sodium. Thiophenol and o-aminothiophenol were available. Diphenylphosphinodithioic acid was freshly prepared[9] and twice crystallized before use. Benzilmonoanils were freshly prepared and twice crystallized before use.[1]

The IR spectra (run in KBr and expressed in cm^{-1}) were recorded with a Beckmann 4220 Infracord Model and the ^{1}H-NMR spectra were measured in ($CDCl_3$ or DMSO-d_6 and expressed in the δ-scale)

TABLE I

Compound	m.p. °C	Solvent of crystallization	Yield %	Formula M. Wt.	Analysis calc./found C	H	N	S	P
III$_a$	162	Benzene	90	$C_{26}H_{21}NSO$	78.99	5.32	3.54	8.10	—
				(395)	79.00	5.53	3.31	8.00	—
III$_b$	63	Ethanol	70	$C_{26}H_{22}N_2SO$	76.09	5.36	6.83	7.80	—
				(410)	76.01	5.33	6.54	7.56	—
III$_c$	146	Pet-ether	80	$C_{32}H_{26}NS_2OP$	71.77	4.86	2.62	11.96	5.79
				(535)	71.50	4.62	2.31	11.62	5.40
III$_d$	103	Benzene pet-ether	85	$C_{27}H_{23}NSO$	79.22	5.62	3.42	7.82	—
				(409)	78.88	5.41	3.21	7.52	—
III$_e$	125	Ethanol	65	$C_{27}H_{24}N_2SO$	76.41	5.66	6.60	7.55	—
				(424)	76.31	5.38	6.30	7.25	—
III$_f$	156	Benzene	75	$C_{33}H_{28}NS_2OP$	72.13	5.10	2.55	11.65	5.65
				(549)	71.98	4.95	2.30	11.35	5.55
III$_g$	185	Benzene	85	$C_{26}H_{20}NSOCl$	72.72	4.65	3.26	7.45	—
				(429.5)	72.50	4.45	3.00	7.25	—
III$_h$	84	Ethanol	60	$C_{26}H_{21}N_2SOCl$	70.27	4.72	6.30	7.20	—
				(444.5)	70.01	4.62	6.20	7.00	—
III$_i$	130	Per-ether	80	$C_{32}H_{25}NS_2OCl$	67.48	4.39	2.46	11.24	5.44
				(569.5)	67.30	4.22	2.30	11.10	5.20

TABLE II

Compound	I.R. cm^{-1}					^{1}H-NMR ppm			
	NH_2	Cl-aryl	OH	C=N	C=C (aromatic)	NH_2	CH_3	Aromatic	—OH
III$_a$	—	—	3400	1620	1500	—	—	7.1–8.0(21H,m)	1.5(1H,s)
III$_b$	1320	—	3430	1610	1500	0.8(2H,s)	—	7.2–8.0(22H,m)	1.6(1H,s)
III$_c$	—	—	3380	1620	1490	—	—	7.5–8.3(26H,m)	1.9(1H,s)
III$_d$	—	—	3520	1630	1480	—	2.2(3H,s)	7.6–8.2(23H,m)	1.8(1H,s)
III$_e$	1330	—	3400	1610	1470	0.7(2H,s)	2.3(3H,s)	7.5–8.1(21H,m)	2.1(1H,s)
III$_f$	—	—	3500	1620	1480	—	2.2(3H,s)	7.5–8.2(28H,m)	1.8(1H,s)
III$_g$	—	1080	3460	1600	1500	—	—	7.2–8.0(20H,m)	1.7(1H,s)
III$_h$	1320	1080	3400	1620	1520	0.8(2H,s)	—	7.2–7.9(21H,m)	1.9(1H,s)
III$_i$	—	1090	3490	1610	1490	—	—	7.3–8.0(25H,m)	1.6(1H,s)

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.

General procedure for the reaction of benzilmonoanils with thiophenol and o-aminothiophenol. A mixture of 0.005 mole of benzilmonoanils and 0.005 mole of reagent was heated in 25 ml dry toluene under reflux with stirring until no more of the starting materials could be detected (TLC). After removal of the volatile materials in vacuo, the residual substance was collected and recrystallized from the proper solvent to give adduct **III$_{a,d,g}$** for the reaction with thiophenol and adduct **III$_{b,e,h}$** for the reaction with o-amino thiophenol.

General procedure for the reaction of benzilmonoanils with diphenylphosphinodithioic acid. To a solution of anil **I$_{a-c}$** (0.1 mole) in benzene (50 ml) was added diphenylphosphinodithioic acid (0.1 mole). The reaction mixture was boiled under reflux for 12 hrs. The mixture was left to cool and the product so obtained was filtered and crystallized to give adducts **II$_{c,f,i}$**.

Degradation experiments with adduct **III$_a$**
a) Oxidation with lead tetraacetate. A solution of **III$_a$** (0.5 g) in dry chloroform (40 ml) was treated with freshly crystallized lead tetraacetate (0.4 g) and the mixture heated on the steam bath for 30 min, then filtered off while hot. After evaporation of the filtrate till dryness, the residue was treated with petroleum ether (b.r. 40–60°C) and left to cool in the refrigerator. The precipitated material was collected, recrystallized from petroleum ether (b.r. 60–80°C) and proved to be benzil (m.p., mixed m.p. and comparative IR spectra).

b) Action of hydrochloric acid on **III$_a$**. Compound **III$_a$** (0.2 g) was refluxed with alcoholic hydrochloric acid (5 ml of hydrochloric acid, sp. gr. 1.18 and 15 ml ethanol) for 2 hrs. The reaction mixture was cooled and the precipitate which separated after neutralization with sodium bicarbonate was collected and crystallized from pet-ether 60–80°C to give benzil (m.p. and mixed m.p. 95°C).

Degradation experiments with dithioate **III$_c$**
a) Alkali hydrolysis. A mixture of **III$_c$** and 10% NaOH aq. (25 ml) was stirred at room temperature for 1 hr. The yellow needles that precipitated were filtered off, washed with water, recrystallized from ethanol and proved to be benzilmonoanil **I$_a$** (yield Ca 85%) (m.p., mixed m.p. and comparative IR spectra).

b) Thermolysis. Compound **III$_c$** was heated in a cold finger sublimator at 200°C (bath temperature) under reduced pressure (5 mm/Hg) for 10 minutes. The substance that sublimed was extracted with boiling ethanol then left to cool in the refrigerator. The precipitated material was collected (70%), recrystallized from ethanol to give yellow crystals proved to be benzilmonoanil **I$_a$** (yield 70%) (m.p. and mixed m.p. 105°C).

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