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THE REACTION OF NITRILES WITH O,O-DIALKYL-DITHIOPHOSPHORIC ACIDS

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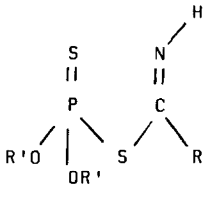
Abstract - Nitriles react with dialkyldithiophosphoric acids 2a-c to give a mixture of corresponding thioamides and O,O-dialkyl-N-thioaceyl-phosphoroamidothioates 3a-e. The structure of compounds 3 are elucidated chemically and from electronic spectra. The yield of thioamides are improved from the reaction of nitriles with compound 2b in presence of water. Mechanistic consideration on the formation of the products are discussed.

INTRODUCTION

It is known from some patents[1,2,3] that nitriles react with $(RO)_2P(S)SH$ to give herbicidal thioamides. The earlier workers[3] identified their pyproduct incorrectly as S-imidoyl-O,O-dialkylditiophosphate derivatives 1. It is now shown to be 3 under the same or different condition.



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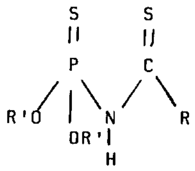

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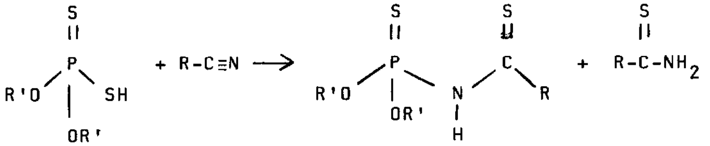
Again, the present work reports on the reaction of nitriles with dialkyldithiophosphoric acids.

RESULTS AND DISCUSSION

Nitriles RCN (R=C_6H_5, C_6H_4-Cl.O, $CH_2COOC_2H_5$) react with dialkyldithiophosphoric acids $\underline{2}$a-c to give a mixture of corresponding known thioamides $\underline{4}$ and O,O-dialkyl-N-thioacylphosphoroamidothioates $\underline{3}$a-e.

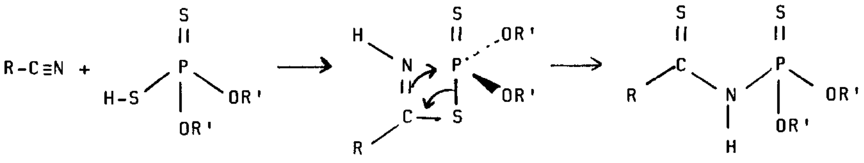


$\underline{2}$a, R'= CH_3
b, = C_2H_5
c, = i-C_3H_7

	R'	R	
$\underline{3}$a	CH_3	C_6H_5	$\underline{4}$
b,	C_2H_5	C_6H_5	
c,	C_2H_5	C_6H_4-Cl.O	
d,	i-C_3H_7	C_6H_5	
e,	i-C_3H_7	CH_2COOCH_3	

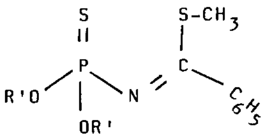
The structures of compounds $\underline{3}$a-e are deduced from microanalysis, MS, ^1H NMR, IR, ^{31}P and ^{13}C NMR (Table 3,4). The IR spectra($CHCl_3$) of compounds $\underline{3}$a-e show NH absorption in the region 1420-1430 cm^{-1}. The ^{13}C NMR spectra contain C=S signal in the range 201-209 ppm (Table 4).

As to the formation of $\underline{3a\text{-}e}$, it is suggested that nucleophilic attack on the nitrile C atom by sulphur of 2 to give the intermediate (5), which collapses to give $\underline{3a\text{-}e}$.



(5)

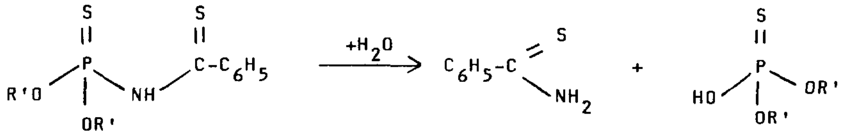
Compounds $\underline{3a,b}$ are methylated using methyl iodide to produce S-methyl derivatives $\underline{6}$a,b.



$\underline{6}$a, R'= CH_3
b, = C_2H_5

The structural proofs of compounds $\underline{6}$a,b are based on microanalysis and spectroscopic data (MS, ^1H NMR, ^{31}P, ^{13}C NMR) Tables 3,4.

Water hydrolysis of compounds 3a,b give thiobenzamide and corresponding phosphoric acid derivatives.



3a, R' = CH_3
b, = C_2H_5

Nitriles RCN (R=C_6H_5 , $C_6H_5CH_2$, $C_6H_5CH_2CH_2$, C_6H_4-Cl.O, C_6H_4-OH.O, C_6H_4-OH.P, $CH_3(CH_2)_4$, CH_3, $ClCH_2$,$CH_2COOC_2H_5$) react with diethyldithiophosphoric acid 2b at 80°C in presence of water to give the corresponding thioamides in high yields (Table 2).

CONCLUSION

The structure of compounds 3a-e are N-thioacyl derivatives and not S-imidoyl derivatives as mentioned before[3]. Compounds 3 are considered as intermediates for the change of nitriles to thioamide using dialkyldithiophosphoric acids.

Table 1

Experimental data for the reaction of nitriles with 2a-c.

R'	R	Temp. °C	Time hr	Product 3 %	Thioamide 4 %
CH_3	C_6H_5	20	24	12	22(4)
C_2H_5	C_6H_5	80	2	58	16(4)
C_2H_5	C_6H_4-Cl.O	20	30	20	15(5)
i-C_3H_7	C_6H_5	20	9	44	28(4)
i-C_3H_7	CH_2COOCH_3	20	21	8	20(6)

Table 2

Experimental data for the reaction of nitriles with 2b in presence of water at 80 °C.

Nitrile (RCN)	Time (hr)	Thioamide %
C_6H_5	1	82(4)
$C_6H_5CH_2$	3	89(7)
$C_6H_5CH_2CH_2$	6	58(8)
C_6H_4-Cl.O	2	65(5)
C_6H_4-OH.O	6	80(9)
C_6H_4 -OH.P	1	78(10)
C_6H_4 -NO_2.P	1	91(11)
$CH_3(CH_2)_4$	6	42(12)
CH_3	6	45(4)
Cl-CH_2	5	55(2)
CH_2COOCH_3	6	56(6)

Table 3

^{31}P; ^{1}H NMR spectra and microanalysis for products 3a-e and 6a,b.

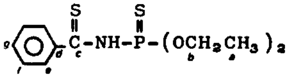
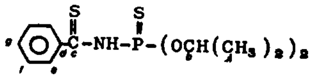
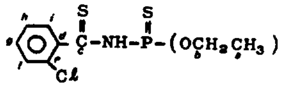
Product	^{31}P	^{1}H NMR	Formula Mol.Wt.	Analysis (Calc./ found) C	H	N	S
3a	62.0	3.7-3.9(6H,d,OCH$_3$),$^3J_{PH}$10.5 Hz; 7.3-7.9(5H,br,aromatic); 8.0-8.3(1H,d,NH); $^2J_{PH}$13.5 Hz.	$C_9H_{12}NO_2PS_2$ 261.3	41.37 41.2	4.63 4.5	5.35 5.4	24.54 24.8
b	61.0	1.3-1.5(6H,t,CH$_3$); 4.1-4.5(4H,dq,OCH$_2$); $^3J_{PH}$10 Hz; 7.2-7.9(5H,br,aromatic); 8.0-8.2(1H,d,NH),$^2J_{PH}$14.5 Hz.	$C_{11}H_{16}NO_2PS_2$ 289.3	45.66 46.0	5.57 5.5	4.84 5.0	22.16 22.0
c	59.5	1.3-1.5(6H,t,CH$_3$); 3.9-4.5(4H,dq,OCH$_2$), $^3J_{PH}$10.5 Hz, 7.1-7.7(4H,br,aromatic); 8.2-8.5(1H,d,NH),$^2J_{PH}$13.5 Hz.	$C_{11}H_{15}NO_2PS_2Cl$ 323.8	40.80 41.0	4.67 4.7	4.32 4.2	19.81 20.0
d	57.1	1.3-1.4(12H,d,CH$_3$), 4.5-5.0(2H,m,OCH), $^3J_{PH}$12.5 Hz; 7.2-7.9(5H,br,aromatic), 8.0-8.3(1H,d,NH),$^2J_{PH}$14.5 Hz.	$C_{13}H_{20}NO_2PS_2$ 317.4	49.19 49.0	6.35 6.2	4.41 4.5	20.20 20.1
e	55.0	1.3-1.5(12H,d,CH$_3$); 3.2(2H,s,CH$_2$CO);3.8 (3H,s,OCH$_3$), 4.6-5.0(2H,m,OCH), $^3J_{PH}$ 11.5 Hz; 8.1-8.3(1H,d,NH),$^2J_{PH}$13.5 Hz.	$C_{10}H_{20}NO_4PS_2$ 313.4	38.33 38.5	6.43 6.4	4.47 4.2	20.47 20.7
6a	59.0	2.5(3H,s,SCH$_3$), 3.7-3.9(6H,d,OCH$_3$), $^3J_{PH}$9.5 Hz, 7.3-8.0(5H,br,aromatic).	$C_{10}H_{14}NO_2PS_2$ 275.3	43.62 43.5	5.13 5.0	5.09 5.2	23.29 23.5
b	60.7	1.1-1.3(6H,t,CH$_3$), 2.4(3H,s,SCH$_3$); 3.8-4.0(4H,dt,OCH$_2$),$^3J_{PH}$9 Hz; 7.3-7.8(5H, br,aromatic).	$C_{12}H_{18}NO_2PS_2$ 303.4	47.51 47.6	5.98 6.0	4.61 4.7	21.14 21.0

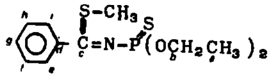
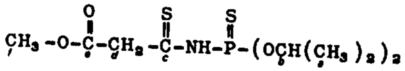
a) The solvent used for ^{1}H NMR spectra is CDCl$_3$.

b) The products 3a-e and 6a,b give $M^{+\cdot}$ in MS.

Table 4

^{13}C NMR spectra for the products 3a-e and 6b.

			
a	15.6; 16.0 $^3J_{PC}$ 8.1 Hz	23.13; 23.48; $^3J_{PC}$ 7.0 Hz	15.7; 16.1 $^3J_{PC}$ 7.5 Hz
b	64.7; 64.9 $^2J_{PC}$ 6.6 Hz	74.1; 74.4; $^2J_{PC}$ 6.0 Hz	64.8; 65.0 $^2J_{PC}$ 4.5 Hz
c	202.4 $^2J_{PC}$ 10.1 Hz	201.0	201.0
d	141.2; 141.7 $^3J_{PC}$ 10.1 Hz	141.5; 142.0; ^3J 9.9 Hz	142.0
e			
f	126.59 128.53	126.5; 128.5	130,35; 127.00 68 130.13 130.00
g	132.1	131.90	
h			
ı			

			
a	16.0; 15.6 $^3J_{PC}$ 7.6 Hz	23.13; 23.49; 23.7	
b	63.1; 63.4 $^2J_{PC}$ 7.5 Hz	74.2; 74.5 $^2J_{PC}$ 5.7 Hz	(74.85, 75.14) $^2J_{PC}$ 5.8Hz)
c	210.0	209.0	
d	138.3; 138.8 $^3J_{PC}$ 9.6 Hz	50.3; 50.7 $^3J_{PC}$ 6.7 Hz	
e		178.4	
f	127.4; 127.8	50.7	
g	130.8		
h	15.20		

EXPERIMENTAL

^{1}H NMR spectra are recorded at 60 MHz on a Varian EM 360 spectrometer. ^{13}C and ^{31}P NMR spectra are recorded at 20 and 32 MHz, respectively, on a Varian CFT-20 spectrometer. TMS is used as internal standered and Chemical shifts are expressed in δ-values. ^{31}P Chemical shifts are related to 85% H_3PO_4. IR spectra were recorded on a Beckman IR spectrometer. Mass spectra are recorded on a micromass 7070 f spectrometer operating at 70 ev using direct inlet.

General procedure for the reaction of nitriles with dialkyldithiophosphoric acids. a) A mixture of 0.005 mole of nitrile and 0.005 mole of compounds 2a-c are heated with stirring at 20-80 °C (Table 1). The reaction mixture, which allowed to obtain room temperature, is extracted with ether (100 ml) and washed with $NaHCO_3$.

Then it is placed on a silica gel column. The thioamides and compounds 3a-e are eluted with CH_2Cl_2 / petroleum ether (50%), Table 1.

b) 0.005 Mole of nitriles; 0.005 mole of compound 2b and 1 ml of water are heated with stirring at 80 °C (Table 2). Then the experiments are completed as in (a) to give the corresponding thioamides in high yield (Table 2).

Hydrolysis of compounds 3a,b. 0.005 Mole of compounds 3a or 3b in 3 ml water is heated at 80 °C with stirring for 3 hours. The reaction mixture which is allowed to obtain room temperature is placed on a silica gel column. The thiobenzamide is eluted with CH_2Cl_2 / petroleum ether (50%) in 60% yield.

Methylation of compounds 3a,b. Amixture of 0.005 mole of compounds 3a or 3b and methyl iodide (0.7 g; 0.006 mole) are dissolved in 30 ml of ethanol containing ½g KOH. The reaction mixture is kept at room temperature with stirring for 4 hours, then it is placed on a silica gel column. The methylated products 6a,b are eluted with CH_2Cl_2 / petroleum ether (40%) in 95% yield.

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