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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS PART 55¹ THE TRANSFORMATION OF NITRILES TO THIOAMIDES WITH *O,O*-DIALKYLDITHIOPHOSPHORIC ACID

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS PART 55¹ THE TRANSFORMATION OF NITRILES TO THIOAMIDES WITH O,O-DIALKYLDITHIOPHOSPHORIC ACID

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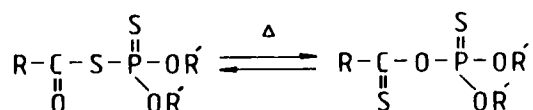
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The reaction between nitriles and O,O-dialkyldithiophosphoric acid (2) under anhydrous conditions produces O,O-diethyl-N-thiobenzoylamidophosphate (5), contrary to literature. When water is present the same reaction gives the corresponding thioamides in reasonable to good yields. Mechanistic considerations and spectral data are presented for the products.

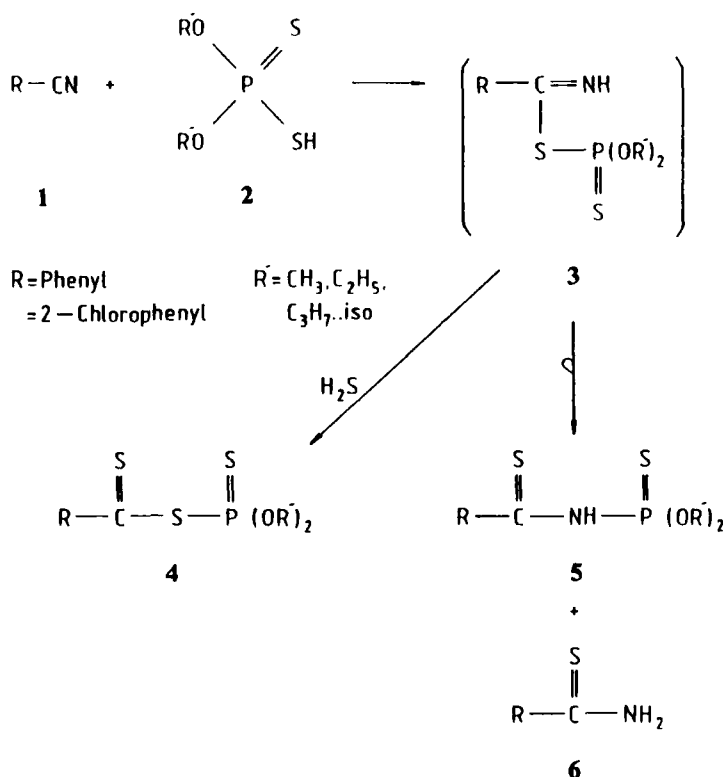
INTRODUCTION

In connection with our investigation on new thioacylating reagents, prepared according to the following transformation.²



Certain limitations were encountered, which we thought could be circumvented by adding O,O-dialkyldithiophosphoric acid (2) to nitriles under anhydrous conditions to give the suggested isolable 1 : 1 adduct (3).^{3,4} Subsequent reaction of 3 with H₂S would then give a thioacylating reagent, 4. (Scheme 1).

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SCHEME 1

However, it was not possible to confirm earlier work,^{3,4} compound **3** was not isolated but instead the rearrangement product, **5**, was the main product. This paper will report on the reaction between **1** and **2** under anhydrous conditions to give **5** and with water present to give thioamides.

TABLE I
Experimental, reaction conditions and the products of the reaction of
O,O-dialkyldithiophosphoric acid, **2**, and nitriles

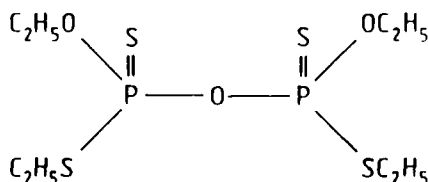
Starting	Molar Ratio 1 : 2	Reaction time (h)	Reaction temp (°C)	Products %	
				5	6
C ₆ H ₅ CN + 2a	1 : 1	24	20	12	22
C ₆ H ₅ CN + 2b	1 : 1	2	80	28.6	5.8
C ₆ H ₅ CN + 2b	2 : 1	2	80	58	9.1
C ₆ H ₅ CN + 2b	1 : 1	22	80	12	26.5
2-ClC ₆ H ₄ CN + 2b	1 : 1	107 [§]	20	19.5	10.5
ClCH ₂ CN + 2b	2 : 1	3 [§]	0	—	43
C ₆ H ₅ CN + 2c	1 : 1	9 [§]	20	44.5	28.4

Notes to table I: 2a, R = CH₃; b, R = C₂H₅; c, R = 2-C₃H₇.

[§]The reaction times in days.

RESULTS AND DISCUSSION

O,O-Dialkyldithiophosphoric acid (2, R' = C₂H₅) was reacted with benzonitrile (1, R = phenyl) in equimolecular amounts at 80°C for 2 hrs to give 29% *O,O*-diethyl-*N*-thiobenzoylamidothiophosphate, 5, and 6% of thiobenzamide, 6, (Table I). A byproduct, tetrathio phosphoric anhydride- P¹-O,S-diethyl ester-P²-O,S-diethyl ester (7), was formed at longer reaction time.



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The structure of the products 5 and 6 has been confirmed by, (Table II-IV) analytical results, derivatives and spectral data. Compound 7 gave M⁺ (354), the phosphorus chemical shift is at δ 94.5 ppm. Compound 6 (R = Ph) is known from literature.⁵ The yellow product 5 (R = phenyl, R' = C₂H₅) exhibits a doublet (1 H) at 8.05–8.17 ppm (²J_{PNH} 14 Hz), which compared to ²J_{PNH} 10 Hz for *O,O*-diphenyl-*N*-phenylamidophosphate⁶ is quite reasonable for structure 5. The size of the coupling constant makes structure 3 improbable, especially as ¹³C NMR also shows an absorption at δ 202.4 ppm which well known for the thiocarbonyl carbon of thioamide.^{7,8} The ³¹P NMR of 5 was found at δ 61.0 ppm which is in accordance with earlier findings.⁹ In UV a strong absorption was found at 280 nm (log ε = 4), typical for thioamide chromophore. In the mass spectra the expected fragmentation pattern was noticed. Also negative ion mass spectra has been investigated. Compound 5 is easily soluble in base and can be extracted from an ether phase by 1 M NaOH. Methylation of the tetrabutylammonium salt of 5 (R = phenyl, R = C₂H₅)

TABLE II

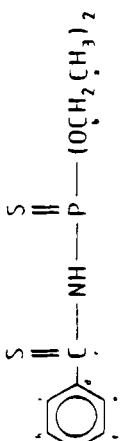
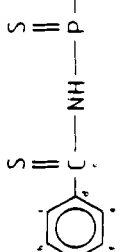
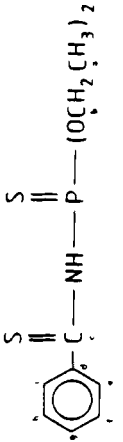


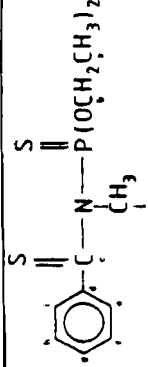
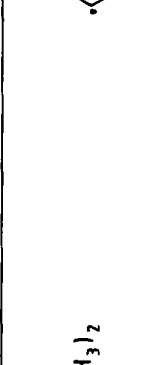


UV and IR Data of Compounds R—C(S)—NH—P(S)(OR)₂, 5, R—C(=S)—N(CH₃)—P(S)(OR)₂, 8,
and R—C(S)—NH—P(O)(OR)₂, 12

Compound	R	R'	UV (CHCl ₃)		IR (CHCl ₃ , cm ⁻¹)	
			nm	log	NH	C=S
5	Ph	Et	280	4.06	3380	1430
5	Ph	Me	295	—	3380	1430
5	Ph	i-C ₃ H ₇	280	4.01	3400	1420
5	2-Cl—C ₆ H ₄	Et	288	3.96	3400	1420
8	Ph	Et	278	—	—	—
12	Ph	Et	256	3.95	3360	—

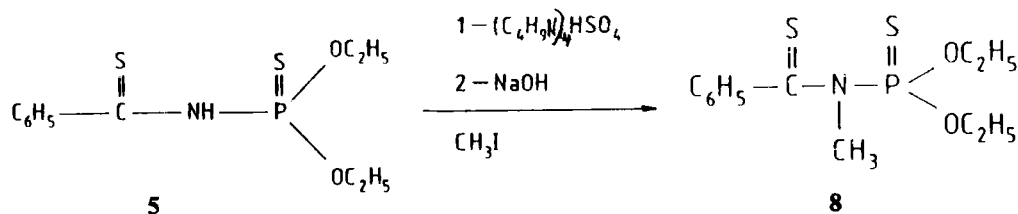
TABLE III
³¹P, ¹H NMR and microanalyses of Compounds 5, 8 and 12

R	R	³¹ P (δ)	¹ H NMR (δ)	Microanalyses (%) Found/Calcd.					
				C	H	N	O	P	Cl
Ph	Et	61.0	1.29–1.45 (6 H, t), 4.11–4.47 (4 H, dq), ³ J _{PH} 10 Hz, 7.24–7.51 (3 H, m), 7.74–7.85 (2 H, m), 8.05–8.17 (1 H, d), ² J _{PH} 13 Hz	45.67	5.68	4.92	10.92	10.74	
Ph	Me	60.5	3.70–3.95 (6 H, d), ³ J _{PH} 14.5 Hz, 7.27–7.6 (3 H, m), 7.67–7.9 (2 H, m), 8.0–8.5 (1 H, d), ² J _{PH} 13–14 Hz	45.60	5.54	4.85	11.08	10.73	
Ph	iso-Pr	57.1	1.32–1.42 (12 H, d), 4.55–5.35 (2 H, d hept.), ³ J _{PH} 12 Hz, 7.2–7.6 (3 H, m), 7.65–7.90 (2 H, m), 8.0–8.4 (1 H, d), ² J _{PH} 14 Hz	36.89	4.19	4.62		10.15	
				37.40	4.19	4.62		10.72	
2-ClC ₆ H ₄	Et	59.5	1.25–1.47 (6 H, t), 3.98–4.50 (4 H, dq), ³ J _{PH} 10 Hz, 7.16–7.65 (4 H, m), 8.2–8.9 (1 H, d), ² J _{PH} 13 Hz	50.26	6.46	4.70	9.97	9.79	
				49.25	6.34	4.41	10.09	9.76	
Ph-C-N-P(S)(OEt) ₂		60.7	1.06–1.21 (6 H, t), 2.47 (3 H, s), 3.82–4.05 (4 H, dt), ³ J _{PH} 9 Hz, 7.29–7.45 (3 H, m), 7.56–7.71 (2 H, m)	40.71	4.78	4.41		9.66	10.89
				40.81	4.64	4.37		9.58	10.97
Ph-C-NH-P(OEt) ₂		-3.5	1.25–1.48 (6 H, t), 4.03–4.53 (4 H, dq), ³ J _{PH} 7.5 Hz 7.3–7.6 (3 H, m), 7.8–8.1 (2 H, m), 9.1–9.5 (1 H, d), ² J _{PH} 10 Hz	47.81	6.07	4.83	10.69	10.02	
				47.50	5.94	4.62	10.56	10.23	
(8)				48.00	5.82	4.92		11.35	
(12)				48.34	5.90	5.13		11.33	

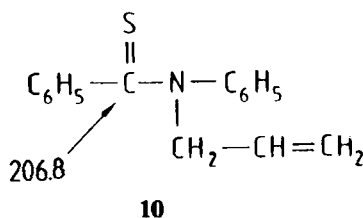
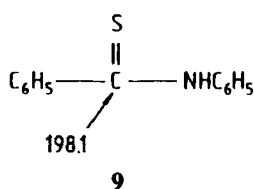
TABLE IV
¹³C NMR Of Compounds 5, 8 and 12

							
a	15.6, 16.0 ³ J _{PC} 8.1 Hz	23.13, 23.48, 27.76 ³ J _{PC} 5.7, 7 Hz	15.7, 16.1 ³ J _{PC} 7.5 Hz				
b	67.7, 64.9 ² J _{PC} 6.6 Hz	74.1, 74.4, ² J _{PC} 600 Hz	64.8, 65.0 ² J _{PC} 4.5 Hz				
c	202.4 ² J _{PC} 10.1 Hz	201.0	201.0				
d	141.2, 141.7 ³ J _{PC} 10.1 Hz	141.5, 142.0 ³ J _{PC} 9.9 Hz	142.0				
e}	126.59, 128.53	126.5, 128.5	130.35, 127.00				
f}	132.1	131.9	130.13				
g			130.00				
h							
i							
							
a	16.0, 15.6 ³ J _{PC} 7.6 Hz	15.9, 16.2 ³ J _{PC} 6 Hz	15.9, 16.2 ³ J _{PC} 6 Hz				
b	63.1, 63.4 ² J _{PC} 7.5 Hz	64.4 ² J _{PC} 5.1 Hz	64.4 ² J _{PC} 5.1 Hz				
c	210.0	204.1	204.1				
d	138.3, 138.8 ³ J _{PC} 9.6 Hz	141.6 ³ J _{PC} 12.4 Hz	141.6 ³ J _{PC} 12.4 Hz				
e}	127.4, 127.8	128.2	128.2				
f}		127.3	127.3				
g	130.8	132.0	132.0				
h							
i							
j	15.20						

gave **8** in quantitative yield.



^{13}C NMR of **8** exhibits absorption at 210.0 ppm and by comparison with the ^{13}C NMR of thiobenzanilide, **9**, and its *N*-alkylated derivatives, **10**, proves the structure of **8**.



As a conclusion we have to state, that the reaction of *O,O*-dialkyldithiophosphoric acids and nitriles produces compounds of the type **5**. It should be added, that making attempts to optimize the reaction, we have found an improved yield when $1/2 = 2$. (Table I).

The mechanism for the formation of **5** from **1** + **2** is indicated in Scheme 1. After the addition of the *S*-acid to the nitrile function, **3** is formed but not isolated. The subsequent *S* → *N* rearrangement (transphosphorylation) produces the final prod-

TABLE V

Experimental and reaction conditions of the reaction of *O,O*-Diethyldithiophosphoric acid and Nitriles in presence of water

Starting Amide	Molar Ratio 1 : 2 : Water	Reaction time (hr)	Reaction temp. (°C)	Yield (%)	M.P. (°C)	M.P. lit.
PhCN	2 : 1 : 1	24	22	49.6	116–7	116–7 ⁵
	2 : 1 : 1	336	22	58.7	—	—
	1 : 1 : 1	1	80	82.5	—	—
	2 : 1 : 2	1.5	80	73.0	—	—
PhCH ₂ CN	2 : 1 : 2	336	22	44.5	96	98 ¹⁴
PhCH ₂ CH ₂ CN	1 : 1 : 1	6	80	46.0	84	—
2-ClC ₆ H ₄ CN	2 : 1 : 1	384	20	65.0	62	62–3 ¹²
2-OHC ₆ H ₄ CN	1 : 1 : 1	6	80	80.0	115–7	117–8 ¹⁵
4-OHC ₆ H ₄ CN	1 : 1 : 1	1	80	78.0	175	175 ¹⁶
4-NO ₂ C ₆ H ₄ CN	1 : 1 : 1	1	80	97.0	155	157 ¹⁷
Hexannitrile	1 : 1 : 1	6	80	42.0	49–51	51 ¹⁸
Cl—CH ₂ CN	2 : 2 : 1	72	2	55.0	77–78	78–79 ¹³
CH ₃ CN	1 : 1 : 1	6	80	45.0	109–111	115–6 ¹⁹
PhCH(CN)COOC ₂ H ₅	1 : 1 : 1	6	80	92.0	118–119	121 ²⁰
CH ₂ (CN)COOCH ₃	1 : 1 : 1	6	40	56.0	76–78	79 ²¹

*New compound with the following microanalysis: Calc. C, 65.54; H, 6.73 N, 8.47; S, 19.35. Found: C, 65.45; H, 6.67 N, 8.49; S, 19.39.

It is noted, that an ethoxycarbonyl group and substituents (Cl, OH, NO₂) on a benzene ring remain unchanged under these reaction conditions. At lower reaction temperature, longer reaction time is needed, and with chloroacetonitrile a reaction temperature of 0–2°C is necessary. Both sulfur atoms of **2** are used in this type of reactions. Benzonitrile (0.01 mole), **2** (R' = C₂H₅, 0.005 mole) and water (0.01 mole) at 80°C for 1.5 hr produce 73% of thioamide. Compound **5** (R = C₆H₅, R' = C₂H₅) is formed, in the presence of water when benzonitrile (0.05 mole), **2** (R' = C₂H₅, 0.025 mole) and water (0.025 mole) were kept at room temperature for 24 hrs to give 49% of thioamide and 3.8% of **5** (R = C₆H₅, R' = C₂H₅). Somewhat unexpected results were observed when benzonitrile, **2** (R' = C₂H₅) and water (ratio 2 : 1 : 1) were allowed to stand for 14 days and nights at 22°C. Besides the thioamide and **5** also *O,O*-diethyl-*N*-thiobenzoylamidophosphate **12**, (Scheme 2) was isolated. The



structure of **12** has been proved by IR, UV, NMR (^1H , ^{13}C and ^{31}P) and microanalysis. In the IR Spectra absorption bands at 3360 cm^{-1} for NH , 1256 cm^{-1} for free $\text{P}=\text{O}$ and 1035 cm^{-1} for $\text{P}-\text{O}-\text{C}_2\text{H}_5$. In the ^1H NMR the NH proton resonates at 9.1–9.5 ppm (d) with $^2J_{\text{PH}} = 10\text{ Hz}$. In the ^{13}C the $\text{C}=\text{S}$ absorbs at 204.1 ppm (Table II, III, IV).

As to the mechanism for the formation of thioamides, **6**, routes 1 and/or 2 are possible (Scheme 2). As **5** hydrolyses very slowly we suggest route 1 to be dominating. The *O,O*-diethylthiophosphoric acid **11**, has not been isolated but its reaction product with benzonitrile has been found (see below). The formation of **12** (Scheme 2) is suggested to occur by addition of **11** (the $\text{P}-\text{SH}$ tautomer) to the nitrile followed by a rearrangement, which has been proven by an independent synthesis when authentic **11** was used.

EXPERIMENTAL

^1H NMR spectra were recorded at 60 MHz on a Varian 360 spectrometer. ^{13}C and ^{31}P NMR spectra were recorded at 20 and 32 MHz, respectively, on a Varian CFT-20 spectrometer. TMS was used as internal standard and chemical shifts are expressed in δ -values. ^{31}P chemical shifts are related to 85% $\text{H}_3\text{PO}_4 \cdot \text{CDCl}_3$, CCl_4 , $(\text{CD}_3)_2\text{CO}$ or $\text{DMSO}-d_6$ were used as solvents. IR spectra recorded on a Beckmann IR-18 spectrometer. Mass spectra were recorded on a Micromass 7070F spectrometer operating at 70 eV using direct inlet. Silica gel 60 (Merck) was used for chromatography. M.P.s are uncorrected. U.V. spectra were recorded on a Perkin-Elmer 402 spectrometer.

1) *Reaction of Benzonitrile + O,O-diethyldithiophosphoric acid (at reflux temperature)*. a) 1.03 g (0.01 mole) of benzonitrile were mixed with 1.86 (0.01 mole) of *O,O*-diethyldithiophosphoric acid and heated for 2 hrs at 80°C , separation on silica gel column gave 0.08 g (6%) of thiobenzamide, m.p. $115\text{--}116^\circ\text{C}$ (lit.⁵ $116\text{--}117^\circ$), 0.83 g (29%) of **5** ($\text{R} = \text{C}_6\text{H}_5$, $\text{R} = \text{C}_2\text{H}_5$), m.p. 68°C .

b) 2.06 g (0.02 mole) of benzonitrile + 1.86 g (0.01 mole) of *O,O*-diethyldithiophosphoric acid as above, yield 1.69 g (58%) of **5** ($\text{R} = \text{C}_6\text{H}_5$, $\text{R} = \text{C}_2\text{H}_5$), and 0.1 g (9.1%) of thiobenzamide.

c) 1.03 g (0.01 mole) of benzonitrile and 1.86 g (0.01 mole) of *O,O*-diethyldithiophosphoric acid were kept at 80°C for 22 hrs to give 0.20 g (12%) of *O,O*-diethyl-*N*-thiobenzoylamidophosphate **5**, 0.25 g (27%) of thiobenzamide **6** and 0.75 g of **7**. The physical data of compound **7** are: ^1H NMR: at δ 1.28–1.43 (12 H, t, 4 CH_3), δ 2.88–3.22 (4 H, dq, 2 CH_2S), 3.99–4.33 (4H, dq, 2 CH_2O), $^3J_{\text{PSCH}} = 16\text{ Hz}$. ^{31}P NMR: δ 94.5. MS: M^+ 354. IR: $\text{P}-\text{O}-\text{C}_2\text{H}_5$ 1025 cm^{-1} , $\text{P}=\text{S}$ 665 cm^{-1} .

2) *At room temperature*. 5.15 g (0.05 mole) of benzonitrile and 4.65 g (0.025 mole) of *O,O*-diethyldithiophosphoric acid were kept at room for 14 days and nights. The mixture was dissolved in ether and extracted with $2 \times 50\text{ ml}$ 1 N NaOH. Addition of petroleum ether to the dried ether phase precipitates 0.32 g of thiobenzamide. The basic H_2O -phase was acidified with 4 N HCl, extracted with ether ($2 \times 100\text{ ml}$), and the combined ether phases washed with water, dried (MgSO_4), concentrated and applied to column chromatography to give 4.24 g (59%) of **5** ($\text{R} = \text{C}_6\text{H}_5$, $\text{R} = \text{C}_2\text{H}_5$) and another 0.24 g of thiobenzamide.

Methylation of compound 5, preparation of 8. 0.34 g (0.001 mole) of tetrabutylammonium hydrogensulfate, 0.08 g (0.002 mole) of NaOH were dissolved in 20 ml H_2O , 0.289 g (0.001 mole) of **5** ($\text{R} = \text{C}_6\text{H}_5$, $\text{R} = \text{C}_2\text{H}_5$) was dissolved in 20 ml chloroform and the solutions were mixed with stirring. Then 0.141 g (0.001 mole) CH_3I was added and stirring continued for 0.5 hr. The CHCl_3 phase was separated and dried (MgSO_4). After removal of CHCl_3 ether was added and the precipitated tetrabutylammonium iodide was removed by filtration. From the ether phase was isolated 0.30 g (99%) of **8** ($\text{R} = \text{C}_6\text{H}_5$, $\text{R} = \text{C}_2\text{H}_5$), $n_D^{25} = 1.5835$.

Compound 5 ($\text{R} = \text{C}_6\text{H}_5$, $\text{R} = \text{CH}_3$). A mixture of 1.13 g (0.011 mole) of benzonitrile and 1.58 g (0.01 mole) of **2** ($\text{R} = \text{CH}_3$) are kept at room temperature for 24 hrs, when **2** is consumed completely. The usual work-up gives 0.30 g (22%) of thiobenzamide and 0.32 g (12%) of the title compound. The reaction gives a complex mixture at $80\text{--}100^\circ\text{C}$.

Compound 5 ($R = C_6H_5$, $R' = 2\text{-Propyl}$). 5.15 g (0.05 mole) of benzonitrile and 10.7 g (0.05 mole) of **2** ($R = 2\text{-propyl}$) were mixed and kept for 19 days at room temperature. 50 ml ether are added and extracted with NaHCO₃-solution. The ether phase is dried (MgSO₄) and after the ether is stripped off, ether-petroleum ether (1/9) is added and 0.99 g of thiobenzamide precipitates. The organic phase is concentrated and by using column chromatography 5.08 g (46%) of the title compound, m.p. 60°C, are isolated. Also 1.50 g benzonitrile was recovered and more thiobenzamide (0.37 g) separated.

Compound 5 ($R = 2\text{-chlorophenyl}$, $R' = C_2H_5$). 4.83 g (0.05 mole) of 2-chlorobenzonitrile and 4.65 g (0.05 mole) of **2** ($R' = C_2H_5$) were mixed together and kept for 107 days at room temperature. The same work-up as above yield 1.64 g (19.5%) of **5** ($R = 2\text{-chlorophenyl}$, $R' = C_2H_5$) m.p. 35°C and 0.18 g (10.5%) of 2-chlorothiobenzamide, m.p. 62°C (Lit.¹² 62.5 – 3°C).

Reaction of chloroacetonitrile with 2 ($R' = C_2H_5$). 3.78 g (0.05 mole) chloroacetonitrile and 4.65 g (0.05 mole) of **2** ($R' = C_2H_5$) were allowed to react for 3 days at 0–2°C to give after working up of the reaction 1.18 g chlorothiobenzamide (43%) m.p. 77°C (lit.¹³ 78–79°C), and 1.1 g from another compound which seems from NMR that $(C_2H_5O)_2P(S)CH_2CN$.

Reaction of O,O-diethyldithiophosphoric acid with nitriles in presence of water. The starting nitrile and O,O-diethyldithiophosphoric acid were mixed together in presence of water and heated or leaved at room temperature (22°C). The molar ratio of the reactants, reaction times, reaction temperature and the yield are listed in Table V. After the reaction has been completed (TLC), the reaction mixture was extracted by ether, washed by NaHCO₃ and dried over MgSO₄ to give the thioamide product.

Note. In case of the reaction of benzonitrile, **2** ($R' = C_2H_5$) and water in ratio (2 : 1 : 1) (entry 2 in Table V) besides the thioamide **6** and **5** (4.2%) also O,O-diethyl-N-thiobenzoylamidophosphate **12** was formed in 4.1% yield, m.p. 116–7°C its physical data (Tables II, III, IV).

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