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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS—XXXV[1]

A NEW ROUTE TO 4-METHOXYPHENYLPHOSPHONOTHIOIC DIAMIDES FROM 2,4-BIS(4-METHOXYPHENYL)-1,3,2,4-DITHIADIPHOSPHETANE-2,4-DISULFIDE AND AMINES

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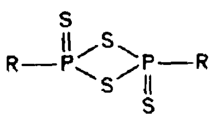
Abstract—By reacting primary and secondary amines with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, **1A**, at 25° ammonium 4-methoxyphenylphosphonamidodithioates, **2**, are formed. Upon heating to 140° **2** eliminates hydrogen sulfide in a new type of reaction yielding 4-methoxyphenylphosphonothioic diamides, **3**, which also are formed directly from primary amines and **1A** at 140°. For dibenzylamine some anomalous results are observed due to N→S rearrangement reactions. NMR spectroscopic data are presented for compounds **2** and **3**.

For some time we have been occupied with thiation reactions using a new thiation reagent 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, **1A**.[1] In an investigation of the reaction of derivatives of urea with **1A** it was unexpectedly found that 4-methoxyphenylphosphonothioic dianilide $MeOC_6H_4PS(NHPh)_2$ was formed when reacting N-phenylurea with **1A**,[2] and the same product was obtained when reacting aniline with **1A**. As a part of our general studies of the chemistry of **1A** these observations and also the fact that phosphonothioic diamides $RPS(NR'R'')_2$ are of potential interest as fungicides, insecticides, and herbicides,[3-10] encouraged and prompted us to make further investigations of the reactions of **1A** with amines. Our results are reported in this paper.



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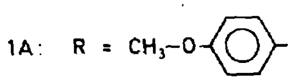

RESULTS AND DISCUSSION

2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, **1A**, reacts with primary amines in ether at 25° to give ammonium N,N'-disubstituted 4-methoxyphenylphosphonamidodithioates, **2a–c, h** (Scheme 1, Table 4), which (after purification) upon heating to 140° in xylene yield 4-methoxyphenylphosphonothioic diamides, **3a–c, h**, under evolution of hydrogen sulfide (Scheme 1, Table 4). By heating **1A** with primary amines at 140° in xylene **3d–k** are formed directly under evolution of hydrogen sulfide (Scheme 1, Table 4). The products **2** and **3** are identified by ^1H NMR, ^{13}C NMR, ^{31}P NMR, MS, and elementary analyses (see section on spectroscopy and Tables 1, 2 and 4).

The primary aliphatic amines (**a–c**) on heating with **1A** at 140° in xylene give complex mixtures, which have not been investigated further. The reagent **1A** does not react with 2- or 4-nitroaniline at 25° in ether or at 140° in xylene. This may be due to the decreased nucleophilicity of the amine due to the nitro group. Compound **1A** reacts with piperidine in ether at 25° to give piperidinium N,N'-pentamethylene-4-methoxyphenylphosphonamidodithioate, **2l**. On heating **1A** and piperidine at 140° in xylene for an extended period of time no evolution of hydrogen sulfide was observed and only **2l** was formed.

Compound **1A** reacts with dibenzylamine in ether at 25° to give a complex mixture. At 140° a mixture consisting of N,N,N'-tribenzyl-4-methoxyphenylphosphonothioic diamide, **4m**, S-benzyl N,N-dibenzyl-4-methoxyphenylphosphonamidodithioate, **5m**, N,N'-dibenzyl-4-methoxyphenylphosphonothioic diamide, **3h**, S-benzyl N-benzyl-4-methoxyphenylphosphonamidodithioate, **6m**, S,S-dibenzyl 4-methoxyphenylphosphonotrithioate, **7m**, and tribenzylamine is formed (Scheme 2, Table 4). When heating **1A** at 230° in excess of dibenzylamine the same products are formed (Table 4). The structure of **3h** has been confirmed by comparison with an authentic sample and the structural proofs of **4m–7m** are based on NMR, MS, and elementary analyses (Tables 3 and 4). Moreover **6m** has been prepared by an independent synthesis: alkylation of benzylammonium N-benzyl-4-methoxyphenylphosphonamidodithioate, **2h**, with benzyl chloride (Experimental)

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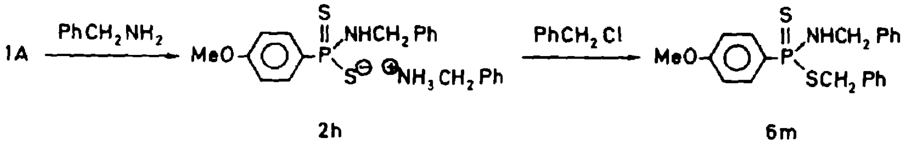
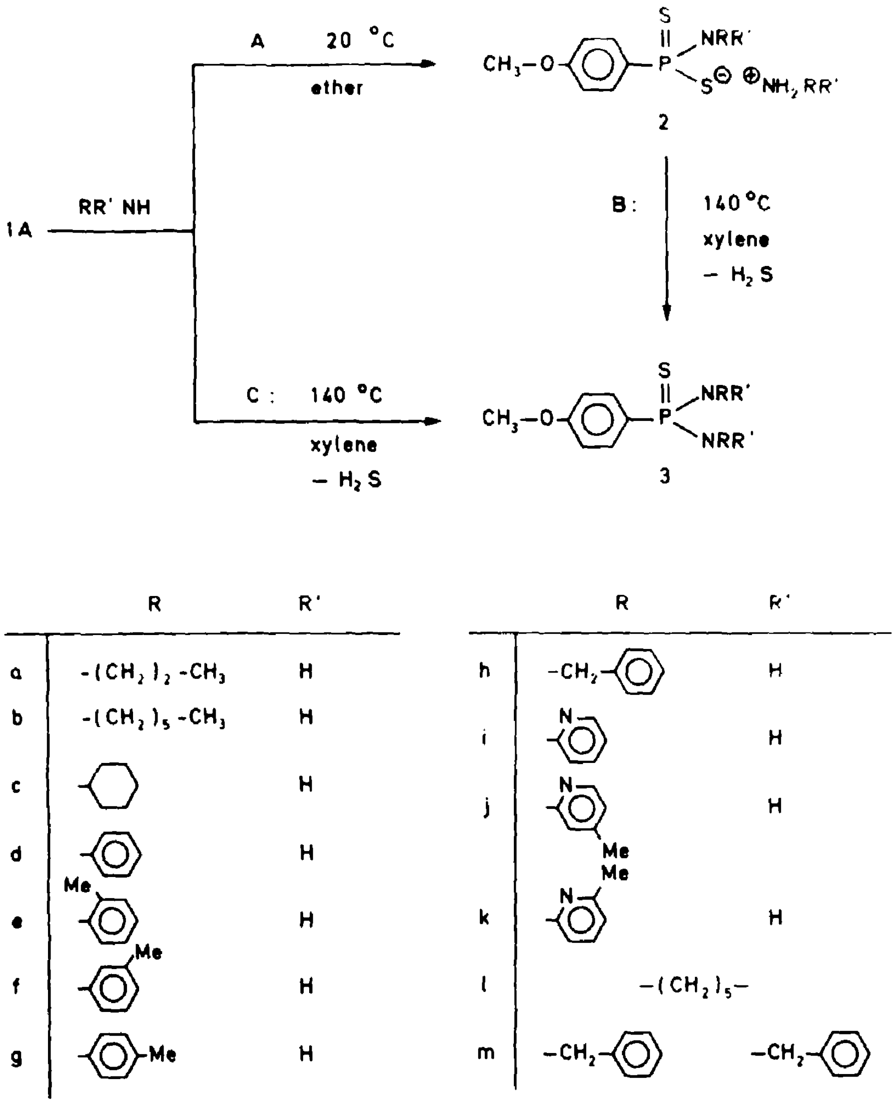
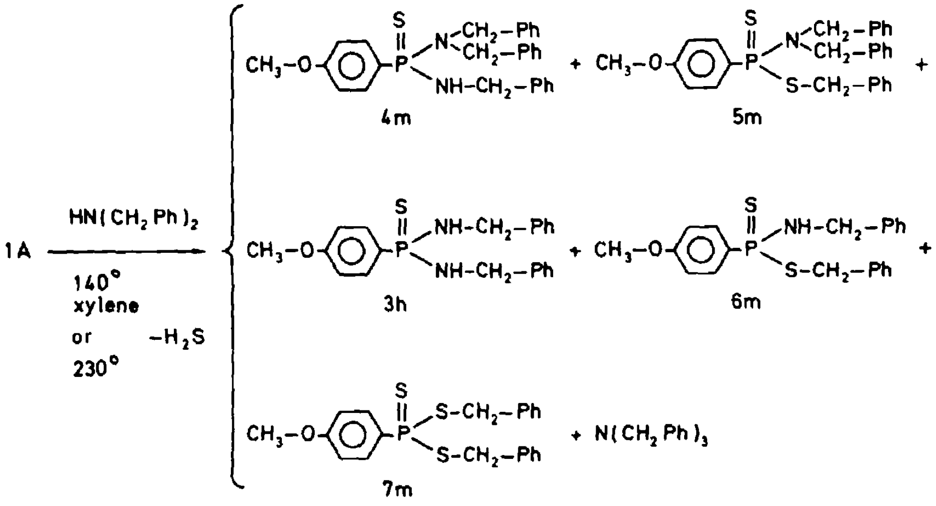




Scheme 1.



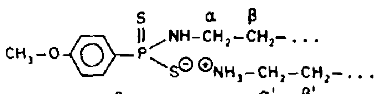
Scheme 2.

Table 1. NMR chemical shifts and P–C coupling constants (Hz) of **2a–c, h, l**

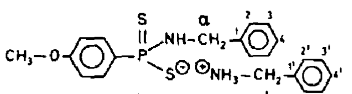
	^1H NMR $(\overset{\oplus}{-}NH_3)$/ $(\overset{\oplus}{-}NH_2)$	^{31}P NMR	^{13}C NMR											
			α	β	γ	δ	ε	ζ	α'	β'	γ'	δ'	ε'	ζ'
<u>2a</u>*	6.2-7.4	87.2	44.5 (3.4)	24.5 (9.9)	11.5	-	-	-	41.5	21.3	11.1	-	-	-
<u>2b</u>*	6.6-7.5	78.2	42.7 (3.5)	31.3 (7.5)	31.4	26.7	22.4	13.9	39.9	27.7	26.3	22.6	22.4	13.9
<u>2c</u>**	5.1-5.8	75.2	50.7 (2.9)	35.1 (4.5)	24.9	25.4	-	-	49.4	30.3	23.7	24.5	-	-
			α	1	2	3	4		α'	1'	2'	3'	4'	
<u>2h</u>**	6.8-7.3	85.1	46.2	142.7 (10.0)	127.9	129.0	128.5	-	42.6	134.2	127.6	128.7	126.2	-
			α	β	γ				α'	β'	γ'			
<u>2l</u>*	8.1-8.4	87.2	45.8	26.5 (9.9)	22.4	-	-	-	44.5	22.4	24.9	-	-	-

* Solvent $CDCl_3$.

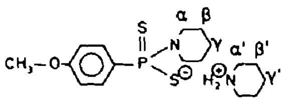
** Solvent DMSO-d_6.



2a-c



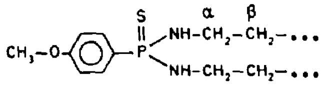
2h



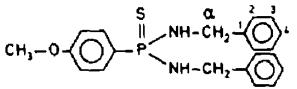
2l

Table 2. NMR chemical shifts and P–C coupling constants (Hz) of **3a–k**

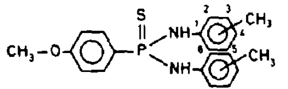
	^1H NMR ($\geq$NH)	^{31}P NMR	^{13}C NMR						
			α	β	γ	δ	ε	ζ	
3a	2.3-2.6	64.1	42.8	24.3 (8.3)	11.0	-	-	-	-
3b	2.1-2.5	64.1	41.1	31.2 (7.5)	31.2	26.3	22.3	13.7	-
3c	2.1-2.5	60.6	50.6	36.0 (4.5)	25.2	25.5	-	-	-
			1	2	3	4	5	6	$-CH_3$
3d	5.1-5.3	52.0	139.9 (2.3)	119.6 (6.2)	129.2	122.5	-	-	-
3e	4.9-5.1	53.07 53.04	138.2 (1.8)	127.8 (7.4)	130.6	122.9	126.7	120.0 (3.6)	17.8
3f	5.1-5.3	52.12 52.10	139.9 (2.1)	120.3 (6.7)	139.0	123.3	129.0	116.6 (6.1)	21.4
3g	5.0-5.2	52.5	137.2 (2.3)	119.9 (6.2)	129.7	132.0	-	-	-
			α	1	2	3	4		
3h	2.6-3.0	65.4	45.1	139.5 (8.5)	127.5	128.3	127.0	-	-
			2	3	4	5	6	$-CH_3$	
3i	arom. region	51.5	153.7	112.3 (4.4)	137.9	117.1	147.9	-	-
3j		51.9	153.8	112.7 (4.8)	149.3	118.5	147.5	21.2	-
3k		51.6	153.0	109.0 (4.3)	138.2	116.4	156.8	23.9	-



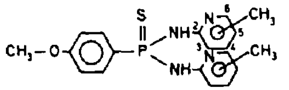
3a-c



3h



3d-g



3i-k

Table 3. NMR chemical shifts and P–C coupling constants (Hz) of **4m–7m**

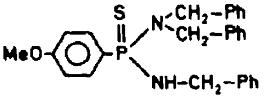
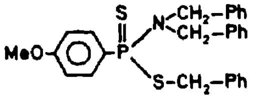
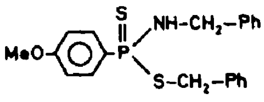
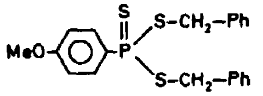
		^1H NMR ($-CH_2-$)	^{31}P NMR	^{13}C NMR				
				α	1	2	3	4
4m		4.25(12)	73.5	48.8(4.6)	137.5(2.7)	128.1	128.3	127
		$4.10\left\{\begin{smallmatrix}(9)\\(7)\end{smallmatrix}\right\}$		45.2	139.4(9.7)	127.6	128.3	127
5m		4.20(12)	88.6	49.1(3.7)	136.8(4.0)	128.2	128.6	127
		4.15(13)		38.3(1.8)	137.1	129.1	128.4	127
6m		$4.05\left\{\begin{smallmatrix}(9)\\(7)\end{smallmatrix}\right\}$	77.0	45.6	138.8(9.5)	127.6	128.3	127
		4.10(13)		37.1(≃0)	137.3(5.6)	128.9	128.3	127
7m		4.15(13)	79.7	37.8(2.3)	136.2(6.2)	129.1	128.3	127

Table 4. Reaction conditions, physical and analytical data

Product	Route*	Yield (%)	Reaction time (h)	Mp. (°C)	Analyses (calc./found) % C	H	N	P	S**
2a	A	97	0.3	101-6	48.72 48.66	7.86 8.05	8.74 8.63		20.01 22.11
2b	A	63	0.3	82-4	56.40 56.12	9.22 9.26	6.92 6.97		15.85 17.58
2c	A	98	0.3	206-8[12]					
2h	A	90	1	148-50	60.58 60.50	6.01 6.20	6.73 6.82	7.45 7.30	15.38 15.87
2l	A C	85 91	7 25	162[12]					
3a	B	32	8	38-40	54.52 54.25	8.10 7.93	9.78 9.30	10.82 11.33	11.20 13.39
3b	B	46	24	$n_D^{23}=1.5386$	61.59 59.55	9.52 9.18	7.56 7.39	8.36 8.34	8.65 9.73
3c	B	14	48	110-12	62.27 62.52	8.53 8.45	7.64 7.58	8.45 8.19	8.75 9.72
3d	C	73	6	137	64.41 63.69	5.37 5.37	7.90 7.48	8.75 7.48	10.78 9.04
3e	C	73	4	120	65.96 65.76	6.29 6.03	7.33 7.00	8.12 8.00	8.38 9.26
3f	C	82	3.5	128	65.96 65.36	6.29 5.88	7.33 7.26	8.12 8.06	8.38 10.54
3g	C	85	3	150	65.96 65.33	6.29 5.98	7.33 6.85	8.12 8.04	8.38 8.33
3h	B C	87 65	10 8	110	65.96 65.15	6.29 5.87	7.33 6.89	8.12 7.87	8.38 9.58
3i	C	66	5	142	57.63 57.26	4.24 4.97	15.82 18.47	8.76 8.61	9.04 10.84
3j	C	44	10	172	59.38 59.33	5.47 6.04	14.58 12.34	8.07 7.26	8.33 9.64
3k	C	39	12	136	59.38 58.87	5.47 5.55	14.58 14.26	8.07 7.94	8.33 9.67
4m***	C D	10 4	18 0.5	97-9					
5m***	C D	6 4	18 0.5	$n_D^{25}=1.6428$					
6m	C D	16 34	18 0.5	$n_D^{25}=1.6354$	63.16 64.47	5.51 5.71	3.51 3.86	7.77 7.24	16.04 15.87
7m***	C D	11 8	18 0.5	$n_D^{25}=1.6640$					

* Route A-C (see text), route D: 230°.

** According to the Microanalytical Laboratory the sulfur analyses are not correct when phosphorus is present.

*** Only spectroscopic proofs.

The fact that no phosphonothioic diamides were obtained when secondary amines as piperidine and dibenzylamine were reacted with 1A is somewhat related to the results of Healy *et al.*,[11] who tried to prepare N,N,N',N'-tetrabenzylphenylphosphonothioic diamide $PhPS[N(CH_2Ph)_2]_2$ from phenylphosphonothioic dichloride $PhPSCl_2$ and dibenzylamine, but instead the mixed amide $PhPS[N(CH_2Ph)_2](NHCH_2Ph)$ was obtained. The present findings with dibenzylamine support to some extent the hypothesis, that steric crowding around the P-atom, also obvious from studies of molecular models, accounts for the rearrangement reactions.

A literature survey reveals that 2,4-disubstituted 1,3,2,4-dithiadiphosphetane-2,4-disulfides, 1, when reacted with primary and secondary amines give ammonium phosphonamidodithioates $RPS(NRR')(S^- \ {}^+NHRR')$,[12–21] while 1 when reacted with ammonia give phosphonothioic diamides $RPS(NH_2)_2$ and diammonium phosphonotrithioates $RPS(S^- \ {}^+NH_4)_2$.[17] Phosphonothioic diamides $RPS(NRR')_2$ have earlier been prepared by three methods: amination of phosphonothioic dichlorides $RPSCl_2$,[11,17,22–49] alkylation of phosphorodiamidothioic chloride $ClPS(NRR')_2$,[5,50,51] and thiation of phosphonous diamides $RP(NRR')_2$ or phosphorodiamidous chlorides $ClP(NRR')_2$.[52–62]

To our knowledge only few spectroscopic data for ammonium phosphonamidodithioates are known. In Table 1 the ¹H NMR shifts of the ammonium protons of

2 are presented. Also the ^{13}C NMR shifts and ^{31}P–^{13}C coupling constants of the carbons in the amine and ammonium parts of the molecules are tabulated. For the 4-methoxyphenyl part of the compounds the ^{13}C NMR shifts and ^{31}P–^{13}C coupling constants are as follows: $\delta_{4\text{-MeO}} = 55.2\text{–}55.3$; $\delta_{C\text{-}4} = 160.9\text{–}161.1$, $^4J_{CCCCP} = 2.5\text{–}3.4$ Hz; $\delta_{C\text{-}3} = 112.7\text{–}113.1$, $^3J_{CCCP} = 13.7\text{–}14.4$ Hz; $\delta_{C\text{-}2} = 132.2\text{–}132.7$, $^2J_{CCP} = 12.3\text{–}13.1$ Hz; $\delta_{C\text{-}1} = 133.7\text{–}134.4$, $^1J_{CP} = 99.2\text{–}102.5$ Hz. Splittings due to P–N–C and P–N–C–C couplings are observed, where the three-bond coupling in agreement with theory is larger than the two-bond coupling, but for the marked carbons no splittings are observed because of the salt bonding. The ^{31}P NMR data are in accordance with the published results for similar compounds,[17] the reported shifts being found in the region 81.1–103.7 ppm. In UV λ_{max} is found in the region 230–240 nm. In MS peaks at *m/e* 202 ($MeOC_6H_4PS_2$, monomer of **1A**) and *m/e* 139 ($MeOC_6H_4PH$) are always observed.

In Table 2 some NMR data for the phosphonothioic diamides, **3**, are given. In ^1H NMR the shifts of the $>$NH protons are found in the range 2.1–7.0 ppm. The values for **3a–c** are in good agreement with reported $>$NH shifts for N,N′-dialkylphenylphosphonothioic diamides which are in the region 2.25–2.5 ppm.[63,64] Also the ^{13}C NMR shifts and ^{31}P–^{13}C coupling constants of the carbons in the amine part of the molecules are given. For the 4-methoxyphenyl part of the compounds ^{13}C NMR shifts and ^{31}P–^{13}C coupling constants are as follows: $\delta_{4\text{-MeO}} = 55.0\text{–}55.4$; $\delta_{C\text{-}4} = 161.8\text{–}162.8$, $^4J_{CCCCP} = 2.6\text{–}3.5$ Hz; $\delta_{C\text{-}3} = 113.3\text{–}114.3$, $^3J_{CCCP} = 14.5\text{–}16.3$ Hz; $\delta_{C\text{-}2} = 132.6\text{–}133.7$, $^2J_{CCP} = 12.2\text{–}14.4$ Hz; $\delta_{C\text{-}1} = 125.6\text{–}126.3$, $^1J_{CP} = 125.9\text{–}136.8$ Hz. Comparing these data with the corresponding data for compounds **2**, the most remarkably deviation is observed for C-1, which is shifted approximately 8 ppm upfield when going from **2** to **3**, and for which the $^1J_{PC}$ coupling constant is increased with approximately 25–30 Hz when going from **2** to **3**. Comparing the respective shifts and coupling constants for the amine parts of compounds **2** and **3**, only slight differences are observed, a common feature being a small upfield shift when going from **2** to **3**. The ^{31}P NMR data are in good agreement with those of similar compounds,[17] the reported shifts for arylphosphonothioic diamides $ArPS(NRR')_2$ being found in the region 57.6–58.2 ppm. For **3e, f** two very close signals (separation ≈ 1 Hz) are observed in the ^{31}P NMR. As this is only observed for the *o*- and *m*-substituted and not for the *p*-substituted compound, it is believed that two isomers exist due to hindered rotation about the N–C bond. In UV λ_{max} is found in the region 240–250 nm. In MS peaks at M^+, M^+–NR, M^+–NR–HS, M^+–2NR–HS, and RNH^+ are always observed.

In Table 3 some NMR data for the products **4m–7m** from the reaction of **1A** with dibenzylamine are given.

As a conclusion it can be stated that new synthetic methods of preparing 4-methoxyphenylphosphonothioic diamides, **3**, from 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, **1A**, have been worked out.

EXPERIMENTAL

^1H NMR spectra were recorded at 60 MHz on a Varian EM 360 spectrometer. ^{13}C NMR spectra and ^{31}P NMR spectra were recorded at 20 MHz 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% H_3PO_4. $CDCl_3$ or DMSO-d6 were used as solvents. IR spectra were recorded on a Beckman IR-18 spectrometer. Mass spectra were recorded on a Micromass 7070 F spectrometer operating at 70 eV using direct inlet. Elementary analyses were carried out by Novo Microanalytical Laboratory A/S, Novo Allé, DK-2880 Bagsvaerd, supervised by Dr. R. E. Amsler. Silica gel 60 (Merck) was used for chromatography. M.ps are uncorrected.

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

General procedure for the preparation of ammonium 4-methoxyphenylphosphonamidodithioates, 2

0.05–0.1 mole of the amine in 20 ml ether was added dropwise at 25° to 0.01 mole of **1A** in 20 ml ether. Stirring was continued until all **1A** was consumed (tlc). The precipitated solid was filtered off and washed several times with ether. Instead of ether CH_2Cl_2 could be used as reaction medium. The experimental, physical, and analytical data are summarized in Table 4.

General procedure for the preparation of 4-methoxyphenylphosphonothioic diamides, 3

Route B. 0.01 mole of **2** was heated in xylene at 140° under N_2, until the starting material was consumed (tlc). After evaporation of the solvent the mixture was worked up by chromatography on silica gel using ether/light petroleum as eluant.

Route C. 0.042 mole of the amine and 0.01 mole of **1A** were refluxed in 15 ml xylene until no more **1A** could be detected (tlc). The products **3d–k** were worked up in the usual manner by column chromatography. The experimental, physical, and analytical data are summarized in Table 4.

Reaction of dibenzylamine with **1A** *at* 140°. 0.01 mole of **1A** and 0.04 mole of dibenzylamine were refluxed in 20 ml xylene for 18 hr. The products were worked up in the usual manner by column chromatography using CH_2Cl_2/light petroleum as eluant. Tribenzylamine, m.p. 92°[65] (1.75 g); N,N′-dibenzyl-4-methoxyphenylphosphonothioic diamide, **3h** (14%). The experimental and physical data for the remaining products **4m–7m** are summarized in Table 4.

Reaction of dibenzylamine with **1A** *at* 230°. 0.01 mole of **1A** was heated at 230° in 10 ml of dibenzylamine for 0.5 hr. Th products were worked up in the usual manner by colum chromatography. Tribenzylamine, m.p. 92°[65] (3.54 g); **3h** (31%) The experimental and physical data for the remaining product **4m–7m** are summarized in Table 4.

Reaction of benzylammonium N-benzyl-4-methoxyphenylphosphonamidodithioate, **2h**, *with benzyl chloride*. 0.01 mole of **2h** wa dissolved in 25 ml CH_2Cl_2, and 0.01 mole of benzyl chlorid dissolved in 15 ml CH_2Cl_2 was added dropwise followed b stirring at 25° for 6 hr. The mixture was then heated at 50° unt no more **2h** could be detected (tlc)(4 hr). Compound **6m** wa isolated in 60% yield.

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