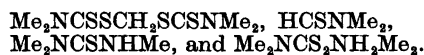


Studies on Organophosphorus Compounds. XI.* Oxidation of Aromatic Compounds with Sulfur in Hexamethylphosphoric Triamide (HMPA). A New Method for Preparation of *N,N*-Dimethylthiocarboxamides

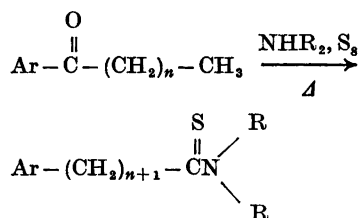
J. PERREGAARD, I. THOMSEN and S.-O. LAWESSON

Department of Organic Chemistry, Chemical Institute, University of Aarhus, DK-8000 Aarhus C, Denmark

Elemental sulfur in HMPA at elevated temperatures has unique oxidizing properties. Alkyl aryl ketones are oxidized to aromatic *N,N*-dimethylthiocarboxamides in reasonable yields. Benzaldehydes give *N,N*-dimethylthiobenzamides and *E*-stilbenes. *N,N*-Dimethylthiobenzamide is demethylated by S_8 in HMPA at about 200 °C. Benzylic compounds $PhCH_2X$ ($X = OH, Cl, SH, NMe_2, OEt, COOEt, CSNMe_2$) all yield *N,N*-dimethylthiobenzamide. α - and γ -Picolines produce the corresponding *N,N*-dimethylthioamides in good yields, while β -picoline does not react under the same conditions. The reaction between S_8 and HMPA is quite complex but the following products have been isolated:



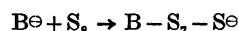
It is a known fact, that by heating sulfur and certain amines with compounds containing oxidizable groups thiocarboxamides are produced. Depending upon reaction conditions also carboxamides and/or carboxylic acids are often isolated.¹ The most well-known reaction of that type is the Willgerodt-Kindler reaction:^{2,3}



* Part X. H. Kolind-Andersen and S.-O. Lawesson, *Acta Chem. Scand. B* 29 (1975) 430.

Good reviews are also available.^{4,5} A drawback is, that working with low-boiling amines the preparation has to be performed in an autoclave in order to reach optimal and quite high reaction temperatures; often also a very high pressure from H_2S is developed.² The synthetic utility of the method is thus limited, if specific amides (thioamides) are wanted. *N,N*-Dimethylformamide has also been used as source of dimethylamine in synthesis of *N,N*-dimethylthiocarboxamides, but due to the low boiling-point of the starting material long reaction times are needed^{6,7} or again an autoclave.⁸ As it has been found, that hexamethylphosphoric triamide (HMPA) at high temperatures can act as a precursor of dimethylamine,⁹⁻¹² we felt prompted to study the behaviour of elemental sulfur in HMPA at elevated temperatures and with different substrates present. This paper reports about oxidation of some aldehydes, ketones, benzylic derivatives, and methylpyridines.

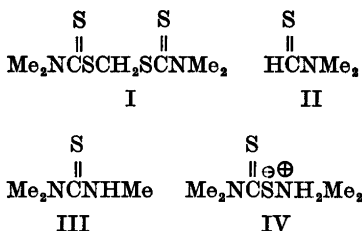
Reaction of HMPA with S_8 . It has been shown earlier that certain bases open up the S_8 -ring and give a sulfur anion:¹



As HMPA is a rather strong base,¹³ its reaction with S_8 is of great potential interest to the organic chemist. Recently Chivers and Drummond¹⁴ claimed that a blue solution is formed when sulfur is dissolved in anhydrous HMPA,

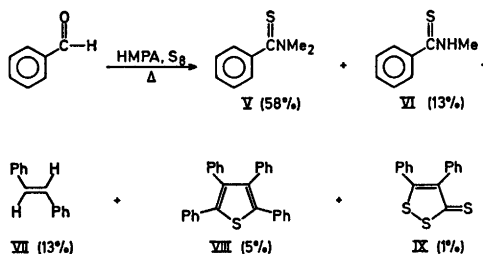
and based on spectroscopic evidence and electrical conductivity measurements they suggested the presence of the species S_3^- . However, we have shown, that HMPA, purified according to Brandsma¹⁵ and kept over molecular sieves, does not give the blue colour or the reported IR absorption at 620 nm with elemental sulfur. But addition of traces of dimethylamine to the HMPA + S_8 solution produces the reported findings.¹⁴ Earlier results¹⁴ have thus to be dealt with with great doubt.

The reaction of HMPA with S_8 at 190 °C is rather complex and within 4 h 2 mol of sulfur (per mol of HMPA) are consumed under development of H_2S . Besides unreacted HMPA the products, I–IV, are isolated, however, only in minor amounts.



The presence of IV strongly indicates the formation of carbon disulphide during the reaction. The products show that oxidation and oxidative demethylation take place on the dimethylamino groups.

Oxidation of benzaldehydes. It is already known that aromatic aldehydes when refluxed with sulfur and a secondary amine, yield the corresponding thioamide in high yields.^{4,16,17} No attempts have been made to isolate other products. The reaction of benzaldehyde with S_8 in HMPA at 205 °C gives a series of products, V–IX, with the thioamide, V, as main product.



o-Methoxybenzaldehyde also produces the *N,N*-dimethylthiobenzamide and the corresponding *E*-stilbene. The *N*-demethylated thioamide was not found in this reaction.

An interesting paper⁷ reports that oxidation of benzaldehydes with S_8 in *N,N*-dimethylformamide produces *N,N*-dimethylbenzamides in considerable yields besides *N,N*-dimethylthiobenzamides. In an experiment with benzaldehyde, S_8 and HMPA, performed at 185 °C, *N,N*-dimethylbenzamide was formed, but obviously at higher temperatures it reacted further to the thioamide.

Oxidations of alkyl aryl ketones. Acetophenone (X, R = CH_3 , R' = H), when heated in HMPA with great excess of S_8 , gave *N,N*-dimethylthiobenzamide, XI, in appreciable yields and also a small yield of the normal Kindler product, XII. Small amounts of 2,5-diphenylthiophene are produced, too. (For other results, see Table 1). In the Willgerodt reaction with great excess of sulfur and quite high reaction temperatures only non-degraded products are produced.¹⁸ Under

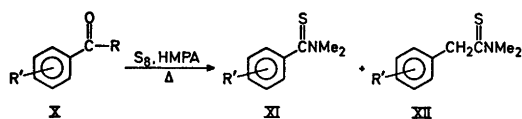
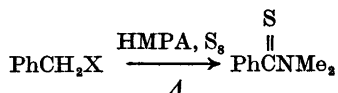


Table 1. Oxidations of alkyl aryl ketones. In all experiments 0.1 mol of ketone was used.

R'	R	S_8 (mol)	HMPA (ml)	React. time (h)	React. temp. (°C)	XI (%)	XII (%)
H	Me ^a	0.6	25	12	172	71	10
<i>p</i> -Me	Me	0.6	25	12	170	64	11
H	Et ^b	0.6	25	10	172	57	19
H	CH_2CO_2Et	1.0	50	12	155	55	5

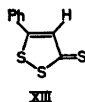
^a 2,5-Diphenylthiophene was isolated. ^b 5-Phenyl-3*H*-1,2-dithiole-3-thione was isolated in 10 % yield.

Table 2. Oxidation of benzylic derivatives. 0.1 mol of benzylic derivative was used in all experiments.



X	S ₈ (mol)	HMPA (ml)	React. time (h)	React. temp. (°C)	V (%)
OH	0.3	25	2	185	75
SH	0.3	25	3.5	173	82
Cl	0.3	25	0.25	190–240	80
NMe ₂	0.3	25	0.75	185	81
OEt	1.0	30	8	200	47 ^a
COOEt	1.0	50	7	188	37 ^b
CSNMe ₂	0.4	30	12	170	78

^a 16 % of PhCSNHMe isolated. ^b 37 % of PhCH₂CSNMe₂ was formed.



almost the same conditions but with HMPA present instead of a free amine the main product, XI, is due to degradation of X. Apparently another mechanism has to be considered. Compound XII might be one of the possible intermediates as it is degraded to XI when heated with sulfur in HMPA. No attempts have been made to get optimal yields of XI, but greater excess of sulfur, possibly also longer reaction times, should decrease the yield of XII and increase that of XI.

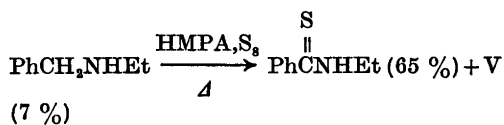
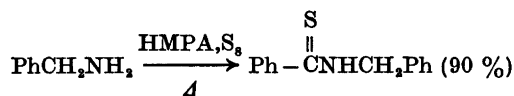
Propiophenone (X, R = Et, R' = H) produced the degradation product XI in 57 % yield, and surprisingly also XII, meaning that a C₃-side-chain has been shortened by one carbon. From the same reaction also the non-degraded 5-phenyl-3H-1,2-dithiol-3-thione, XIII, was isolated.

Oxidation of ethyl benzoylacetate gave, besides XI and XII, also *N,N*-dimethylthioacetamide. As the same thioamide also is formed by oxidizing ethyl phenylacetate with S₈ in HMPA it might be possible that the ethyl group is responsible for this compound. A separate paper¹⁹ on oxidation of esters will be published in due time.

Oxidation of benzylic derivatives. A series of derivatives, PhCH₂X, where X = OH, SH, Cl,

NMe₂, OEt, COOEt and CSNMe₂, was oxidized by sulfur in the presence of HMPA, and the main product, V, was isolated in quite high yields (Table 2). No attempts were made to reach optimal yields.

Also other benzylamines than *N,N*-dimethylbenzylamine have been investigated.

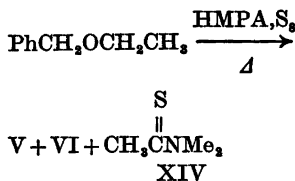


N-Benzylthioacetamide has earlier been produced without the presence of HMPA.²⁰ From the second reaction it is concluded that transamidation does not seem to occur to any great extent.

Benzyl alcohols yield *N,N*-dimethylbenzylamines when heated at about 230 °C with HMPA.¹² Reaction in the presence of sulfur at 185 °C gives V in quite high yields. Benzyl mercaptan also yields V. However, under the same reaction conditions without sulfur present no reaction between benzyl mercaptan and HMPA occurred. At higher temperatures dibenzylsulfide was formed. These results indicate that *N,N*-dimethylbenzylamine is not initially formed in these reactions.

Oxidation of benzyl ethyl ether required rather severe reaction conditions, but when all

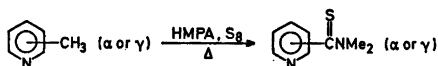
the ether had been reacted three compounds could be isolated:



V and XIV are supposed to be formed first by oxidation of the ether to two different thionacids, or derivatives thereof, and subsequent reaction with HMPA to the corresponding thioamides. VI is formed from V as has been shown in a separate experiment. When *N,N*-dimethylthiobenzamide was heated with sulfur in HMPA for 2 hours at 225 °C about 20 % of *N*-methylthiobenzamide was isolated, besides non-reacted starting material. Compound VI was recognized as minor product (by NMR) in most of the reaction mixtures. Thus it is noted that long reaction times and high reaction temperatures cause an appreciable demethylation of V to give VI.

Ethyl phenylacetate, after reaction with sulfur in HMPA, gave 37 % yield of V and the same yield of phenyl-*N,N*-dimethylthioacetamide. That means that an ester can be directly converted to a thiocarboxamide.¹⁹

Oxidation of picolines. Both α - and γ -picolines are converted into the corresponding *N,N*-dimethylthiocarboxamides when heated at 130–160 °C for 20–22 h with DMF in the presence of sulfur. With HMPA the same results were obtained after only one hour's reflux.



The β -picoline was recovered unchanged after reflux in HMPA for 20 h, which is in agreement with earlier observed reactivities of the methyl groups of picolines in oxidation with sulfur.¹

Conclusion. The results presented in this paper show that S₈ in HMPA is a rather strong oxidizing reagent, which easily converts many different types of aromatic compounds into aromatic *N,N*-dimethylthiocarboxamides. A preparative advantage is that all reactions can be run in open vessels contrary to previously described reactions with dimethylamine. It is foreseen that elemental sulfur + HMPA at

elevated temperatures should comprise unique reactivities, which now are being studied on a whole range of different substrates.

EXPERIMENTAL

NMR spectra were recorded at 60 MHz on a Varian A-60 spectrometer. TMS was used as internal reference standard. The chemical shifts are expressed in δ values (ppm) (s=singlet, d=doublet, t=triplet, m=multiplet). IR spectra were recorded on a Beckman IR-18 spectrophotometer. Mass spectra were recorded on a CEC 21-104 operating at 70 eV, using direct inlet. Ion source temperature 250 °C. Column chromatography was carried out with silicagel 60 (Merck), using light petroleum as eluent and then stepwise raising the polarity by addition of ether. Commercial HMPA dried over molecular sieves (3A) was used. Elemental analyses were performed by Novo Industry A/S, Copenhagen. M.p.'s and b.p.'s are uncorrected.

Oxidation of HMPA with sulfur. HMPA (17.9 g) was heated with S₈ (6.4 g) at 190 °C for 4 h. After cooling to room temperature the mixture was dissolved in 100 ml of hot CH₂Cl₂. On addition of ether a gum precipitated. The solution was decanted and the solvent evaporated. Column chromatography yielded: I. 140 mg of *methylene dimethyldithiocarbamate* (I), m.p. 150–151 °C (lit.²¹ m.p. 150–151 °C). (Found: C 32.97; H 5.63; N 11.03; S 49.92. C₇H₁₄N₂S₄ requires: C 33.07; H 5.51; N 11.02; S 50.39). NMR (CDCl₃): 3.4 (d, 12 H); 5.4 (s, 2 H). MS: *m/e* 254 (M⁺, \approx 1 %); 164 (Me₂NCS⁺, 60 %); 88 (Me₂NCS⁺, 100 %). II. 1.1 g of *N,N*-dimethylthioformamide (II), b.p. 96–98 °C/11 mmHg (lit.²² b.p. 95–100 °C/10 mmHg). An NMR spectrum was in accordance with literature.²² III. 2.2 g of *N,N,N'*-trimethylthiourea (III), m.p. 84 °C (lit.²³ m.p. 87 °C). NMR (CDCl₃): 3.1 (d, 3 H); 3.3 (s, 6 H); \approx 6.0 (m, 1 H). IR(KBr): 1550, 2940 and 3280 cm⁻¹. Further elution with CH₃CN yielded some very hygroscopic crystals which could not be purified for identification. Finally elution with MeOH afforded a mixture of products, which after distillation (b.p. 60–66 °C/0.3 mmHg) yielded 3.8 g of HMPA. From a condenser a crystalline material was collected, dissolved in CHCl₃ and on addition of ether 400 mg of *dimethylammonium dimethyldithiocarbamate* (IV), m.p. 130–131 °C was obtained (lit.²⁴ m.p. 130–132 °C). NMR (D₂O): 2.7 (s, 6 H); 3.5 (s, 6 H); 4.7 (s, 2 H).

In all the following experiments a common working-up procedure was used: When cooled down to room temperature the reaction mixtures were poured into 250 ml of brine and 100 ml of ether. Non-reacted sulfur was filtered off. After ether extraction (3 \times 100 ml) (except for the picolines where extraction was performed with benzene) and washing with brine (2 \times 50 ml)

the combined ether phases were dried (CaSO₄), the ether evaporated and the crude organic phases were further purified according to the procedures below.

Benzaldehydes

Benzaldehyde (10.6 g) was heated with 9.6 g of S₈ in 25 ml of HMPA at 205 °C for 75 min. Column chromatography of the organic phase yielded: I. 1.2 g (13 %) of *E-stilbene* (VII), m.p. 122–123 °C (lit.²⁴ m.p. 124 °C). NMR (CDCl₃): 7.1 (s, 2 H); 7.3 (m, 10 H). IR (CCl₄): 960, 1490, 1600 and 3030 cm⁻¹. II. 500 mg (5 %) of *tetraphenylthiophene* (VIII), m.p. 181–183 °C (lit.²⁵ m.p. 183–184 °C). (Found: C 86.54; H 5.13; S 8.47. C₂₈H₂₀S requires: C 86.56; H 5.19; S 8.25). NMR (CS₂): 7.0 (m). MS: *m/e* 388 (M⁺, 100 %); 311 (M-Ph, 13 %); 121 (PhCS⁺, 5 %); 77 (5 %). III. 200 mg (1 %) of orange-red *4,5-diphenyl-3H-1,2-dithiole-3-thione*, m.p. 158–159 °C (lit.²⁶ m.p. 159 °C). (Found: C 62.40; H 3.41; S 33.31. C₁₆H₁₀S₃ requires: C 62.90; H 3.52; S 33.58). NMR (CS₂): 7.2 (m). IR (CHCl₃): 830, 1040, 1150, 1510, 3000 cm⁻¹. MS: *m/e* 286 (M⁺, 88 %); 285 (100 %); 178 (PhCCPh, 36 %); 165 (M-PhCS, 32 %); 145 (PhC₂S⁺, 44 %); 121 (PhCS⁺, 54 %); 77 (46 %). IV. 9.2 g (55 %) of *N,N-dimethylthiobenzamide*, m.p. 67 °C (lit.⁷ m.p. 67 °C). NMR (CDCl₃): 3.1 (s, 3 H); 3.5 (s, 3 H); 7.3 (m, 5 H). A mass spectrum was in accordance with literature.²⁷ V. 2.0 g (13 %) of *N-methylthiobenzamide*, m.p. 77–78 °C (lit.²⁸ m.p. 79 °C). NMR (CDCl₃): 3.2 (s, 1.5 H); 3.3 (s, 1.5 H); 7.5 (m, 5 H); 8.0 (m, 1 H). A mass spectrum was in accordance with literature.²⁷

In another reaction of benzaldehyde run at 185 °C for 2 h the organic phase yielded after column chromatography besides the products found above 2.7 g (18 %) of *N,N-dimethylbenzamide*, m.p. 40–42 °C (lit.²⁹ m.p. 43 °C). NMR (CDCl₃): 3.0 (s, 6 H); 7.4 (m, 5 H). IR (CCl₄): 1075, 1380, 1630, 2900 and 3020 cm⁻¹.

o-Methoxybenzaldehyde (13.6 g) was heated with 9.6 g of S₈ in 25 ml of HMPA at 200 °C for 30 min. Column chromatography of the organic phase first yielded 1.5 g of a mixture of products, which could not be further separated. Then 1.3 g (11 %) of *2,2'-dimethoxy-E-stilbene* was isolated, m.p. 135–136 °C (lit.³⁰ m.p. 140 °C). NMR (CDCl₃): 3.8 (s, 6 H), 7.3 (m, 10 H). IR (CHCl₃): 970, 1230, 1450, 1480, 1590, 2920 and 3050 cm⁻¹. Finally 13.6 g (70 %) of *o-methoxy-N,N-dimethylthiobenzamide* was eluted, m.p. 84 °C. (Found: C 61.39; H 6.72; N 7.18; S 16.49. C₁₀H₁₃NOS requires: C 61.54; H 6.67; N 7.18; S 16.41). NMR (CDCl₃): 3.1 (s, 3 H); 3.6 (s, 3 H); 3.8 (s, 3 H); 7.1 (m, 4 H).

Alkyl aryl ketones

Reaction conditions are given in Table 1.

Acetophenone. Column chromatography of the organic phase yielded as the first fraction 2.6 g of a mixture of products. Distillation (until 200 °C/0.3 mmHg) followed by separation on preparative TLC (silica gel, elution with 15 % ether in light petroleum) yielded 160 mg of *2,5-diphenylthiophene*, m.p. 148–150 °C (lit.³¹ m.p. 150.5 °C). NMR (CDCl₃): 7.3 (m). A mass spectrum was in accordance with literature.³¹ Further elution of the organic phase yielded 13.4 g of a mixture of *N,N-dimethylthiobenzamide* (XI) (71 %) and *phenyl-N,N-dimethylthioacetamide* (XII) (10 %). The yields are calculated according to NMR. Authentic phenyl-*N,N*-dimethylthioacetamide was prepared.⁹ NMR (CDCl₃): 3.2 (s, 3 H); 3.5 (s, 3 H); 4.3 (s, 2 H); 7.3 (m, 5 H).

p-Methylacetophenone. Column chromatography of the organic phase gave first 2.0 g of a mixture of products, which was not further purified. Then 13.6 g of a mixture of two thioamides was eluted. Crystallization of the mixture twice from ether yielded pure *p-methyl-N,N-dimethylthiobenzamide*, m.p. 49–50 °C (lit.³² m.p. 49–49.5 °C). NMR (CDCl₃): 2.3 (s, 3 H); 3.1 (s, 3 H); 3.5 (s, 3 H); 7.1 (m, 4 H). From the mixture *p-methylphenyl-N,N-dimethylthioacetamide* was recognized according to an NMR-spectrum (CDCl₃): 2.3 (s, 3 H); 3.1 (s, 3 H); 3.4 (s, 3 H); 4.2 (s, 2 H); 7.1 (m, 4 H).

Propiophenone. Column chromatography of the organic phase yielded: I. 2.2 g (10 %) of *5-phenyl-3H-1,2-dithiole-3-thione*, m.p. 121–123 °C (lit.³³ m.p. 126 °C). (Found: C 51.44; H 2.86; S 45.08. C₈H₆S₃ requires: C 51.39; H 2.88; S 45.73). NMR (CS₂): 7.2 (s, 1 H); 7.5 (m, 5 H). II. 12.9 g of a mixture of *N,N-dimethylthiobenzamide* (57 %) and *phenyl-N,N-dimethylthioacetamide* (19 %).

Ethyl benzoylacetate. Column chromatography of the organic phase yielded: I. 5.9 g of a mixture of products which were not further purified. II. 10.0 g of a mixture of *N,N-dimethylthiobenzamide* (55 %) and *phenyl-N,N-dimethylthioacetamide* (5 %). III. 2.1 g (20 %) of *N,N-dimethylthioacetamide*. M.p. 72 °C (lit.³⁴ m.p. 73–74 °C). NMR (CDCl₃): 2.7 (s, 3 H); 3.3 (s, 3 H); 3.5 (s, 3 H).

Benzyl derivatives

In most reactions the organic phase was simply distilled twice, yielding pure *N,N*-dimethylthiobenzamide. Reaction conditions and yields are given in Table 2. The following are exceptions to the general procedure.

Benzyl ethyl ether. Column chromatography of the organic phase yielded 7.8 g (47 %) of *N,N-dimethylthiobenzamide* and 2.4 g (16 %) of *N*-

methylthiobenzamide. Further elution yielded 600 mg (6 %) of *N,N*-dimethylthioacetamide.

Ethyl phenylacetate. The reaction mixture was very stiff, when cooled down, so it was dissolved in boiling CH_2Cl_2 , cooled to room temperature and filtered. Filtration through a silica gel column (eluted with CH_2Cl_2) followed by column chromatography yielded 12.8 g of an approximately 1:1 mixture of *N,N*-dimethylthiobenzamide and *phenyl-N,N*-dimethylthioacetamide. Further elution yielded 2.3 g of a mixture of *N,N*-dimethylthioformamide (~80 %) and *N,N*-dimethylthioacetamide (~20 %).

Benzylamine (10.7 g) was heated with 9.6 g of S_8 in 25 ml of HMPA at 175 °C for 45 min. After the general working-up procedure, the organic phase was recrystallized from light petroleum-ether (1:1), yielding 10.2 g (90 %) of *N*-benzylthiobenzamide, m.p. 82–83 °C (lit.³⁰ m.p. 84–85 °C). NMR (CDCl_3): 4.8 (d, 2 H); ~7.5 (m, 11 H).

Benzylethylamine (13.5 g) was heated with 9.6 g of S_8 in 25 ml of HMPA at 185 °C for 45 min. Distillation of the organic phase yielded a fraction (11.9 g) with b.p. 135–143 °C/0.25 mmHg. An NMR-spectrum showed that it contained *N,N*-dimethylthiobenzamide (7 %) and *N*-ethylthiobenzamide (65 %) (lit.³⁵ b.p. 148–150 °C/1 mmHg). NMR (CDCl_3): 1.3 (t, 3 H); 3.8 (m, 2 H); 7.3 (m, 3 H); 7.7 (m, 2 H); 7.9 (m, 1 H).

Reaction of HMPA with benzylmercaptan. Benzylmercaptan (12.4 g) was heated in 25 ml of HMPA at 172 °C for 3 ½ h. Distillation of the organic phase yielded benzylmercaptan almost quantitatively. Another reaction performed at 205 °C for 3 h afforded a very complex reaction mixture. However, column chromatography of the organic phase yielded a mixture of products, containing dibenzylsulfide. Gentle distillation gave 2.4 g (22 %) of pure *dibenzylsulfide*, m.p. 48–49 °C (lit.³⁷ m.p. 49 °C). NMR (CDCl_3): 3.5 (s, 4 H); 7.2 (m, 10 H).

Picolines

General working-up procedure: After cooling to room temperature the reaction mixtures were poured into 250 ml of NaHCO_3 -saturated H_2O and 100 ml of benzene. Non-reacted S_8 was filtered off. After benzene extraction (4 × 100 ml) the combined benzene phases were washed with 50 ml of NaHCO_3 -saturated H_2O , dried (CaSO_4) and the benzene evaporated.

α -Picoline (9.3 g) was refluxed in 25 ml of HMPA with 12.8 g of S_8 for 50 min. Distillation of the worked-up reaction mixture twice yielded 8.8 g (53 %) of *N,N*-dimethyl- α -thiopicolinamide, b.p. 119–122 °C/0.2 mmHg (lit.⁶ 129–133 °C/0.55 mmHg). NMR (CDCl_3): 3.2 (s, 3 H); 3.6 (s, 3 H); 7.5 (m, 3 H); 8.4 (m, 1 H).

γ -Picoline (9.3 g) was refluxed in 25 ml of HMPA with 12.8 g of S_8 for an hour. Distillation

of the worked-up reaction mixture, followed by recrystallization from light petroleum-ether (4:1) yielded 7.9 g (48 %) of *N,N*-dimethylthioisonicotinamide, m.p. 62–64 °C (lit.⁶ m.p. 64–65 °C). NMR (CDCl_3): 3.2 (s, 3 H); 3.6 (s, 3 H); 7.2 (m, 2 H); 8.5 (m, 2 H).

β -Picoline (9.3 g) was refluxed in 25 ml of HMPA with 12.8 g of S_8 for 20 h. Distillation of the worked-up reaction mixture gave 7.6 g of picoline.

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