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 $N,N$-dimethylthiourea and $E$-stilbenes. $N,N$-Dimethylthiourea is demethylated by $S_8$ in HMPA at about 200 °C. Benzyl compounds PhCH$_2$X (X = OH, Cl, SH, NMe$_2$, OEt, COOEt, CSNMe$_3$) all yield $N,N$-dimethylthiourea. α- and γ-Piclines produce the corresponding $N,N$-dimethylthiocarboxamides 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:

$\text{Me}_2\text{NCSCH}_2\text{SCH}_2\text{NCMe}_3$, $\text{HCSNMe}_2$,
$\text{Me}_2\text{NCSNHMe}_2$, and $\text{Me}_2\text{NCS}_2\text{NHMe}_2$.

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. The most well-known reaction of that type is the Willgerodt-Kindler reaction:

$$\begin{align*}
\text{O} \\
\text{Ar} \text{–} \text{C} \text{–} (\text{CH}_2)_n \text{–} \text{CH}_3 & \xrightarrow{\text{NHR}, S_8, \Delta} \text{Ar} \text{–} \text{C} \text{–} (\text{CH}_2)_{n+1} \text{–} \text{CN} \xrightarrow{\text{S}} \text{Ar} \text{–} \text{C} \text{–} (\text{CH}_2)_{n+1} \text{–} \text{CN} \xrightarrow{\text{R}}
\end{align*}$$

Good reviews are also available. 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$_2$S is developed. 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 or again an autoclave. As it has been found, that hexamethylphosphoric triamide (HMPA) at high temperatures can act as a precursor of dimethylamine, we felt prompted to study the behavior of elemental sulfur in HMPA at elevated temperatures and with different substrates present. This paper reports about oxidation of some aldehydes, ketones, benzyl 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: $\text{B}^\ominus + S_8 \rightarrow \text{B} – \text{S}_7 – S^\ominus$

As HMPA is a rather strong base, its reaction with $S_8$ is of great potential interest to the organic chemist. Recently Chivers and Drummond 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 $S_2^-$. However, we have shown, that HMPA, purified according to Brandsma\textsuperscript{15} 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+$S_2$ solution produces the reported findings.\textsuperscript{14} Earlier results\textsuperscript{14} have thus to be dealt with great doubt.

The reaction of HMPA with $S_2$ 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.

\[
\begin{align*}
\text{S} & \quad \text{S} \\
\text{Me}_2\text{NCSCH}_2\text{SCNMe}_2 & \quad \text{HCNMe}_2 \\
\text{I} & \quad \text{II} \\
\text{S} & \quad \text{S} \quad \oplus \\
\text{Me}_2\text{NCNHMe} & \quad \text{Me}_2\text{NCSNMe}_2 \\
\text{III} & \quad \text{IV}
\end{align*}
\]

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.\textsuperscript{4,14,17} No attempts have been made to isolate other products. The reaction of benzaldehyde with $S_2$ in HMPA at 205 °C gives a series of products, V−IX, with the thioamide, V, as main product.

\[
\begin{align*}
\text{H} & \quad \text{Me}^a \\
p\text{-Me} & \quad \text{Me} \\
\text{H} & \quad \text{Et}^b \\
\text{H} & \quad \text{CH}_2\text{CO}_2\text{Et}
\end{align*}
\]

\[\text{X} \quad \text{S}_2\text{HMPA} \quad \text{XI} \quad \text{XII}\]

\[\text{R}^+ \quad \text{R}^- \quad \text{R}^+ \quad \text{R}^- \quad \text{R}^+ \quad \text{R}^- \quad \text{R}^+ \quad \text{R}^- \]

\[\text{XI} \quad \text{XII}\]

\[
\begin{align*}
\text{XI} & \quad \text{XII} \\
0.6 & \quad 25 & 12 & 172 & 71 & 10 \\
0.6 & \quad 25 & 12 & 170 & 64 & 11 \\
0.6 & \quad 25 & 10 & 172 & 57 & 19 \\
1.0 & \quad 50 & 12 & 155 & 55 & 5
\end{align*}
\]

\textsuperscript{a} 2,5-Diphenylthiophene was isolated. \textsuperscript{b} 5-Phenyl-3H-1,2-dithiole-3-thione was isolated in 10% yield.

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

---

*Acta Chem. Scand. B 29 (1975) No. 5*
Table 2. Oxidation of benzylic derivatives. 0.1 mol of benzylic derivative was used in all experiments.

\[
\begin{align*}
\text{PhCH}_2\text{X} & \xrightarrow{\text{HMPA}, S_8} \text{PhCNMe}_2 \\
\text{OH} & \quad 0.3 \quad 25 \quad 2 \quad 185 \quad 75 \\
\text{SH} & \quad 0.3 \quad 25 \quad 3.5 \quad 173 \quad 82 \\
\text{Cl} & \quad 0.3 \quad 25 \quad 0.25 \quad 190 - 240 \quad 80 \\
\text{NMe}_2 & \quad 0.3 \quad 25 \quad 0.75 \quad 185 \quad 81 \\
\text{OEt} & \quad 1.0 \quad 30 \quad 8 \quad 200 \quad 47^a \\
\text{COOEt} & \quad 1.0 \quad 50 \quad 7 \quad 188 \quad 37^b \\
\text{CSNMe}_2 & \quad 0.4 \quad 30 \quad 12 \quad 170 \quad 78 \\
\end{align*}
\]

* 16 % of PhCSNHMe isolated. ^ 37 % of PhCH_4CSNMe_2 was formed.

![Diagram](image)

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 C_4-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 benzoyleacetate gave, besides XI and XII, also N,N-dimethylthioacetamide. As the same thioamide also is formed by oxidizing ethyl phenylacetate with S_8 in HMPA it might be possible that the ethyl group is responsible for this compound. A separate paper on oxidation of esters will be published in due time.

Oxidation of benzylic derivatives. A series of derivatives, PhCH_2X, where X = OH, SH, Cl, NMe_2, OEt, COOEt and CSNMe_2, 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.

\[
\begin{align*}
\text{PhCH}_2\text{NH}_2 & \xrightarrow{\text{HMPA}, S_8} \text{PhCNHCH}_2\text{Ph (90 %)} \\
\text{PhCH}_2\text{NHEt} & \xrightarrow{\text{HMPA}, S_8} \text{PhCNHEt (65 %)} + V \\
\end{align*}
\]

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

Benzylic alcohols yield N,N-dimethylbenzylamines when heated at about 230 °C with HMPA. 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:

$$\text{PhCH}_2\text{OCH}_2\text{CH}_3 + \text{HMPA}, S\rightarrow \text{V} + \text{VI} + \text{CH}_3\text{CNMe}_3$$

[XIV]

V and XIV are supposed to be formed first by oxidation of the ether to two different thiono-

acids, or derivatives thereof, and subsequent reaction with HMPA to the corresponding thio-

amides. VI is formed from V as has been shown in a separate experiment. When N,N-dimethyl-

thiobenzamide was heated with sulfur in HMPA for 2 hours at 225 °C about 20 % of N-methyl-

thiobenzamide 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

to a thioicarboxamide. 19

Oxidation of picolines. Both α- and γ-picolines are converted into the corresponding N,N-di-

methylthiocarboxamides 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.

$$\text{N} - \text{CH}_3 \quad (\text{a or } \gamma) \quad \text{HMPA}, S \rightarrow \text{N} - \text{CNMe}_2 \quad (\text{a or } \gamma)$$

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

amidines, 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 eluant 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 CHCl₃. On addi-
tion of ether a gum precipitated. The solution was decanted and the solvent evaporated.

Column chromatography yielded: 1. 140 mg of

methylene dimethylthiocarbamate (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. C₆H₅N,S₄ requires: C 33.07; H 5.61; N 11.02; S 50.39). NMR

(CDCl₃): 3.4 (d, 12 H); 5.4 (s, 2 H). MS: m/e 254 (M⁺, ∼ 1 %); 164 (Me₃NCSCH⁺, 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. 3.2 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); ≥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 puri-
fied 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 was a crystalline material was collected, dissolved in CHCl₃ and on addition of ether 400 mg of dimethylammo-
nium dimethylthiocarbamate (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 x 100 ml) (except for the

picolines where extraction was performed with benzene) and washing with brine (2 x 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 HMFA 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.¹² 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.¹⁵ m.p. 183–184 °C). (Found: C 86.64; H 5.13; S 8.47. C₉H₅S requires: C 86.56; H 5.19; S 8.25). NMR (CS₂): 7.0 (m). MS: m/e 358 (M⁺, 100 %); 311 (M⁺–Ph, 13 %); 121 (PhCC⁺, 5 %); 77 (5 %). III. 200 mg (1 %) of orange-red 4,4'-diphenyl-3H-1,2-dithiole-3-thione, m.p. 158–159 °C (lit.¹⁶ m.p. 159 °C). (Found: C 82.40; H 3.41; S 33.3. C₁₂H₁₂S₃ 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 (PhCCPP, 36 %); 165 (M⁺–PhCS, 32 %); 145 (PhCS⁺, 44 %); 121 (PhC⁺, 54 %); 77 (46 %). IV. 9.2 g (56 %) of N,N-dimethylthiobenzamide, m.p. 67 °C (lit.⁶ 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.⁷⁻⁹ V. 2.0 g (13 %) of N,N-dimethylthiobenzamide, m.p. 77–78 °C (lit.¹⁰ 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.⁷⁻⁹

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-dimethylthiobenzamide, m.p. 40–42 °C (lit.¹² 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 HMFA 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.¹² 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. C₈H₅NOS 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).

**Alkylarylketones**

Reaction conditions are given in Table 1. *Acetophenone*. Column chromatography of the organic phase yielded as the first fraction 2.2 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.¹⁴ m.p. 150.5 °C). NMR (CDCl₃): 7.3 (m). A mass spectrum was in accordance with literature.¹¹ 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-Methylocetophenone*. 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 thiocarboxamides was eluted. Crystallization of the mixture twice from ether yielded pure p-methyl-N,N-dimethylthiobenzamide, m.p. 49–50 °C (lit.¹⁴ 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): 2.5 (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.¹⁶ m.p. 126 °C). (Found: C 51.44; H 2.86; S 45.08. C₁₁H₉S₃ 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 benzoyleacetate**. 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.¹⁶ m.p. 73–74 °C). NMR (CDCl₃): 2.7 (s, 3 H); 3.3 (s, 3 H); 3.5 (s, 3 H).

**Benzylidervatives**

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-
methyliobenzamide. Further elution yielded 600 mg (6 %) of N,N-dimethyliothioacetamide.

Ethyl phenylacetate. The reaction mixture was very stiff, when cooled down, so it was dissolved in boiling CH₂Cl₂, cooled to room temperature and filtered. Filtration through a silica gel column (eluted with CH₂Cl₂) followed by column chromatography yielded 12.8 g of an approximately 1:1 mixture of N,N-dimethyliothio- benzamide and phenyl-N,N-dimethyliothioacetamide. Further elution yielded 2.3 g of a mixture of N,N-dimethyliothioformamid (30%) and N,N-dimethyliothioacetamide (30%).

Benzylamine (10.7 g) was heated with 9.6 g of S₈ 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-benzylthio benzamide, m.p. 82–83°C (lit.³⁸ m.p. 84–85°C). NMR (CDCl₃): 4.8 (d, 2 H); 7.5 (m, 11 H).

Benzylthiobenzamide (13.5 g) was heated with 9.6 g of S₈ 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-dimethyliothio benzamide (7%) and N-ethylthio benzamide (65%) (lit.³⁸ m.p. 148–150°C/1 mmHg). NMR (CDCl₃): 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 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.³⁸ m.p. 49°C). NMR (CDCl₃): 5.5 (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 NaHCO₃-saturated H₂O and 100 ml of benzene. Non-reacted S₈ was filtered off. After benzene extraction (4 × 100 ml) the combined benzene phases were washed with 50 ml of NaHCO₃-saturated H₂O, dried (CaSO₄) and the benzene evaporated.

α-Picoline (9.3 g) was refluxed in 25 ml of HMPA with 12.8 g of S₈ for 50 min. Distillation of the worked-up reaction mixture twice yielded 8.8 g (50%) of N,N-dimethyliothiopicolinamide, b.p. 119–122°C/0.2 mmHg (lit.³⁸ b.p. 129–133°C/0.55 mmHg). NMR (CDCl₃): 8.4 (s, 3 H); 7.5 (m, 3 H); 8.4 (m, 1 H).

β-Picoline (9.3 g) was refluxed in 25 ml of HMPA with 12.8 g of S₈ 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-dimethyliothiopicolinamide, m.p. 62–64°C (lit.³⁸ m.p. 64–65°C). NMR (CDCl₃): 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 S₈ for 20 h. Distillation of the worked-up reaction mixture gave 7.6 g of picoline.

REFERENCES


Received December 16, 1974.