Preparation of \(\text{N,N'-Dimethyl-}
\text{and N,N'-Diethy1sulfamide}

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In the course of the work on certain ring-closure reactions\(^1\), rather large amounts of \(\text{N,N'-dimethylsulfamide}\) were needed. The previously reported preparations of \(\text{N,N'-dimethylsulfamide}\)\(^2-3,4\) \(\text{(2, } R = \text{CH}_3\text{)}\) or \(\text{N,N'-diethy1sulfamide}\)\(^5\) \(\text{(2, } R = \text{C}_2\text{H}_4\text{)}\) gave low yields \(26\%\) and \(16\%\), respectively and were contradictory, even though the synthesis of the higher \(\text{N,N'-dia1kyl-}\)\(^-3,5\) or \(\text{N,N'-diarylsulfamides}\)\(^6\) has been adequately described. Moreover, some reactions with \(\text{2 (R = CH}_3\text{)}\) have been presented\(^6,7,8\) recently without stating how the compound was made. We therefore developed a reproducible way for obtaining \(\text{2 (R = CH}_3\text{)}\) and \(\text{2 (R = C}_2\text{H}_4\text{)}\) in reasonable yields \(60\%\) and \(70\%\), respectively and purity from the reaction:

\[
4 \text{R-NH}_2 + \text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2\text{NH-NH}_2 \text{Cl} + 2 \text{R-NH}_3 \text{Cl}
\]

As pointed out earlier\(^9\), the yield of \(\text{2}\) is never quantitative due to the presence of \(3\), the formation of which cannot be prevented completely. We carried out a preliminary investigation of the possibility that \(3\) might be formed in the thermal decomposition of \(\text{2}\) by local overheating

\[
2 \text{SO}_2\text{NH-NH}_2 \rightarrow \text{SO}_2\text{NH-NH} + \text{R-NH}_2 \text{Cl}
\]

since it is observed that at higher reaction temperatures \(\text{(i.e. ca. -50 to -40°)}\) this by-product is formed in significantly larger amounts. Differential thermal analysis at \(\text{5°/min}\) and thermogravimetric studies in nitrogen \(\text{10°/min}\) give evidence for a series of overlapping decomposition processes, with decomposition starting at the melting point and leveling off at \(\text{275°}\), with another set of processes taking over at higher temperatures. When a series of \(\text{1H-N.M.R. spectra were taken over a period of 2 1/2 hours in two differently boiling solvents (dichloroethane and}
\text{sym-tetrachloroethane, decomposition was evident; but the spectral pattern corresponding to 3 was not identified.}

The previously reported\(^4\) unsatisfactory yields of \(2\) for \(R = \text{CH}_3\) or \(C_2H_4\) are attributable to too high a reaction temperature. Indeed by our method of preparation \(\text{(78°)}, \text{1H-N.M.R. shows no detectable 3 (R = C}_2\text{H}_4\text{). Obviously, the statement\(^4\) that the direct reaction of the components at low temperature in pentane gives no product has been disproven by our work.

The I.R. spectra of \(2 (R = \text{CH}_3, C_2H_4)\) can readily be assigned and are similar to those of higher \(\text{N,N'-dia1kylsulfamides}\)\(^9\). Thus, \(\nu_{\text{NH}}\) is found at \(3280 \text{ cm}^{-1}\) and \(\delta_{\text{NH}}\) asym. at \(1440\) and \(\delta_{\text{NH}}\) sym. at \(1420 \text{ cm}^{-1}\) for both \(2 (R = \text{CH}_3)\) and \(2 (R = C_2H_4)\); the weak \(\nu_{\text{NH}}\) asym. are found at \(2940 \text{ cm}^{-1}\) for \(2 (R = \text{CH}_3)\) and at \(2980 \text{ cm}^{-1}\) for \(2 (R = C_2H_4)\) and \(\nu_{\text{NH}}\) sym. for \(2 (R = \text{CH}_3)\) at \(2820 \text{ cm}^{-1}\). The characteristic
\(v_{\text{SO}_3}\) are at 1320 cm\(^{-1}\) for 2 (R = CH\(_3\)) or 1315 cm\(^{-1}\) for 2 (R = C\(_2\)H\(_5\)) for the asymmetric vibration and at 1155 cm\(^{-1}\) for the symmetric vibrations. The band at 955 cm\(^{-1}\) for 2 (R = C\(_2\)H\(_5\)) may be assigned to the NSN asymmetric stretch vibration whereas \(v_{\text{SN}}\) sym. occurs at 870 cm\(^{-1}\) for 2 (R = CH\(_3\)) or 895 cm\(^{-1}\) for 2 (R = C\(_2\)H\(_5\)), significantly higher than in sulfamide.\(^{10,11}\) The broad NH-rocking vibration appears at 700–690 cm\(^{-1}\) for 2 (R = CH\(_3\)) and at 690–670 cm\(^{-1}\) for 2 (R = C\(_2\)H\(_5\)) and the SO\(_2\)-bending modes are found at 545 cm\(^{-1}\).

The \(^1\)H-N.M.R. spectra are consistent with the structures and exhibit the theoretical pattern.

**N,N'-Dimethylsulfanamide (2, R = CH\(_3\))**: Dry dimethylamine (~250 ml) is condensed in a three-necked 500 ml flask equipped with a sodium hydroxide-filled drying tube, an adapter (or a 5 cm glass elongation) with a stopper on the middle joint, and a gas-inlet tube. The whole system is kept at -78°C. A solution of freshly distilled sulfuric chloride (71.3 g) in petroleum ether (70 ml; b.p. 35–55°C) is added dropwise with a dropping funnel on the adapter (30–45 min) with occasional shaking. (The adapter prevents clogging.) After addition is completed, two layers are formed; the upper one consists mainly of petroleum ether and the lower one of a solution of methylamine hydrochloride and compound 2 (R = CH\(_3\)) in excess methylamine. The whole apparatus is taken out of the cooling bath and overnight evaporation of the excess methylamine produces a white slurry. Striping of the residual methylamine and petroleum ether gives a pure white heterogeneous precipitate (123.3 g, theor. 125.7 g). This is then extracted two times with hot dichloromethane (200 ml) and filtered, leaving essentially methylamine hydrochloride. The solvent is distilled off from the combined filtrates giving 49.0 g of impure (slightly yellow) compound 2 (theor. 59.7 g). \(^1\)H-N.M.R. shows it to contain on the average 10 to 15% of methylmimo-bis-methylaminoisulfone (methylimidodisulfuric acid bis-[monomethylamide] 3, R = CH\(_3\)). This crude product is taken up in water (100 ml), 2% hydrochloric acid (10 ml) is added, and the system is kept at 40°C for 5 min. Water is distilled off by means of a rotary evaporator (bath temperature at 50–55°C but not higher) leaving a mixture of 2 (R = CH\(_3\)) and methylamidodisulfuric acid. This mixture is extracted with boiling ether (8 × 200 ml) with the ethereal solutions always being decanted from the oily-sesquiisol residue. It is convenient to reuse distilled ether from a previous extraction so that only a total of ~800 ml is necessary.\(^{12}\) Evaporation of the ether gives pure N,N'-dimethylsulfanamide as colorless crystals; yield: 35–39 g (53.6–59.8%, m.p. 75–76°C (dec.) (Ref. 7, m.p. 78°C; Ref. 8, 75–76°C). Very soluble in water, dichloromethane, chloroform, methanol, ethanol, dimethyl sulfoxide; moderately soluble in benzene and carbon tetrachloride.

C\(_2\)H\(_6\)N\(_2\)O\(_2\)S calc. C 19.35 H 6.49 N 22.56 S 25.82 O 25.77 found 19.24 6.32 22.02 26.23 26.10 (by diff.)

I.R. (KBr, 0.5%): 3200 vs (v), 2940 (m), 2820 (w), 1440 (m), 1420 (m), 1320 (vs), 1155 (s), 1120 (s), 1070 (m), 870 (w), 810 (w), 700–690 (w, b), 545 (m), 490 (w) cm\(^{-1}\).

\(1\)N-N.M.R. of 2, R = CH\(_3\) (CDCl\(_3\), TMS): \(t_{\text{CH}}=5.95\) (broad, s), \(t_{\text{CH}}=7.28\) (s).

\(1\)H-N.M.R. (CDCl\(_3\), TMS) of 3, R = CH\(_3\) [CH\(_3\)\(_2\)N(SO\(_2\)NCH\(_3\))\(_2\)] as from the reaction mixture: \(t_{\text{CH}_2}=7.70\) (s), \(t_{\text{CH}_2}=6.77\) (d), J\(_{\text{NH}t_{\text{NH}}}=2.55\) Hz; the signal for the NH group was not detected.

**N,N'-Diethylsulfanamide (2, R = C\(_2\)H\(_5\))**: As previously, a solution of sulfuric chloride (41.5 g) in petroleum ether (50 ml) is added to liquid ethylamine (~250 ml). Excess ethylamine and petroleum ether are distilled off leaving 93.5 g of a yellow-brownish mass (theor. 97.4 g). Extraction with dichloromethane (200 ml) at 40°C and filtration removes most of the ethylamine hydrochloride. The solvent is evaporated from the filtrate and the residue extracted 5 times with boiling ether; the ethereal solutions are decanted and combined, and then evaporated to dryness. The resultant essentially pure product is recrystallized from small amounts of methanol to give colorless crystals; yield: 33.0 g (70.0%, m.p. 67°C (Ref. 7, m.p. 67°C). C\(_2\)H\(_5\)N\(_2\)O\(_2\)S calc. C 31.56 H 7.45 N 18.40 S 21.06 O 21.02 found 31.54 7.44 18.14 21.30 21.12 (by diff.)

I.R. (KBr, 0.5%): 3260 vs (v), 2980 (m), 2840 (w), 1440 (m), 1420 (m), 1315 (vs), 1155 (vs), 1120 (s), 1060 (s), 955 (w), 895 (w), 800 (w), 690–670 (m, b), 560 (m), 490 (w) cm\(^{-1}\).

\(1\)H-N.M.R. (CDCl\(_3\), TMS): \(t_{\text{CH}}=6.05\) (broad, s), \(t_{\text{CH}}=6.89\) (q), \(t_{\text{CH}_2}=8.79\) (t), J\(_{\text{NH}}=7.35\) Hz.

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10. R. SOWADA, J. Prakt. Chem. 311, 228 (1969), and references therein.
13. All \(t_{\text{NH}}\) values are extrapolated to the c = 0 limit.