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SYNTHESIS OF STABLE ALIPHATIC SULFUR DIIMINES

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We wish to report a new synthesis of stable aliphatic sulfur diimines (I)[1].

$$R\text{-}N{=}S{=}N\text{-}R$$

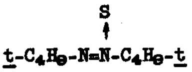
I

When the aliphatic group R in structure I is a bulky tertiary-carbinyl group, stable sulfur diimines are readily prepared from the corresponding *t*-alkylamines and sulfur dichloride. Analogous to the results of earlier studies with methylamine[2] or ethylamine[3], the initial condensation product from *t*-butylamine and SCl_2 had the composition $(C_4H_9NS)_x$. However, this product on heating under reduced pressure did not undergo explosive decomposition[2,3a], but rather a *smooth pyrolysis with formation of sulfur and distillation of the sulfur diimine*.

Thus, dropwise addition of 343 g. (3.3 moles) of freshly distilled sulfur dichloride in 300 ml. of anhydrous ether to a solution of 733 g. (10.0 moles) of *t*-butylamine in 1250 ml. of anhydrous ether at 5-10° gave an immediate precipitate of *t*-butylamine hydrochloride. After standing for two days, the solid was removed by filtration and washed with ether. Evaporation of the solvent and excess *t*-butylamine to 40° (0.1 mm) left 287 g. of a yellow oil, n_D^{25} 1.5083. *Anal.* Calcd.

for $(C_4H_9NS)_x$: C, 46.56; H, 8.79; N, 13.58; S, 31.07. Found: C, 46.47; H, 8.90; N, 13.30; S, 31.06.

On attempted distillation of 123 g. of the above oil at reduced pressure, a smooth decomposition began at a pot temperature of 63° and continued until the pot temperature reached 160°, when 72 g. of a straw-colored liquid had collected in the receiver. Redistillation gave 70 g. of pure di-t-butylsulfur diimine (I,R = t-C_4H_9), b.p. 60-62° (15 mm), n_D^{25} 1.4558. Anal. Calcd. for $C_8H_{18}N_2S$: C, 55.12; H, 10.41; N, 16.08; S, 18.39. Found: C, 55.13; H, 10.44; N, 16.37; S, 18.47. The infrared spectrum showed only one absorption band (at 9.4μ) not present in t-butylamine. The n.m.r. spectrum, consisting of a sharp singlet at τ8.60, would appear to rule out the possible alternative structure II, which should, like di-t-butyldiimide N-oxide (azoxyisobutane)[5], possess two distinct resonances.

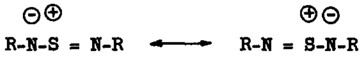

$\underline{t}\text{-}C_4H_9\text{-}\overset{\overset{S}{\uparrow}}{N=N}\text{-}C_4H_9\text{-}\underline{t}$

II

Di-t-butylsulfur diimine is stable at its normal boiling point (167-169°). It hydrolyzes slowly in water, but rapidly in dilute hydrochloric acid to produce sulfur dioxide and t-butylamine (isolated as the hydrochloride). Oxidation with dilute aqueous hydrogen peroxide gave N,N'-di-t-butylsulfamide, m.p. 135-137°, identified by comparison with an authentic sample prepared from t-butylamine and sulfuryl chloride.

In a similar manner, di-t-octylsulfur diimine (I,R = t-C_8H_{17}), b.p. 88-90°C. (0.15 mm), n_D^{25} 1.4785, was obtained from t-octylamine and sulfur dichloride. Both sulfur diimines were also obtained by pyrolysis of the reaction products of sulfur monochloride with excess *t*-alkylamine, but in somewhat lower yields.

From the structural relationship of the sulfur diimines to sulfur dioxide (Goehring and Weis[1] regarded their compound as a "diimide of sulfurous acid.") and the thionylamines[5], we believe that they are best represented as resonance hybrids to which structures Ia and Ib make significant contributions.



$$R-\overset{\ominus}{N}-\overset{\oplus}{S}=N-R \longleftrightarrow R-N=\overset{\oplus}{S}-\overset{\ominus}{N}-R$$

Ia Ib

This indicates a pronounced *ylid* character for these compounds and suggests the possibility of their reaction with various functional groups, e.g., by nucleophilic attack of the negative nitrogen on a carbonyl group. Some reactions fulfilling this expectation are discussed in the following communication.

REFERENCES

1. The only previous reference to an aliphatic sulfur diimine is that of M. Goehring and G. Weis, *Angew. Chem.*, **68**, 678 (1956), who reported that *n*-butylamine and sulfur tetrachloride at -65° gave di-*n*-butylsulfur diimine (I,R=*n*-C_4H_9) as a yellow oil stable only below 50°. R. Cramer, *J. Org. Chem.*, **26**, 3476 (1961), prepared an aromatic analog, diphenylsulfur diimine (I,R=C_6H_5), as a red liquid by the reaction of aniline with sulfur tetrafluoride or with phenyliminosulfur difluoride.

2. B.D. Stone and M.L. Nielsen, *J. Am. Chem. Soc.*, **81**, 3580 (1959).

3. (a) F. Lengfeld and J. Steiglitz, *Ber.*, **28**, 2742 (1895),
(b) A. Meuwsen, Ber., **64**, 2301 (1931).

4. J.P. Freeman, *J. Org. Chem.*, **28**, 2508 (1963).

5. K.A. Jensen and N. Hofman Bang, Ann. **548**, 95 (1941).