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REACTIONS OF ALIPHATIC SULFUR DIIMINES

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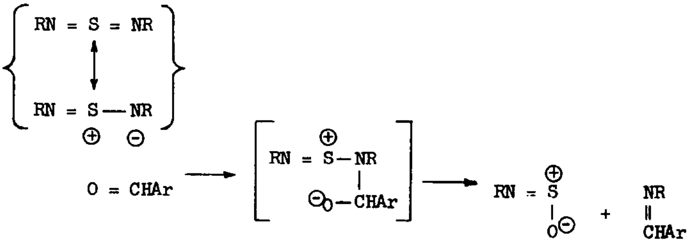
The possibility of a pronounced ylid character for sulfur diimines has been suggested[1]. We have found that these compounds do indeed react with a number of reagents to give products whose formation is, in some cases, consistent with the general mechanistic pattern of the Wittig and related reactions[2]. Thus, heating of a mixture of 10.3 g. (0.036 mole) of di-t-octylsulfur diimine and 3.8 g. (0.036)mole of benzaldehyde at 125-130° for two hours followed by direct distillation of the reaction mixture gave 3.7 g. (60%) of N-t-octylbenzaldimine, b.p. 126-130° (10 mm), n_D^{25} 1.5096 (lit.[3] b.p. 129-131° (8 mm), n_D^{25} 1.5130) and 1.7 g. (30%) of t-octylthionylamine, b.p. 61-62° (10 mm), n_D^{25} 1.4513. Anal. Calcd. for $C_8H_{17}NOS$: C, 54.81; H, 9.78; N, 7.99; O, 9.13; S, 18.29. Found: C, 54.91; H, 9.66; N, 7.97; O, 9.05; S, 18.19).

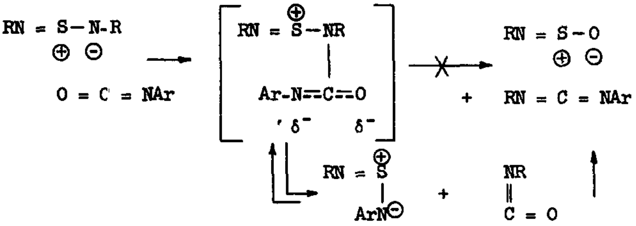


(1)

The course of this reaction (eq. 1) parallels that of benzaldehyde with phosphinimines[4], phosphoramidate anions[5], and thionylamines[6].

In a similar manner, reaction of di-*t*-octylsulfur diimine with furfural for 9 hours at 125° gave some *t*-octylthionylamine and an 87% yield of N-*t*-octylfurfuraldimine, b.p. 132-135° (24 mm), n_D^{25} 1.4940 (lit.[3] b.p. 138-141° (30 mm), n_D^{25} 1.4965).

In the reaction of di-*t*-butylsulfur diimine with phenyl isocyanate, a surprising result was obtained. The products which might be predicted by analogy to previous reports[4,5] (and to eq. 1) are *t*-butylthionylamine and the mixed carbodiimide (eq. 2a). However, heating of 10.5 g. (0.05 mole) of di-*t*-butylsulfur diimine with 7.1 g. (0.06 mole) of phenyl isocyanate to 118° (held at reflux for 30 minutes) followed by distillation gave (eq. 2b) 3.6 g. (71%) of *t*-butyl isocyanate, b.p. 86-90°, n_D^{25} 1.3856 (lit.[7] b.p. 85-87°, n_D^{25} 1.3824) and 6.65 g. (68%) of N-phenyl-N'-*t*-butylsulfur diimine, b.p. 75-77° (1 mm), n_D^{25} 1.5966. *Anal.* Calcd. for $C_{10}H_{14}N_2S$: C, 61.81; H, 7.26; N, 14.42; S, 16.50. Found: C, 61.89; H, 7.11; N, 14.08; S, 16.39. The n.m.r. spectrum of the latter consisted of a sharp singlet at τ8.52 and a complex multiplet centered at τ2.51. It seems likely that an equilibrium is involved between the reactants and the products of eq. 2b and that the reaction is driven to completion by distillation of the more volatile t-butyl isocyanate.

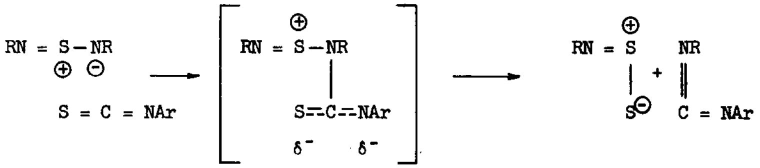


(2a)

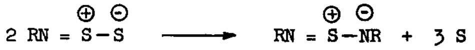
(2b)

Similarly, di-*t*-butylsulfur diimine reacted with *two equivalents* of p-chlorophenyl isocyanate to give *t*-butyl isocyanate (75%) and a 70% yield of di(p-chlorophenyl)sulfur diimine[8], m.p. 60.5-61°. *Anal.* Calcd. for $C_{12}H_8Cl_2N_2S$: C, 50.89; H, 2.85; Cl, 25.04; N, 9.90; S, 11.32. Found: C, 50.77; H, 2.81; Cl, 24.84; N, 9.98; S, 11.10.

On the other hand, reaction of 6.8 g. (0.039 mole) of di-t-butylsulfur diimine with 10.4 g. (0.078 mole, 2 equiv.) of phenyl isothiocyanate for 4 hours at 120° gave 9.9 g. (72% based on phenyl isothiocyanate) of N-phenyl-N'-t-butylcarbodiimide, b.p. 90-92° (4.0 mm), n_D^{25} 1.5382, (*Anal.* Calcd. for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.13; H, 8.00; N, 15.51.) as the sole reaction product in addition to sulfur and recovered starting materials. The formation of the mixed carbodiimide and the observed stoichiometry may be rationalized on the basis of a two-stage process involving fragmentation of the intermediate betaine (eq. 3a), followed by decomposition of the other product to form sulfur and regenerate sulfur diimine (eq. 3b).



(3a)



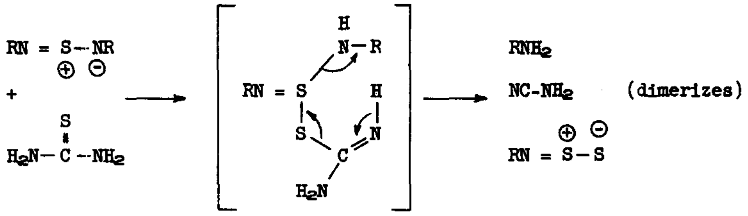
$$2\,RN=\overset{\oplus}{S}-\overset{\ominus}{S} \longrightarrow RN=\overset{\oplus}{S}-\overset{\ominus}{N}R + 3\,S$$

(3b)

Isothiocyanates react readily with phosphinimines to give carbodiimides in unspecified yield[4], but reportedly do not react with phosphoramidate anions "under ordinary conditions[5]."

The difference in the course of the reaction of isocyanates (eq. 2b) and isothiocyanates (eq. 3a) is striking and may be related to greater nucleophilicity of nitrogen over oxygen in the former case, and of sulfur over nitrogen in the latter.

Surprisingly, di-t-butylsulfur diimine also reacts readily with thiourea. Thus, heating a mixture of 4.7 g. (0.027 mole) of di-t-butylsulfurdiimine and 4.15 g. (0.054 mole, 2 equiv.) of thiourea at 86°C. resulted in distillation of 2.0 g. (50%) of t-butylamine. Washing the remaining solid with carbon disulfide removed 2.45 g. (94%) of sulfur and left 2.2 g. (97%) of dicyandiamide, m.p. 206-208°C. (lit.[9] m.p. 209°). Although the organic products might conceivably arise by decomposition of t-butylguanidine (expected on the basis of a "Wittig-type" mechanism) we feel that the result is better rationalized in terms of an initial attack of the nucleophilic sulfur atom of thiourea on the positive sulfur atom of the sulfur diimine (eq. 4).



(4)

The observed stoichiometry is again explained by decomposition of one of the products to sulfur diimine and sulfur (cf. eq. 3b). Fragmentation of the proposed intermediate to produce cyanamide (which dimerizes) finds precedent in the conversion of methyl isothiuronium sulfate to methyl mercaptan and dicyandiamide by the action of base[10].

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