

A New Reaction, a One-step Synthesis of *N*-Substituted Thioamide from Nitriles

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We have found that the reaction of nitriles with *N*-substituted dithiocarbamates constitutes a facile one-step synthesis of *N*-substituted thioamides. Thus, when a mixture of benzonitrile, dimethylammonium *N,N*-dimethyldithiocarbamate, and benzene was heated for several hours under pressure by shaking, *N,N*-dimethyl benzthioamide was obtained; it proved to be identical with an authentic sample prepared by the thionation of *N,N*-dimethylbenzamide with phosphorus pentasulfide.¹⁾

This reaction can be successful with a number of aromatic nitriles and aralkyl nitriles, and with a variety of heterocyclic nitriles, as is shown in Table 1.

The reaction mechanism will be described and discussed in detail in the near future elsewhere.

Synthesis of *N,N*-Dimethylthiobenzamide.

5.15 g (0.05 mol) of benzonitrile was added to a suspension of 8.5 g (0.05 mol) of dimethylammonium *N,N*-dimethyldithiocarbamate in 25 ml of

absolute benzene. The mixture was heated in an autoclave by shaking it at 150°C for 3 hr. The reaction mixture was then allowed to stand overnight. To this 100 ml of ether were added in order to remove a small quantity of an insoluble material. The ethereal solution was dried over anhydrous sodium sulfate, the solvent was removed on a rotating evaporator, and the resulting red-brownish residue was fractionated under reduced pressure. *N,N*-Dimethylbenzthioamide distilled over at 153—163°C/7—8 mmHg as a light yellow oil which was soon solidified. After recrystallization from methyl acetate, light yellow crystals (mp 59—64°C) resulted. UV: $\lambda_{max}^{CH_3OH}$ 278 m μ (ϵ_{max} 9181), IR: 1515 cm⁻¹, 1295 cm⁻¹, 1140 cm⁻¹ (—C—N^{||}S) 1450

cm⁻¹, 1490 cm⁻¹ (benzene ring). *R_f* value (thin layer, silica gel) 0.916 (EtOH: CHCl₃: AcOEt = 4 : 3 : 2).

TABLE 1

| Nitrile | <i>N</i> -Dimethylcarbamate | Solvent | Reaction temp., °C | Reaction time, hr | Yield % |
|---|-----------------------------|--------------------|--------------------|-------------------|---------|
| Benzo- | Dimethylamine salt | Benzene | 150—160 | 3 | 79.9 |
| Benzo- | Dimethylamine salt | Dimethylcellosolve | 145—150 | 3 | 35.9 |
| Benzo- | Dimethylamine salt | Pyridine | 150—155 | 3 | 35.6 |
| Phenylaceto- | Dimethylamine salt | Xylene | 190—210 | 3 | 35.5 |
| Butyro- | Dimethylamine salt | Xylene | 190—210 | 3 | 48.6 |
| 3-Cyano-4-methoxymethyl-6-methyl 2-pyridone | Dimethylamine salt | Xylene | 150—170 | 3 | 9.3 |

1) K. Kindler, *Ann.*, **431**, 210 (1923).