

Synthesis of Organic Isocyanates. I. Thermal Decomposition of Substituted 1,3,2,4-Dioxathiazole S-Oxides

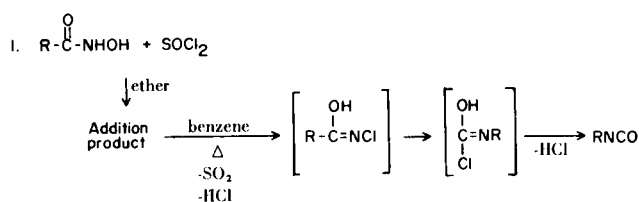
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A new synthesis of aromatic isocyanates from hydroxamic acids is described which involves pyrolysis of the derived 1,3,2,4-dioxathiazole S-oxides.

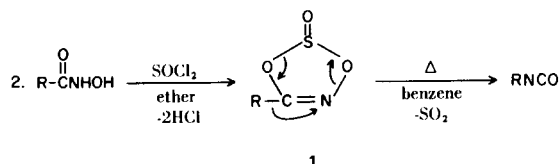
Of the methods of synthesis of both alkyl and aryl isocyanates, only the amine phosgenation route has reached commercial significance. Pyrolysis of acid azides has been restricted to the laboratory, while alkyl halide-methyl cyanate reactions have found use solely in the aliphatic series. The dehydration of hydroxamic acids and their derivatives (1-3) (Lossen rearrangement) as well as the Hofmann rearrangement give isocyanates; however, these procedures have found little use as practical methods for preparing isocyanates.

In 1906 Marquis (1) showed that reaction of benzo-hydroxamic acid with thionyl chloride led to formation of phenyl isocyanate. To account for this transformation he suggested the reaction scheme shown in equation 1. While



N-haloamides are known to rearrange to isocyanates by reaction with base (Hofmann rearrangement), earlier work on our part has shown that heat alone will not generally effect such a transformation.

We have found that the reaction of a hydroxamic acid with thionyl chloride forms, according to equation 2, a substituted 1,3,2,4-dioxathiazole S-oxide (1) which ther-

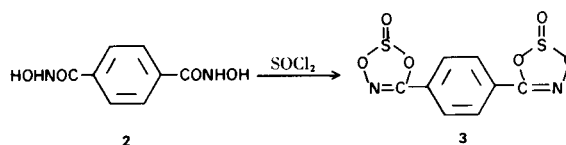


mally rearranges to give isocyanate and sulfur dioxide. While this ring system has been recently synthesized (4,5), it was not shown that such a ring would thermally re-

arrange to an isocyanate (6). For simplicity we will throughout this paper refer to compounds of type 1 as substituted nitrile sulfites.

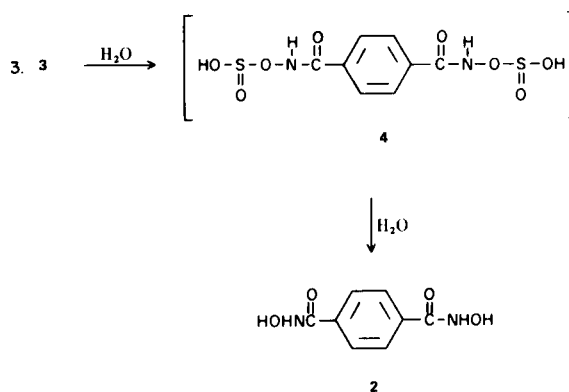
Results.

The reaction of terephthalodihydroxamic acid (2) with excess thionyl chloride at 45° gives 96% yield of a crystalline solid (m.p. 136° dec.) which has been shown to be terephthalonitrile disulfite, 3. Compound 3 was stable at



room temperature and was characterized by elemental analysis, and by its infrared and N.M.R. spectra (see experimental).

The sulfite 3 reacted rapidly with water, presumably through the intermediate 4 to give 2 (equation 3). This observation is consistent with the proposed structure, 3.



Reaction of 3 at room temperature with 2-propanol alcohol in the absence of base catalyst gave 2, as shown in equation 4.

Thermal Decomposition of Isophthalonitrile Disulfite.

Similarly, 40.0 g. (0.14 mole) of isophthalonitrile disulfite was added in small portions to 200 ml. of refluxing *n*-octane which contained, in suspension, 1.0 g. of Super-Cel. After addition was complete, the reaction mixture was refluxed for an additional ten minutes. The reaction mixture was filtered while hot and the filtrate cooled to about 0° to precipitate 16.8 g. of product. An additional 4.6 g. was obtained upon evaporation of the filtrate. There was obtained a total of 21.4 g. (97%) of *m*-phenylene diisocyanate, m.p. 51-52° (lit. 51° (9)). An infrared spectrum (Nujol mull) of the product was identical to that of an authentic sample of *m*-phenylenediisocyanate.

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