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### NITROSYLSULFURIC ACID HYDROLYSIS OF PRIMARY AMIDES

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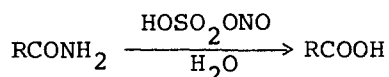
NITROSYLSULFURIC ACID HYDROLYSIS OF PRIMARY AMIDES<sup>†</sup>

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Use of a nitrosation reaction to hydrolyze primary amides, presumably via an acyl diazonium salt, has been well established.<sup>1</sup> These procedures have achieved fair to good yields using nitrous acid generated in situ, generally from sodium nitrite and mineral acid; there is one report of the use of nitrosonium fluoroborate as the nitrosating agent.<sup>2</sup>

We have found that wet nitrosylsulfuric acid (NSA) can be used as the diazotizing reagent to hydrolyze primary amides, resulting in shortened reaction times and improved yields.



Treatment of a primary amide with 50-85% NSA<sup>3</sup> at 20-45° for 1-3 hrs generally affords the acid<sup>4</sup> in good yield and in sufficiently high purity for direct use in succeeding reactions. The enhanced efficiency observed using this reagent is probably due to both the reactivity of the NSA solution and the moderate solubility of many of the starting materials in NSA.

## EXPERIMENTAL

Hydrolysis of Cinnamide. General Procedure.<sup>5</sup> Cold commercial nitrosylsulfuric acid (3.5 ml) was cautiously added to 1.5 ml

Table 1. Hydrolysis of Primary Amides with NSA

	NSA <sup>3</sup> (%)	Time (hrs)	Temp (°C)	Yield (%)	mp (°C) crude	lit. <sup>a</sup>
stearamide	70	2	45	99	65-69	69
4-phenylbutanamide	50	3	20	98	47-49	50
cinnamide	70	2	20	83	127-128	133
benzamide	60	2	20	89	120-121	122
<i>o</i> -bromobenzamide	70	1.5	20	82	143-144	147
2,6-dichlorobenzamide	70	2	35	93	138-139	139

<sup>a</sup>Handbook of Chemistry and Physics

of water in an ice bath. Cinnamide (0.429 g, 2.92 mmole) was added to this solution, and the mixture was allowed to come to ambient temperature and stirred for 2 hrs. The reaction mixture was poured over ice (10 g) and extracted with dichloromethane. The dichloromethane layer was dried and evaporated under reduced pressure to give 0.357 g (82.6%) of crystalline cinnamic acid, mp. 128°, lit.<sup>mp.</sup> 133°.

## REFERENCES

- † This work was supported by a Biological Research Support Grant from Colorado State University.
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  2. G.A. Olah and J. A. Olah, *J. Org. Chem.*, 30, 2386 (1965).
  3. DuPont nitrosylsulfuric acid is composed of 40% NSA, 52.5%

sulfuric acid, and 7.8% water. As used in the above table (% NSA), "60% NSA" would indicate a mixture of 60% DuPont NSA solution and 40% added water (by volume). The addition of water results in partial decomposition (with vigorous evolution of  $\text{NO}_x$  vapors) as well as dilution of the NSA. NSA concentrations and temperatures used were selected by determining the mildest conditions which would allow the hydrolysis to proceed at a convenient rate. In some cases, dichloromethane was added to the NSA solution to form a two-phase reaction mixture.

4. Structures assigned to the carboxylic acids were confirmed by comparison with authentic samples.

#### SYNTHESIS OF ARYL HALIDES via ORGANOBORANE CHEMISTRY

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Aryl halides are generally formed via reaction of aryl diazonium salts with halide ions. These reactions are quite sensitive to temperature, solvent, and other factors. Nevertheless, the products are isomerically pure, in contrast to the mixtures which are obtained via direct halogenation of arenes. We recently developed new halogenation methods which involve the reaction of organoboranes with halide ions in the presence of chloramine-T.<sup>1</sup> we have found these reactions to be