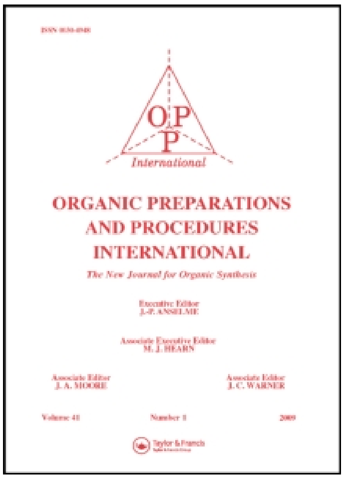

**Organic Preparations and Procedures International**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

# NITROSYLSULFURIC ACID HYDROLYSIS OF PRIMARY AMIDES

L. G. Wade Jr.[a]; William B. Silvey[a]
[a] Department of Chemistry, Colorado State University, Fort Collins, Colorado

**To cite this Article** Wade Jr., L. G. and Silvey, William B.(1982) 'NITROSYLSULFURIC ACID HYDROLYSIS OF PRIMARY AMIDES', Organic Preparations and Procedures International, 14: 5, 357 — 359

**To link to this Article: DOI:** 10.1080/00304948209354931

**URL:** http://dx.doi.org/10.1080/00304948209354931

# NITROSYLSULFURIC ACID HYDROLYSIS OF PRIMARY AMIDES[†]

Submitted by L. G. Wade, Jr.* and William B. Silvey
(11/30/81)
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

Use of a nitrosation reaction to hydrolyze primary amides, presumably *via* an acyl diazonium salt, has been well established.[1] 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.[2]

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.

$$RCONH_2 \xrightarrow[H_2O]{HOSO_2ONO} RCOOH$$

Treatment of a primary amide with 50-85% NSA[3] at 20-45° for 1-3 hrs generally affords the acid[4] 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.-[5] Cold commercial nitrosylsulfuric acid (3.5 ml) was cautiously added to 1.5 ml

Table 1. Hydrolysis of Primary Amides with NSA

| | NSA[3] (%) | Time (hrs) | Temp (°C) | Yield (%) | mp(°C) crude | lit.[a] |
|---|---|---|---|---|---|---|
| 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 |
| o-bromobenzamide | 70 | 1.5 | 20 | 82 | 143-144 | 147 |
| 2,6-dichlorobenzamide | 70 | 2 | 35 | 93 | 138-139 | 139 |

---

[a] 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.$^{mp}$. 133°.

REFERENCES

† This work was supported by a Biological Research Support Grant from Colorado State University.

1. L. Bouveault, Bull. Soc. Chim. France, 9, 368 (1893); J. J. Sudborough, J. Chem. Soc., 67, 601 (1895); N. Sperber, D. Papa and E. Schwenk, J. Am. Chem. Soc., 70, 3091 (1948); S. Sarel and M. S. Newman, ibid., 78, 5416 (1956); H. Ladenheim and M. L. Bender, ibid., 82, 1895 (1960).
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 $NO_x$ 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

Submitted (12/21/81)

by George W. Kabalka*, Kunda A. R. Sastry, Usha Sastry and Vishwanatha Somayaji

Department of Chemistry
University of Tennessee
Knoxville, Tennessee 37996-1600

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.[1] we have found these reactions to be