

peratures, **3** can also extrude **1**, leaving the coordinatively unsaturated dinuclear complex **B** which rapidly dimerizes to **5**. At no time do we observe any **2** in these reactions³ and therefore suggest that it is formed by reaction of **1** or a derived photoproduct with trace amounts of atmospheric oxygen.

Acknowledgments. We are grateful to the National Science Foundation and the Chevron Research Corporation for partial support of this work.

(13) Camille and Henry Dreyfus Foundation Teacher-Scholar, 1970-1975.

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Received January 2, 1974

Convenient Synthesis of Silver Hyponitrite

Sir:

Silver hyponitrite is the starting material for the synthesis of alkyl hyponitrites, which are useful low-temperature sources of alkoxy radicals.¹⁻⁵ Numerous syntheses of sodium and silver hyponitrites have appeared in the literature.⁵⁻⁹ Most are tedious, hazardous, poorly described, or require large quantities of mercury. In our hands, one procedure gave no product and the reaction mixture from another ignited during work-up.

The method described below is a modification of that of Weitz and Vollmer¹⁰ which takes advantage of the known solubility of sodium in benzophenone solutions.¹¹ The yield is low (it might be improved by inverse addition), but the synthesis is shorter and more convenient than earlier procedures. The reaction of sodium in hexamethylphosphoramide¹² with nitric oxide proceeded exothermically, but the product was more difficult to isolate.

A 500-ml three-necked flask was equipped with a gas inlet, a magnetic stirrer, and an outlet connected to a bubbler. The inlet tube was connected by a T-joint so either N₂ or NO could be added. The flask was charged with 100 ml of 1,2-dimethoxyethane and 150 ml of toluene (each distilled from blue Na and benzophenone solutions). Benzophenone (26 g) was added and the solution was flushed with N₂. Sodium (6.9 g) was then extruded as wire into the solution, and the flask was surrounded by an ice bath. After flushing with N₂, stirring was begun, and nitric oxide was admitted at a rate such as to maintain a slight positive pressure. Shaking the flask greatly increased the rate of gas uptake. The re-

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action was nearly complete within 20 min. After stirring 1 hr under NO, the solution was flushed with N₂. Water (10 ml) was added dropwise with stirring (foaming), and the solution was extracted with additional water (70 ml) in three portions. Absolute ethanol (200 ml) was added to the combined extracts, and the solution was swirled with cooling if necessary to induce crystallization. The Na salt was filtered off and washed with absolute ethanol and ether. After drying in air, the cream solid weighed 3.5 g but contained bound ethanol and water.

A solution of silver nitrate (6.0 g) in water (600 ml) was added slowly with vigorous stirring to a 1% solution of the Na salt until the precipitate began to discolor.¹³ About 420 ml was required. The product was filtered off, washed with water, and dried over P₂O₅ at 25° and 0.5 Torr. The yellow solid contained 77.5% Ag (Volhard method¹⁴) and weighed 3.5 g (8% based on Na). With excess methyl bromide the product afforded methyl hyponitrite, a spontaneously explosive liquid that will be described elsewhere in detail.

Acknowledgment. This work was supported, in part, by Grant R 802288 from the Environmental Protection Agency.

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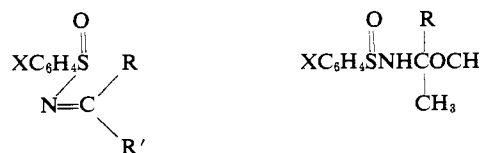
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Received April 1, 1974

Chemistry of the Sulfur-Nitrogen Bond. VIII. *N*-Alkylidenesulfonamides¹

Sir:

We wish to report the synthesis of a new class of reactive sulfur-nitrogen compounds,² *N*-alkylidenesulfonamides (*N*-(arylsulfinyl)imines), **1**. Compounds **1a-e** were prepared in good yield by dropwise addition of 1 equiv of *m*-chloroperbenzoic acid to a two-phase system containing the corresponding *N*-alkylidenesulfenamides³ in chloroform and water-sodium bicarbonate. Although the C-N double bond in imines is known to be oxidized to oxaziridines⁴ under these conditions, we were unable to detect any of these products.



- 1a**, X = H; R = R' = CH₃ **2a**, X = H; R = CH₃
b, X = H; R = H; R' = C₆H₅ **b**, X = 3-NO₂; R = H
c, X = 4-Cl; R = H; R' = C₆H₅
d, X = 3-NO₂; R = H; R' = CH₃
e, X = 3-NO₂; R = H; R' = C₆H₅

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