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On the α-Nitrosation of Tetrahydroisoquinoline-type Schiff Bases: a Simplified Procedure

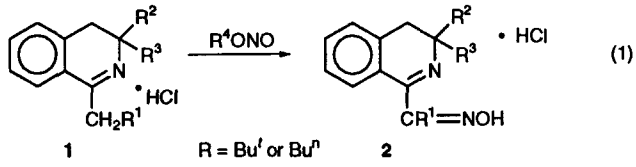
Electron A. Mistryukov* and Olga N. Sorokina

N. D. Zelinsky Institute of Organic Chemisry, Russian Academy of Sciences, 117913 Moscow, Russian Federation. Fax: +7 095 135 5328

Interaction of alkyl nitrite and chloride **1** leads to a high yield of oxime chloride **2**.

In the previous communication[1] we described the nitrosation of some isoquinolinic imines by a new reagent: trimethyl silylchloride (TMSCl)/alkyl nitrite. The mechanism of this reaction is not clear and among probable intermediates may include the imine chloride **1**. As shown in this communication, interaction of hydrochloride **1** and butyl- or *tert*-butyl nitrite produces a high yield of oxime hydrochlorides **2**, reaction (1). Thus, from this simple and practically useful imine nitrosation procedure follows the conclusion that *C*- or *N*-silylated derivatives of starting free base **1**, when TMSCl/RONO is the

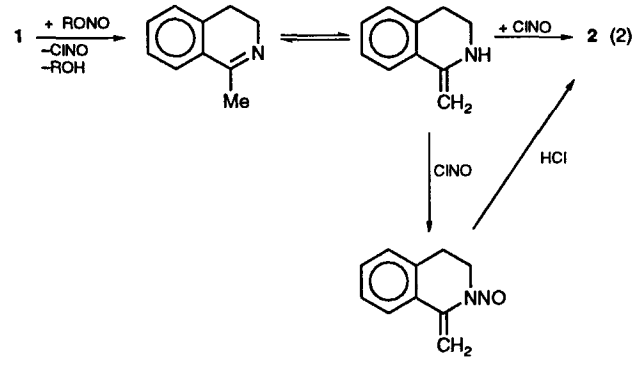
reagent, are not the required precursors for imino oximes. Therefore, the pathway *via* chloride **1** with TMSCl/alkyl nitrite reagent may be assumed as a probable one.†



(1)

1 R = Bu^t or Bu^n **2**

a $R^1 = R^2 = R^3 = H$
b $R^1 = Me$, $R^2 = R^3 = H$
c $R^1 = Ph$, $R^2 = R^3 = H$
d $R^1 = H$, $R^2 = R^3 = Me$



† *Typical procedure for the oximination of chloride* **1a**. To a solution of **1a** (180 mmol) in 20 ml of alcohol-free chloroform under argon was added 300 mmol of *tert*-butyl nitrite and the mixture was kept at 50 °C. After 1 h, copious crystallisation of **2a** occurred and the reaction was left to proceed overnight at room temperature. The crystals were filtered off, washed with 15 ml of the same solvent, and then dried. The yield was 3.1 g (82%); the product was identical with the one previously synthesized, **2a**·HCl (NMR, TLC, m.p). In the same way were prepared imino oxime chlorides **2b-d**; yields are comparable with those obtained in TMSCl/alkyl nitrite oximination.[1]

Nevertheless, with alkyl nitrite and **1** the formation of **2** is not a straightforward process but should include the prior formation of a strong electrophile ClNO, reaction (2), and free base **1** equilibrating between imine and enamine forms. Then, if the *N*-nitroso derivative is a primary product, acidic isomerisation into **2** follows. A similar *N*- to *C*-migration in *N*-nitrosoenamines has been described.[2] Interestingly, the experiment pertinent to the above consideration is the formation of the *N*-nitroso derivative from diethylamine hydrochloride and butyl nitrite at room temperature in acetonitrile solution with liberation of HCl. The latter is known to form ClNO with alkyl nitrite. From this it might be decided that the optimal reagent for nitrosation of **1** as free base would be ClNO. However, in practice, the reagent and free base **1** react together very exothermally but fail to produce **2**. The probable success of reaction of chloride **1** with alkyl nitrite is connected with the controlled liberation of both ClNO and base **1**. It is not quite clear why only alkyl nitrites were successful with chlorides **1**: with lithium nitrite or aqueous sodium nitrite only low yields of **2** were obtained. The same is true for interaction of free bases **1** in acetic acid with lithium or sodium nitrites or alkyl nitrites.

References

1 E. A. Mistryukov, Y. Rozpravka and O. N. Sorokina, *Mendeleev Commun.*, 1993, preceding paper.
2 R. E. Lylle, W. E. Kruger and V. E. Gunn, *J. Org. Chem.*, 1983, **48**, 3574.

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