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# IONIC DENITROHYDROGENATION OF α-NITRO OR β-NITRO SULFIDES WITH TRIETHYLSILANE

Noboru Ono,* Toshihiro Hashimoto, Tuo Xiao Jun, and Aritsune Kaji
Department of Chemistry, Faculty of Science, Kyoto University,
Kyoto 606, Japan

Summary: The nitro groups of α-nitro or β-nitro sulfides are replaced by hydrogen on treatment with triethylsilane in the presence of a Lewis acid.

Replacement of aliphatic nitro groups by hydrogen is becoming an important process in organic synthesis, for the nitro group serves as an excellent activating group for carbon-carbon bond forming reactions.1) Although radical denitration using tributyltin hydride has been used for this transformation, the radical method cannot be applied to all kinds of denitrohydrogenation.1) For example, the reaction of α-nitro sulfides with tributyltin hydride results in the selective cleavage of the C-S bond to give the nitro compounds, and the reaction of β-nitro sulfides with tin radicals results in the concurrent cleavage of the C-N and C-S bonds to give the corresponding alkenes.2) In this paper we report a new method for replacing nitro groups by hydrogen via ionic hydrogenation,3) which can be used for denitrohydrogenation of α-nitro or β-nitro sulfides.

Procedure: A mixture of $R-NO_2$, $Et_3SiH$ (2 equiv), and a Lewis acid (1-2 equiv) in $CH_2Cl_2$ was stirred at 0-20 °C for 0.5-5 h. The reaction mixture was poured into water and extracted with $CH_2Cl_2$. After the removal of the solvent, the residue was purified either by distillation or column chromatography (silica gel/benzene-hexane) to give R-H in good yields. The results are summarized in Table 1. The nitro function might be converted into triethylsilyl nitrite, for 1,1,1,3,3,3-hexaethyldisiloxane was isolated in 90-100% yield.4)

$$R\text{-}NO_2 \quad + \quad Et_3SiH \xrightarrow{\text{Lewis acid}} R\text{-}H \quad + \quad Et_3SiONO \qquad (1)$$

The present method is applicable to denitration of the nitro compounds which are activated by a phenyl or phenylthio group at the α- or β-position. Other secondary or tertiary nitro groups are not denitrated by this method. Radical denitration with tributyltin hydride is more suitable for such denitration than the present method. However, the present method is very

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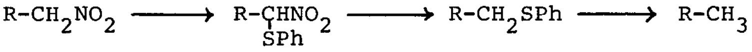
This paper is dedicated to the late Professor Ryozo Goto, Kyoto University.

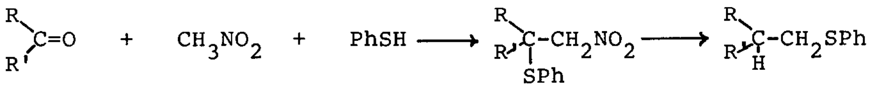
useful for reductive denitration of α-nitro and β-nitro sulfides, for these nitro groups are not replaced by hydrogen on treatment with tributyltin hydride or other radical denitration agents.1)

α-Nitro sulfides are prepared either by the reaction of nitro compounds with diphenyl disulfide,5) or alkylation of α-phenylthionitromethane with alkyl halides or other electrophiles.6) Subsequent denitration with triethylsilane followed by desulfurization provides a new method for the conversion of the nitromethyl group to the methyl group.7)



$$R\text{-}CH_2NO_2 \longrightarrow R\text{-}\underset{SPh}{C}HNO_2 \longrightarrow R\text{-}CH_2SPh \longrightarrow R\text{-}CH_3 \qquad (2)$$

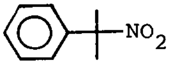
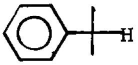
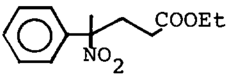
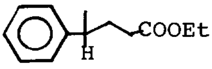
β-Nitro sulfides are generally prepared by the Michael addition of thiols to nitroolefins or related reactions.8) The reaction of ketones with nitromethane in the presence of thiophenol gave the nitromethylsulfide. Subsequent denitration with triethylsilane gave the sulfide, where hydride attacked the more substituted carbon atom. The reaction may proceed via episulfonium intermediates.9)



(3)

The present ionic denitrohydrogenation can be applied to the nitro compounds which have the thio function at the α- or β-position. The thio function stabilizes the carbocation intermediates via an alkylidene sulfonium ion or an episulfonium ion. Thus, ionic denitrohydrogenation may compensate the defects of radical denitration, and most nitro groups are now replaced by hydrogen via ionic or radical procedures.1)

Table 1 Ionic Denitrohydrogenation with Triethylsilane

| $R\text{-}NO_2$ | Lewis acid (equiv) | Temp °C | Time h | R-H | yield % |
|---|---|---|---|---|---|
|  | $SnCl_4$ (1.5) | 20 | 1 |  | 75 |
|  | $SnCl_4$ (1.5) | 20 | 2 |  | 65 |

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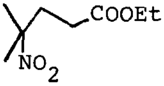
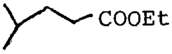
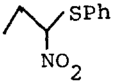
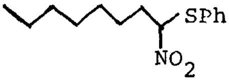
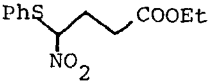
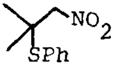
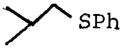
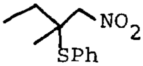
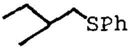
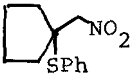
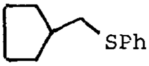
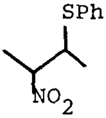
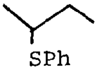
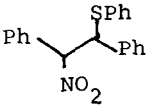
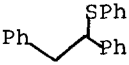
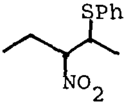
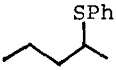
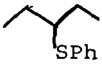
|---|---|---|---|---|---|
|  a) | $SnCl_4$ (2.0) | 20 | 8 |  | 0 |
|  | $SnCl_4$ (1.5) | 0 | 0.5 |  | 94 |
|  b) | $SnCl_4$ (1.5) | 0 | 0.5 |  | 93 |
|  | $SnCl_4$ (1.5) | 0 | 1 |  | 75 |
|  | $AlCl_3$ (2) | 20 | 2 |  | 77 |
|  | $AlCl_3$ (2) | 20 | 2 |  | 81 |
|  | $AlCl_3$ (2) | 20 | 2 |  | 70 |
|  | $AlCl_3$ (2) | 20 | 2 |  | 89 |
|  c) | $SnCl_4$ (1.5) | 20 | 2 |  | 50 |
|  | $AlCl_3$ (2) | 20 | 2 |  <br>1 : 1 mixture | 86 |

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(a) Radical denitration with $Bu_3SnH$ gave the denitrated product in 86% yield.

(b) Treatment of this compound with $Bu_3SnH$ in the presence of azobisisobutyronitrile gave 1-nitrooctane in 80% yield.

(c) Heating a mixture of this compound, $Bu_3SnH$, and azobisisobutyronitrile in benzene at 80 °C gave (E)-stilbene in 95% yield.

References

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2) N. Ono, A. Kamimura, A. Kaji, Tetrahedron Lett., 25, 5319 (1984).

3) Review: D. N. Kursanov, Z. N. Parnes, N. M. Loim, Synthesis, 633 (1984); where hydrogenation of C=C, C=O, C=N multiple bonds and for a number of single bonds such as C-OH, C-Hal, etc are described.

4) K. Kobayashi, M. Kawanishi, K. Kozima, Synth. Reac. Inorg. Metalorg. Chem., 8, 75 (1978), where trimethylsilyl nitrite is described to be decomposed readily to hexamethyldisiloxane.

5) W. R. Bowman, G. D. Richardson, J. Chem. Soc. Perkin I, 1407 (1980), and references therein.

6) D. Seebach, F. Lehr, Angew. Chem., Int. Ed. Engl., 15, 505 (1976).

7) Primary nitro groups are not replaced by hydrogen via radical procedures, see, ref 1.

8) W. E. Parham, F. L. Ramp, J. Am. Chem. Soc., 73, 1293 (1951).

9) Assumption of episulfonium ion intermediates is based on the following facts: 1) Simple secondary or tertiary nitro compounds which have not a phenylthio group at β-position were inert to the present procedure. (ii) Rearrangement of a phenylthio group was observed in the reaction of β-nitro sulfides with $Et_3SiH$ in the presence of a Lewis acid. Generation of episulfonium ions from β-nitro sulfides may promise a potential utility for organic synthesis, for the nitro group may be replaced by various nucleophiles via episulfonium ions.

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