

SELECTIVE REDUCTION OF THE N-O BOND IN N-OXIDES AND IN NITRONES
BY SODIUM HYDROGEN TELLURIDE

Derek H.R. Barton, Abdelwaheb Fekih and Xavier Lusinchi

Institut de Chimie des Substances Naturelles, C.N.R.S.,
91190 Gif-sur-Yvette, France

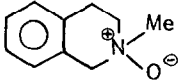
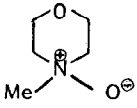
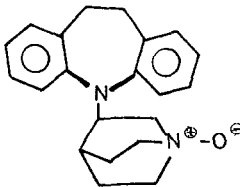
Abstract. - Sodium hydrogen telluride reduces *tert.*-amine N-oxides to the corresponding amines in very high yield, but does not reduce sulphoxides. This reagent also reduces nitrones to sec.-amines at pH6 and to imines at alkaline pH (10-11).

Sodium hydrogen telluride is an efficient but selective reducing agent for a number of functional groups.¹ It is easily prepared² by reduction of metallic tellurium and, at the end of the reaction, the original tellurium can be recovered quantitatively. In addition the reducing power of the reagent can be usefully changed¹ by variation of pH, suitably in the range of 2 to 12. For example¹ an imine is smoothly reduced under mild acid conditions, but is not touched at alkaline pH. We now describe the reduction of N-oxides and of nitrones.

Table 1 shows that a range of N-oxides are reduced, in general quantitatively, to the corresponding amines. In contrast, $(\text{PhCH}_2)_2\text{S}=\text{O}$ was not reduced to sulphide, at either acid or alkaline pH under reflux in ethanol.

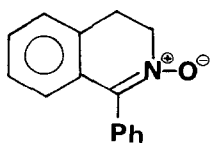
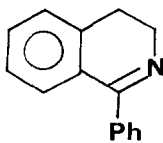
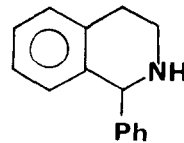
Since N-oxides are not reduced by sodium borohydride³ the tellurium can be used catalytically. Thus about 15% of the theoretical amount of tellurium with the usual excess of sodium borohydride gives the same result as the usual conditions.^{1,2}

Table 1

| N-Oxide | Time a) | Yield (%) of Amine b) |
|--|---------|--------------------------|
| $(\text{PhCH}_2)_3\text{N}^{\oplus}\text{-O}^{\ominus}$ <u>1</u> | 15 min. | 98 |
| $\text{PhMe}_2\text{N}^{\oplus}\text{-O}^{\ominus}$ <u>2</u> | 18 hr | 88 |
|  <u>3</u> | 2 hr | 96 |
|  <u>4</u> | 2 hr | 70 ^{c)} |
|  <u>5</u> | 6 hr | 94 |

a) Time of reflux in ethanol. b) Yields of amine isolated and compared with authentic specimens. c) Low yield because of volatility of the product.

Nitrones are known to be reduced by sodium borohydride to furnish hydroxylamines.⁴ To study their reduction by sodium hydrogen telluride we, therefore, adjusted^{1,2} the pH to 6 to destroy excess borohydride. The results are given in Table 2.

678

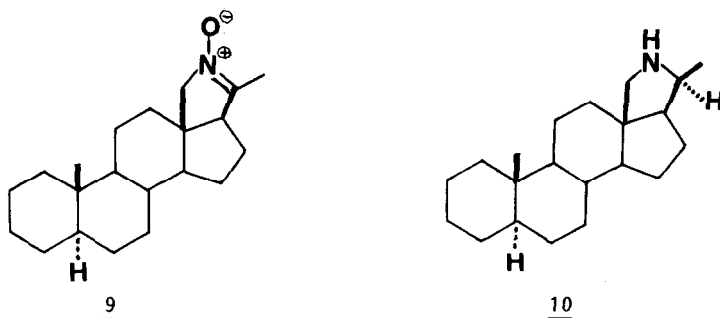
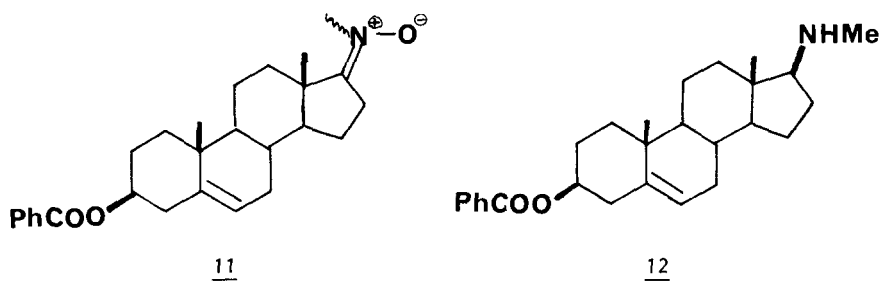


Table 2

| Nitronone | Time ^a | Yield (%) ^b of Amine |
|-----------|-------------------|------------------------------------|
| <u>6</u> | 6 hr | <u>8</u> (80) |
| <u>9</u> | 20 hr | <u>10</u> (54) |
| <u>11</u> | 2 hr | <u>12</u> (85) |

a) Time of reflux in ethanol.

b) Yield of Secondary amine isolated and compared
(except for 12) with authentic material.



For the nitronones 9⁵ and 11⁶ the reduction was stereoselective as judged by N.M.R. The secondary amine 10 was prepared by the known route.⁷ The amine 12⁸ is unknown and the configuration is assigned by analogy.

When the nitronone 6 was reduced (18 hr, under reflux) at alkaline pH (pH 6 adjusted to pH 10-11 by addition of NaOH) the reaction gave only the imine 7 (88%), in accordance with our previous findings.¹

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REFERENCES

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2. D.H.R. Barton and S.W. McCombie, J. Chem. Soc., Perkin Trans 1, 1574 (1975).
3. A blank experiment was made with $(\text{PhCH}_2)_3\text{N}^{\oplus}-\text{O}^{\ominus}$ and an excess of NaBH_4 under reflux in ethanol for 2 hrs. All the starting material was recovered unchanged.
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8. M.p. 150-152° (from EtOAc-hexane), $[\alpha]_{\text{D}} -17^\circ$ (CHCl_3 , $c=1$).

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