A New Synthesis of Amines with Diborane[1]

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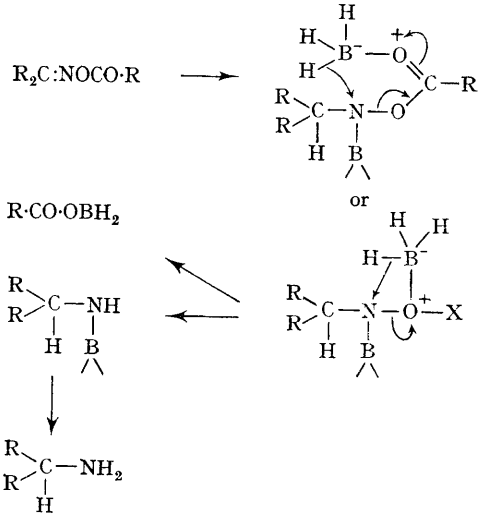
HYDROBORATION, or addition of diborane to olefins, is of considerable value in stereospecific organic syntheses.[2] It has been extended to carbonyl and azo-compounds, acetylenes, epoxides, nitriles, amides, and oximes.[2-4]

We report our results on the preparation of amines from ketoxime acetates or tosylates by reduction with an excess of diborane in tetrahydrofuran at room temperature. This reaction greatly extends the usefulness of diborane reductions, since Feuer and his co-workers[4] have shown that aldoximes and ketoximes are hydroborated to hydroxylamines. Furthermore, whereas diaryl ketoximes such as fluorenone and benzophenone oxime are not affected by diborane,[4] we found that fluorenone oxime acetate was easily reduced to the corresponding amine in 75% yield. After addition of diborane the mixture is worked-up with water, or preferably with dilute sodium hydroxide, and the products are usually isolated as the corresponding acetamides [ν_{max} 3300—3400 (NH), 1640—1680 cm.$^{-1}$ (NH·C=O), CH_3 singlet at τ 8·0] after treatment with acetic anhydride. The overall yields from oxime acetates are 60—75%.

A few examples are given in the Table. As can be seen, the reduction at the C=N at the 3- and 17-position in steroids occurs stereospecifically from the sterically less hindered α-side.

It is noteworthy that the reduction can also be applied successfully to the synthesis of 10-aminothioxanthenes. Recent attempts to reduce xanthone oxime and thioxanthone oxime with lithium aluminium hydride led to deaminated products.[5] We likewise were unable to reduce 2,3-dimethoxythioxanth-10-one 5,5 dioxide oxime



TABLE†

Diborane reduction of oxime derivatives to amines[a]

Indan-1-one oxime acetate	1-Acetamidoindane
Indan-1-one oxime tosylate	1-Acetamidoindane
Indan-2-one oxime acetate	2-Acetamidoindane
Fluoren-9-one oxime acetate	9-Acetamidofluorene
Cholestan-3-one oxime acetate	3-Acetamidocholestane
Androstan-3β-ol-17-one oxime diacetate	17β-Acetamido-3β-acetoxyandrostane
2,3-Dimethoxythioxanth-10-one 5,5-dioxide oxime acetate	10-Acetamido-2,3-dimethoxythioxanthene 5,5-dioxide

[a] Overall yields of pure amides from oxime derivative ranged between 60 and 75%.

using a variety of reducing agents until we applied the diborane reduction to the oxime acetate.

The fact that oximes are reduced by diborane to hydroxylamines while oxime acetates yield amine can be explained by co-ordination of borane with one of the acetate oxygens, thus providing a good leaving group that facilitates internal hydride transfer. This is consistent with the fact that *O*-oxime ethers are reduced to amines and is substantiated by the analogous behaviour of oxime tosylates (see Table).‡

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† Consistent elemental analyses and spectral data were obtained for all products not already reported in the literature.

‡ An alternative elimination of HOX from $R_2CH{\cdot}NB{\cdot}OX$ cannot be ruled out at this time.

[1] For previous paper see A. Hassner and P. Catsoulacos, *Chem. Comm.*, 1967, 121.

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