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REDUCTION OF OXIMES TO HYDROXYLAMINE(N-B)BORANES WITH SODIUM HYDRIDOBORATE ON SILICA GEL

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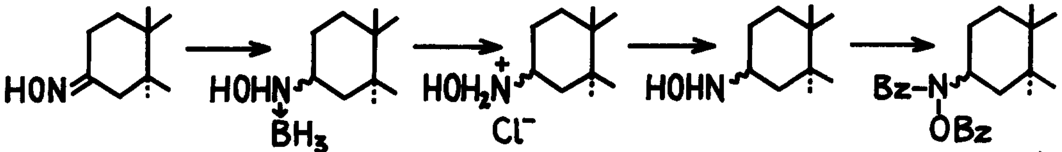
We observed that the previously reported[1] reduction of ketones to alcohols in non-polar solvents using sodium hydridoborate on alumina ($NaBH_4/Al_2O_3$) proceeds also with silica gel as adsorbent ($NaBH_4$/SG). Testing the reducing power of the latter on compounds which under usual conditions are not reducible with sodium hydridoborate we found that $NaBH_4$/SG reacts with oximes at room temperature in benzene solution. For instance, on reacting 5α-cholestan-3-one oxime (I) with $NaBH_4$ two boron compounds could be isolated by TLC. The major product was found to be the 3β-hydroxylamine(N-B)borane IIa (decomp. 185-190°) and the less polar, minor one, the corresponding 3α-epimer IIb (decomp. 55-60°). The IR spectra of these compounds taken in cyclohexane exhibit sharp O-H and N-H stretching bands at 3480 and 3250 cm^{-1}, respectively, and a rather complex absorption between 2265-2410 cm^{-1} which may be assigned to the BH_3 group.[2] The hydroxylamine (N-B)borane IIa was readily converted with hydrochloric acid into the hydrochloride IIIa (decomp. 175-182°) from which sodium hydroxide liberated the rather unstable hydroxylamine IVa (m.p. 159-165°); the Schotten-Baumann benzoylation of the latter gave the O,N-dibenzoyl compound Va (m.p. 153-156°). Similarly, the epimeric hydroxylamine(N-B)borane IIb was converted into the hydrochloride IIIb (decomp. 185-200°) and then without isolation of the free hydroxylamine IVb into the O,N-dibenzoyl derivative Vb (m.p. 113-115°). Starting with 5α-androstan-17-one oxime the corresponding 17β- and 17α-hydroxylamine-borane (decomp. 192-194° and 165-167°, respectively) were obtained.

The expected reducing property of the hydroxylamine(N-B)boranes was demonstrated by converting 5α-cholestan-3-one with these reagents to the epimeric cholestanols.

The hydroxylamine(N-B)borane IIa could be obtained also by treatment of free hydroxylamine IVa with $NaBH_4$/SG. Analogously, triethylamine afforded the



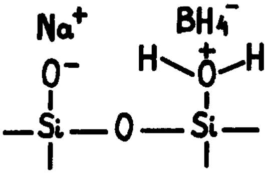
I IIa,b IIIa,b IVa,(b) Va,b

already known triethylamine-borane.[2] Moreover, in the reaction mixture obtained by reduction of the 17-oxime a very unstable boron compound was found which is most likely the borane adduct of the initial product  $>C=N\overset{OH}{\underset{\searrow BH_3}{<}}$. Consequently, a generalization according to the equation

$$=\ddot{N}- \;+\; NaBH_4 \;+\; HO-\overset{|}{\underset{|}{Si}}- \longrightarrow \overset{BH_3}{\overset{\uparrow}{=N-}} \;+\; H_2 \;+\; NaO-\overset{|}{\underset{|}{Si}}-$$

is possible.

As far as the reduction mechanism is concerned, we suggest the formation on the silica gel surface of an active reducing species as follows:



able to transfer simultaneously a hydride ion and a proton to a suitable acceptor (e.g. an oximino group). It is dificult to establish the moment when the complexation with borane occurs, but we consider that it accompanies the hydrogenation step, taking place before the reduced molecule leaves the reaction site. A more detailed dissoussion of the mechanism along with other experimental data will be published soon.

References

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[2] H. Nöth and H. Beyer, Chem. Ber. 93, 928 (1960); R. Köster, G. Bruno and P. Bingen, Liebigs Ann. Chem. 644, 1 (1961)