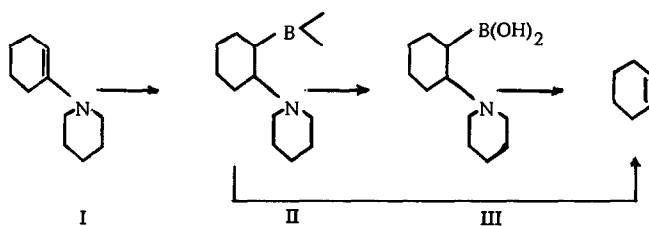


ALKENES FROM ENAMINES VIA HYDROBORATION

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We recently reported (1) the formation of alkenes from enamines by hydrogenolysis with a 'mixed hydride' reagent (AlH_2Cl): we now report similar results achieved by reaction of enamines with diborane followed by treatment of the resulting boranes with a carboxylic acid.

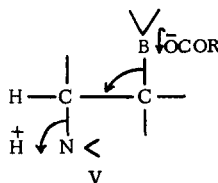
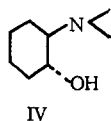
It has recently been shown (2) that when the pyrrolidine enamine of cholestan-3-one is reacted with diborane in tetrahydrofuran and the resulting solution of the borane is refluxed with acetic acid, 3-N-cholestanylpyrrolidine is formed. We followed this procedure with N-cyclohex-1-enylpiperidine (I) and obtained, in almost quantitative yield, 2-N-piperidylcyclohexylboronic acid (III), m.p. $114-116^\circ$ (Found: C, 62.4, H, 10.3; $\text{C}_{11}\text{H}_{22}\text{NO}_2\text{B}$ req. C, 62.3, H, 10.5%). When (III) was refluxed with acetic or propionic acids in diglyme, cyclohexene was formed. The intermediate borane (II) was unaffected when it was boiled in diglyme but it was



converted to cyclohexene when a carboxylic acid was added. This procedure has been applied to a number of enamines of cyclic and acyclic ketones and the alkenes have been obtained in yields of greater than 80%.

<u>Enamine</u>			
<u>Ketone:</u>	<u>Amine</u>	<u>Product</u>	<u>% Yield</u>
Cyclohexanone	Pyrrolidine	Cyclohexene	94
Cyclohexanone	Piperidine	Cyclohexene	95
Cyclohexanone	Hexamethylene-imine	Cyclohexene	93
Cyclohexanone	Morpholine	Cyclohexene	96
Cyclopentanone	Pyrrolidine	Cyclopentene	90
Cycloheptanone	Pyrrolidine	Cycloheptene	98
Cyclo-octanone	Pyrrolidine	Cyclo-octene	98
2-Methylcyclohexanone	Pyrrolidine	3-Methylcyclohexene	95
2-n-Butylcyclohexanone	Pyrrolidine	3-n-Butylcyclohexene	98
4-t-Butylcyclohexanone	Pyrrolidine	4-t-Butylcyclohexene	90
Pentan-3-one	Pyrrolidine	Pent-2-ene	85
Heptan-4-one	Pyrrolidine	Hept-3-ene	86
Ethyl acetoacetate	Pyrrolidine	Ethyl Crotonate	97

Confirmation of the expected cis-addition of diborane to enamines has been obtained in the isolation of a trans-2-hydroxycyclohexylamine derivative (IV) by hydroboration of an unspecified cyclohexanone enamine followed by oxidative cleavage of the borane with alkaline hydrogen peroxide*. The trans-relationship of the amine and boron functions favours a concerted elimination mechanism in the present reaction (V).



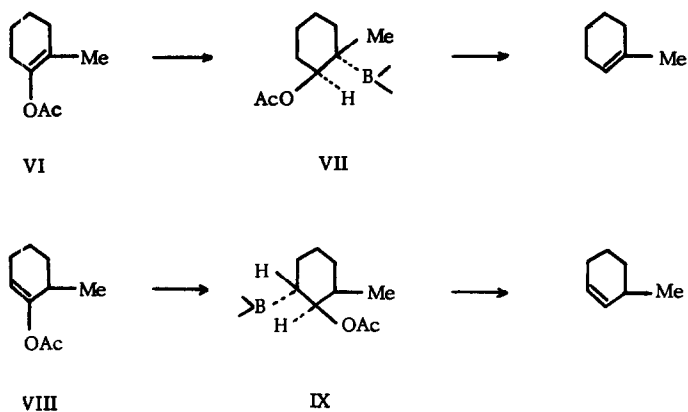
An analogous reaction is the conversion of the enol acetate of cholestan-3-one to cholest-2-ene by hydroboration followed by treatment with acetic anhydride (3). However, enol acetate formation preferentially involves the more substituted α -carbon atom of a ketone (4) whereas enamine formation involves the less substituted α -carbon atom (5). In the case of unsymmetrical ketones therefore, the hydrogenolysis of enol acetate and enamine would be expected to lead to different alkenes as main product.

We have confirmed this in the case of 2-methylcyclohexanone. The enamine gave only 3-methylcyclohexene (95%) whereas under analogous conditions the enol acetate** gave 1-methylcyclohexene (64%), 3-methylcyclohexene (17%) and methylcyclohexane (19%). The latter presumably arises by a spontaneous

*G. Stork, reported before the Organic Chemistry Division at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 6, 1961.

**Mixture of 2- and 6-methylcyclohex-1-enyl acetates (VI and VIII) prepared by slow distillation of acetic acid from a mixture of the ketone, acetic anhydride and a little p-toluenesulphonic acid (4).

elimination from one of the α -acetoxyboranes (VII) or (IX) followed by a second hydroboration and protonolysis. Similar mechanisms have been suggested to account for the formation of cyclohexanol from cyclohexenyl acetate (6) and *n*-propanol from allyl acetate (7) by procedures which involve hydroboration and oxidative cleavage. In the present reaction it appears that hydroboration of 2-methylcyclohex-1-enyl acetate (VI) gives only (VII) indicating that the addition is electronically controlled by the acetoxy-group.



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