

A CONVENIENT REDUCTION OF α,β -UNSATURATED NITROALKENES TO
ALKYLAMINES USING BORON HYDRIDES

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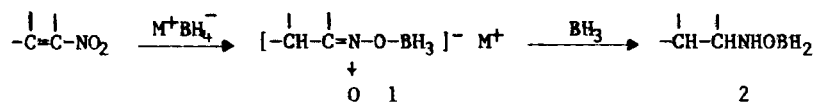
α,β -Unsaturated nitroalkenes are reduced to
alkylamines in good yields by excess of borane-
THF in presence of catalytic amount of sodium
borohydride.

In connection with our ongoing program directed toward the
synthesis of radiolabeled amphetamine derivatives¹, we required a
convenient procedure for synthesis of amines from α,β -unsaturated
nitroalkenes. The reduction of conjugated nitroalkenes to alkyl-
amines is conventionally accomplished using lithium aluminum
hydride.²⁻⁵ Generally, mixtures of products are obtained and
yields are modest. Catalytic hydrogenation⁶ has also been used on
rare occasions with limited success.

We recently reported⁷ a sodium borohydride catalyzed reaction
of borane complexes with α,β -unsaturated nitroalkenes.

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The reaction presumably proceeds via a nitronate intermediate, 1, which is then reduced to a hydroxylamine ester 2 by borane.



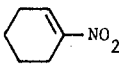
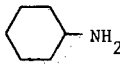
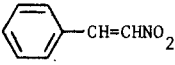
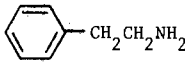
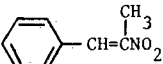
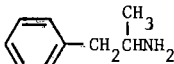
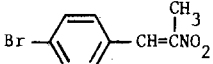
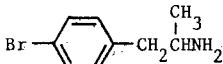
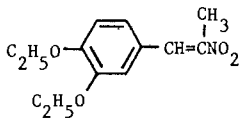
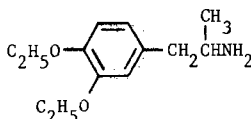
Since earlier studies⁸ demonstrate that hydroxylamines as well as their precursor oxime derivatives are reduced by diborane to amines at elevated temperature (105–110°C), we decided to investigate the reduction of the boron esters of hydroxylamines, 2, to amines.

We wish to report that the borohydride catalyzed reduction of α,β -unsaturated nitroalkenes to alkylamines can be carried out in good yields at room temperature using an excess of borane-THF. Our results are summarized in Table 1.

EXPERIMENTAL

All glassware was thoroughly dried in an oven and cooled under dry nitrogen just before using. THF was dried over CaH_2 , distilled from $LiAlH_4$ and stored under dry nitrogen. The BH_3 -THF solution was prepared and standardized according to the published procedure.¹³ Commercially available samples of 1-nitro-1-cyclohexene and β -nitrostyrene (Aldrich) were used as received. Other nitroalkenes were prepared via published procedures.^{5,12,14} Amine hydrochloride salts were prepared in a usual manner according to standard procedure³ by bubbling anhydrous hydrogen chloride through a solution of the amine in absolute ether and recrystal-

Table I. Reduction of α,β -Unsaturated Nitroalkenes with $\text{BH}_3\cdot\text{THF}$ and Sodium borohydride (catalytic amount).

Nitroalkene	Product	Yield ^b (%)	M.p. ^c (°C)	Ref.
		89(84)	207 ^d	9,15
		88(82)	215-16 ^e	10,16
		91(86)	146-47 ^f	3,17
		85(79)	202-3 ^g	11
		87(82)	139-40	12

a. All products were characterized by their physical properties and spectral characteristics (^1H -NMR, ^{13}C -NMR etc.). b. Yields in parentheses are for the hydrochloride salts. c. Melting points (hydrochloride salts) are uncorrected. d. (Lit.⁹ 209-10); e. (Lit.¹⁰ 218-19); f. (Lit.³ 147-48), hygroscopic; g. (Lit.¹¹ 204-6).

lized from ethanol-ether.

Synthesis of Alkylamines. General Procedure

The synthesis of β -phenylethylamine is representative of the procedure employed. A flame-dried, nitrogen-flushed, 100 mL flask, equipped with a septum inlet, magnetic stirring bar and reflux condenser was cooled to 0°C. A $\text{BH}_3\text{-THF}$ solution (16mmol, 9.5 mL of

1.7M) was injected into the reaction flask via a syringe, followed by the slow addition of a solution of β -nitrostyrene in THF (4 mmol, 0.6g in 6 mL THF). After the addition, the ice-bath was removed and a catalytic amount (~40 mg) of NaBH_4 was added to the stirred reaction mixture by means of a spatula. A moderately exothermic reaction ensued. The reaction was then allowed to proceed for 6 days at 25°C. The reaction mixture was poured on to ice-water mixture (50 mL), acidified with 10% HCl (~20 mL) and then stirred at 60–65°C for 2h. After cooling to room temperature, the acidic layer was washed with ether (2x50 mL), and then the β -phenylethylamine was liberated via the addition of aqueous sodium hydroxide. Solid NaCl was added and the product extracted into ether (3x50 mL). The combined ethereal extracts were dried over anhydrous MgSO_4 and the solvent removed under reduced pressure to yield 0.43 g (88%) of β -phenylethylamine. The product exhibited physical properties¹⁰ and spectral characteristics¹⁶ in accord with an authentic sample.

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