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THE REDUCTION OF α,β-UNSATURATED NITROALKENES TO NITROALKANES WITH TRIALKYLBOROHYDRIDES

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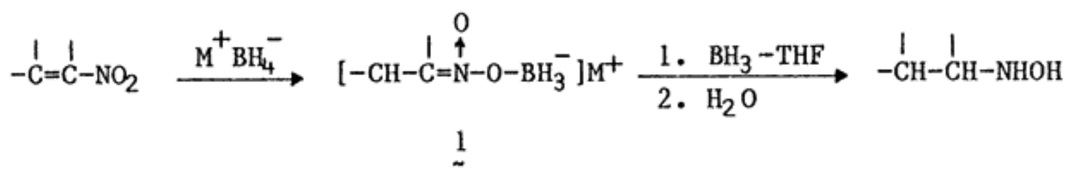
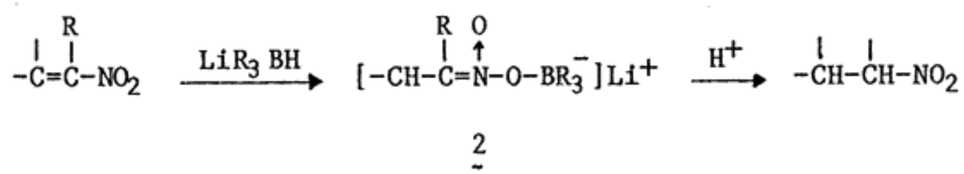
α,β-Unsaturated nitroalkenes are reduced to nitronate salts by trialkylborohydrides. These salts are readily hydrolyzed on silica gel to the corresponding nitroalkanes in good yields.

An attractive route to nitroalkanes involves reduction of the olefinic bond in the corresponding α,β-unsaturated nitroalkenes[1] and a number of reagents have been used to affect this transformation.[1-5] These reagents include complex metal hydrides,[1] sodium borohydride,[2-4] sodium cyanoborohydride[5] and catalytic hydrogenation.[6] The borohydride reagents have been found to be the most effective although yields greater than 60% are normally unattainable unless careful pH control is maintained.[3] The loss of product is due to a dimerization caused by the addition of the nitronate intermediate to the nitroalkene (via a Michael addition); this dimerization is especially prevalent for β-nitrostyrene derivatives.[2,3]

We recently reported[7] a synthesis of hydroxylamines involving the reduction of α,β-unsaturated nitroalkenes which presumably proceeds via the nitronate intermediate, 1.



We envisioned that the hydrolysis of intermediate 1 would produce the corresponding nitroalkane if 1 could be intercepted before complete reduction had occured. We investigated the use of trialkylborohydrides for the formation of intermediate 1 via the reduction of conjugated nitroalkenes because they had been successfully utilized in conjugate additions to α,β-unsaturated carbonyl compounds.[8] We found that lithium triethylborohydride[9] and lithium tri-sec-butylborohydride[10] cleanly reduce conjugated nitroalkenes to the desired nitronate, 2.

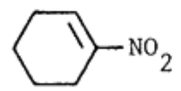
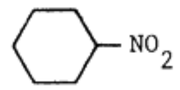
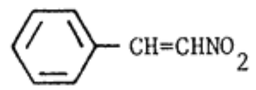
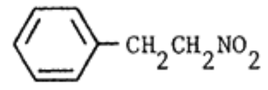
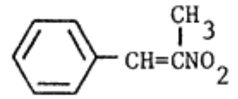
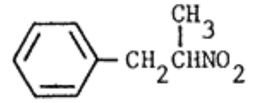
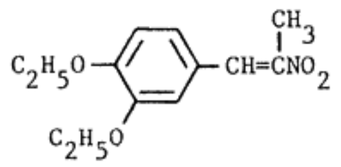
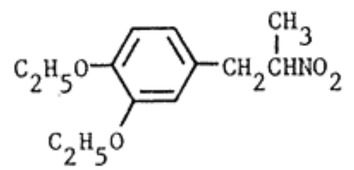
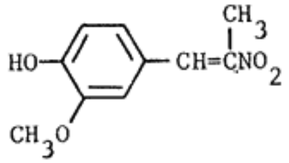
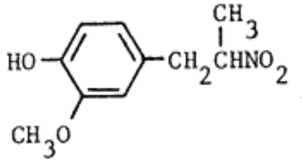


In an earlier study, Kornblum observed that nitroalkanes could be obtained by hydrolyzing nitronate salts with dilute acids.[11] We found that the most efficient hydrolysis of 2 was achieved using ordinary silica gel. The results are summarized in Table I.

The ready availability, mild reducing characteristics, and ease of manipulation of the trialkylborohydrides as well as the shorter reaction times and efficiency of this procedure make it an especially attractive route to a variety of nitroalkanes.

Acknowledgement. We wish to thank the Department of Energy for support of this research.

Table I. Reduction of α,β-Unsaturated Nitroalkenes to Nitroalkanes

Nitroalkene	Product[a]	Yield (isolated) (%)	Ref.
		69	12,13
		78	1,14
		81	1,15
		69	-
		65	-

a. Products exhibited physical and spectral properties in accord with the assigned structures.

EXPERIMENTAL

Commercially available 1-nitro-1-cyclohexene and the trialkylborohydrides (Aldrich) were used as obtained (L-Selectride, 1.0M in

THF; Super hydride, 1.0M in THF). All other nitroalkenes, were prepared by procedure as described earlier.[16] The products were characterized by their physical properties and spectral characteristics (^{1}H-NMR, ^{13}C-NMR etc.).

NMR spectra were recorded on a JEOL-FX90Q spectrometer and referenced to Me_4Si. Mass spectra were recorded on a Hewlett Packard HP 5982-A-GC-mass spectrometer equipped with a HP-5934 data package. All glassware was thoroughly flame-dried and cooled under dry nitrogen just before using. THF was dried over CaH_2, distilled from $LiAlH_4$ and stored under dry nitrogen. Air and moisture sensitive borohydride solutions were transferred using oven-dried hypodermic syringes.

General Procedure for the Synthesis of Nitroalkanes

The reduction of β-methyl-β-nitrostyrene is representative of the procedure employed. Lithium tri-sec-butylborohydride (4.5 mmol, 4.5 mL of a 1.0M solution) was placed in a 100 mL flask, equipped with a septum inlet and a magnetic stirring bar. β-Methyl-β-nitrostyrene in THF (4 mmol, 0.65 g in 5 mL of THF) was added dropwise to the stirred solution of the trialkylborohydride at room temperature. A mildly exothermic reaction ensued with the disappearance of the yellow coloration (nitroalkene). The reaction mixture was stirred for 30 min., cooled to 0°C, and then silica gel (10g) was added in 4 portions. The mixture was washed with ether (5x50 mL) to remove the adsorbed 2-nitro-1-phenylethane from the silica gel. The ethereal solution was washed with concentrated ammonium hydroxide, water, dried over anhydrous $MgSO_4$, and the

solvent removed under reduced pressure. The crude product was purified by column chromatography (silica gel, 2% ether/petroleum ether eluant) to yield 0.53g (81%) of 2-nitro-1-phenylethane. The product exhibited physical properties[1] and spectral characteristics[15] in accord with an authentic sample.

1-(3,4-Diethoxyphenyl)-2-nitropropane. The reaction was performed as described in the general procedure to yield 0.69g (69%) of the product as colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.43 (t,6H,CH_2-CH_3), 1.52 (d,3H,-CH-CH_3), 3.1 (m,2H,CH_2), 4.06 (q,4H,-OCH_2), 4.73 (sextet,1H,CH), 6.7-6.9 (m,3H,Ar-H); ^{13}C NMR ($CDCl_3$) δ 84.7 ($CHNO_2$), 64.6 (OCH_2), 40.9 (CH_2), 18.7 (CH_3), 14.9 (CH_2CH_3); MS m/e: 253 (M^+), 206 (base peak, M^+-HNO_2).[17]

1-(4-Hydroxy-3-methoxyphenyl)-2-nitropropane. The reaction was carried out as described in the general procedure using 2 equivalents of L-selectride to yield 0.55g (65%) of the product as pale yellow gum; ^{1}H NMR ($CDCl_3$) δ 1.54 (d,3H,CH_3), 3.1 (m,2H,CH_2), 3.87 (s,3H,OCH_3), 4.74 (sextet,1H,CH), 5.5 (bs,1H,-OH; exch. with D_2O), 6.6-6.91 (m,3H,Ar-H); ^{13}C NMR ($CDCl_3$) δ 84.8 ($CHNO_2$), 56.0 (OCH_3), 41.0 (CH_2), 18.8 (CH_3); MS m/e: 211 (M^+), 164 (base peak, M^+-HNO_2).[17]

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