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Reaction of Nitroolefins with Raney Nickel and Sodium Hypophosphite. A Mild Method for Converting Nitroolefins into Ketones (or Aldehydes).

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Summary: *Nitroolefins are converted into the corresponding saturated ketones or aldehydes in high yield by treatment with Raney nickel and sodium hypophoshite in aqueous ethanol at pH 5.*

Nitroolefins are of great synthetic potential in organic chemistry and several ways are known to convert them into carbonyl or amino derivatives (*1-4*). However, current methods for reducing vinyl nitro compounds to saturated ketones or aldehydes (*2*) either require reagents which are incompatible with acid-sensitive and reducible functional groups within the molecule (*1d,3,4*) or proceed by a two-step process (*4*).

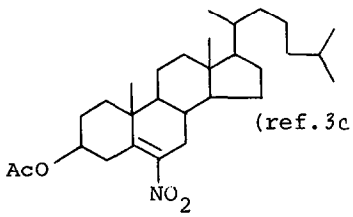
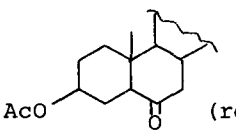
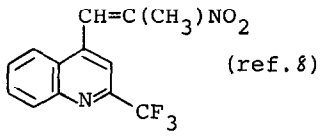
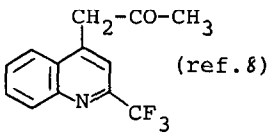
We wish to report here a chemoselective method for effecting the direct conversion of nitroalkenes into ketones or aldehydes in high yield under mild conditions This method involves the treatment of the nitroolefin with sodium hypophosphite and Raney nickel in ethanolic solution at pH 5 (see Table). Ester groups, C=C bonds, nitro and halogen substituents on aromatic nuclei, carbonyl groups are not affected by this reducing system (*5*).

General Experimental Procedure: *A suspension of Raney nickel (2.5 ml) and an aqueous solution of sodium hypophosphite (14 g in 60 ml) were added (in several portions and under stirring) to a solution of the nitroolefin (14 mmol) in ethanol-aqueous acetate buffer, pH 5 (2:1, ca. 400 ml). After 2 hr at 40-60°C the catalyst was filtered off, water added and the solution extracted with ether. Evaporation of the solvent yielded the carbonyl compound that could be purified by either distillation or crystallisation.*

It must be pointed out that under the conditions reported here nitroparaffins are reduced to amines whilst oximes give the corresponding carbonyl compounds in almost quantitative yields (*6*). Thus the above procedure represents also a very mild method for deoximation which appears complementary to those in the literature (*7*).

Work is in progress to clarify the mechanism of each step from nitroolefins to carbonyl compounds.

TABLE

	Nitroolefins	Carbonyl compounds	Isolated yields
1)	$C_6H_5-CH=C(CH_3)NO_2$	$C_6H_5-CH_2-CO-CH_3$	88
2)	$p-CH_3O-C_6H_4-CH=C(CH_3)NO_2$	$p-CH_3O-C_6H_4-CH_2-CO-CH_3$	92*
3)	$p-Br-C_6H_4-CH=C(CH_3)NO_2$	$p-Br-C_6H_4-CH_2-CO-CH_3$	77*
4)	$o-OH-C_6H_4-CH=C(CH_3)NO_2$	$o-OH-C_6H_4-CH_2-CO-CH_3$	70
5)	$p-OH-C_6H_4-CH=C(CH_3)NO_2$	$p-OH-C_6H_4-CH_2-CO-CH_3$	56
6)	$C_6H_5-CH=CH-CH=C(CH_3)NO_2$	$C_6H_5-CH_2-CH=CH-CO-CH_3$	64
7)	 (ref.3c,d)	 (ref.3c,d)	52
8)	 (ref.8)	 (ref.8)	86
9)	$p-CH_3O-C_6H_4-CH=CH-NO_2$	$p-CH_3O-C_6H_4-CH_2-CHO$	53

(*Glc yield.) Satisfactory elemental analyses were obtained for all compounds isolated and ^{1}H-NMR data were in agreement with structure of the products.

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