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THE CONVERSION OF NITRO GROUPS TO CARBONYLS WITH VANADIUM II CHLORIDE

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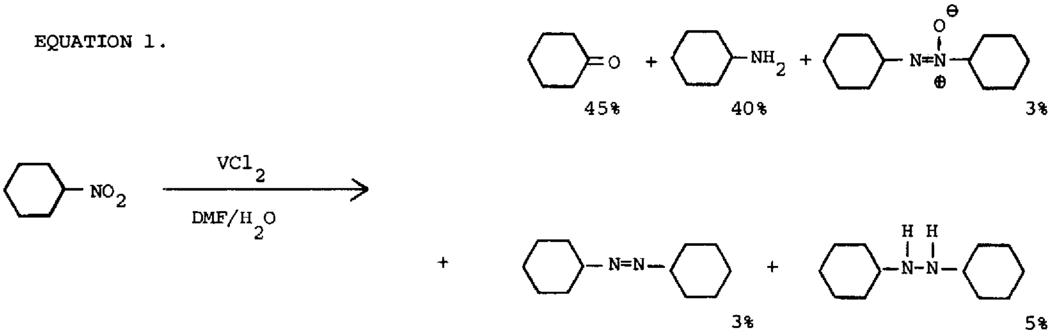
The conversion of primary and secondary nitro groups into carbonyls is a transformation of considerable synthetic utility. Several methods exist for carrying out this transformation in moderate to good yield.[2-6] Perhaps the most useful of these methods is the one originated by McMurry.[6] This procedure involves the simultaneous reduction and hydrolysis of nitro compounds with aqueous titanium III chloride. In the course of this work, McMurry investigated the reduction of nitro compounds with divalent vanadium and found that it too yielded carbonyl compounds but in low yield. We have reinvestigated this reaction and found that under conditions of low pH, vanadium II chloride converts primary and secondary nitro compounds into carbonyls in moderate to good yield.

The addition of one equivalent of nitrocyclohexane to five equivalents of vanadium II chloride in dimethylformamide at pH 0.3 resulted in a rapid and exothermic reaction. Upon work up, the products shown in equation 1 were isolated and identified. The low yield of cyclohexanone was consistant with McMurry's report. Interestingly, a considerable amount of cyclohexylamine was also produced along with nitroso coupling and reduction products.[7] In order to improve the yield of ketone, various conditions of solvent and pH were tried. It was found that by adding the aqueous vanadium II chloride to the nitro compound dissolved in a mixture of water, hydrochloric acid and dimethylformamide, the yield of ketone could be raised to 73% by glc (53% isolated). Under these conditions, the pH of the reaction mixture is much less than zero and the initial product of the reduction is the carbonyl imine which is stable. Subsequent hydrolysis at pH 4.0 readily affords the carbonyl compound.[8] The imine need not be isolated but may

EQUATION 1.



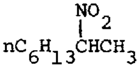
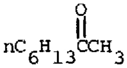
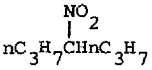
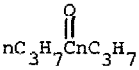
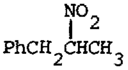
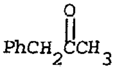
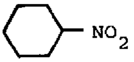
Yields by glc.

be hydrolyzed in the reaction mixture by adjusting the pH to 4.0 with sodium hydroxide after the reduction step.

Table 1 shows various nitro group to carbonyl conversions by means of aqueous vanadium II chloride. The low yield of aldehydes is due to their aldolization and polymerization under the strongly acidic reaction conditions.

Table 1

Conversion of Nitro Compounds to Carbonyls with Vanadium II Chloride

Nitro Compound	Product	% Yield (isolated)
$nC_7H_{15}CH_2NO_2$	$nC_7H_{15}CHO$	24
 $nC_6H_{13}\overset{NO_2}{\overset{\vert}{C}}HCH_3$	 $nC_6H_{13}\overset{O}{\overset{\Vert}{C}}CH_3$	71
 $nC_3H_7\overset{NO_2}{\overset{\vert}{C}}HnC_3H_7$	 $nC_3H_7\overset{O}{\overset{\Vert}{C}}nC_3H_7$	63
 $PhCH_2\overset{NO_2}{\overset{\vert}{C}}HCH_3$	 $PhCH_2\overset{O}{\overset{\Vert}{C}}CH_3$	65
		53

2-Nitrooctane (2.47 g, 0.015 mol) was dissolved in a mixture of 10 ml of water, 30 ml of 12 M hydrochloric acid and 70 ml of dimethylformamide. The solution was stirred in a water *bath at room temperature under an atmosphere of nitrogen. Vanadium II chloride*[9] *(150 ml of* 0.5 M soln., 0.075 mol) was then added dropwise over 20 min. After addition, the mixture was stirred at room temperature for 30 min and then diluted with 250 ml of water. The pH of the mixture was adjusted to 4.0 with 20% sodium hydroxide. Ether (100 ml) was added and the mixture was stirred for 1 hr. The ether layer was separated and saved and the aqueous phase was extracted with four 50 ml portions of ether. The ether extracts were combined and washed with four 25 ml portions of water and dried over magnesium sulfate. The drying agent was filtered off and the filtrate evaporated to yield the crude product. This was purified by vacuum distillation to give 1.36 g (71%, bp 110° @ 40 mm) of 2-octanone.

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7. Control experiments have shown that the amine formed is not the result of further reduction of the imine intermediate by vanadium II. The detailed mechanism of this transformation will be discussed in a forthcoming full paper.
8. Control experiments have shown that this is not an acid catalyzed conversion of the nitro group to the aci form followed by Nef type hydrolysis.
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