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# A NEW NITRO GROUP TO ACETAL TRANSFORMATION

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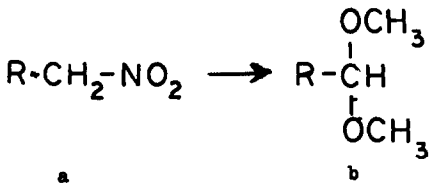
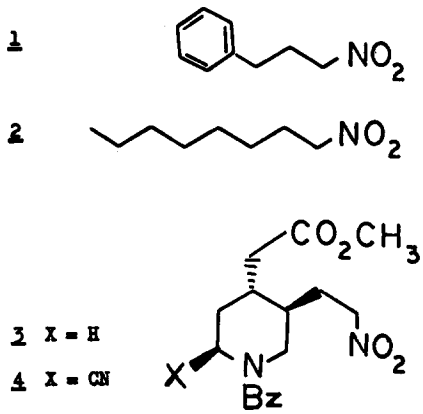
The preparation of medium and high molecular weight aldehydes and ketones from the corresponding nitro compounds by the Nef reaction is usually a much lower yield process than that for low molecular weight analogs, presumably because of the insolubility of the nitronate anion and/or the aci-nitro compound in the aqueous reaction medium.[2] The alternate method of Schecter[3] likewise requires nitronate anion solubility in roughly 0.5 molar aqueous magnesium sulfate and hence also suffers lower yields at higher molecular weights. The only other commonly used method for effecting the nitro to aldehyde/ketone conversion is that of McMurry and Melton[4] which allows the use of a cosolvent, dimethoxyethane, but gives only moderate yields for the primary nitro to aldehyde case.

We have found that the Nef reaction can be easily modified, using methanol in place of water, to give high yields of dimethyl acetals of even high molecular weight nitro compounds.




a b

78-99%




3 X = H

4 X = CN

The procedure is illustrated with the preparation of ester acetal benzamide 3b. A solution of 987 mg (2.96 mmole) of nitro ester benzamide 3a[5] in 7.0 ml of 0.5 N methanolic sodium methoxide (3.5 mmole) was added dropwise at a rate of 1 drop per second to a solution of 7.0 ml of sulfuric acid in 27 ml of methanol cooled to -35°. When the addition was complete the mixture was poured into 150 ml of methylene chloride and washed with 75 ml of ice water and 50 ml of dilute aqueous sodium hydroxide. The organic layer was dried over potassium carbonate and concentrated in vacuo yielding 810 mg (2.42 mmole, 78%) of ester acetal 3b[6] of high purity. The acetal 3b could be hydrolysed to the appropriate aldehyde in quantitative yield.

Use of the conventional (aqueous) Nef reaction or the methods of Schecter or McMurry gave variable low yields (always below 20%) of impure aldehyde.

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6. all new compounds have spectral properties consistent with their structures. Solids have correct elemental analyses.