Conjugated Aldehydes from Nitromethylalkenes

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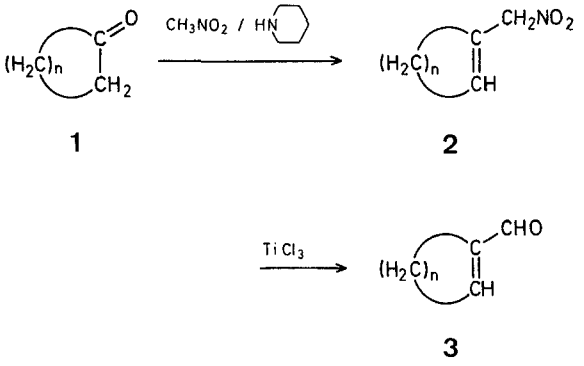
The synthesis of α,β-unsaturated aldehydes[1] by one-carbon homologation of ketones has been a focus of current interest. However, most of the existing methods suffer from low yields and require lengthy manipulation.

We wish to report the preparation of 1-cyclohexene- and 1-cycloheptenecarboxaldehyde from the corresponding 1-nitromethylcycloalkenes by reduction with titanium(III) chloride. This reagent has been used to generate ketones[2] from secondary nitroalkanes. Reaction with nitroalkanes and nonaromatic nitroalkenes has apparently not been attempted. Since the nitroalkenes **2** are readily available from cyclic ketones (**1**) by condensation with nitromethane[3],

the present produre constitutes a mild and useful route to these conjugated aldehydes.



1 2 3

1-Cycloalkenecarboxaldehyde:
A mixture of the 1-nitromethylcycloalkene (**2**, n = 4,5; 20 mmol) and titanium(III) chloride (20% solution, 75 ml) was degassed, sealed under vacuum (ca. 60 torr) and shaken at room temperature for 40 hr. The unsaturated aldehyde was extracted into ether and purified by bulb-to-bulb distillation.

1-Cyclohexenecarboxaldehyde: yield: 55%; b.p. 80°/20 torr [lit.[4,5] b.p. 70°/13 torr].

^{1}H-N.M.R. (CCl_4): $\delta = 9.33$ (s, 1H, CHO), 6.68 (m, 1H, =CH—), 2.0—2.5 (m, 4H), 1.3—1.9 ppm (m, 4H); [lit.[4] $\delta(CCl_4) = 9.33$ ppm].
I.R. (CCl_4): $\nu_{max} = 1690$ cm^{-1} [lit.[5] ν_{max} ($CHCl_3$) = 1690 cm^{-1}]
U.V. (hexane): $\lambda_{max} = 227$ nm ($\varepsilon = 10\,800$) [lit.[4] λ_{max} (hexane) = 227 nm ($\varepsilon = 11000$)].
1-Cycloheptenecarboxaldehyde: yield: 57%; b.p. 95°/20 torr [lit[4,5] b.p. 80°/10 torr].

^{1}H-N.M.R. (CCl_4): $\delta = 9.25$ (s, 1H, CHO), 6.77 (t, 1H, =CH—, $J = 6$ Hz), 2.2—2.7 (m, 4H), 1.20—2.0 ppm (m, 6H) [lit.[4] $\delta(CCl_4) = 9.26$ ppm].
I.R. (CCl_4): $\nu_{max} = 1690$ cm^{-1} [lit.[5] ν_{max} ($CHCl_3$) = 1690 cm^{-1}].
U.V. (hexane): $\lambda_{max} = 228$ nm ($\varepsilon = 11500$) [lit.[4] λ_{max} (hexane) = 228 nm ($\varepsilon = 11\,500$)].

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