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Aziridination of Conjugated Nitroalkenes

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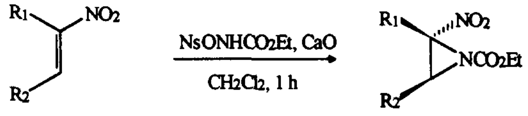
Abstract: **The recently proposed amination methodology based on solid bases induced decomposition of arenesulphonyloxycarbamates ($ArSO_3NHCO_2Et$) has been applied to α-nitroalkenes. α-Nitroaziridines have been obtained in high yields and purity, under mild conditions.**

Our continuous interest in alkene amination reactions, has been recently focused on a novel methodology employing a solid inorganic base, mainly CaO, K_2CO_3 or Cs_2CO_3, as the deprotonating agent of $NsONHCO_2Et$ and $TsONHCO_2Et$.[1] In this way it was possible to usefully extend the amination reaction to electron poor alkenes such as homoallylic acetals,[2] unsaturated acetonides[3] and α,β-unsaturated esters.[4]

In this communication we report on our first results concerning the aziridination by the same methodology of conjugated nitroalkenes, an important class of electrophilic alkenes, commercially available or easily synthesized.[5,6] To the best of our knowledge only one example of direct amination of these compounds by a *N*-nitrene has been reported.[7]

The aziridination was performed using a threefold excess of both CaO and $NsONHCO_2Et$ in the presence of a small amount of solvent (dichloromethane) and very good conversions were observed.



	Yield
$R_1 = R_2 = Me$	82%
$R_1 = Me$; $R_2 = Et$	84%
$R_1 = Me$; $R_2 = i\text{-}Pr$	70%
$R_1 \cdots R_2 = \text{-}(CH_2)_4\text{-}$	80%
$R_1 \cdots R_2 = \text{-}(CH_2)_6\text{-}$	71%
$R_1 = Me$; $R_2 =$ Cyclohexyl	62%

Other combinations of reagents, for example Et_3N-$NsONHCO_2Et$ or Cs_2CO_3-$TsONHCO_2Et$, gave lower yields of the same products.

The crude reaction mixtures showed satisfactory IR, ^1H and ^{13}C NMR spectra indicating the high purity of the products. The reaction products can be purified by flash chromatography eluting with a mixture of hexane/ethyl acetate/Et_3N (80:19:1), but sometimes the yields decreased owing to partial decomposition of aziridines on silica gel. The structures of the aziridines were confirmed by spectral data.[8]

The nitroaziridines so obtained are promising synthetic intermediates, since the nitro group offers a wide range of efficient methods for its transformation into other functionalities.[9] They are strained systems for which a stabilisation has been calculated by an *ab initio* method.[10]

The potential of this procedure is now under further investigation in our laboratories.

General Procedure. To 3 mmol of nitroalkene in 3 ml of CH_2Cl_2, 9 mmol of both $NsONHCO_2Et$ and CaO were added. After 1 h of stirring, 30 ml of CH_2Cl_2 and 300 ml of petroleum ether were added to precipitate the salt. After filtration, the crude product was concentrated *in vacuo*.

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8. For $R_1=R_2=Me$: IR (CCl_4) 1754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (*t*, 3 H, $CH_2C\mathit{H}_3$), 1.35 (*d*, 3 H, $C\mathit{H}_3CH$), 1.87 (*s*, 3 H, CH_3), 3.30 (*q*, 1 H, CH), 4.19 (*q*, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 13.44, 13.79 (CH_3), 14.23 (CH_2CH_3), 44.32 (CH), 63.14 (CH_2), 76.39 (C), 157.71 (CO); GC-MS *m/z* 158 (M^+ -30, 0.04), 114 (29), 70 (40), 69 (27), 68 (27), 44 (12), 43 (43), 42 (100), 41 (16).
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