Lewis Acid-induced Nucleophilic Substitution Reactions of α -Nitro Sulphides

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The nitro group of α -nitro sulphides is displaced by a cyano, allyl, or 2-oxocyclohexyl group on treatment with trimethylsilylcyanide, allyltrimethylsilane, or 1-trimethylsilyloxycyclohexene, respectively, in the presence of a Lewis acid.

In a previous paper we reported that tertiary, benzyl, and allylic nitro compounds undergo nucleophilic substitution reactions with carbon nucleophiles such as electron-rich aromatic compounds, allylsilanes, or silyl enol ethers in the presence of a Lewis acid.¹ Such nucleophilic displacement of aliphatic nitro groups is a useful process in organic synthesis, as nitro groups activate carbon–carbon bond formation very effectively. In this paper we report Lewis acid-induced nucleophilic substitution reactions of α -nitro sulphides, where the nitro group is displaced by nucleophiles.²

 α -Nitro sulphides are prepared either by sulphenylation of nitro compounds² or alkylation of α -phenylthionitromethane with alkyl halides.³ Thus prepared α -nitro sulphides (1) reacted with trimethylsilylcyanide or allyltrimethylsilane very rapidly, the reaction being complete in 20 min at 0 °C in the presence of SnCl₄ (1 equiv.), to give α -cyano sulphides (2, Y =



Reagents and conditions: SnCl₄ (1 equiv.), CH₂Cl₂, 0 °C, 20 min.

CN) or the allylated sulphides (2, $Y = CH_2=CHCH_2$), respectively, equation (1).[†] The results are summarized in Table 1.

When silyl enol ethers were used as nucleophiles, α -phenylthioalkylation of carbonyl compounds occurred to give (3) in good yields, equation (2).

R	Y	% Yield of (2)
Et	CN	92
$n - C_7 H_{15}$	CN	91
$n - C_9 H_{19}$	CN	95
[CH ₂] ₂ CO ₂ Me	CN	80
Et	$CH_2 = CHCH_2$	82
$n-C_7H_{15}$	$CH_2 = CHCH_2$	90
n-C ₉ H ₁₉	$CH_2 = CHCH_2$	84
$[CH_2]_2CO_2Me$	CH ₂ =CHCH ₂	78

Table 1. Nucleophilic substitution of NO_2 in (1) by Y.

† A typical procedure is as follows. To a mixture of (1) (10 mmol) and Me_3SiCN (15 mmol) in CH_2Cl_2 (10 ml) was added $SnCl_4$ (10 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 20 min and then poured into water. The usual work-up consisted of extraction with CH_2Cl_2 , washing with water, and drying with MgSO₄, followed by column chromatography (silica gel/benzene-hexane) to give (2).

differently. The synthetic utility of α -phenylthioalkylation of silylated nucleophiles has been well documented.⁴

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References

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The reaction may proceed via an S_N1 mechanism involving α -thio carbonium ion intermediates. This method for phenylthioalkylation of various silylated nucleophiles under Friedel-Crafts conditions is complementary to the existing method for such phenylthioalkylation using α -chloro sulphides,⁴ since, as well as being more stable, α -nitro sulphides are made