

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 trimethylsilyl cyanide, 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

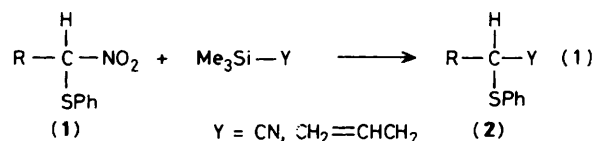
α -Nitro sulphides are prepared either by sulphenylation of nitro compounds² or alkylation of α -phenylthionitromethane with alkyl halides.³ Thus prepared α -nitro sulphides (1) reacted with trimethylsilyl cyanide or allyltrimethylsilane very rapidly, the reaction being complete in 20 min at 0°C in the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

CN) or the allylated sulphides (2, Y = CH₂=CHCH₂), 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).

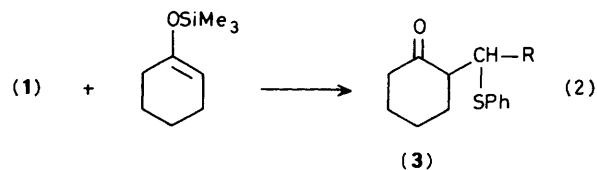
Table 1. Nucleophilic substitution of NO₂ in (1) by Y.

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 ₇ H ₁₅	CH ₂ =CHCH ₂	90
n-C ₉ H ₁₉	CH ₂ =CHCH ₂	84
[CH ₂] ₂ CO ₂ Me	CH ₂ =CHCH ₂	78



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

[†] A typical procedure is as follows. To a mixture of (1) (10 mmol) and Me₃SiCN (15 mmol) in CH₂Cl₂ (10 ml) was added SnCl₄ (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 CH₂Cl₂, washing with water, and drying with MgSO₄, followed by column chromatography (silica gel/benzene-hexane) to give (2).



- R = Et (85%)
 R = n-C₉H₁₉ (86%)
 R = [CH₂]₂CO₂Me (75%)

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

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

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

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