

Lewis Acid-catalysed Nucleophilic Displacement of the Nitro Group from Nitroalkanes

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Reaction of trimethylsilyl phenyl sulphide with tertiary and benzyl nitro compounds in the presence of SnCl_4 gives the corresponding sulphides.

Although some examples of nucleophilic substitution reactions of aliphatic nitro compounds are known, a general procedure for nucleophilic substitution reactions of nitro compounds is still far from realization. Electron transfer substitution ($S_{\text{RN}}1$) of nitro compounds,¹ palladium-catalysed allylic alkylation of allylic nitro compounds,² and nucleophilic substitution of allylic nitro compounds with dialkyl cuprates,³ or sodium benzenethiolate⁴ are representative examples, but are not general reactions and the substrates and nucleophiles are activated. For example, α,p -dinitrocumene reacts with sodium benzenethiolate rapidly to give the sulphide in good yield,⁵ but α -nitrocumene and 2-methyl-2-nitropropane do not react. Thus, the *para*-nitro group is essential for the smooth $S_{\text{RN}}1$ reaction with sodium benzenethiolate, and replacement of the nitro group for other nitro compounds is very difficult, except for nitromethane.⁶

We now report a new type of nucleophilic substitution reaction of nitro compounds; the nitro group of tertiary and benzyl nitro compounds is replaced by a phenylthio group on treatment with PhSSiMe_3 in the presence of SnCl_4 , which extends the scope and limitation of nucleophilic substitution of nitro compounds. The reaction was carried out by stirring a mixture of the nitro compounds (1), PhSSiMe_3 (2 equiv.), and SnCl_4 (2 equiv.) in CH_2Cl_2 at room temperature for 1–25 h.

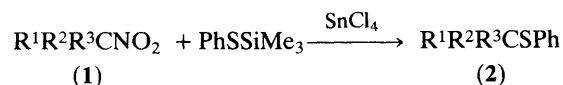
Tertiary and benzyl nitro compounds were converted into the corresponding sulphides (2) by this procedure. Simple primary and secondary nitro compounds such as 1- and 2-nitropropane were not converted into the sulphide by this procedure. The best results were obtained when 2 equiv. of SnCl_4 were used; other Lewis acids such as AlCl_3 , TiCl_4 , and ZnCl_2 were less effective than SnCl_4 for the present conversion. The results are summarized in Table 1. The nitro compounds in

Table 1. Conversion of nitro compounds (1) into sulphides (2).

R ¹	R ²	R ³	Time/h	(2), yield, % ^a
Me	Me	Me	14	67
Ph	Me	Me	1	55
Ph	Me	SPh	1	68
Ph	Me	H	2	71 ^b
Ph	Et	H	3	61
Ph	H	$[\text{CH}_2]_2\text{CO}_2\text{Et}$	16	61
	$-\text{[CH}_2\text{]}_4-$	$[\text{CH}_2]_2\text{CO}_2\text{Et}$	20	35
Me	<i>n</i> -C ₆ H ₁₃	$[\text{CH}_2]_2\text{CO}_2\text{Et}$	20	38

^a Yields refer to pure isolated products. ^b The yield was reduced to 35% when 1 equiv. of SnCl_4 was used.

Table 1 were not converted into (2) under $S_{RN}1$ reaction conditions (PhSNa in dipolar aprotic solvents with visible irradiation).⁵



It is noteworthy that the nitro group is replaced by a phenylthio group after the Michael addition of the nitro compounds. Thus, nitro compounds serve as both nucleophiles and electrophiles in this reaction.

Other nucleophiles also participated in the Lewis acid-catalysed nucleophilic substitution of nitro compounds. Preliminary results show that PhSO₂Na, active methylene compounds, and electron rich aromatic compounds react with nitro compounds in the presence of SnCl₄.

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