

## 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  $\text{SnCl}_4$  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,<sup>1</sup> palladium-catalysed allylic alkylation of allylic nitro compounds,<sup>2</sup> and nucleophilic substitution of allylic nitro compounds with dialkyl cuprates,<sup>3</sup> or sodium benzenethiolate<sup>4</sup> are representative examples, but are not general reactions and the substrates and nucleophiles are activated. For example,  $\alpha,p$ -dinitrocumene reacts with sodium benzenethiolate rapidly to give the sulphide in good yield,<sup>5</sup> but  $\alpha$ -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.<sup>6</sup>

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  $\text{PhSSiMe}_3$  in the presence of  $\text{SnCl}_4$ , 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),  $\text{PhSSiMe}_3$  (2 equiv.), and  $\text{SnCl}_4$  (2 equiv.) in  $\text{CH}_2\text{Cl}_2$  at room temperature for 1–25 h.

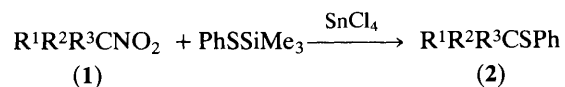
Tertiary and benzyl nitro compounds were converted into the corresponding sulphides (2) by this procedure. Simple primary and secondary nitro compounds such as 1- and 2-nitropropane were not converted into the sulphide by this procedure. The best results were obtained when 2 equiv. of  $\text{SnCl}_4$  were used; other Lewis acids such as  $\text{AlCl}_3$ ,  $\text{TiCl}_4$ , and  $\text{ZnCl}_2$  were less effective than  $\text{SnCl}_4$  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 <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Time/h	(2), yield, % <sup>a</sup>
Me	Me	Me	14	67
Ph	Me	Me	1	55
Ph	Me	SPh	1	68
Ph	Me	H	2	71 <sup>b</sup>
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	$n\text{-C}_6\text{H}_{13}$	$[\text{CH}_2]_2\text{CO}_2\text{Et}$	20	38

<sup>a</sup> Yields refer to pure isolated products. <sup>b</sup> The yield was reduced to 35% when 1 equiv. of  $\text{SnCl}_4$  was used.

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



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 PhSO<sub>2</sub>Na, active methylene compounds, and electron rich aromatic compounds react with nitro compounds in the presence of SnCl<sub>4</sub>.

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