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 ($S_{RN}1$) 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 benzenethiolate[4] 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 $S_{RN}1$ 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 produre. 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	$[CH_2]_2CO_2Et$	16	61
$-[CH_2]_4-$		$[CH_2]_2CO_2Et$	20	35
Me	$n-C_6H_{13}$	$[CH_2]_2CO_2Et$	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]

$$\underset{(\mathbf{1})}{R^1R^2R^3CNO_2} + PhSSiMe_3 \xrightarrow{SnCl_4} \underset{(\mathbf{2})}{R^1R^2R^3CSPh}$$

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 $PhSO_2Na$, active methylene compounds, and electron rich aromatic compounds react with nitro compounds in the presence of $SnCl_4$.

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