CHEMISTRY LETTERS, pp. 509-510, 1992.

Facile Synthesis of Organic Thiocyanates from Organozinc(II) Thiocyanates and N-Chlorosuccinimide

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The reaction of organozinc(II) compounds, generated in situ from organolithiums and zinc(II) thiocyaniate, with N-chlorosuccinimide (NCS) afforded the corresponding organic thiocyanates in good yields.

Organic thiocyanates are interesting groups of pharmacological, insecticidal, and bactericidal activities, and also of potential intermediates in synthesizing heterocycles.[1] A wide variety of methods have been hitherto reported for preparing organic thiocyanates, but efficient ones are still required.[2] In this paper, we report that a replacement of organozinc(II) compounds with thiocyanate anion is readily attained by the assistance of NCS, thereby providing an efficient and facile synthetic method of organic thiocyanates.

$$\text{R-Li} \xrightarrow{\text{Zn(SCN)}_2} [\text{R-Zn-X}] \xrightarrow{\text{NCS}} \text{R-SCN}$$

X = SCN or R

As shown in Table 1, the reaction of phenylzinc(II) compound, generated in situ from $Zn(SCN)_2$ and equimolar amount of phenyllithium in THF, with CH_2Cl_2 solution of NCS at 0 °C produced phenyl thiocyanate in a yield of 94%. In the reaction mixture, other product such as chlorobenzene or diphenylsulfide was detected in the yield of less than 1% and phenyl isothiocyanate was not detected. It is to be noted that 1) phenyllithium itself did not produce phenyl thiocyanate at all even if NCS in CH_2Cl_2 was added to the mixture of phenyllithium and KSCN in THF but 2) phenylzinc(II) compound, generated in situ from $ZnCl_2$ and phenyllithium or from $Zn(SCN)_2$ and twice amounts of phenyllithium, produced the aimed compound (see Table 1). Consequently, for a successful reaction, bond between phenyl and zinc(II) is essential but one between zinc(II) and thiocyanate anion is not necessarily the case. N-Bromosuccinimide also induced the reaction of phenylzinc(II) compounds with thiocyanate anion, albeit accompanied by a fairly large amount of bromobenzene (15%). These results might suggest an intervention of thiocyanogen halide as an active thiocyanating agent.[3] Various aryl, alkynyl, or alkyl thiocyanates (1-8) were likewise obtained in good yields from corresponding organolithiums via organozinc(II) intermediates. Thus, this new procedure not only provides an efficient and facile synthetic method of organic thiocyanates but also exhibits the utility of organozinc(II) compounds in synthetic organic chemistry.[4]

Table 1. Synthesis of Phenyl Thiocyanate

MX	(Molar ratio of MX/PhLi/NCS)	Yield/%[a]
$Zn(SCN)_2$	(1 / 1 / 1)	94 (89)
$Zn(SCN)_2$	(0.5 / 1 / 1)	85
$ZnCl_2$+2KSCN	(0.5 / 1 / 1)	15
KSCN	(1 / 1 / 1)	0

a) Yields were determined by GLC. Yields in parentheses were isolated ones.

R-SCN (R; Yield isolated)

1 (4-$CH_3OC_6H_4$; 87%)
2 (4-$CF_3C_6H_4$; 89%)
3 (4-ClC_6H_4; 90%)
4 (2,6-$(CH_3)_2C_6H_3$; 81%)
5 (PhC≡C; 79%)
6 (n-BuC≡C; 83%)
7 (n-Bu; 90%)
8 (t-Bu; 60%)

Typical procedure is as follows: To a suspension of $Zn(SCN)_2$ (364 mg, 2.0 mmol) in THF (4 cm^3) was added 2,6-dimethylphenyllithium, prepared by the reaction of 1-bromo-2,6-dimethylbenzene (0.266 cm^3, 2.0 mmol) with buthyllithium (1.31 cm^3 of a 1.6 M solution in hexane, 2.1 mmol) in THF (2 cm^3), at -78 °C under nitrogen and was allowed to stir for 1 h. Then, NCS (267 mg, 2.0 mmol) in CH_2Cl_2 (4.4 cm^3) was added to the solution at 0 °C and the reaction mixture was allowed to stir for 10 min. The resulting solution was treated with aqueous NaOH and organic products were subsequently extracted with ether. The condensate of the ether solution was chromatographed on a silica-gel column using hexane as an eluent, affording 265 mg of 2,6-dimethylphenyl thiocyanate (81%). Mp 62-62.5 °C (lit,[5] 56 °C). IR 2159 cm^{-1}.

References

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3) It is known that 1) thiocyanogen bromide tends to dissociate into thiocyanogen and bromine in organic solvent and 2) thiocyanogen, which is a weaker electrophilic thiocyanating agent than thiocyanogen chloride, reacts with organozinc compounds but the yields are low. See, P. G. Guy, "Syntheses and Preparative Applications of Thiocyanates," in "The Chemistry of Cyanates and Their Thio Derivatives," ed by S. Patai, John Wiley & Sons, New York (1977), p. 819.
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(Received January 6, 1992)