CHEMISTRY LETTERS, pp. 1093-1094, 1975. Published by the Chemical Society of Japan

THIOL-ACTIVATED SODIUM BOROHYDRIDE REDUCTION OF NITRO COMPOUNDS

Yuji MAKI, Hiroshi SUGIYAMA,* Katsuo KIKUCHI, and Shuichi SETO*
Department of Chemistry, Yamagata University, Koshirakawa, Yamagata 990
*Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira,
Sendai 980

Sodium borohydride under the presence of thiols reduced nitro compounds to amine, hydroxylamine, azo, and azoxy compounds.

Sodium borohydride hardly reduces nitro compounds, but few cases have been reported.[1] Recently, Lalancette and Brindel have shown that sulfurated sodium borohydride can reduce nitro aromatics to amine and nitro aliphatics to nitrile and oxime via the corresponding nitroso compounds.[2] In this paper, it will be shown that sodium borohydride under the presence of thiols reduced nitro compounds to amine, hydroxylamine, azo, and azoxy compounds.

As shown in the table, sodium borohydride in refluxing tetrahydrofuran reduced nitrobenzene to azoxybenzene. However, sodium borohydride with thiols in refluxing tetrahydrofuran reduced nitrobenzene mainly to aniline along with azo and azoxybenzenes. The comparison among ethanedithiol, benzenethiol, and ethanethiol showed that ethanedithiol was the best activating agent and that benzenethiol was the next. Hence, we tried to reduce various nitro compounds under the presence of ethanedithiol or benzenethiol. The reactions with ethanedithiol were faster and the yields were better than those with benzenethiol. In the case of p-bromonitrobenzene, the thiol substituted anilines were obtained as well as p-bromoaniline. In the case of 1-nitronaphthalene, the reaction with benzenethiol gave mainly a thiohydroxylamine derivative, but that with ethanedithiol gave only naphthylamine. In the case of nitrocyclohexane, Lalancette has shown that their reagent gives cyclohexanone and its oxime as main products,[2] but the reactions with thiols gave cyclohexylamine and cyclohexylhydroxylamine as main products. The products were identified by GLC, GC-MS, and IR.

Table. Thiol-activated sodium borohydride reduction of nitro compounds.[a]

Substrate	Thiol	(reaction time, hr)	Products (%)[b]
nitrobenzene	none	(20)	azoxybenzene (20)
"	$(CH_2SH)_2$	(10)	aniline (95), azobenzene (1), azoxybenzene (4)
"	"	(")	aniline (94), azobenzene (5)[c]
"	PhSH	(20)	aniline (70), azobenzene (2), azoxybenzene (1)
"	EtSH	(")	aniline (14), azobenzene (32), azoxybenzene (37)
p-nitroanisole	(CH_2SH)	(10)	p-anisidine (85), azo-p-anisole (12)
p-nitrotoluene	"	(")	p-toluidine (73), azo-p-toluene (4)
p-nitrobromobenzene	"	(")	p-bromoaniline (61), p-(2-mercaptoethylthio)-aniline (24)
m-dinitrobenzene	"	(")	m-nitroaniline (100)
1-nitronaphthalene	"	(")	1-naphthylamine (100)
nitrocyclohexane	"	(")	cyclohexylamine (54), N-cyclohexylhydroxylamine (29), cyclohexanone oxime (17)
p-nitroanisole	PhSH	(20)	p-anisidine (71), azo-p-anisole (4)
p-nitrotoluene	"	(")	p-toluidine (58), N-(p-tolyl)-S-phenylthiohydroxylamine (18)
p-nitrobromobenzene	"	(")	p-bromoaniline (22), p-phenylthioaniline (50)
m-dinitrobenzene	"	(")	m-nitroaniline (34), N-(m-aminophenyl)-S-phenylthiohydroxylamine (9)
1-nitronaphthalene	"	(")	1-naphthylamine (36), N-(1-naphthyl)-S-phenylthiohydroxylamine (50)
nitrocyclohexane	"	(")	cyclohexylamine (32), N-cyclohexylhydroxylamine (37), cyclohexanone oxime (12)

---

a) Mole ratio of (substrate:$NaBH_4$:thiol) was (1:3:4). (2.5 mmol of the substrate in 20 ml of dry tetrahydrofuran). b) The yields were estimated by GLC. The rests of the products were unreduced nitro compounds. c) Mole ratio of (substrate:$NaBH_4$: thiol) was (1:3:2). (The concentration was as mentioned in a)).

REFERENCES

1. C.E. Weill and G.S. Pauson, J. Org. Chem., 21, 803 (1956); H.J. Shine and M. Tsai, J. Org. Chem., 23, 1592 (1958); R.D. Hutchins, D.W. Lamson, L. Rua, C. Milewski, and B. Maryanoff, J. Org. Chem., 36, 803 (1971); G. Otani, Y. Kikugawa, and S. Yamada, Chem. Pharm. Bull., 16, 1840 (1968).
2. J.M. Lalancette and J.R. Brindel, Can. J. Chem., 49, 2990 (1971).

(Received August 14, 1975)