CHEMISTRY LETTERS, pp. 13-14, 1978. Published by the Chemical Society of Japan

REACTIONS OF ARYL HALIDES WITH THIOLATE ANIONS IN THE PRESENCE OF CATALYTIC AMOUNTS OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM
PREPARATION OF ARYL SULFIDES

Masanori KOSUGI, Tomiya SHIMIZU, and Toshihiko MIGITA
Department of Chemistry, Faculty of Technology, Gunma University,
Kiryu, Gunma 376

Aryl bromide and iodide were found to react with aliphatic and aromatic thiolate anions to give the corresponding sulfides in the presence of Pd(0). The reaction was not inhibited by p-dinitrobenzene which is a good inhibitor for the $S_{RN}1$.

Recently, synthetic application of oxidative-adducts of aryl halides to low-valent transition metal has received much attention.[1] Among these, there have been known only a few examples which show that nucleophilic substitution of "unactivated" aromatic halides by anions can proceed smoothly in the presence of a catalytic amount of transition metal complexes. Thus, aryl halide can react with cyanide anion and enolate anion of acetophenone under moderate conditions in the presence of Pd(II) or Pd(0)[2] and Ni(0),[3] respectively. Here, we wish to add another example; that is the reaction of aryl bromide or iodide with aliphatic or aromatic thiolate anion catalyzed by tetrakis(triphenylphosphine)palladium.

$$\text{Ph-X} + \text{R-S}^- \xrightarrow{\text{(Pd)}} \text{Ph-SR} + \text{X}^-$$

X: I, Br. R: Ph, Et.

Aryl halides react easily with thiolate anions in dimethyl sulfoxide (DMSO) to give aryl sulfides in satisfactory yields. Reactions were carried out as follows; a mixture of 2 m mol of iodobenzene and 0.08 m mol of palladium(0) complex in 5 ml of DMSO was stirred and heated at 100° for 1 h. under a nitrogen atmosphere, and then solution of 2 m mol of thiophenol and of 4 m mol of sodium t-butoxide in 20 ml of DMSO was added dropwise. After 18 h., the products were analyzed by GLC and identified by comparing their spectroscopic data with those of the authentic samples. Typical examples are shown in Table.

It can be seen that the presence of the catalyst remarkably accelerates the reactions. The reaction of bromobenzene, as well as of iodobenzene, gave satisfactory results, but chlorobenzene was much less reactive. Not only arenethiolates but also alkanethiolates were found to be good reagents. These findings suggest that this reaction has a potential utility for the synthesis of diaryl and alkyl aryl sulfides.

Similar reaction of "unactivated" aryl iodide with arenethiol giving sulfide has been known to proceed without metal complex, in liquid ammonia under irradiation by Pyrex-filtered light, and the $S_{RN}1$ chain mechanism involving electron transfer was proposed for the reaction.[4] Our reaction presented here, however, is thought to

Table. Reactions of aryl halides with thiolate anions in the presence of palladium(0) complex at 100° for 18 h.

Substrates (m mol)					Product Yields (%)
PhX		RSH		Pd(0)	PhSR
PhI	2	PhSH	2	0.08	75
	2		2	—	22
p-$CH_3C_6H_4I$	2		2	0.08	78
	2		2	—	trace
p-$CH_3OC_6H_4I$	2		2	0.08	49
	2		2	—	6
p-ClC_6H_4I	2		2	0.08	79
	2		2	—	33
PhI	2	EtSH	2	0.08	78
PhBr	2	PhSH	2	0.08	82
	2		2	—	7
p-$CH_3C_6H_4Br$	2		2	0.08	51
	2		2	—	4
p-$CH_3OC_6H_4Br$	2		2	0.08	52
	2		2	—	3
p-ClC_6H_4Br	2		2	0.08	53
	2		2	—	28
PhBr	2	EtSH	2	0.08	98
	2		2	—	24
PhCl	2	PhSH	2	0.08	trace

proceed through the path different from the $S_{RN}1$, because the reaction is not inhibited by the presence of p-dinitrobenzene which is known to be a good inhibitor for the $S_{RN}1$ reaction. Our results obtained so far support the following reaction mechanism involving an oxidative-adduct of aryl halide to Pd(0).

$$\text{Ph-X} + \text{Pd(0)} \longrightarrow \text{Ph-Pd(II)-X}$$

$$\text{Ph-Pd(II)-X} + \text{RS}^- \longrightarrow \text{PhSR} + \text{X}^- + \text{Pd(0)}$$

Further more comprehensive studies on the scope and limitation of the reaction and on the comparison with the $S_{RN}1$ are in progress.

References

1) J. Tsuji, "Organic Synthesis with Palladium Compounds", J. Synth. Org. Chem. Japan, 35, 94 (1977). p 101.
2) K. Takagi, T. Okamoto, Y. Sakakibara, and S. Oka, Chem. Lett., 1973, 471.
A. Sekiya and N. Ishikawa, ibid, 1975, 277.
3) M. F. Semmelhack, R. D. Stauffer, and T. D. Rogerson, Tetrahedron Lett., 1973, 4519.
4) J. F. Bunnett and X. Creary, J. Org. Chem., 39, 3173, 3611 (1974).

(Received November 1, 1977)