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Nickel(0)-catalyzed Synthesis of Diaryl Sulfides from Aryl Halides and Aromatic Thiols[1]

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Facile and selective syntheses of various diaryl sulfides from aryl halides and aromatic thiols by the aid of an in situ generated nickel(0) catalyst are reported. The nickel(0) induces a C-S cleavage, as well.

Several types of nucleophilic displacement of aryl halides are known to be catalyzed by transition metals. For example, in the presence of catalytic amounts of nickel(0) or palladium(0) complexes, a thiation of aryl halides with thioureas or thioamides readily takes place, though both of them are otherwise inert nucleophiles.[2] Here, we will report an additional thiation of the type using an aromatic thiol as a nucleophile, which affords a facile and selective procedure for the preparation of various diaryl sulfides at ambient temperature. Although several procedures have been reported for the thiation of non-activated aryl halides with arenethiolate anions, they still suffer from an utility of special solvent,[3a,c] a manipulation of preformed air-sensitive complexes,[3b,d,e] or an operation under rather severe conditions.[3c-g]

As the table indicates, in the presence of both a base and a catalytic amount of a nickel(0) complex generated in situ from nickel(II) bromide, 1,1'-bis(diphenylphosphino)ferrocene (dppf), and zinc powder, thiophenol reacted with an equimolar amount of iodobenzene at 25 °C or bromobenzene at 60 °C to afford phenyl sulfide in an excellent yield. Attempted syntheses of unsymmetrical sulfides, however, afforded not only aimed sulfides but also two symmetrical ones (Runs 8-10). For example, by the reaction of thiophenol with p-iodotoluene under conventional conditions, phenyl p-tolyl sulfide, phenyl sulfide, and p-tolyl sulfide were obtained in a molar ratio of 15:1:1.

Table 1. Synthesis of Diaryl Sulfides[a]

Run	Aromatic thiol	Aryl halide		Temp	Time	Yield/%[b]		
	$R-C_6H_4-SH$	$R'-C_6H_4-X$		°C	h	$R-C_6H_4-S-C_6H_4-R'$	$R-C_6H_4-S-C_6H_4-R$	$R'-C_6H_4-S-C_6H_4-R'$
	R	R'	X					
1	H	H	I	25	10	97		
2[c]	H	H	I	40	3	96		
3	H	H	Br	60	3	96		
4[d]	H	H	Br	60	5	91		
5	H	H	Cl	80	10	13		
6[e]	$4-CH_3$	H	SC_6H_5	80	10	11		
7	$4-CH_3$	$4-CH_3$	I	60	5	96		
8	H	$4-CH_3$	I	60	5	86	7	5
9	$4-CH_3$	H	Br	60	2	80	10	6
10	H	$4-CH_3CO$	Br	40	3	80	10	10
11[f]	$4-CH_3$	$4-CH_3$	I	60	2	76		
12	$4-CH_3$	H	I	40	2	97	<1	<1
13	$4-CH_3$	H	I	25	10	99	<1	<1
14	$4-CH_3O$	H	I	25	10	(93)		
15	$2-CH_3$	H	I	25	10	(88)		
16	H	$4-CH_3CO$	I	25	5	95(91)	2	2
17	H	$3-CH_3O_2C$	I	25	5	(95)		
18	H	2-CN	I	40	5	(97)		
19	$4-CH_3O$	$4-CH_3CO$	I	25	5	(91)		

a) Every runs were carried out in N-methyl-2-pyrrolidone (NMP) under nitrogen. Molar ratio of each component (aromatic thiol/aryl halide/K_2CO_3/Ni(II)Br_2/dppf/Zn) was 1.0/1.0/1.0/0.04/0.08/0.2 (Runs 1-11) or 1.0/1.5/1.0/0.04/0.08/0.2 (Runs 12-19).

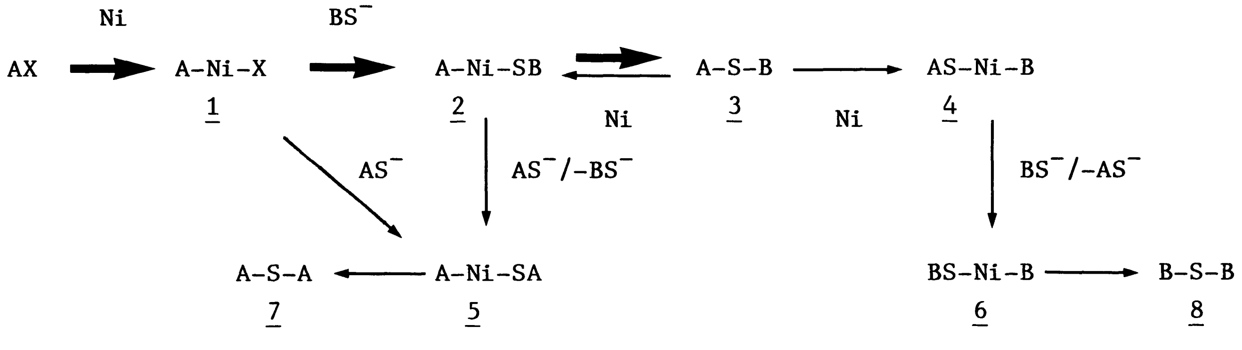
b) Yields were determined by GLC using internal standards. Yields in parentheses were isolated ones.

c) Run using 2 mol% of nickel catalyst.

d) Run in N,N-dimethylformamide (DMF).

e) Thiophenol was obtained in a yield of 9%.

f) This run was carried out in the presence of phenyl sulfide (Ph_2S/aryl halide= 0.4/1). Thirty% of phenyl sulfide was consumed and phenyl p-tolyl sulfide was obtained in a yield of 40% (based on phenyl sulfide initially added).



A and B represent arene nucleus.
➡ represents the path, giving aimed sulfides.
→ represents the path, giving objectionable sulfides.

Scheme 1.

The most plausible pathway leading to these by-products (7 and 8) is outlined in Scheme 1: An oxidative addition of an initial product (3) to nickel(0) formed two kinds of C-S cleaved products (2 and 4). Once 4 was originated, its reaction with a thiolate anion, BS^-, would happen to afford 6 along with a new thiolate anion, AS^-. The expelled AS^- subsequently converted 2 and/or 1 to 5. Thus formed 5 and 6 gave symmetrical sulfides, 7 and 8, respectively.[4)] This scheme indicates that the formation of undesired sulfides should be reduced by an introduction of a more electron-rich arene-nucleus as an aromatic thiol and a less one as an aryl halide, and especially an addition of the latter in excess.[5)] Indeed, under the altered conditions, unsymmetrical sulfides were produced almost solely (Runs 12-19). Thus, this nickel(0)-catalyzed reaction not only affords a facile and efficient procedure for the synthesis of a great variety of diaryl sulfides but also exhibits a possibility of nucleophilic displacement of diaryl sulfides which might make possible a new type of transformation of sp^2C-S bond in sulfides.[6)]

A typical procedure is as follows: A mixture of potassium carbonate (138 mg, 1.0 mmol), a 0.17 mol dm^{-3}-DMF solution of nickel(II) bromide (0.235 cm^3, 0.04 mmol), dppf (44 mg, 0.08 mmol), zinc powder (13 mg, 0.2 mmol), and NMP (1 cm^3) was stirred at 25 °C for 1 h under nitrogen. In the course of this stirring, the green mixture turned to dark red, showing the formation of nickel(0) complex. Thiophenol (110 mg, 1.0 mmol) and p-iodoacetophenone (369 mg, 1.5 mmol) were then introduced and the mixture was kept at 25 °C for 3 h under nitrogen. The resulting mixture was chromatographed on a silica-gel column using hexane-ethyl acetate as the eluent, affording 208 mg of 4-(phenylthio)acetophenone (91%). Mp 63-64 °C (lit.,[7)] 67 °C).

References

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3) a) J. F. Bunnett and X. Creary, J. Org. Chem., 39, 3137 (1974); b) A. Alemagna, P. D. Buttero, C. Gorini, D. Landini, E. Licandro, and S. Maiorana, ibid., 48, 605 (1983); c) H. Suzuki, H. Abe, and A. Osuka, Chem. Lett., 1980, 1363; d) T. Migita, T. Shimizu, Y. Asami, J. Shiobara, Y. Kato, and M. Kosugi, Bull. Chem. Soc. Jpn., 53, 1385 (1980); e) M. Kosugi, T. Ogata, M. Terada, H. Sano, and T. Migita, ibid., 58, 3657 (1985); f) T. Yamamoto and Y. Sekine, Inorg. Chim. Acta, 83, 47 (1984); g) H. J. Cristau, B. Chabaud, R. Labaudiniere, and H. Cristol, Organometallics, 4, 657 (1985).

4) Supporting evidence for the scheme is as follows: (1) C-S cleavage by transition metals involving nickel(0) is precedented,[6] and (2) regarding diaryl sulfides, C-S cleavage and exchange by thiolate anions had been ascertained (Runs 6 and 11). These results mean that a nucleophilic displacement of diaryl sulfides with thiolate anions takes place by the assistance of nickel(0) catalyst.

5) Electron-withdrawing groups on arene-nucleus generally increase the reactivities of aryl halides in oxidative addition.[8] Then, under the altered conditions, nickel(0) will have little opportunity to react with 3 to form 4 and, moreover, 2 will be restricted to turn to 5, since BS^- is a stronger base than AS^-.

6) Transition metal-induced conversion of sp^2C-S into C-C or C-H bonds is well-known: B. M. Trost and A. C. Lavoie, J. Am. Chem. Soc., 105, 5075 (1983) and references cited therein. See also J. J. Eisch, L. E. Hallenbeck, and K. I. Han, ibid., 108, 7763 (1986); S. C. Shim, S. Antebi, and H. Alper, J. Org. Chem., 50, 149 (1985); M. Chan, K. Cheng, M. K. Li, and T. Luh, J. Chem. Soc., Chem. Commun., 1985, 1610; E. Wenkert, J. M. Hanna, Jr., M. H. Leftin, E. L. Michelotti, K. T. Potts, and D. Usifer, J. Org, Chem., 50, 1125 (1985).

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8) See, e. g., J. P. Collman and L. S. Hegedus, "Principles and Applications of Organotransition Metal Chemistry," University Science Books, Mill Valley (1980), p. 201.

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