

Preliminary communication

PHASE-TRANSFER CATALYSIS IN THE NICKEL- AND PALLADIUM-CATALYZED FORMATION OF ARYL AND ALKENYL SULFIDES

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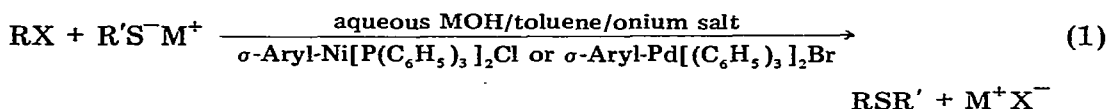
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Summary

Aryl and alkenyl sulfides can be conveniently prepared from the corresponding halides and alkaline thiolates under phase transfer conditions in the presence of σ -Aryl-Ni[P(C₆H₅)₃]₂Cl or σ -Aryl-Pd[P(C₆H₅)₃]₂Br.

Some examples of nickel- and palladium-catalyzed nucleophilic substitutions of aromatic and vinylic halides under phase transfer conditions have been reported recently [1–4]. We now report the application of phase transfer technique to nickel- and palladium-catalyzed formation of aryl and alkenyl sulfides from the corresponding halides and alkaline thiolates (eq. 1).



(R = aryl or alkenyl group; R' = aryl or alkyl group; M = alkaline metal; X = Cl, Br)

It is known that aryl [5] and alkenyl [6] sulfides can be prepared from the corresponding bromides and iodides under homogeneous conditions in the presence of palladium tetrakis(triphenylphosphine) as catalyst. The application of the phase-transfer technique provides a simple method of utilizing nickel complexes which have not been previously reported as catalysts for this reaction and under these conditions even aryl chlorides appear to be effective substrates. Moreover remarkable improvements over the corresponding reactions in homogeneous phase can be obtained when the phase-transfer technique is used with palladium catalysts. The number of catalytic cycles is generally increased owing the fact that catalyst deactivation by thiolates is more easily

TABLE 1

NICKEL- AND PALLADIUM-CATALYZED REACTIONS

Catalyst A = *trans*-bromo(phenyl)bis(triphenylphosphine)palladium + triphenylphosphine (1/1)Catalyst B = *trans*-chloro(1-naphthyl)bis(triphenylphosphine)nickel + triphenylphosphine (1/1)

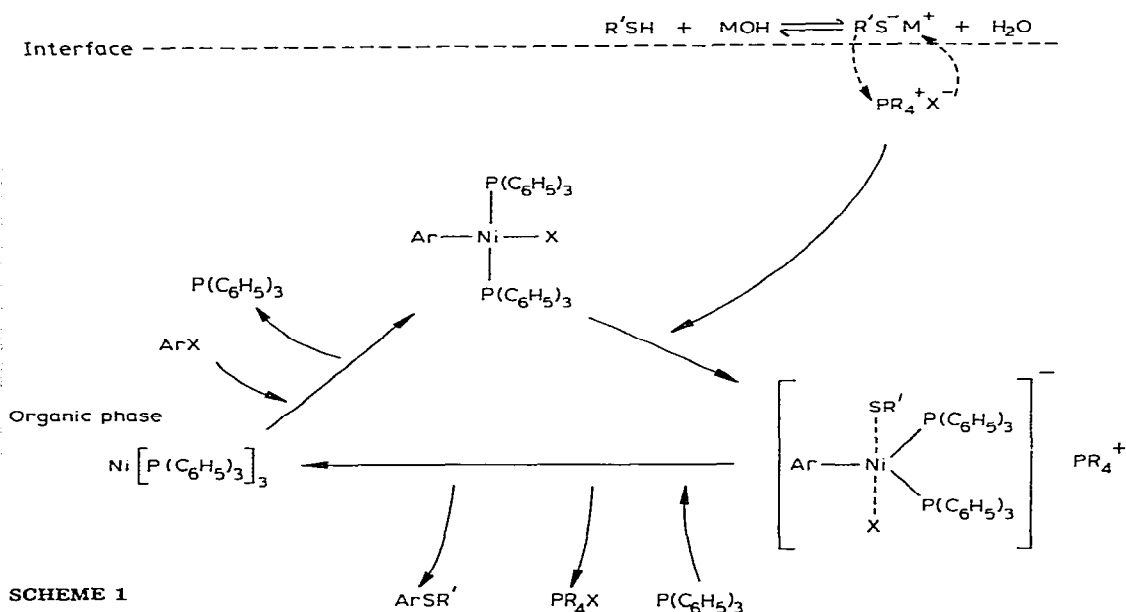
RX (mmol)	Catalyst ^d (mmol)	R'SH (mmol)	Phosphonium salt (mmol)	Time ^e (h)	Temperature (°C)	Product	Yield ^b
C ₆ H ₅ Br (24)	A (0.24)	C ₆ H ₅ SH ^c (24)	1.3	7.5	100	C ₆ H ₅ SC ₆ H ₅	97
C ₆ H ₅ Br (24)	A (0.24)	C ₆ H ₅ SH ^c (24)	—	5	100	C ₆ H ₅ SC ₆ H ₅	94
C ₆ H ₅ Br (24)	B (1.3)	C ₆ H ₅ SH ^c (24)	1	23	55	C ₆ H ₅ SC ₆ H ₅	95
C ₆ H ₅ Br (24)	B (1.3)	C ₆ H ₅ SH ^c (24)	—	23	55	C ₆ H ₅ SC ₆ H ₅	97
C ₆ H ₅ Br (24)	B (1.3)	C ₆ H ₅ SH ^c (24)	—	7 ^f	55	C ₆ H ₅ SC ₆ H ₅	50
C ₆ H ₅ Cl (24)	B (1.3)	C ₆ H ₅ SH ^c (24)	—	20	55	C ₆ H ₅ SC ₆ H ₅	70
C ₆ H ₅ Br (12)	A (0.24)	C ₆ H ₅ CH ₂ SH ^d (12)	1	15	100	C ₆ H ₅ SCH ₂ C ₆ H ₅	89
C ₆ H ₅ Br (12)	A (0.24)	C ₆ H ₅ CH ₂ SH ^d (12)	—	21	100	C ₆ H ₅ SCH ₂ C ₆ H ₅	49
C ₆ H ₅ CH=CHBr (24)	A (0.24)	C ₆ H ₅ SH ^c (24)	1	9	80	C ₆ H ₅ CH=CHSC ₆ H ₅	85
C ₆ H ₅ CH=CHBr (24)	A (0.24)	C ₆ H ₅ SH ^c (24)	—	20	80	C ₆ H ₅ CH=CHSC ₆ H ₅	25
C ₆ H ₅ CH=CHBr (12)	B (1.3)	C ₆ H ₅ SH ^c (12)	1	7	35	C ₆ H ₅ CH=CHSC ₆ H ₅	75

^aThe ratio RX/catalyst was not optimized. ^bYields, calculated by GLC, are based on the organic halide allowed to react.^cDissolved in NaOH 30%. ^dDissolved in NaOH 50%. ^eThe reaction was over 30 min after the last addition of thiolate solution. ^fThe thiolate was added all at once.

prevented. Furthermore it is not necessary to use strong bases such as sodium *t*-butoxide [5] or butyllithium [6] to produce thiolates or coordinating solvents (DMSO) because the thiolate anion, extracted from the aqueous solution, is able to attack the complexed organic group directly.

The thioethers were produced under nitrogen by slowly adding the aqueous alkaline thiolate solution to the organic layer, containing the organic halide, the catalyst and the onium salt. In a typical experiment a solution of thiophenol (2.6 g, 24 mmol) in NaOH (25 ml, 30%) was gradually added during 20 h at 55°C to a solution of chlorobenzene (2.7 g, 24 mmol), $C_{10}H_7Ni[P(C_6H_5)_3]_2Cl$ [7] (1.0 g, 1.3 mmol) and $P(C_6H_5)_3$ (0.35 g, 1.3 mmol) in toluene (20 ml). Diphenyl sulfide was obtained in 70% yield (GLC analysis).

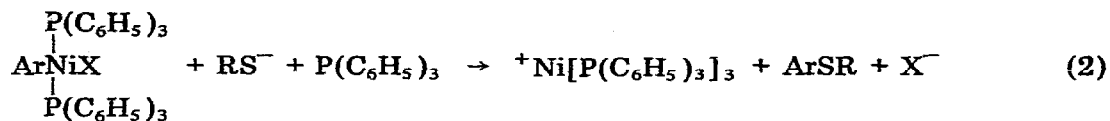
Aqueous phase



SCHEME 1

The results obtained are summarised in Table 1. It can be observed that in many cases the reaction occurs in high yield even without the onium salt. The same result was observed for the nickel-catalyzed cyanation of aryl halides [2] and the rhodium-catalyzed isomerisation of allylic alcohols [8]. Probably, as previously pointed out [2], the organometallic complex can also act as phase transfer catalyst [9]. Nevertheless the onium salt improves the yield when the reagents are alkenyl halides or thioalcohols. Hexadecyltributylphosphonium bromide was mostly used as the onium salt because of its thermal stability.

Owing to their air stability σ -arylbis(triphenylphosphine)-nickel or -palladium halides were used as catalysts instead of the corresponding phosphine-nickel(0) or -palladium(0) complexes, which are formed in the reaction medium (eq. 2),



The scheme summarises the reactions probably involved in the catalytic cycle.

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