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METALLIC NICKEL AS A REAGENT FOR THE COUPLING OF AROMATIC AND BENZYLIC HALIDES

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SUMMARY: The oxidative addition of aromatic and benzylic halides to activated metallic nickel occurred under mild conditions to give the corresponding dehalogenative coupled products in good yields.

Zero-valent, transition metals in the metallic state generally do not undergo smooth oxidative addition of organic halides under mild conditions in spite of the well known easy oxidative addition to metal atoms produced by the vaporization technique[1] and to metal complexes coordinated with ligands.[2] In the Ullmann synthesis of biaryls, metallic copper is employed, however, drastic conditions in the range of 150°C to 280°C were required.[3] Thus, organic synthesis using metallic transition metals as reagents under mild conditions is quite limited. Among the group VIII elements, a few examples have been reported of the direct preparation of π-allylpalladium chloride from palladium sponge[4] and of the Grignard type addition of allyl chloride to aldehydes by cobalt or nickel metal.[5] We now report that the oxidative addition of aromatic and benzylic halides to activated metallic nickel prepared by the reduction of nickel iodide occurred under mild conditions to give the corresponding dehalogenative coupled products in good yields.

The activated nickel was prepared in glyme (30 ml) by the reduction of nickel iodide (10 mmol) with lithium (23 mmol) in the presence of naphthalene (1 mmol). After stirring these reagents at room temperature for 12 hr, the finely divided nickel metal powders were formed as black slurries which settled out leaving a clear colorless solution. The reaction of the nickel powder with aromatic and benzylic halides were carried out in glyme and the results are summarized in Table I.

Aromatic and benzyl halides afforded the corresponding coupled products and the substituents such as acetyl, cyano, and nitro groups were compatible with the reaction conditions employed. Benzylic di- and trihalides gave mixtures of cis and trans isomers of the corresponding olefins. In the case of α,α,α-trichlorotoluene, 1,2-dichloro-1,2-diphenylethene was formed at 85°C and the intermediate, 1,2-diphenyl-1,1,2,2-tetrachloroethane, was obtained in 50% yield at room temperature for 12 hr.

The oxidative addition of iodopentafluorobenzene to the nickel powder proceeded even at room temperature, and the quantitative yield of decafluorobiphenyl was attained under refluxing glyme. The intermediate oxidative adduct of iodopentafluorobenzene to nickel was trapped as the triethylphosphine complex. A mixture of iodopentafluobenzene (8 mmol), nickel powder (10 mmol), and triethylphosphine (20 mmol) was stirred at room temperature for 24 hr. Usual work-up gave bis(triethylphosphine)pentafluorophenylnickel(II) iodide in 15% yield.[6] In a previous communication,[7] we

Table I. Dehalogenative coupling of aromatic and benzylic halides by activated metallic nickel[a]

Halide	Conditions	Product	Yield (%)[b]
Iodopentafluorobenzene	85°C, 2 hr	Decafluorobiphenyl	100[c]
4-Bromoacetophenone	85°C, 8 hr	4,4'-Diacetylbiphenyl	46
4-Iodobenzonitrile	85°C, 2 hr	4,4'-Dicyanobiphenyl	85[c]
2-Bromothiophene	85°C, 3 hr	2,2'-Bithiophene	45
4-Nitrobenzyl chloride	r.t., 1 hr	4,4'-Dinitrobibenzyl	80
4-Cyanobenzyl bromide	r.t., 1 hr	4,4'-Dicyanobibenzyl	75
Dichlorodiphenylmethane	r.t., 2 hr	Tetraphenylethene	99
α,α-Dibromotoluene	r.t., 1 hr	Stilbene[d]	65
α,α,α-Trichlorotoluene	85°C, 1 hr	1,2-Dichloro-1,2-diphenylethene[e]	71

[a] 1.25 eq. of nickel powder were used per one halogen atom of halide. [b] Isolated yield unless otherwise noted. [c] Glpc yield. [d] cis/trans = 27/73. [e] cis/trans = 74/26.

reported that bis(pentafluorophenyl)nickel(II) was isolated in 69% yield as the triethylphosphine complex by adding triethylphosphine to the reaction mixture prepared from iodopentafluorobenzene and nickel powders at 40°C for 9 hr. These facts suggest that the smooth oxidative addition of aryl halide to metallic nickel did occur and the coupled product was formed via the arylnickel(II) halide followed by disproportionation to the bisarylnickel(II) complex.

The results show that the reactivity of the activated metallic nickel is comparable or greater than that of zero-valent nickel complexes such as bis(1,5-cyclooctadiene)nickel(0) or tetrakis(triphenylphosphine)nickel(0).[8] Further advantages of the highly reactive nickel powders are that the preparation of the metal is quite simple and convenient and that the reactions proceed in an ethereal solvent.

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