

CuI.PPh₃ Based Functionalized Aromatic Organocopper Reagents Efficient in the Formation of Carbon-Carbon Bond with Epoxides

Santosh S. Devkate*, Arvind S. Burungale, Sunil D. Jadhav, Ashok S. Pise, Ramesh B. Gawade, Mohan B. Kale

S.M. Joshi College Hadapsar, Pune, Maharashtra, India

ABSTRACT

We have observed that the lithium naphthalenide reduction of solution of CuI.PPh₃ complex produced a highly reactive zero valent copper complex. The choice of phosphine based ligand was found to be crucial for the formation of subsequent reactivity of the organocopper species. The aromatic copper reagents derived from aromatic halides reacts with epoxides to form carbon carbon bond which are synthetically useful.

Keywords: Lithium naphthalenide, epoxide, active, copper, triphenylphosphine, Napthalene, zerovalent.

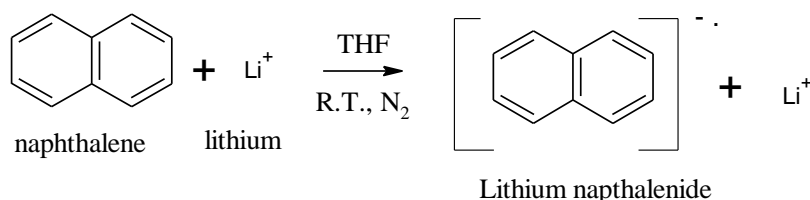
I. INTRODUCTION

Aromatic copper reagents obtained from copper (I) iodide triphenylphosphine complexes are very reactive in epoxide ring opening reactions¹⁻¹⁰. Molecules containing both an epoxide and a halide which can undergo an intramolecular cyclization¹¹⁻¹⁴. Epoxy aromatic copper species using triphenyl phosphine copper are able to undergo intramolecular cyclization via an epoxide ring opening process¹⁵⁻¹⁷. The regioselectivity of intramolecular epoxide ring opening reactions usually follows Baldwin's rule¹⁸. The activity of the reagent at low temperature is significant. The copper species prepared at 0°C is superior to that prepared at room temperature¹⁹⁻²⁰.

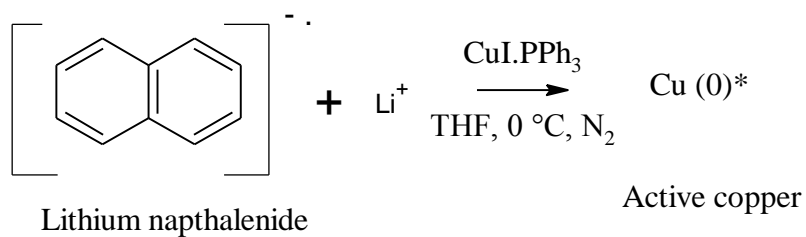
II. RESULT AND DISCUSSION

The reactivity of the copper reagent was determined by measuring its ability to coupling with aromatic halides and epoxides. This copper species was found to be more

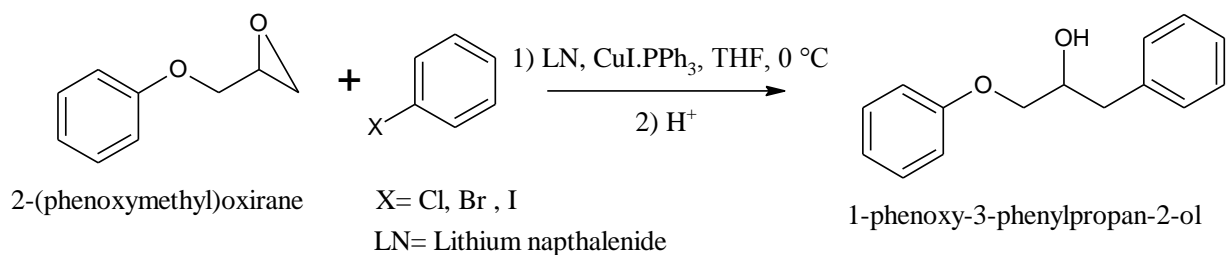
reactive than ordinary copper bronze used in the traditional Ullmann reaction. The copper in this experiment were activated by Rieke method²¹⁻²³. It should be observed that homocoupling of aromatic halides completely eliminated when CuI.PPh₃ complex was used. These reactive forms of copper (0) i.e. Rieke copper reagents have been developed by reducing copper (I) salts. The reduction of copper (I) iodide with lithium and naphthalene in THF solvent gives a highly reactive forms of copper (0). The yield of aryl copper obtained from bromobenzene is lower than that obtained from iodobenzene. Intramolecular reactions of aryl copper derivatives derived from 2-chloroaryl substituted epoxides proceeds to give both five and six membered rings by exo and endo ring opening reactions. The progress of reaction studied by thin layer chromatography. The products obtained were purified by column chromatography and analyzed by I.R. and ¹H NMR spectroscopy.



Scheme 1. Fomation of Lithium naphthalenide.

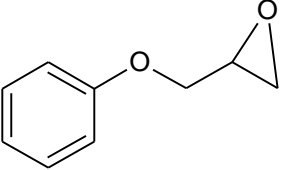
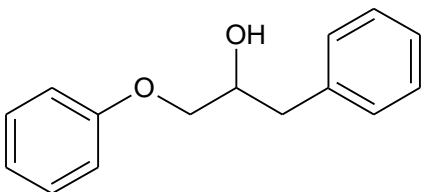
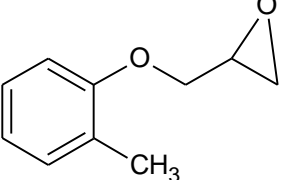
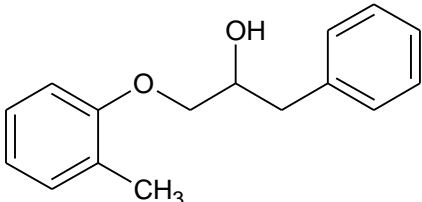
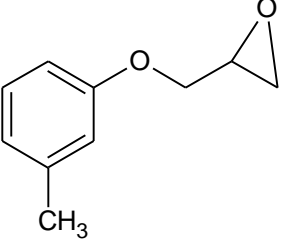
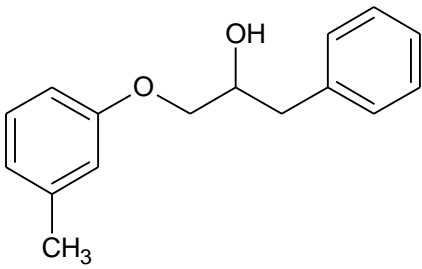
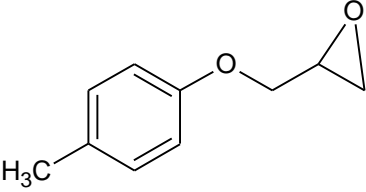
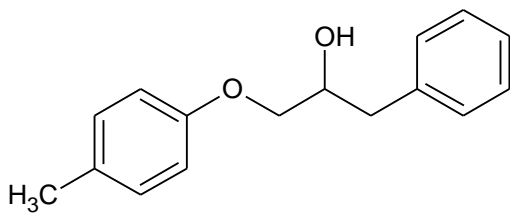


Scheme 2. Formation of triphenyl phosphine based copper (0).



Scheme 3. Formation of coupled product (carbon –carbon bond) with epoxide.

Table 1. synthesis of coupled product from organocopper reagent with epoxide

Reactant	Product	Time (hrs)	Yield (%)
		1.5	76
		3.0	60
		2.5	63
		2.0	67

		1.0	80
		1.5	82
		2.75	64

III. EXPERIMENTAL

Procedure for preparation of lithium naphthalenide:

In a 50 ml two necked round bottom flask charged naphthalene (10 mmol) and lithium metal (10 mmol) to which added 10 ml dry THF and continued magnetic stirring for 4 hrs under atmosphere of nitrogen at room temperature, the green coloured homogeneous solution has been formed which is stable under anhydrous conditions for several days.

Procedure for preparation functionalized copper reagent:

In a 50 ml two necked round bottom flask charged solution of CuI.PPh₃ complex (10 mmol) to which added lithium naphthalenide solution (10 mmol) by syringe under magnetic stirring and continued stirring for about 30 min. at 0°C temperature in the atmosphere of nitrogen gas. The very reactive form of reduced copper is formed from copper (I) to copper (0).

Procedure for preparation of coupled product form aromatic copper reagents with epoxide:

In a 50 ml two necked round bottom flask charged epoxide (10 mmol) to which added halobenzene (aromatic halide) (10 mmol), added 10 ml dry THF under stirring and added solution of functionalized copper reagent by syringe under nitrogen atmosphere, after completion of reaction, product isolated by extraction with ethyl acetate (3x10 ml), organic layers dried over sodium sulphate.

IV. CONCLUSION

We have used copper (I) iodide triphenyl phosphine as a efficient reagent for the replacement of halide from aromatic compounds and its addition to epoxide to form carbon –carbon bond and found that it has tremendous applications in synthesis.

V. REFERENCES

- [1]. Suzuki, Y.; Suzuki, T.; Kawagishi, T.; Noyori, R.; Tetrahedron Letters, 1980, 21, 1247.
- [2]. Ebert, G. W.; Rieke, R. D.; J. Org. Chem., 1984, 49, 5280.
- [3]. Smith, J. G.; Synthesis, 1984, 629.
- [4]. Stark, G.; Cohen, J. F.; J. Am. Chem. Soc., 1974, 96, 5270.
- [5]. Stark, G.; Cama, L. D.; Coulson, D. R.; J. Am. Chem. Soc., 1974, 96, 5268.
- [6]. Hodgson, D. M.; Robinson, L. A.; Jones, M. L.; Tetrahedron Letters, 1999, 40, 8637.
- [7]. Reddy, L. R.; Reddy, M. A.; Chanumathi, N.; Rao, K. R. Synlett, 2000, 339.
- [8]. Sabitha, G.; Reddy, G. S. K. K.; Reddy, K. B.; Yadav, J. S.; Synthesis, 2003, 2298.
- [9]. Bartoli, G.; Bosco, M.; Carlone, A.; Locatelli, M.; Mechiorre, P.; Sambri, L.; Org Lett. 2004, 6, 3973.
- [10]. Zhao, P. Q.; Xu, L. W.; Xia, C. G.; Synlett, 2004, 846.

- [11]. Fink, D. M.; Synlett, 2004, 2394.
- [12]. Iranpoor, N.; Kazemi, F.; Synth. Commun., 1999, 29, 561.
- [13]. Sabitha, G.; Babu, R. S.; Rajkumar, M.; Yadav, J. S.; Org. Lett., 2002, 4, 343.
- [14]. Kalita, B.; Barua, N. C.; Bezbarua, M.; Bez, G.; Synlett., 2001, 1411.
- [15]. Fujiwara, M.; Tanaka, M.; Baba, A.; Ando, H.; Souma, Y.; Tetrahedron Letters, 1995, 36, 4849.
- [16]. Campbell, J. R.; Jones, J. K. N.; Wolfe, S.; Can. J. Chem., 1966, 44, 2339.
- [17]. Isaacs, N. S.; Kirkpatrick, D.; Tetrahedron Letters, 1972, 3869.
- [18]. Baldwin, J. E.; J. Chem. Soc. Chem. Commun. 1976, 734.
- [19]. Sartillo-Piscil, F.; Quinero, L.; Villegas, C.; Santacruz Juarez, E.; de Parrrodi, C. A.; Tetrahedron Letters, 2002, 43, 15.
- [20]. Harder, S.; Vanlenthe, J. H.; Van Eikkema Hommes, N. J. R.; Schleyer, P. V. R.; J. Am. Chem. Soc., 1994, 116, 2508.
- [21]. Rieke, R. D.; Rhyne, L. D.; J. Org. Chem., 1984, 49, 3445.
- [22]. Rieke, R. D.; CRC Crit. Rev. Surf. Chem., 1991, 1, 131.
- [23]. Rieke, R. D.; Science, 1989, 246, 12160.