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A FACILE METHOD FOR THE PREPARATION OF FUNCTIONALIZED

2-HALO-1-OLEFINS

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ABSTRACT Highly functionalized 2-halo-1-olefins were prepared by the reaction of functionalized organozinc halides with 2,3-dihalopropene catalyzed by Cu(I) salts. Yields are high to excellent.

2-Halo-1-olefins are important intermediates in organic and natural product synthesis.¹ Addition of hydrogen halides to terminal alkynes² and hydrogen substitution reactions of terminal alkenes³ are two of the most used methods for the preparation of these compounds. Grignard reagents have been reported to react with 2,3-dichloropropene to give 2-chloro-1-alkene in 45 to 60% yields.⁴ In addition to relatively low yields, the approach precludes most functional groups.

We have reported that highly reactive zinc, prepared by the lithium naphthalenide reduction of $ZnCl_2$, readily undergoes oxidative addition to highly fuctionalized alkyl, aryl and vinyl halides under mild conditions to

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generate the corresponding organozinc compounds in excellent yields.⁵ In this communication, we would like to report a facile method for the preparation of highly functionalized 2-halo-1-olefins (I) by the cross-coupling of organozinc compounds with 2,3-dibromopropene or 2,3-dichloropropene mediated with CuCN·2LiBr.⁶



The presence of the copper(I) salt is essential for these coupling reactions. In the absence of Cu(I) salts, the reactions are very slow or sluggish and the yields are usually poor to moderate. In the presence of 5-10 mol% CuCN·2LiBr, the reaction is complete in 1-2 h. The excess Zn* should be removed before the cross coupling step. This is readily accomplished by allowing the excess Zn* to settle and then transferring the THF/organozinc solution via cannula to the copper cyanide-lithium bromide solution. 2,3-Dichloropropene was used to prepare the 2-chloro-1-olefins and 2,3-dibromopropene was used to prepare 2-bromo-1-olefins. Both provided excellent yields of the corresponding products. The experimental results are summarized in Table I. The following is a typical procedure for the preparation of 6-bromohept-6-ennitrile: 4-bromobutyronitrile (1.0 equiv., 35 mmol) was added directly to Zn*⁷ (1.3 equiv., 45 mmol) neat via syringe at

f	Time ₹X + Zn∗ Temp [.]	→	RZnX	uCN 2LiBr	R /	Ύ,
No	RX	Y	Rx/Zn* ^a	Temp	Time	Yields ^b
				(°C)	(h)	(%)
1.	p-BrC ₆ H ₄ CN	Br	1:2.5	reflux	1	85
2.	p-BrC ₆ H ₄ COCH ₃	Br	1:2.0	reflux	1	81
3.	p-IC ₆ H ₄ CO ₂ Et	Br	1:1.5	reflux	0.3	90
4.	<i>p</i> -BrC ₆ H ₄ Cl	Br	1:1.7	reflux	1.5	82
5.	Br(CH ₂) ₃ CO ₂ Et	Br	1:1.2	rt	2	96
6.	Br(CH ₂) ₃ CN	Br	1:1.5	reflux	0.5	94
7.	Br(CH ₂) ₆ Cl	Br	1:1.2	rt	2	88
8.	Br(CH ₂) ₃ CO ₂ Et	Cl	1:1.2	rt	2	95
9.	Br(CH ₂) ₃ CN	Cl	1:1.5	rt	1	78
_10.	m-IC ₆ H ₄ CO ₂ Et	Cl	1:1.5	reflux	1	83

Table I. Preparation of 2-Bromo-1-alkene

^a ratio in mole; ^b isolated yield, compounds were fully characterized by ¹H and ¹³C NMR, FT-IR, and Elemental analysis or HREI.

RT. The mixture was stirred at reflux for 30 min with complete consumption of 4-bromobutyronitrile as indicated by GC. Stirring was stopped to allow the excess amount of zinc settle out of the organozinc solution. After 2-5 hours, the top dark brownish organozinc solution was slowly transferred via cannula to the CuCN 2LiBr/THF solution (0.35 mmol CuCN and 0.70 mmol LiBr in 20 mL THF) which was precooled to -30°C. After stirring for 10 min., 2,3dibromopropene (0.9 equiv., 31.5 mmol) was added neat via syringe, stirred at this temp., for 1 h and additionally at RT for another 1 h. After workup and purification, 6-bromohept-6-en-nitrile was recovered as a colorless liquid in 94% yield. ¹H NMR 1.68-1.74 (m, 4H), 2.35-2.51 (m, 4H), 5.44 (d, J=1.7 Hz, 1H), 5.61 (t, J=0.9 Hz, 1H) ¹³C NMR 16.80, 23.92, 26.62, 40.22, 117.24, 119.25, 133.06. IR 2247, 1735, 1630 cm⁻¹. HREI calcd for $C_7H_{10}^{79}BrN$ m/e 186.9997, found 186.9993 ; calcd for $C_7H_{10}^{81}BrN$ m/e 188.9977, found 188.9976.

In summary, cross-coupling reactions of highly functionalized organozinc reagents with 2,3-dihalopropene provides an important and useful method to prepare functionalized 2-halo-1-olefins. The reaction is simple, clean and the yields are excellent.

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- 7. In this experiment, we modified the method (ref. 5) for the preparation of highly reactive zinc by using 5-10 mol% of naphthalene based on lithium as an electron carrier. After the mixture of lithium and naphthalene in THF was stirred for about 5 min, ZnCl₂/THF solution was transferred by cannula to it at a rate such that the greenish color persisted until all the lithium was consumed. The activity of the zinc was the same as the method reported earlier.⁵ The advantages of this method are three fold: using a catalytic amount of naphthalene, shortening the reduction times and ease of product purification.

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