Iron-Catalyzed Coupling Reaction between 1,1-Dichloro-1-alkenes and Grignard Reagents

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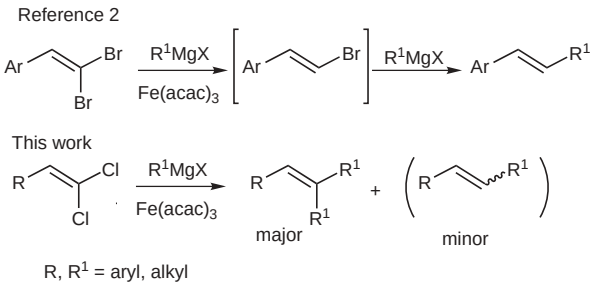
Abstract: This letter reports the coupling reaction of Grignard reagents with 1,1-dichloro-1-alkenes in the presence of the environmentally friendly iron(III) catalyst. This non-toxic procedure is general and provides the di-coupled products as the major compounds. The scope and limitations of this new reaction are described.

Key words: Grignard reagents, iron, 1,1-dichloro-1-alkenes, trisubstituted alkenes

Recently, during our investigations on Fe(III)-catalyzed cross-coupling reactions of vinyl- and/or aryl halides with Grignard reagents,[1] we observed that 2-aryl-1,1-dibromo-1-alkenes undergo selective hydrodebromination under usual conditions [RMgX 1 equiv, THF–NMP, $Fe(acac)_3$ 5 mol%, –10 °C, 0.5 h] to afford stereoselectively (*E*)-vinyl bromides in good yields.[2] Interestingly, we have found that if a second Grignard reagent was added to the reaction mixture the desired *E*-alkenes were thus obtained in good overall yields (Scheme 1). In this work, we decided to extend this study and focused our attention on the use of less reactive 1,1-dichloro-1-alkenes in the Fe-catalyzed coupling reaction with Grignard reagents.



Scheme 1

Although the reactivity of 1,1-dibromo-1-alkenes with organometallic reagents under classical transition metal catalysis (Pd, Ni) is now well documented,[3] the coupling of 1,1-dichloro-1-alkenes has received little attention,[4] probably because of their weaker reactivity compared to the bromo derivatives (*vide infra*). Previously, Tamao et al.[5] have studied the palladium-catalyzed reaction of aryl Grignard reagents with 1,1-dichloro-1-alkenes to afford stereoselectively the *Z*-chloro cross-coupled alkenes, which then could be engaged in a second cross-coupling reaction with alkyl or aryl Grignard reagents producing trisubstituted alkenes. However, these authors have pointed out that alkyl Grignard reagents do not react with 1,1-dichloro-1-alkenes in the presence of the palladium catalyst used. Under nickel-catalysis, Okamoto et al.[6] have reported that the reaction of 1,1-dichloro-2-phenyl-1-alkenes with phenyl-magnesium bromide fails to stop at the monoarylation stage and affords the reduced monoarylated (*E*)-1,2-diphenyl-1-alkenes as the major products. The cobalt-catalyzed coupling reaction of 1,1-dichloroethylene or 1,1,2-trichloroethylene has also been studied by Cahiez et al.[7] but no reaction was observed when Grignard reagents were used.

Recently, a new environmentally friendly procedure using the non-toxic iron(III) acetylacetonate was reported allowing the coupling of Grignard and organozinc reagents with simple halogenoalkenes (e.g. chloro-, iodo- and bromoalkenes) in a stereoselective manner.[8] To the best of our knowledge, no study has been reported on the iron catalyzed-reaction with 1,1-dichloro-1-alkenes. Therefore, we turned our attention to investigate the reactivity of these derivatives towards Grignard reagents in the presence of the non-toxic iron(III) acetylacetonate catalyst. The results of this study are now reported.

At first, we studied the reactivity of 1,1-dichloro-2-(4-methoxyphenyl)ethylene (**1**) with butylmagnesium bromide in the presence of $Fe(acac)_3$ under different reaction conditions (solvent, temperature, amount of catalyst and Grignard reagent used, Equation 1, Table 1). The required substrate **1** was readily prepared from *para*-methoxybenzaldehyde and triphenylphosphine–tetrachloromethane mixture in dichloromethane.[9]

When BuMgBr (1.5 equivalents) was added to 1,1-dichloro-2-(4-methoxyphenyl)ethylene (**1**) in a THF–NMP solution at –10 °C, in the presence of a catalytic amount of $Fe(acac)_3$ (3 mol%), no reaction occurred and the starting material was recovered unchanged (entry 1). However, when the same reaction was run in THF alone for one hour, the dehydrochlorinated-coupled product **3**(*Z*) was

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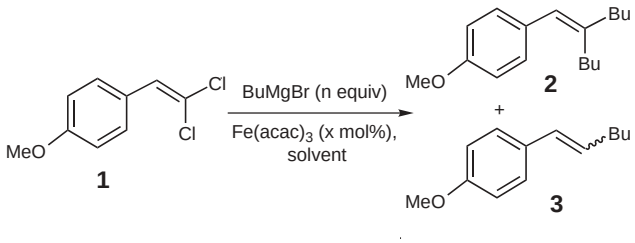


Equation 1

Table 1 Reaction of 1,1-Dichloro-2-(4-methoxyphenyl)ethylene (**1**) with BuMgBr, in the Presence of $Fe(acac)_3$

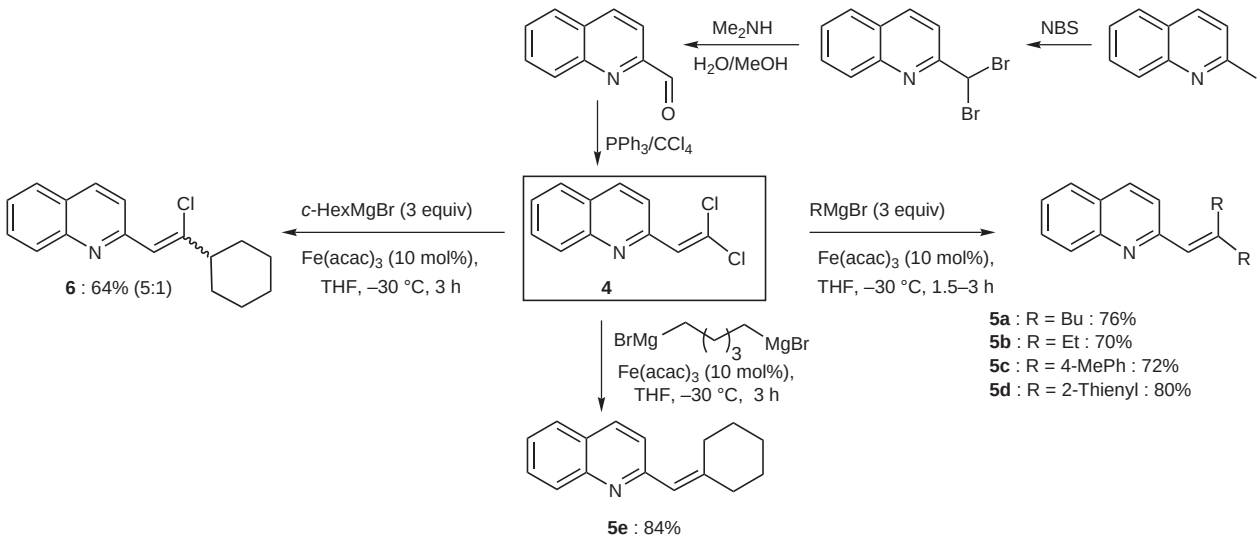
Entry	BuMgBr (equiv)	$Fe(acac)_3$ (mol%)	Solvent	Time (°C)	Yield (%)[a]		
					2	**3**(*E*)	**3**(*Z*)
1	1.5	3	THF–NMP	–10	Nr[b]		
2	1.5	3	THF	–10	51	0	20[c]
3	3	3	THF	–10	32	2	10[d]
4	3	10	THF	–10	45	7	10[e]
5	3	10	THF	–30	65	9	17[f]

[a] Yields of isolated products.
[b] Exclusively recovered starting material.
[c] 14% Of recovered starting material.
[d] 34% Of recovered starting material.
[e] 18% Of recovered starting material.
[f] No starting material was recovered.

obtained in 20% yield, together with the di-coupled product **2** (51%) and the starting material was recovered (14%, entry 2). This result is interesting and shows that 2-aryl-1,1-dichloro-1-alkenes afford mainly di-coupled products, whereas 2-aryl-1,1-dibromo-1-alkenes give the hydrodebrominated products under the almost identical reaction conditions (THF–NMP, *vide infra*).[2] The solvent effect was then studied, but more polar solvents (DMSO) or less polar solvents (Et_2O, CH_2Cl_2, toluene) did not allow the reaction to occur (results not shown). When the amount of Grignard reagent was increased the conversion was not improved (entry 3), and some starting material was recovered (34%). Thus, the catalyst and the Grignard amounts were increased to 10 mol% and three equivalents, respectively, leading to approximately the same amounts of the different compounds (entry 4) with a higher ratio of di-coupled **2** versus mono-coupled reduced compounds **3**, and 18% of starting material was recovered. Finally, when the temperature was brought to –30 °C a higher yield of the di-coupled product **2** was thus obtained (entry 5), and we observed complete disappearance of starting material.

We then decided to apply these reaction conditions to 1,1-dichloro-2-(2-quinolyl)ethylene (**4**), since 2-substituted quinoline derivatives have shown interesting in vitro and in vivo leishmanicide activities.[10] In a structure–activity relationships study numerous quinolines have been synthesized,[11] and the crucial role of unsaturation (e.g. double or triple bond) at the 2-position of the quinoline ring has been highlighted for biological activity. Thus, we were interested in preparing quinolines substituted at the 2-position by a disubstituted alkenyl moiety. Quinoline **4**, prepared in good yield from 2-quinaldine in a three-steps sequence (*i*. 2.5 equiv NBS in refluxed $CHCl_3$, *ii*. Me_2NH treatment in a methanol–water mixture under reflux,[12] *iii*. CCl_4–PPh_3 treatment of 2-quinaldehyde so obtained), was treated by several Grignard reagents (3 equivalents) in THF at –30 °C, in the presence of 10 mol% of $Fe(acac)_3$, and the results are reported in Scheme 2.

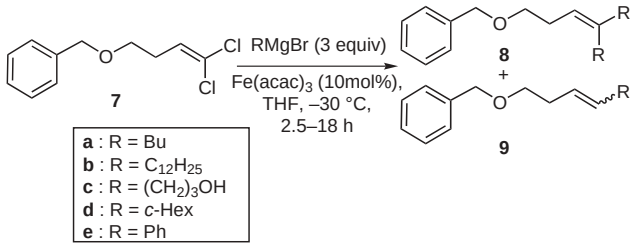
It is noteworthy that primary aliphatic as well as aromatic Grignard reagents gave the di-coupled products **5a**–**d** in high yields (70–80%) as the single products. Interestingly, the 1,5-di-Grignard reagent gave exclusively the cyclized product **5e** in excellent isolated yield (84%) through an intramolecular coupling reaction; no products resulting from intermolecular reactions could be isolated.



Scheme 2

When 1,1-dichloro-2-(2-quinolyl)ethylene (**4**) was treated by 3 equivalents of *c*-hexylmagnesium bromide, surprisingly, the reaction stopped at the monoalkylation stage and a 5:1 mixture of undetermined *E*/*Z* mono-coupled chloro alkenes **6** was obtained in 64% yield, and no di-coupled product could be isolated.

We then decided to study the reaction of aliphatic 1,1-dichloro-1-alkenes (Equation 2 and Table 2), and choose 4-benzyloxy-1,1-dichlorobut-1-ene (**7**) as starting material. This latter compound was prepared as described above from the corresponding aldehyde. We already reported that when the corresponding aliphatic 1,1-dibromo-1-alkenes were subjected to Grignard reagents in the presence of Fe(III) catalyst, no coupling reactions occured.[2] Instead, alkynes were obtained through a Fritsch–Buttenberg–Wiechell rearrangement.



Equation 2

Table 2 Reaction of 4-Benzyloxy-1,1-dichlorobut-1-ene (**7**) with Grignard Reagents in the Presence of 10 mol% of $Fe(acac)_3$ at –30 °C in THF

Entry	RMgBr (*R*)	Time (h)	Yield (%)[a]		
			8	**9**(*E*)	**9**(*Z*)
1	Bu	2.5	59	–	–
2	$C_{12}H_{25}$	2.5	59	–	–
3	$BrMgO(CH_2)_3$	18	21	30	–
4	*c*-Hex	2.5	12	29	16
5	Ph	3	–	33	2

[a] Yields of isolated products.

When 3 equivalents of primary alkyl Grignard reagents were reacted with 4-benzyloxy-1,1-dichlorobut-1-ene (**7**) as described above [2.5–18 h at –30 °C in THF in the presence of 10 mol% of $Fe(acac)_3$], the expected di-coupled products **8a**,**b** were obtained in good yields (entries 1 and 2). Again, these results are quite remarkable since the corresponding aliphatic 1,1-dibromo-1-alkenes do not lead to the cross-coupled products.[2] In the case of less reactive alkyl Grignard reagents, such as the functionalized β-hydroxylated reagent or the cyclohexyl reagent, the mono-coupled-reduced compounds **9c**,**d** were obtained as the major products of the reaction (as the *E*-isomer or as a mixture of *E*- and *Z*-isomers). This result is unexpected in regards to the reactivity of *c*-hexylmagnesium bromide with 1,1-dichloro-2-(2-quinolyl)ethylene (**4**) which led to the mono-cross-coupled product **6**. With an aryl Grignard reagent, the dicoupled product **8e** was not formed but instead the alkene **9e**(*E*) was obtained as the major product with only trace amount of the **9e**(*Z*)-isomer.

In conclusion, we describe herein the iron(III)-catalyzed cross-coupling reaction of 1,1-dichloro-1-alkenes with Grignard reagents.[13] This reaction leads mainly to the di-coupled products in good to excellent yields and requires mild conditions (–30 °C in a few hours). Nevertheless, in one case we obtained the mono-coupled adduct, where the remaining chloride atom could be engaged in a second coupling reaction, leading to unsymmetrical trisubstituted alkenes. Furthermore, these results highlight the difference of reactivity of 1,1-dichloro-1-alkenes and 1,1-dibromo-1-alkenes towards Grignard reagents in the presence of iron(III) catalyst. Further studies for elucidation of the mechanism of this reaction are undertaken in our laboratories. Furthermore, the quinoleine derivatives prepared in this study are now evaluated for their anti-parasitic properties against several trypanosomia species, and the results will be published elsewhere.

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(12) Through the slightly modified procedure of: Bankston, D. *Synthesis* **2004**, 283.

(13) **Typical Procedure and Selected Spectroscopic Data:** In a round-bottomed flask, under a nitrogen atmosphere, containing the 1,1-dichloro-1-alkene (1.00 mmol) and $Fe(acac)_3$ (35.3 mg, 0.10 mmol) was added THF (1.2 mL). The reaction mixture was cooled to –30 °C and the desired Grignard reagent (3.00 mmol of typically 1 M solution in THF) was added dropwise. The red colored solution turned dark brown to black (depending on the Grignard reagent). The reaction mixture was stirred for 1.5 h to 18 h, until the disappearance of starting material as judged by TLC. A 1 M aq HCl solution (5.0 mL) was then added, and the two layers were separated. After extraction of the organic layer by EtOAc (2 × 20 mL), the combined organic layers were washed three times with H_2O, then dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude residue was then purified by silica gel column chromatography to yield the expected adducts (see in the text for yields).
1,1-Dibutyl-2-(4-methoxyphenyl)ethylene (2): ^{1}H NMR (200 MHz): δ = 7.14 (d, *J* = 8.7 Hz, 2 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 6.20 (s, 1 H), 3.81 (s, 3 H), 2.16 (m, 4 H), 1.42 (m, 8 H), 0.94 (t, *J* = 7.1 Hz, 3 H), 0.90 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (50 MHz): δ = 157.7, 142.6, 131.4, 129.7, 124.1, 113.5, 55.2, 37.1, 30.5, 30.4, 22.9, 22.6, 14.0, 13.9 ppm.
1,1-Dibutyl-2-(2-quinolyl)ethylene (5a): ^{1}H NMR (200 MHz): δ = 8.04 (d, *J* = 8.4 Hz, 2 H), 7.74 (d, *J* = 8.1 Hz, 1 H), 7.66 (td, *J* = 8.2, 1.1 Hz, 1 H), 7.45 (t, *J* = 7.4 Hz, 1 H), 7.30 (d, *J* = 8.4 Hz, 1 H), 6.47 (s, 1 H), 2.67 (t, *J* = 7.3 Hz, 2 H), 2.28 (t, *J* = 6.9 Hz, 2 H), 1.60 (m, 4 H), 1.37 (m, 4 H), 0.97 (t, *J* = 7.4 Hz, 3 H), 0.93 (t, *J* = 7.3 Hz, 3 H) ppm. ^{13}C NMR (50 MHz): δ = 157.6, 151.3, 148.0, 135.4, 129.2, 129.1, 127.2, 126.2, 125.6, 124.4, 122.4, 38.1, 31.3, 30.6, 30.3, 23.0, 22.6, 14.0, 13.9 ppm. ESI-MS: *m*/*z* (%) = 268 (100) [MH^+].
1,1-Diethyl-2-(2-quinolyl)ethylene (5b): ^{1}H NMR (200 MHz): δ = 8.07 (d, *J* = 6.9 Hz, 1 H), 8.02 (d, *J* = 6.4 Hz, 1 H), 7.73 (d, *J* = 8.1 Hz, 1 H), 7.66 (td, *J* = 7.1, 1.5 Hz, 1 H), 7.45 (t, *J* = 7.4 Hz, 1 H), 7.31 (d, *J* = 8.6 Hz, 1 H), 6.47 (br s, 1 H), 2.65 (q, *J* = 7.6 Hz, 2 H), 2.30 (qd, *J* = 7.4, 1.1 Hz, 2 H), 1.19 (t, *J* = 7.2 Hz, 3 H), 1.16 (t, *J* = 7.3 Hz, 3 H) ppm. ^{13}C NMR (50 MHz): δ = 157.5, 153.4, 147.8, 135.6, 129.2, 129.0, 127.2, 126.2, 125.6, 123.1, 122.2, 30.3, 24.6, 12.9, 12.5 ppm. ESI-MS: *m*/*z* (%) = 234 (35) {M + Na^+], 212 (100) [MH^+].
1,1-Di-*p*-toluyl-2-(2-quinolyl)ethylene (5c): ^{1}H NMR (200 MHz): δ = 8.04 (d, *J* = 8.8 Hz, 1 H), 7.72 (d, *J* = 8.7 Hz, 1 H), 7.64 (m, 2 H), 7.44 (t, *J* = 7.3 Hz, 1 H), 7.31 (m, 3 H), 7.15 (m, 6 H), 6.84 (d, *J* = 8.8 Hz, 1 H), 2.40 (s, 3 H), 2.38 (s, 3 H) ppm. ^{13}C NMR (50 MHz): δ = 157.5, 148.1, 147.3, 139.8, 138.1, 137.8, 136.9, 134.7, 130.3, 129.3, 128.9, 128.1, 127.9, 127.3, 126.5, 126.0, 122.0, 21.3, 21.1 ppm. ESI-MS: *m*/*z* (%) = 358 (10) [M + Na^+], 336 (100) [MH^+].
1,1-Dithienyl-2-yl-2-(2-quinolyl)ethylene (5d): ^{1}H NMR (200 MHz): δ = 8.03 (d, *J* = 8.2 Hz, 1 H), 7.80 (d, *J* = 8.7 Hz, 1 H), 7.69 (d, *J* = 7.6 Hz, 1 H), 7.65 (dd, *J* = 7.1, 1.6 Hz, 1 H), 7.45 (m, 3 H), 7.32 (dd, *J* = 5.0, 1.9 Hz, 1 H), 7.08 (s, 1 H), 7.05 (m, 3 H), 6.91 (d, *J* = 8.7 Hz, 1 H) ppm. ^{13}C NMR (50 MHz): δ = 156.1, 147.9, 146.4, 139.3, 135.0, 133.1, 129.4, 129.1, 129.0, 128.9, 127.5, 127.4, 127.3, 127.1, 126.6, 126.5, 126.4, 121.5 ppm. ESI-MS: *m*/*z* (%) = 342 (15) [M + Na], 320 (100) [MH^+].
1,1-Cyclohexyliden-2-(2-quinolyl)ethylene (5e): ^{1}H NMR (200 MHz): δ = 8.05 (d, *J* = 8.5 Hz, 2 H), 7.75 (d, *J* = 7.9 Hz, 1 H), 7.67 (td, *J* = 8.3, 1.3 Hz, 1 H), 7.46 (t, *J* = 7.8 Hz, 1 H), 7.32 (d, *J* = 8.5 Hz, 1 H), 6.48 (s, 1 H), 2.75 (m, 2 H), 2.36 (t, *J* = 5.6 Hz, 2 H), 1.66 (m, 6 H) ppm. ^{13}C NMR (50 MHz): δ = 157.6, 149.9, 147.9, 135.7, 129.3, 129.1, 127.3, 126.3, 125.8, 122.6, 122.4, 38.1, 29.9, 28.6, 27.8, 26.5 ppm. ESI-MS: *m*/*z* (%) = 224 (100) [MH^+].
4-Benzyloxy-1,1-dibutylbut-1-ene (8a): ^{1}H NMR (200 MHz): δ = 7.36 (m, 5 H), 5.13 (br t, *J* = 7.0 Hz, 1 H), 4.53 (s, 2 H), 3.47 (t, *J* = 7.2 Hz, 2 H), 2.36 (q, *J* = 7.1 Hz, 2 H), 2.00 (m, 4 H), 1.33 (m, 8 H), 0.91 (t, *J* = 6.8 Hz, 6 H) ppm. ^{13}C NMR (50 MHz): δ = 142.0, 138.7, 128.3, 127.6, 127.4, 119.9, 72.8, 70.5, 36.6, 30.7, 30.4, 30.0, 28.5, 22.9, 22.5, 14.0 ppm. ESI-MS: *m*/*z* (%) = 297 (81) [M + Na^+], 275 (16) [MH^+].
4-Benzyloxy-1,1-didodecylbut-1-ene (8b): ^{1}H NMR (200 MHz): δ = 7.34 (m, 5 H), 5.12 (br t, *J* = 7.0 Hz, 1 H), 4.56 (s, 2 H), 3.46 (t, *J* = 7.2 Hz, 2 H), 2.35 (q, *J* = 7.1 Hz, 2 H), 2.00 (m, 4 H), 1.27 (m, 40 H), 0.89 (t, *J* = 6.4 Hz, 6 H) ppm. ^{13}C NMR (50 MHz): δ = 142.1, 138.7, 128.3, 127.6, 127.4, 119.9, 72.8, 70.5, 37.0, 31.9, 29.8, 29.7, 29.5, 29.4, 28.5, 28.2, 22.7, 14.1 ppm. ESI-MS: *m*/*z* (%) = 499 (100) [MH^+].