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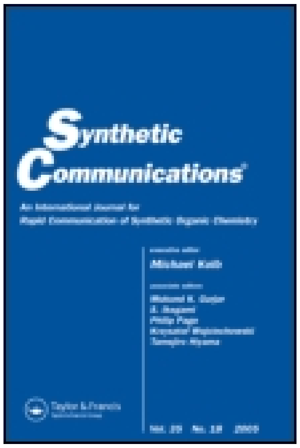

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Ruthenium-Catalyzed Coupling Reaction of Benzylic Halides

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ABSTRACT

Reported herein is a novel method on dechlorination coupling reaction of halides by using $RuCl_2(PPh_3)_3$ catalyst under a hydrogen atmosphere with benzene as the solvent, which affords alkanes in excellent yields.

Key Words: Dechlorination; Coupling reaction; Radical reaction; Ruthenium catalyst.

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INTRODUCTION

Metal-catalyzed radical coupling reaction with olefins have been carried out by utilizing metal complex catalysts[1] such as $CuCl_2$,[2] Cu_2Cl_2,[3] $Fe_2(CO)_9$,[4] and (naphthalene) $Cr(CO)_3$.[5] Also the nickel or palladium catalyzed cross-coupling reaction of organic halides or triflates with alkenes (the Heck reaction),[6] organoborons (the Suzuki reaction),[7] organotins (the Stille reaction)[8] are powerful and widely used on carbon–carbon bond formation. In addition, low valent ruthenium complexes have proven to be one of the effective catalysts for generating radical from various organic halides due to their ability to promote fast electron transfer.[9] However to our knowledge, dechlorination coupling reaction of halides to afford alkanes by using ruthenium catalyst has never been reported. Here we present a novel method on dechlorination coupling of halides to produce alkanes induced by utilizing $RuCl_2(PPh_3)_3$. The dechlorination coupling reaction was investigated, 1,1,2,2-tetraphenylethane, 1,2-diphenyl-1,2-di-*p*-tolylethane, and 1,2-diphenyl-1,2-di-*p*-bromophenylethane were prepared by using $RuCl_2(PPh_3)_3$ catalyst under a hydrogen atmosphere with benzene as the solvent in high yields respectively (Sch. 1).

RESULTS AND DISCUSSION

Benzophenone can be reduced to diphenyl methanol in 64% yield by formic acid with ruthenium complex $RuCl_2(PPh_3)_3$ without solvent.[10] However 1,1,2,2-tetraphenylethane **3a** was obtained with benzophenone as starting material using $RuCl_2(PPh_3)_3$ in the presence of concentrated hydrochloric acid (Entry 1). The effect of concentrated hydrochloric acid was investigated. The results are summarized in Table 1. Just a little change of yield was observed (Entry 2), when the quality of ruthenium catalyst was increased. Without HCl aq. **3a** was obtained in 25% low

1a: R = H
1b: R = CH_3
1c: R = Br

Scheme 1.

Table 1. Synthesis of 1,1,2,2-tetraarylethane by utilizing $RuCl_2(PPh_3)_3$ complex.[a]

Entry	Ketone	Halide	Conc. HCl (mol%)	Solvent	Sub./Ru (mol/mol)	Temp. (°C)	Yield[c] (%)
1	**1a**		0.1	Toluene	100	180	76
2	**1a**		0.1	Toluene	50	180	78
3	**1a**			Xylene	100	180	25
4	**1a**	**2a**	0.2	Xylene	100	180	90
5	**1a**	**2a**		Xylene	100	180	55
6	**1b**		0.1	Xylene	100	180	15
7	**1b**	**2a**		Xylene	100	180	43 (**3a**)
8		**2a**		Xylene	100	180	89
9[b]		**2a**		Xylene	100	180	—
10		**2a**		Benzene	100	90	95
11		**2b**		Benzene	100	90	96
12		**2c**		Benzene	100	90	85

[a] The reaction was carried out in autoclave under 15 kg/cm^2 of hydrogen atmosphere for 24 h.
[b] Without hydrogen atmosphere.
[c] Isolated yield.

yield (Entry 3). The reaction of benzophenone **1a** and alpha chlorodiphenylmethane **2a** afforded 1,1,2,2-tetraphenylethane **3a** in high yield (90%), which was carried out using $RuCl_2(PPh_3)_3$ in xylene at 180°C under 15 kg/cm^2 hydrogen atmosphere in the presence of 0.2 mol% concentrated hydrochloric acid (Entry 4). The ruthenium-catalyzed reaction of benzophenone **1a** and alpha chlorodiphenylmethane **2a** afforded 1,1,2,2-tetraphenylethane **3a** in 55% yield in the absence of concentrated hydrochloric acid (Entry 5). Because concentrated hydrochloric acid can promote the yield of diphenyl methanol in the procedure of ruthenium-catalyzed hydrogenation of benzophenone, and then converts diphenyl methanol into alpha chlorodiphenylmethane **2a**. Until now the fact we found that it is alpha chlorodiphenylmethane **2a** that presented the product 1,1,2,2-tetraphenylethane **3a** in all case. Low conversion of 4-methylbenzophenone led to afford 1,2-diphenyl-1,2-di-*p*-tolylethane **3b** in 15% yield (Entry 6). It identifies further that alpha chlorodiohenylmethane **2a** can afford **3a** in high yield (Entry 7).

On the basis of these results, the dechlorination coupling reaction of halides (**2a–b**) was carried out and the results were illustrated in Table 1. The dechlorination coupling reaction of halide **2a** was performed by using ruthenium complex $RuCl_2(PPh_3)_3$ with xylene as solvent at 180°C under 15 kg/cm^2 hydrogen atmosphere for 24 h, and alkane **3a** was produced in 89% yield (Entry 8). In the absence of hydrogen atmosphere ruthenium-catalyzed dechlorination coupling reaction could not carry out under the same reaction condition (Entry 9). When benzene was employed as solvent and the reaction temperature decreased to 90°C, 1,1,2,2-tetraphenylethane **3a** was obtained in 95% yield (Entry 10). Another halide **2b** was investigated under the same condition, 1,2-diphenyl-1,2-di-*p*-tolylethane **3b** was obtained in 96% yield (Entry 11). Because so many compounds can be synthesized from bromides, **2c** was employed as substrate to challenge dechlorination coupling reaction, it afforded **3c** in 85% yield (Entry 12). These results show that without corrosive concentrated hydrochloric acid the dechlorination coupling reaction can also afford tetraarylethane **3a–c** in high yields.[12] The crystal structure of **3a**, **3b**, and **3c** were rendered by using Chem 3D (Fig. 1).

As a redox transfer radical chain mechanism in ruthenium(II)-catalyzed addition of aryl or methanesulfonyl chlorides to olefin,[11] we speculate that the mechanism is as shown in Sch. 2. At the beginning of the reaction, ruthenium(II) catalyst $RuCl_2(PPh_3)_3$ reacts with alpha chlorodiphenyl–methane **2a** to form the diphenylmethyl radicals, $Ru^{III}Cl$ is yielded simultaneously which will be reduced to Ru^{II} by hydrogen atmosphere. Finally the diphenylmethyl radicals undergo nearly diffusion-controlled, radical–radical coupling to quantitatively form 1,1,2,2-tetraphenylethane **3a**.

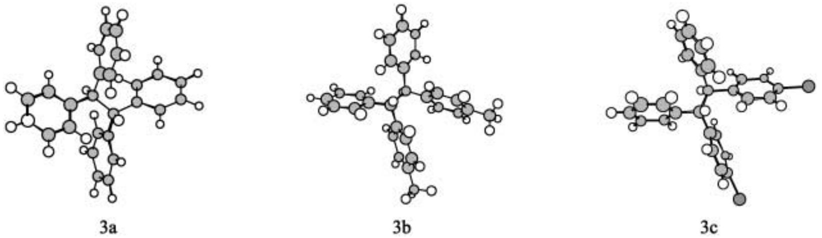
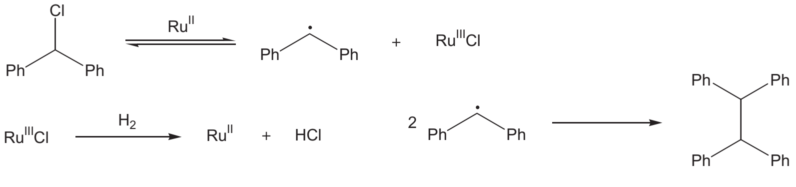


Figure 1. Chem 3D rendering of the crystal structure of **3a**, **3b**, and **3c**.



Scheme 2.

In conclusion, *tris*-triphenylphosphine ruthenium(II) dichloride $RuCl_2(PPh_3)_3$ is an efficient catalyst on dechlorination coupling reaction of halides to afford alkanes in excellent yields.

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12. *Tris*-triphenylphosphine ruthenium(II) dichloride $RuCl_2(PPh_3)_3$ was prepared according to the literature procedure.[13] The solvents were used without further purification. Melting point was determined on a Micro capillary melting point apparatus and uncorrected. ^{1}H NMR was recorded on Varian 500 MHz spectrometer. All reactions were run in autoclave under hydrogen atmosphere (15 kg/cm^2). Alpha chlorodiohenylethane (**2a**, 1.0 g, 5.0 mmol), $RuCl_2(PPh_3)_3$ (0.049 g, 0.05 mmol), and benzene (20 mL) were added to autoclave (100 mL), under 15 kg/cm^2 hydrogen pressure at 90°C stirring for 24 h. After removal of benzene, the cruel product was purified by recrystallization with chloroform to give 1,1,2,2-tetraphenylethane **3a** as a colorless needle crystal 0.78 g (95%). **3a**. M.p.: 212°C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.77 (2H, s), 6.99–7.17 (20H, m). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 57.05, 126.55, 128.84, 129.22, 144.17. IR (KBr) cm^{-1}: 3420, 3025, 3014, 1494, 1449, 1072, 746, 698, 608. **3b**. M.p.: 178°C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.17 (6H, d, $J = 8.6$ Hz), 4.72 (2H, s), 6.89–7.11 (18H, m). ^{13}C NMR ($CDCl_3$, 500 MHz) δ: 21.65, 56.58, 126.38, 128.82, 129.00, 129.15,

129.55, 135.83, 141.30, 144.62. IR (KBr) cm^{-1}: 3430, 3019, 2913, 1513, 1492, 1108, 1070, 788, 723, 694. **3c**. M.p.: 221–222°C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.70 (2H, dd, $J = 20.3$ Hz, $J = 6.3$ Hz), 7.04–7.28 (18H, m). ^{13}C NMR ($CDCl_3$, 500 Hz) δ: 57.04, 126.55, 126.68, 128.85, 128.98, 129.05, 129.13, 129.22, 130.92, 131.96, 142.92, 144.17. IR (KBr) cm^{-1}: 3060, 3023, 2890, 1489, 1448, 1072, 1008, 744, 696.

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