

Ruthenium-catalyzed carbon–carbon formation to synthesize tetraarylethanes and tetraarylxylylene through dechlorinative dimeric reaction

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Abstract

Dechlorinative coupling–dimerization reaction is studied to synthesize alkanes by using tris-triphenylphosphine ruthenium (II) in the presence of hydrogen atmosphere. Two types of halides (α -chlorodiarylmethanes **1a–d** and bis(chlorophenylmethyl)-1,3-phenylene **6**) are employed as substrates to form radical species and then dimerized to generate alkanes in high yields. To our knowledge, it is the first time that the formation of 1,1,2,2-tetraarylethanes and 1,2,9,10-tetraphenyl-di-*m*-xylylene over typical ruthenium-catalyzed dehalogenative coupling–dimerization conditions is reported.

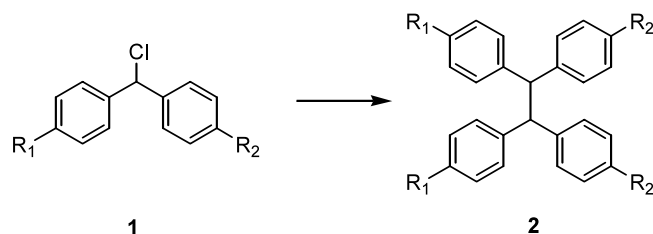
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1. Introduction

The Ullmann reaction [1], initially reported in 1901, illustrated dechlorinative coupling–dimerization reactions of aryl halides to generate a C–C bond between two aromatic nuclei. Considerable improvements have been made through the last century, Sessler et al. [2] developed an efficient procedure for the preparation of alkyl-substituted 2,2'-bipyroles through dechlorination symmetrical coupling reaction. Liebeskind et al. [3] reported a CuTC-mediated Ullmann-reductive coupling of substituted aromatic iodides and bromides, 2-iodo-heteroaromatics, at room temperature. As already mentioned, Kende et al. [4] reported a simple method to generate in situ tris(triphenylphosphine)nickel(0), the reactive species undergoing further oxidative additions with aryl halides. Ruthenium complex catalyzed dechlorination coupling–dimerization reaction has never

been reported. Although Sawamoto et al. [5] described the generation of radical species R^\bullet via the reaction of **1a** with ruthenium complex $RuCl_2(PPh_3)_3$ in living radical polymerizations, it is called Kharasch [6] or atom-transfer radical addition reactions in organic chemistry. We focus on the dehalogenation dimerization of halides (**1a–d** and **6**) by using ruthenium complex $RuCl_2(PPh_3)_3$ in the presence of hydrogen atmosphere. Herein we report the synthesis of 1,1,2,2-tetraarylethanes (**2a–d**) and 1,2,9,10-tetraphenyl-di-*m*-xylylene (1,2,9,10-TPDX, **9**) using ruthenium-catalyzed dechlorinative dimeric reaction.



Conditions: cat. $RuCl_2(PPh_3)_3$; H_2 15 kg/cm²; 24 h.

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Table 1
Ruthenium-catalyzed dechlorination coupling reaction of halides (**1a–d**)^a

Entry	Substrate	R ₁	R ₂	Solvent	Temperature (°C)	Yield ^b (%)
1	1a	H	H	Xylene	180	89
2	1a	H	H	Benzene	90	95
3	1b	Me	H	Benzene	90	96
4	1c	Br	H	Benzene	90	85
5 ^c	1d	OMe	OMe	Benzene	90	86

^a All reactions were carried out in the autoclave under 15 kg cm⁻² for 24 h, the mole ratio of substrate and catalyst was 100, except for Entry 5.

^b Isolated yields.

^c The mole ratio of substrate and catalyst was 50.

Table 2
Effect of free radical inhibitors in the Ru(II)-catalyzed reaction of α -chlorodiphenylmethane^a

Entry	Radical inhibitor	Yield ^b (%)
1	None	95
2	<i>p</i> -Benzoquinone (0.3%)	90
3	<i>p</i> -Benzoquinone (0.5%)	61
4	<i>p</i> -Benzoquinone (1.0%)	24
5	Galvinoxyl (0.3%)	78

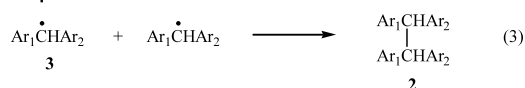
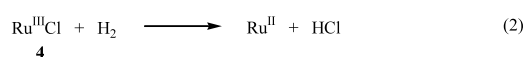
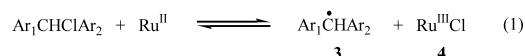
^a All reactions were carried out in autoclave under 15 kg cm⁻², at 90 °C for 24 h.

^b Isolated yields.

2. Results and discussion

2.1. Ruthenium-catalyzed dechlorination coupling of halides

The reaction of α -chlorodiphenylmethane was carried out in benzene, using ruthenium (II) complex RuCl₂(PPh₃)₃ as a catalyst, by heating the reaction mixture at 90 °C, for 24 h in the autoclave. In the absence of the hydrogen atmosphere, no reaction was observed, and all the starting material was recovered. In the absence of RuCl₂(PPh₃)₃ the reaction could not be performed. Roberge et al. [7] gave an example about the formation of 4,4'-dimethylbiphenyl through dehalogenation under 101 kPa hydrogen, however in this case Ru(1%)/silica was employed as a catalyst, and the yield was too low. Therefore all the reactions were carried out using RuCl₂(PPh₃)₃ under 15 kg cm⁻² hydrogen atmosphere, and the results were shown in Table 1. The dechlorination coupling reaction of halide **1a** was performed by using ruthenium complex RuCl₂(PPh₃)₃ with xylene as solvent at 180 °C under 15 kg cm⁻² hydrogen atmosphere for 24 h, and alkane **2a** was produced in 89% yield (Entry 1). When benzene was employed as solvent and the reaction temperature decreased to 90 °C, 1,1,2,2-tetraphenylethane **2a** was obtained in 95% yield (Entry 2). Another halide **1b** was investigated under the same condition, 1,2-diphenyl-1,2-di-*p*-tolylethane **2b** was obtained in 96% yield (Entry 3).



Scheme 1.

Dechlorination coupling reaction of bromide **1c** was carried out, which afforded product **2c** in 85% (Entry 4). 4,4'-Dimethoxybenzhydrylchloride **1d** was practiced, when the mole ratio of substrate **1d** and ruthenium catalyst was 100, it afforded **2d** in 56% yield and 40% of starting material was recovered. When the mole ratio was changed to 50, the product **2d** was obtained in 86% yield (Entry 5) (Table 1).

One plausible reaction mechanism for the ruthenium (II)-catalyzed reaction involves a free-radical, redox-transfer chain process (Scheme 1).

In Scheme 1, the ruthenium catalyst RuCl₂(PPh₃)₃ first abstracts a chlorine atom from α -chlorodiphenylmethane to give a diarylmethane radical **3** and the Ru (III) species **4** (eq 1). In the second step, the Ru (III) species **4** is hydrogenated by hydrogen atmosphere to regenerate the ruthenium (II) catalyst (eq 2). Finally the diarylmethane radicals undergo nearly diffusion controlled, radical–radical coupling to quantitatively form tetraarylethane **2** (eq 3).

Inhibitors can stop every radical and radical reaction is completely halted until they are consumed [8]. The effect of free-radical inhibitors was also studied and the results were shown in Table 2. When 0.3% mol of *p*-benzoquinone employed as an inhibitor was added, the yield of 1,1,2,2-tetraphenylethane (**2a**) was affected to only a small extent. However, addition of 0.5% mol and 1.0% mol of *p*-benzoquinone led to a definite reduction in yields of **2a**. Another inhibitor, galvinoxyl (0.3% mol) afforded **2a** in 78% yield. All these results support the free-radical mechanism of Scheme 1.

(8H, d, $J = 7.7$ Hz). ^{13}C -NMR (CDCl_3 , 500 MHz) δ : 55.64, 55.77, 114.20, 129.99, 137.03, 158.07. IR (KBr) cm^{-1} : 3534, 3029, 2929, 2834, 1608, 1509, 1249, 1172, 1035, 809, 767. Anal. Calc. for $\text{C}_{30}\text{H}_{30}\text{O}_4$: C, 79.37; H, 6.65. Found: C, 79.01; H, 6.61%.

4.3. Synthesis of 1,2,9,10-tetraphenyl-di-*m*-xylylene (**9**)

Bis(chlorophenylmethyl)-1,3-phenylene (**6**, 1.0 g, 3.1 mmol), $\text{RuCl}_2(\text{PPh}_3)_3$ (0.06 g, 0.031 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 crude product was purified by recrystallization with chloroform to give 1,2,9,10-tetraphenyl-di-*m*-xylylene (**9**) as a colorless solid 0.63 g (80%).

4.3.1. 1,2,9,10-tetraphenyl-di-*m*-xylylene (**9**)

Column chromatography (SiO_2 , Chloroform); m.p.: 190–192 °C. MS/FAB (70 eV), m/z (relative intensity) 512 (6.5), 345 (13.5), 256 (37.0), 165 (100.0), 91 (60.0), 77 (13.0). ^1H -NMR (CDCl_3 , 500 MHz) δ : 4.33 (4H, s), 6.43–7.20 (28H, m). ^{13}C -NMR (CDCl_3 , 500 MHz) δ : 56.72, 126.25, 127.26, 128.55, 129.19, 144.15. IR (KBr) cm^{-1} : 3083, 3023, 1598, 775, 754, 698, 678. Anal. Calc. for $\text{C}_{40}\text{H}_{32}$: C, 93.71; H, 6.29. Found: C, 93.31; H, 6.38%.

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