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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. \bigcirc 2003 Elsevier B.V. All rights reserved.

Keywords: Dechlorination; Radical reaction; Coupling-dimerization; Ruthenium catalyst

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'-bipyrroles through dechlorination symmetrical coupling reaction. Liebeskind et al. [3] reported a CuTC-mediated Ullmann-reductive coupling of substituted aromatic iodides and bromides, 2-iodoheteroaromatics, 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

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been reported. Although Sawamoto et al. [5] described the generation of radical species \mathbf{R}^{\bullet} via the reaction of **1a** with ruthenium complex $\operatorname{RuCl_2(PPh_3)_3}$ 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 $\operatorname{RuCl_2(PPh_3)_3}$ 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 dechorinative dimeric reaction.



Conditions: cat. $RuCl_2(PPh_3)_3$; $H_215 \text{ kg/cm}^2$; 24 h.

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Table 1		
Ruthenium-catalyzed dechlorination	n coupling reaction	of halides (1a-d)

Entry	Substrate	R ₁	R_2	Solvent	Temperature (°C)	Yield ^b (%)
1	1a	Н	Н	Xylene	180	89
2	1a	Н	Н	Benzene	90	95
3	1b	Me	Н	Benzene	90	96
4	1c	Br	Н	Benzene	90	85
5°	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.

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		

 $^{\rm a}$ All reactions were carried out in autoclave under 15 kg cm $^{-2},$ at 90 °C for 24 h.

^b Isolated yields.

Table 2

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 $RuCl_2(PPh_3)_3$ 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 $RuCl_2(PPh_3)_3$ the reaction could not performed. Roberge et al. [7] gave an example about the formation of 4,4'-dimethylbiphenyl though 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 $RuCl_2(PPh_3)_3$ 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-1,2di-*p*-tolylethane **2b** was obtained in 96% yield (Entry 3).



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 -chlorodiarylmethane 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.

2.2. Didechlorination coupling reactions

In order to popularize and apply this novel method of carbon-carbon formation, the dechlorinative couplingdimerization reaction of 1,2-dichloro-1,2-diphenylethane **5** and 1,3-dichlorobenzylbenzene **6** have been carried out using ruthenium catalyst $\text{RuCl}_2(\text{PPh}_3)_3$ in the presence of hydrogen atmosphere. Herein these experimental results are reported.



The reaction of 1,2-dichloro-1,2-diphenylethane **5** was carried out in benzene using ruthenium (II) complex RuCl₂(PPh₃)₃ as a catalyst under 15 kg cm⁻² hydrogen atmosphere at 90 °C for 24 h. After purification, *trans*-1,2-diphenylethylene **8** was obtained in 70% yield, but no 1,2,3,4-tetraphenylcyclobutane **7** at all could be detected by NMR and MS. These results show that adjacent chlorine contained compound **5** can practice dechlorination reaction, but coupling–dimerization reaction is never practiced in this case. In addition, under the same reaction condition, ruthenium-catalyzed dechlorination coupling reaction of bis(chlorophenylmethyl)-1,3-phenylene **6** was performed, which afforded compound 1,2,9,10-TPDX, **9** in 80% yield.

3. Conclusion

We have described that dechlorination of halides (1a-d), 1,2-dichloro-1,2-diphenylethane 5 and bis-(chlorophenylmethyl)-1,3-phenylene 6 catalyzed by RuCl₂(PPh₃)₃ lead to radical coupling reaction. The ruthenium complex RuCl₂(PPh₃)₃ is found to be an efficient catalyst on dechlorination coupling-dimerization reaction, which affords a novel significant method of carbon-carbon formation. Numerous benzylic halides have successfully been converted to the corresponding alkanes in high yields.

4. Experimental

4.1. General considerations

Tris-triphenylphosphine ruthenium (II) dichloride $RuCl_2(PPh_3)_3$ was prepared according to the literature procedure [9]. The solvents were used without further purification. Melting point was determined on a Micro capillary melting point apparatus and uncorrected. ¹H-NMR and ¹³C-NMR were recorded on Varian 500 MHz spectrometer. IR spectra were recorded on a Horiba FT-710 infrared spectrophotometer as KBr pellets. Mass spectra were performed with a Hitachi RMU-6M mass spectrograph. All reactions were run in autoclave under hydrogen atmosphere (15 kg cm⁻²).

4.2. Synthesis of 1,1,2,2-tetraarylethanes

Alpha chlorodiphenylethane (1a, 1.0 g, 5.0 mmol), RuCl₂(PPh₃)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-tetra-phenylethane **2a** as a colorless needle crystal 0.78 g (95%).

4.2.1. 2a

M.p.: 211–212 °C (lit. 211 °C). ¹H-NMR (CDCl₃, 500 MHz) δ : 4.77 (2H, s), 6.99–7.17 (20H, m). ¹³C-NMR (CDCl₃, 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.

4.2.2. 2b

M.p.: 178–179 °C. ¹H-NMR (CDCl₃, 500 MHz) δ : 2.17 (6H, d, J = 8.6 Hz), 4.72 (2H, s), 6.89–7.11 (18H, m). ¹³C-NMR (CDCl₃, 500 MHz) δ : 21.65, 56.58, 126.38, 128.82, 129.00, 129.15, 129.55, 135.83, 141.30, 144.62. (KBr) cm⁻¹: 3430, 3019, 2913, 1513, 1492, 1108, 1070, 788, 723, 694. Anal. Calc. for C₂₈H₂₆: C, 92.77; H, 7.23. Found: C, 92.17; H, 7.23%.

4.2.3. 2c

M.p.: 221–222 °C. ¹H-NMR (CDCl₃, 500 MHz) δ : 4.70 (2H, dd, J = 20.3 Hz, J = 6.3 Hz), 7.04–7.28 (18H, m). ¹³C-NMR (CDCl₃, 500 MHz) 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. Anal. Calc. for C₂₆H₂₆Br₂: C, 63.44; H, 4.10. Found: C, 63.85; H, 4.21%.

4.2.4. 2d

M.p.: 192–193 °C. ¹H-NMR (CDCl₃, 500 MHz) δ : 3.69 (12H, s), 4.57 (2H, s), 6.64 (8H, d, J = 7.7 Hz), 7.02

(8H, d, J = 7.7 Hz). ¹³C-NMR (CDCl₃, 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 C₃₀H₃₀O₄: 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), RuCl₂(PPh₃)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 cruel 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 (SiO₂, 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 (CDCl₃, 500 MHz) δ : 4.33 (4H, s), 6.43–7.20 (28H, m). ¹³C-NMR (CDCl₃, 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 C₄₀H₃₂: C, 93.71; H, 6.29. Found: C, 93.31; H, 6.38%.

References

- (a) F. Ullmann, J. Bielecki, Chem. Ber. 34 (1901) 2174;
 (b) P.E. Fanta, Synthesis 1 (1974) 9;
 (c) G. Bringmann, R. Walter, R. Weirich, Angew. Chem. Int. Ed. Engl. 29 (1990) 977.
- [2] J.L. Sessler, M.C. Hoehner, Synlett 3 (1994) 211.
- [3] S. Zhang, D. Zhang, L.S. Liebeskind, J. Org. Chem. 62 (1997) 2312.
- [4] A.S. Kende, L.S. Liebeskind, D.M. Braitsch, Tetrahedron Lett. (1975) 3375.
- [5] (a) M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, Polym. Prepr. Jpn. 43 (1994) 1792;
 (b) M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, Macromolecules 28 (1995) 1721;
 (c) M. Kamigaito, T. Ando, M. Sawamoto, Chem. Rev. 101 (2001) 3689.
- [6] (a) D.P. Curran, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 4, Pergamon, Oxford, UK, 1991, p. 715;
 (b) J. Iqbal, B. Bhatia, N.K. Nayyar, Chem. Rev. 94 (1994) 519.
- [7] D.M. Roberge, W.F. Holderich, Appl. Catal. A 194–195 (2000) 341.
- [8] (a) W.T. Anderson, Jr., H.S. Taylor, J. Am. Chem. Soc. 45 (1923) 650;
- (b) H.S. Taylor, A.A. Vernon, J. Am. Chem. Soc. 53 (1931) 2527.
- [9] P.S. Hallam, T.A. Stephenson, G. Wilkinson, Inorg. Synth. 12 (1972) 238.