Chinese Journal of Catalysis 39 (2018) 1194–1201 催化学报 2018年 第39卷 第7期 | www.cjcatal.org

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc

Article

Photocatalytic hydrogen-evolution dimerization of styrenes to synthesize 1,2-dihydro-1-arylnaphthalene derivatives using Acr⁺-Mes and cobaloxime catalysts

Wenxiao Cao [a,b], Chengjuan Wu [a], Tao Lei [a], Xiulong Yang [a], Bin Chen [a,b,*], Chenho Tung [a,b], Lizhu Wu [a,b,#]

[a] *Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

ARTICLE INFO

Article history:
Received 20 April 2018
Accepted 27 April 2018
Published 5 July 2018

Keywords:
Hydrogen-evolution dimerization
Styrenes
1,2-Dihydro-1-arylnaphthalene derivatives
Photocatalysis
Cobaloxime catalysts

ABSTRACT

We report a hydrogen-evolution dimerization of styrenes *via* the synergistic merger of Acr⁺-Mes photocatalyst and cobaloxime proton reduction catalysts. By utilizing this dual catalyst system, 1,2-dihydro-1-arylnaphthalene derivatives can be directly constructed from commercially available styrenes. Our reaction proceeds smoothly under mild conditions without the need for oxidants or hydrogen atom transfer reagents, and the sole byproduct is hydrogen gas. Mechanistic investigation suggests that the reaction is initiated by photoinduced electron transfer under visible-light irradiation.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.
Published by Elsevier B.V. All rights reserved.

1. Introduction

1,2-Dihydro-1-arylnaphthalene derivatives are common structural units in many biologically active natural products and pharmaceuticals [1–6]. This skeleton contains an alkene C=C bond that can be easily derivatized; for example, podophyllotoxin with high anticancer activity can be constructed by using this skeleton as a precursor [7, 8]. Over the past decades, a variety of effective methods such as Friedel-Crafts reaction [9], Heck reaction [10], metal-catalyzed intramolecular epoxidation [11], and others [12, 13] have been developed for the construction of 1,2-dihydro-1-arylnaphthalenes [14–21]. Nevertheless, these methods often require substrate pre-functionalization and high temperatures, and have limited product regioselectivity. In recent years, visible-light-induced chemical transformations have attracted increasing interest from organic chemists because of their green and sustainable features [22–27]. Despite their high oxidation potential, sty-

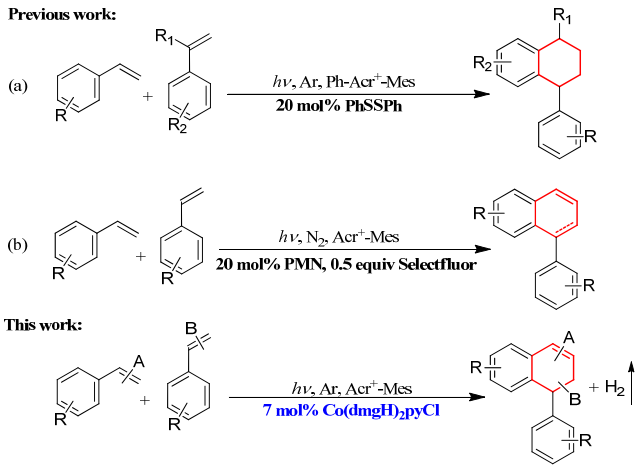
* Corresponding author. Tel/Fax: +86-10-82543576; E-mail: chenbin@mail.ipc.ac.cn
# Corresponding author. Tel/Fax: +86-10-82543580; E-mail: lzwu@mail.ipc.ac.cn
This work was supported by the Ministry of Science and Technology of China (2014CB239402, 2017YFA0206903), the National Natural Science foundation of China (21390404), the Strategic Priority Research Program of the Chinese Academy of Science (XDB17000000), the Key Research Program of Frontier Sciences, the Chinese Academy of Sciences (QYZDY-SSW-JSC029).
DOI: 10.1016/S1872-2067(18)63095-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 7, July 2018

renes can undergo dimerization by acridinium-based organic dyes in the presence of a stoichiometric oxidant or hydrogen atom transfer (HAT) reagent [28,29]. 9-Mesityl-10-acridinium-based organic dye shows a strong absorption band in the visible region (λ = 430 nm) and high oxidizing ability in the excited state, and has been successfully employed in the transformation of a diverse range of alkenes into cation radicals under irradiation [30–34]. Huang *et al.* [28] recently reported the [4+2] cycloaddition of styrenes by using 9-mesityl-10-phenylacridinium tetrafluoroborate (Ph-Acr$^+$-Mes BF_4^-) as the photosensitizer and PhSSPh as an HAT reagent for the synthesis of 1,2,3,4-tetrahydro-arylnaphthalenes (Scheme 1(a)). Liang and co-workers [29] took the lead in the oxidative synthesis of 1,2-dihydro-1-arylnaphthalene derivatives from styrenes by using 9-mesityl-10-methyl acridinium perchlorate (Acr$^+$-Mes ClO_4^-) as the photosensitizer, and 2-phenylmalononitrile (PMN) and Selectfluor as the oxidants (Scheme 1(b)). However, the use of an HAT reagent always leads to the reduced product (tetralins) rather than 1,2-dihydronaphthalenes. The use of an oxidant, on the other hand, can result in overoxidized products, naphthalene derivatives. We contemplated whether we could combine catalytic amounts of the Acr$^+$-Mes photosensitizer and cobalt catalyst [35–37] to synthesize 1,2-dihydro-1-arylnaphthalene derivatives by a cross-coupling hydrogen-evolution (CCHE) reaction [38–50], which avoids the use of any sacrificial oxidant and yields hydrogen gas (H_2) as the sole byproduct. To our delight, the use of Acr$^+$-Mes ClO_4^- and cobaloxime catalyst $Co(dmgH)_2pyCl$ helped us execute our idea under visible-light irradiation at room temperature.

2. Experimental

2.1. General methods

^{1}H NMR spectra were recorded using a Bruker Avance DPX 400MHz instrument with tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were obtained at 100 MHz and referenced to the internal solvent signals. Hydrogen gas was analyzed by gas chromatography (7890-II, Tianmei, China)



Scheme 1. Representative synthesis of 1-arylnaphthalene derivatives *via* photocatalysis.

using a thermal conductivity detector (TCD) with a 5 Å molecular sieve column and nitrogen as the carrier gas. Mass spectra were recorded using a Trio-2000 GC-MS spectrometer. Commercially available reagents and solvents were used without further purification. Blue LEDs (3 W, λ = 440 ± 10 nm, 145 lm @700mA) were used as the irradiation light sources.

2.2. General procedure for the preparation of 1,2-dihydro-1-arylnaphthalene

A 10 mL Pyrex tube equipped with a magnetic stir bar was charged with styrene (73 μL, 0.7 mmol) Acr$^+$-Mes (8.82 mg, 0.003 mmol), $Co(dmgH)_2pyCl$ (19.6 mg, 0.007 mmol), NaH_2PO_4 (210 mg, 1.75 mmol), and dry MeCN (5 mL). Then, the system was degassed with a stream of argon for 30 min. The mixture was irradiated by blue LEDs under an argon atmosphere for 24 h. After removal of the solvent under vacuum, the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent to obtain the products.

1,2-dihydro-1-arylnaphthalene (**2**): colorless oil, yield 60%, petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, J = 8.0 Hz, 2H), 7.27–7.24 (m, 3H), 7.20 (t, J = 7.6 Hz, 1H), 7.13–7.08(m, 2H), 6.83 (d, J = 7.6 Hz, 1H), 6.56 (d, J = 9.6 Hz, 1H), 6.04–6.00 (m, 1H), 4.16 (t, J = 8.8 Hz ,1H), 2.69–2.64 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 137.9, 134.1, 128.5, 128.4, 128.0, 127.9, 127.3, 127.2, 126.8, 126.5, 126.2, 43.9, 32.0. HRMS (EI) calcd. for $C_{16}H_{14}$ [M]: 206.1096, found: 206.1099.

7-Methyl-1-(*p*-tolyl)-1,2-dihydronaphthalene (**3**): colorless oil, yield 66%, petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04–7.00 (m, 4H), 6.94–6.87 (m, 2H), 6.57 (s, 1H), 6.41 (d, J = 9.6 Hz, 1H), 5.84–5.80 (m, 1H), 3.96 (t, J = 7.6 Hz, 1H), 2.54–2.50 (m, 1H), 2.49–2.46 (m, 1H), 2.24 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 137.9, 137.0, 135.9, 131.5, 129.1, 128.6, 128.3, 127.8, 127.3, 126.1, 126.0, 43.5, 32.2, 21.3, 21.0. HRMS (EI) calcd. for $C_{18}H_{18}$ [M]: 234.1409, found: 234.1412.

5-Methyl-1-(*o*-tolyl)-1,2-dihydronaphthalene (**4**): colorless oil, yield 71%, petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, J = 3.2 Hz, 1H), 7.16–7.13 (m, 2H), 7.11 (t, J = 6.4 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.95 (t, J = 6.4 Hz, 1H), 6.78 (d, J = 9.6 Hz, 1H), 6.54 (d, J = 7.6 Hz, 1H), 6.10–6.05 (m, 1H), 4.38–4.34 (m, 1H), 2.59–2.54(m, 2H), 2.39 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 138.1, 136.2, 133.2, 132.6, 130.4, 128.5, 128.4, 127.6, 126.9, 126.3, 126.1, 125.3, 124.7, 40.1, 30.2, 19.8, 19.3. HRMS (EI) calcd. for $C_{18}H_{18}$ [M]: 234.1409, found: 234.1409

4-(2,5-Dimethylphenyl)-5,8-dimethyl-1,2-dihydronaphthalene (**5**): colorless oil, isolated yield 55%, petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 15.2 Hz, 1H), 7.08 (s, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.90 (s, 1H), 6.47 (s, 1H), 5.91–5.71 (m, 1H), 4.39 (d, J = 8.9 Hz, 1H), 2.87 (ddd, J = 11.4, 6.0, 3.2 Hz, 1H), 2.48 (s, 3H), 2.44 (s, 3H), 2.41–2.37 (m, 1H), 2.14 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 135.9, 135.1, 133.6, 132.8, 131.8, 131.0, 130.3, 129.3, 128.9, 128.4, 126.8, 125.3, 125.1, 34.6, 29.9, 21.3, 19.5, 18.9, 18.4. HRMS (EI) calcd. for $C_{20}H_{22}$ [M]: 262.1722, found: 262.1711

7-Methyl-4-(*m*-tolyl)-1,2-dihydronaphthalene (**6**) and

5-methyl-4-(*m*-tolyl)-1,2-dihydro-naphthalene (**6'**): colorless oil, isolated yield 76%, petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.74 (m, 2H), 7.46 (m, 1H), 7.41–7.32 (m, 2H), 7.30 (m, 3H), 6.98–6.91 (m, 3H), 6.87 (m, 1H), 6.78 (m, 1H), 6.70 (m, 1H), 6.50 (t, 2H), 6.03–5.95 (m, 1H), 5.80–5.70 (m, 1H), 4.20 (t, J = 8.4 Hz, 1H), 4.05 (t, J = 8.9 Hz, 1H), 2.91 (m, 2H), 2.62–2.57 (m, 2H), 2.32 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7 , 137.9, 137.6, 137.0, 136.2, 136.1, 135.5, 134.1, 134.0, 130.8, 130.4, 129.6, 129.2, 128.5, 128.3, 128.0, 127.8,127.7,127.3, 127.2, 126.9, 126.7 , 125.5, 125.1, 124.9, 124.5, 124.3, 43.4, 38.4, 32.4, 32.2, 21.6, 21.0. HRMS (EI) calcd. for $C_{18}H_{18}$ [M]: 234.1409, found: 234.1409

6-Methoxy-4-(4-methoxyphenyl)-1,2-dihydronaphthalene (**7**): colorless oil, yield 47%, petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (m, 3H), 7.02 (s, 1H), 6.84 (d, J = 1.8 Hz, 2H), 6.70 (m, 1H), 6.39 (m, 1H), 5.94–5.73 (m, 1H), 4.14–3.97 (m, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 2.27 (d, J = 3.3 Hz, 1H), 2.06 (d, J = 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 157.9, 140.0, 137.0, 129.3, 127.5, 127.4, 127.2, 124.7, 114.5, 113.9, 113.7, 111.3, 111.0, 55.4, 54.9, 48.0, 26.0. HRMS (EI) calcd. for $C_{18}H_{18}O_2$ [M]: 266.1307, found: 266.1309

6-Ethoxy-4-(4-ethoxyphenyl)-1,2-dihydronaphthalene (**8**): colorless oil, isolated yield 41%, petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 1H), 7.11 (s, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.80 (s, 1H), 6.68 (m, 1H), 6.48 (d, J = 9.6 Hz, 1H), 6.39 (d, J = 2.4 Hz, 1H), 5.94–5.78 (m, 1H), 4.01 (m, 2H), 3.90 (m, 2H), 3.44 (m, 1H), 2.58–2.53 (m, 1H), 2.27–2.25 (m, 1H), 2.07 (t, J = 5.0 Hz, 1H), 1.39 (s, 3H), 1.32 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 157.6, 157.4, 140.2, 136.4, 136.2, 129.5, 127.6, 127.0, 124.6, 115.0, 114.8, 114.3, 111.7, 63.3, 63.0, 43.5, 26.0, 15.0, 14.8. HRMS (EI) calcd. for $C_{20}H_{22}O_2$ [M]: 294.1620, found: 294.1620

6-(*tert*-Butyl)-4-[4-(tert-butyl)phenyl]-1,2-dihydronaphthalene (**9**): white solid, isolated yield 62%, petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.3 Hz, 2H), 7.26–7.23 (m, 1H), 7.14 (m, 2H), 7.07 (d, J = 8.0 Hz, 1H), 6.96 (s, 1H), 6.53 (d, J = 9.6 Hz 1H), 5.99–5.91 (m, 1H), 4.12 (t, J = 7.8 Hz, 1H), 2.75–2.69 (m, 1H), 2.66–2.61 (m, 1H), 1.34 (s, 9H), 1.25 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 149.0, 141.6, 137.4, 131.6, 127.8, 127.7, 126.3, 125.7, 125.3, 125.1, 123.5, 43.3, 34.6, 34.4, 31.4, 31,3. HRMS (EI) calcd. for $C_{24}H_{30}$ [M]: 318.2348, found: 318.2350

6-Fluoro-4-(4-fluorophenyl)-1,2-dihydronaphthalene (**10**): colorless oil, yield 67%, petroleum ether/ethyl acetate = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.15 (m, 2H), 7.06 (m, 1H), 7.04–6.98 (m, 2H), 6.88–6.84 (m, 1H), 6.52–6.48 (m, 2H), 5.98–5.93 (m, 1H), 4.10–4.07 (m, 1H), 2.64–2.58 (m, 1H), 2.57–2.49 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 160.5, 140.3, 139.3, 130.3, 129.8, 127.6, 127.1, 126.2, 115.5, 115.0, 113.5, 43.3, 31.6. HRMS (EI) calcd. for $C_{16}H_{12}F_2$ [M]: 242.0907, found: 242.0909

6-Chloro-4-(4-chlorophenyl)-1,2-dihydronaphthalene (**11**): colorless oil, isolated yield 62%, petroleum ether/ethyl acetate = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 2.5 Hz, 2H), 7.12 (dd, J = 6.9, 4.9 Hz, 2H), 7.00 (dd, J = 10.1, 8.3 Hz, 2H), 6.80–6.74 (m, 1H), 6.49 (d, J = 9.6 Hz, 1H), 6.10–5.79 (m, 1H), 4.06–3.98 (m, 1H), 2.89–2.74 (m, 1H), 2.59–2.49 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 139.2, 132.7, 132.6, 132.5, 129.7, 129.2, 128.8, 128.7, 128.0, 127.9, 127.4, 127.3, 127.2, 127.1, 43.2, 31.6. HRMS (EI) calcd. for $C_{16}H_{12}Cl_2$ [M]: 274.0316, found: 274.0353

5-Chloro-1-(*o*-chlorophenyl)-1,2-dihydronaphthalene (**12**): colorless oil, isolated yield 50%, petroleum ether/ethyl acetate = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, J = 7.4, 2.0 Hz, 1H), 7.25–7.20 (m, 2H), 7.17–7.16 (m, 1H), 7.15-7.13(m, 1H), 7.03–7.01 (m, 1H), 7.01–6.98 (m,1H), 6.72 (d, J = 7.4 Hz, 1H), 6.10–6.05 (m, 1H), 4.69 (t, J = 8.0 Hz, 1H), 2.68-2.63 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 138.8, 133.7, 131.9, 131.5, 129.9, 129.7, 128.7, 128.1, 127.9, 127.8, 126.9, 126.5, 125.2, 124.0, 39.9, 29.7. HRMS (EI) calcd. for $C_{16}H_{12}Cl_2$ [M]: 274.0316, found: 274.0266

6-Bromo-4-(4-bromophenyl)-1,2-dihydronaphthalene (**13**): colorless oil, isolated yield 62%, petroleum ether/ethyl acetate = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 10.0 Hz, 1H), 7.21 (dd, J = 8.4, 8.8 Hz, 1H),7.07 (d, J = 8.4 Hz, 2H), 6.97(d, J = 4.0 Hz, 1H), 6.48 (d, J = 9.6 Hz, 1H), 6.02–5.99 (m, 1H), 4.08–4.03 (m, 1H), 2.63–2.60 (m, 1H), 2.57–2.53 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 139.3, 132.9, 131.7, 131.6, 130.7, 130.0, 127.6, 127.8, 127.4, 127.2, 120.6, 43.1, 31.6. HRMS (EI) calcd. for $C_{16}H_{12}Br_2$ [M]: 361.9306, found: 361.9251

5-Bromo-1-(*o*-bromophenyl)-1,2-dihydronaphthalene (**14**): colorless oil, isolated yield 48%, petroleum ether/ethyl acetate = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.9, 1.1 Hz, 1H), 7.42 (dd, J = 12.6, 4.7 Hz, 2H), 7.35–7.27 (m, 1H), 7.22–7.12 (m, 1H), 7.06 (dd, J = 7.7, 1.9 Hz, 1H), 6.97–6.90 (m, 1H), 6.75 (d, J = 7.8 Hz, 1H), 6.14–5.91 (m, 1H), 4.66 (t, J = 8.1 Hz, 1H), 2.85 (d, J = 6.2 Hz, 1H), 2.63 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 142.4, 136.4, 133.0, 131.9, 130.1, 129.4, 128.4, 127.7, 127.0, 126.9, 126.6, 126.0, 123.6, 42.4, 30.0. HRMS (EI) calcd. for $C_{16}H_{12}Br_2$ [M]: 361.9306, found: 361.9183.

6-Ethoxy-4-(4-ethoxyphenyl)-1,2-dihydronaphthalene (**15**): colorless oil, yield 53%, petroleum ether/ethyl acetate = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.5 Hz, 2H), 7.15–7.03 (m, 2H), 7.01 (dd, J = 13.7, 8.4 Hz, 2H), 6.90 (dd, J = 8.1, 2.2 Hz, 1H), 6.51 (d, J = 11.4 Hz, 1H), 6.06–5.91 (m, 1H), 4.08 (dt, J = 50.1, 25.2 Hz, 1H), 2.58 (s, 1H), 2.56 (s, 1H), 2.31–2.24 (m, 3H), 2.18 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 169.5, 149.6, 149.4, 141.3, 139.2, 131.9, 129.4, 127.2, 126.9, 121.6, 121.0, 119.9, 43.5, 31.8, 21.2. HRMS (EI) calcd. for $C_{18}H_{18}O_4$ [M]: 322.1205, found: 322.1205

6-Benzyl-4-(4-benzylphenyl)-1,2-dihydronaphthalene (**16**): colorless oil, isolated yield 60%, petroleum ether/ethyl acetate = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.44 (d, J = 8.1 Hz, 3H), 7.39 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 7.4 Hz, 3H), 7.25 (d, J = 8.1 Hz, 3H), 7.23–7.17 (m, 3H), 7.13–7.05 (m, 2H), 6.51 (d, J = 9.6 Hz, 1H), 6.05–5.84 (m, 1H), 4.14 (t, J = 8.2 Hz, 1H), 2.71–2.56 (m, 1H), 2.05 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 143.6, 141.0, 141.1, 140.2, 139.4, 138.2, 133.4, 129.3, 128.9, 127.8, 128. 7, 127.8, 127.3, 127.2, 127.1, 127.1, 127.1, 127.0, 126.9, 126.7, 125.7, 43.8, 32.1. HRMS (EI) calcd. for $C_{28}H_{22}$ [M]: 358.1722, found: 358.1722

1-(Naphthalen-1-yl)-1,2-dihydronaphthalene (**17**): white

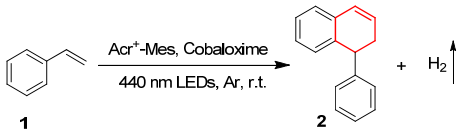
solid, isolated yield 58%, petroleum ether/ethyl acetate = 100/1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 15.5, 8.6 Hz, 2H), 8.01–7.92 (m, 1H), 7.93–7.89 (m, 1H), 7.83–7.70 (m, 3H), 7.57–7.49 (m, 4H), 7.41–7.37 (m, 1H), 7.29 (d, J = 3.5 Hz, 1H), 7.04 (d, J = 6.4 Hz, 1H), 6.20–6.07 (m, 1H), 5.13 (t, J = 8.0 Hz, 1H), 3.05–2.78 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 135.0, 134.4, 133.0, 131.4, 129.6, 129.2, 128.6, 127.8, 127.5, 127.2, 126.8, 126.2, 125.9, 125.6, 125.5, 125.4, 125.3, 123.1, 122.8, 39.8, 37.8. HRMS (EI) calcd. for $C_{24}H_{18}$ [M]:306.1409, found: 306.1407

3. Results and discussion

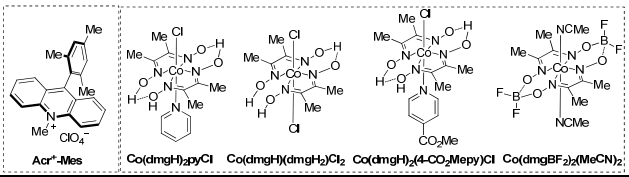
Initially, styrene was chosen as the standard substrate for the desired product. As shown in Table 1, when using Acr$^+$-Mes ClO_4^- (3 mol%) as the photocatalyst and Co(dmgH)$_2$pyCl (7 mol%) as the proton reduction catalyst, 35% yield of the desired product **2** was obtained after 24 h of irradiation (Table 1, entry 1). The produced hydrogen gas was also detected by GC–TCD. No other product was detected, except for a very small amount of tetralin derivative. We hypothesized that the generated hydrogen and the target product were further hydrogenated to give a hydrogenated compound. To enhance the reaction efficiency, various concentrations of **1** were screened (Table 1, entries 1–4). At a high concentration, the yield of product **2** was increased to 56% (Table 1, entry 3) due to the bimolecular reaction character. Further increasing the concentration led to a decrease in the product yield (Table 1, entry 4). Then, several cobaloxime catalysts were evaluated (Table 1, entries 3, 5–7), and Co(dmgH)$_2$pyCl was found to be the best (Table 1, entry 3), indicating that the structure of the cobalt complex has a greater impact on the reaction. In order to further optimize the yield, we added additives, including Na_2CO_3, $NaHCO_3$, NaH_2PO_4, DMAP, and K_2CO_3, to the system and found that 2.5 equiv. NaH_2PO_4 could increase the yield of the desired product **2** to 72% (Table 1, entry 8), where NaH_2PO_4 might aid in proton transfer. Other photocatalysts such as rose bengal, rhodamine B, [Ir(dtbbpy)(ppy)$_2$][PF_6], eosin Y, and Ru(bpy)$_3$Cl$_2$ did not afford the desired product at all. In the control experiments, no desired product was observed without the photosensitizer Acr$^+$-Mes, cobalt catalyst, or visible light, indicating that Acr$^+$-Mes and cobalt catalysts are essential for this transformation (Table 1, entries 9–11).

With the optimal conditions in hand, we attempted to explore the scope of the visible-light catalytic 1,2-dihydro-1-arylnaphthalene formation. As summarized in Scheme 2, most of the styrenes containing elec-

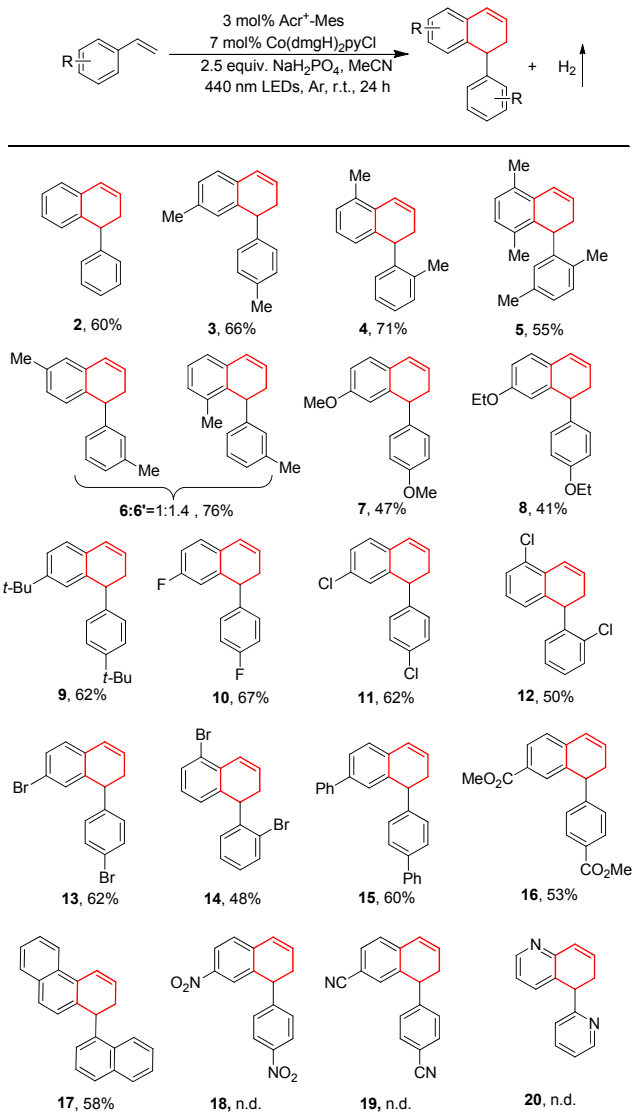
Table 1
Optimization of reaction conditions [a].



Entry	**1** (mmol)	Co catalyst	Yield [b] (%)
1	0.3	Co(dmgH)$_2$pyCl	35
2	0.5	Co(dmgH)$_2$pyCl	46
3	0.7	Co(dmgH)$_2$pyCl	56
4	1.0	Co(dmgH)$_2$pyCl	36
5	0.7	Co(dmgH)(dmgH$_2$)Cl$_2$	10
6	0.7	Co(dmgH)$_2$(4-CO$_2$Mepy)Cl	28
7	0.7	Co(dmgBF$_2$)$_2$(MeCN)$_2$	38
8 [c]	**0.7**	**Co(dmgH)$_2$pyCl**	**72**
9 [d]	0.7	Co(dmgH)$_2$pyCl	n.d.
10	0.7	—	n.d.
11 [e]	0.7	Co(dmgH)$_2$pyCl	n.d.
12 [f]	0.7	Co(dmgH)$_2$pyCl	n.d.



[a] Reaction conditions: corresponding **1**, Acr$^+$-Mes ClO_4^- (3 mol%), Co catalyst (7 mol%) in 5 mL of dry MeCN under argon atmosphere, irradiation with blue LEDs (λ = 440 nm), at room temperature for 24 h; [b] Yields detected by ^{1}H NMR, using diphenylacetonitrile as the internal standard; [c] 2.5 equiv. NaH_2PO_4; [d] Without Acr$^+$-Mes ClO_4^-; [e] In the dark; [f] In air.



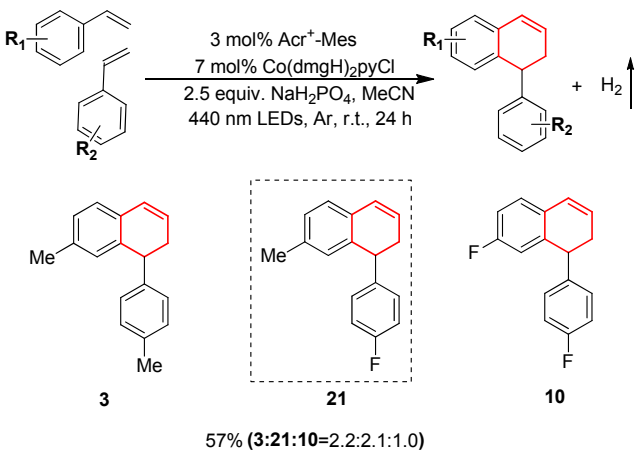
Scheme 2. Substrate scope for the dimerization of styrenes.

tron-withdrawing groups or electron-donating groups could afford the corresponding 1,2-dihydro-1-arylnaphthalenes in moderate yields under standard conditions. Meanwhile, styrenes with halo group substitution at the *ortho* or *para*-position were also smoothly converted into the 1,2-dihydro-1-arylnaphthalene products in moderate yields, which have the potential for further transformation. When a *meta*-methyl styrene derivative was employed in the reaction, two region-isomers **6** and **6'** were obtained. The presence of a methoxy group or ethyloxy group at the *para*-position of styrene afforded 1,2-dihydro-1-arylnaphthalene (**7**,**8**) in only 47% and 41% yields because of the formation of some unidentified byproducts. Styrene with a tertiary butyl substituent at the *para*-position also gave the desired product **9** in 62% yield. Interestingly, 2-vinyl-naphthalene also worked well for this protocol and afforded the product **17** in 58% yield. However, the electron-deficient 2-pyridylethylene failed to afford the corresponding annulation product, similar to the results observed for 4-nitrostyrene and 4-cyanogroup. A large gram-scale reaction (10 mmol **1** in 50 mL dry CH_3CN) was performed to obtain 1,2-dihydro-1-arylnaphthalene **2** in 55% yield after 48 h of irradiation.

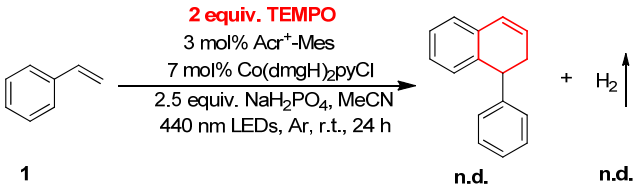
A cross-dimerization reaction using two styrenes with different substituents on the phenyl ring (e.g., a 1:1 mixture of 4-methylstyrene and 4-fluorostyrene) was also conducted (Scheme 3). The corresponding homodimerized and cross-dimerized products were obtained as a mixture (**3**:**21**:**10** = 2.2:2.1:1.0) in 57% total isolated yield, which further broadened the scope of our substrates.

Mechanistic studies were conducted to gain insights into the aforementioned transformation. When 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was used as the radical scavenger, no desired products were formed (Scheme 4), implying that radicals are involved in our reaction process. To shed more light on the process of the reaction, we examined the interaction between styrene **1** and the excited Acr^+-Mes. The luminescence of the excited Acr^+-Mes could be significantly quenched by **1** with a rate constant of 9.6×10^8 $(mol/L)^{-1}$ s^{-1}. On the other hand, $Co(dmgH)_2pyCl$ could also quench the luminescence of Acr^+-Mes with a quenching rate constant of 1.6×10^7 $(mol/L)^{-1}$ s^{-1}, which is two orders of magnitude smaller than that of **1**. The concentration of styrene was also much higher than that of $Co(dmgH)_2pyCl$. Thus, we considered that the excited Acr^+-Mes preferentially reacted with styrene than with $Co(dmgH)_2pyCl$ (Fig. 1(a)). Furthermore, upon irradiation, the absorption spectrum (Fig. 1(b)) of the system containing styrene, Acr^+-Mes, and $Co(dmgH)_2pyCl$ in degassed dry MeCN immediately exhibited absorption bands at 440–500 nm and 550–650 nm, which indicated the formation of Co^{II} and Co^{I} species, respectively, based on reports in the literature [49].

Based on the above results, we proposed a plausible mechanism for this reaction (Scheme 5). Photosensitizer Acr^+-Mes is



Scheme 3. Cross-over reaction between 4-methylstyrene and 4-fluorostyrene.



Scheme 4. Free radical capture experiment.

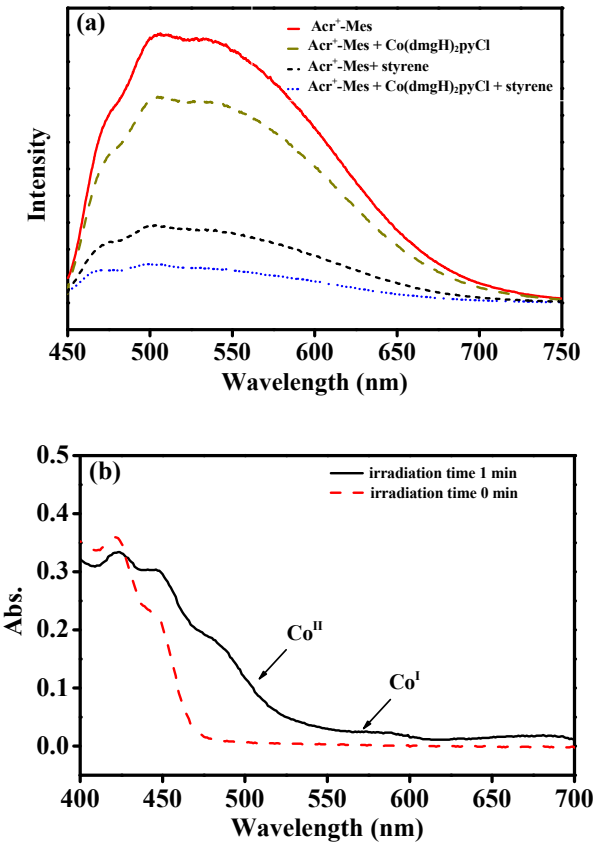
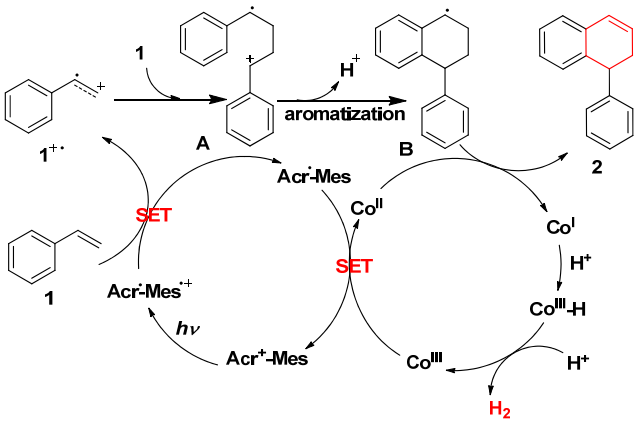


Fig. 1. (a) Emission spectra of Acr^+-Mes (0.03 mmol/L) in the absence and respective presence of $Co(dmgH)_2pyCl$ (0.07 mmol/L) (dash line) and styrene **1** (1.0 mmol/L, short dash line) in degassed dry CH_3CN, and Acr^+-Mes (0.03 mmol/L) in the presence of $Co(dmgH)_2pyCl$ (0.07 mmol/L), and styrene **1** (1.0 mmol/L) in degassed dry CH_3CN (dot line). (b) UV-vis absorption spectra of a mixture of Acr^+-Mes (0.03 mmol/L), $Co(dmgH)_2pyCl$ (0.07 mmol/L) and styrene **1** (1.0 mmol/L) in degassed dry MeCN before and after irradiation under blue LEDs.



Scheme 5. Possible mechanism.

irradiated by visible light to reach its excited state Acr•-Mes•+ ($E_{1/2}^{red}$ = + 2.06 V *vs.* SCE) [30–34], which undergoes single-electron transfer (SET) with styrene to generate styrene radical cation **1**+• and Acr•-Mes radical anion. Electrophilic trapping of intermediate **1**+• by a neutral alkene molecule gives distal 1,4-radical cation **A**, which readily undergoes Friedel–Crafts annulation to form intermediate **B** via deprotonation and aromatization. The generated Acr•-Mes radical anion donates an electron to $Co(dmgH)_2pyCl$ (Co^{III}) to produce Co^{II} species and regenerate the photosensitizer Acr+-Mes. The carbon- centered radical **B** is further oxidized by Co^{II} to afford Co^{I} species and product **2**. Protonation of the Co^{I} species provides Co^{III}-H [52,53], which can react with a proton to release H_2 eventually and regenerate the generate Co^{III} catalyst.

4. Conclusions

In summary, we have developed a hydrogen-evolution dimerization methodology for the synthesis of 1,2-dihydro-1-arylnaphthalenes by combining photocatalysis and proton reduction catalysis under visible-light irradiation. By using the dual catalyst system of photosensitizer Acr+-Mes and cobaloxime catalyst $Co(dmgH)_2pyCl$, various styrenes can be transformed into the desired products in moderate to good yields, and H_2 is the only byproduct. As opposed to previous methods, this reaction proceeds smoothly under extremely mild conditions, and no oxidized products (naphthalene derivatives) are produced. We believe that this methodology would be significant for application to a series of organic reactions.

References

[1] C. Canel, R. M. Moraes, F. E. Dayan, D. Ferreira, *Phytochemistry,* **2000**, 54, 115–120.

[2] H. M. L. Davies, X. Dai, M. S. Long, *J. Am. Chem. Soc.,* **2006**, 128, 2485–2490.

[3] L. F. Silva. Jr, F. A. Siqueira, E. C. Pedrozo, F. Y. M. Vieira, A. C. Doriguetto, *Org. Lett.,* **2007**, 9, 1433–1436.

[4] S. O. De Silva, C. St. Denis, R. Rodrigo, *J. Chem. Soc. Chem. Comm.,* **1980**, 995–997.

[5] V. Nair, V. Sheeba, S. B. Panicker, T.G. George, R. Rajan, L. Balagopal, M. Vairamani, S. Prabhakar, *Tetrahedron,* **2000**, 56, 2461–2467.

[6] B. L. Yvon, P. K. Datta, T.N. Le, J. L. Charlton, *Synthesis,* **2001**, 1556–1560.

[7] T. Linker, F. Rebien, G. Toth, A. Simon, J. Kraus, G. Bringmann, *Chem. Eur. J.,* **1998**, 4, 1944–1951.

[8] J. C. T. Reddel, K. E. Lutz, A. B. Diagne, R. J. Thomson, *Angew. Chem. Int. Ed.,* **2014**, 53, 1395–1398.

[9] R. R. Malladi, N. S. Li, D. Tejedor, G. W. Kabalka, *Synth. Commun.,* **2000**, 30, 3613–3616.

[10] K. Maeda, E. J. Farrington, E. Galardon, B. D. John, J. M. Brown, *Adv. Synth. Catal.,* **2002**, 344, 104–109.

[11] C. K. Chan, N. C. Hsueh, Y. L. Tsai, M. Y. Chang, *J. Org. Chem.,* **2017**, 82, 7077–7084.

[12] K. R. Kopecky, M. C. Hall, *Can. J. Chem.,* **1981**, 59, 3095–3104.

[13] M. Y. Chang, Y. C. Cheng, *Org. Lett.,* **2016**, 18, 1682–1685.

[14] J. J. M. Lamberts, T. J. H. M. Cuppen, W. H. Laarhoven, *J. Chem. Soc. Perkin Trans.,* **1985**, 1819–1827.

[15] J. Yun, S. L. Buchwald, *J. Org. Chem.,* **2000**, 65, 767–774.

[16] T. Kudoh, T. Mori, M. Shirahama, M. Yamada, T. Ishikawa, S. Saito, H. Kobayashi, *J. Am. Chem. Soc.,* **2007**, 129, 4939–4947.

[17] Z. Yu, W. Dan, H. Jie, Z. Li, *Med. Chem. Res.,* **2009**, 19, 71–76.

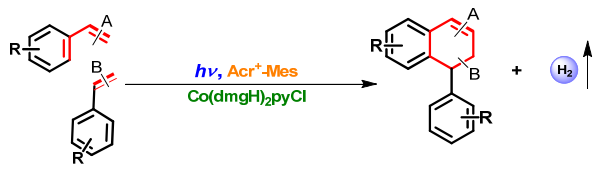
[18] M. L. N. Rao, D. N. Jadhav, V. Venkatesh, *Eur. J. Org. Chem.,* **2009**, 2009, 4300–4306.

Graphical Abstract

Chin. J. Catal., 2018, 39: 1194–1201 doi: 10.1016/S1872-2067(18)63095-5

Photocatalytic hydrogen-evolution dimerization of styrenes to synthesize 1,2-dihydro-1-arylnaphthalene derivatives using Acr+-Mes and cobaloxime catalysts

Wenxiao Cao, Chengjuan Wu, Tao Lei, Xiulong Yang, Bin Chen *, Chenho Tung, Lizhu Wu *
Technical Institute of Physics and Chemistry, Chinese Academy of Sciences; University of Chinese Academy of Sciences



By combining Acr+-Mes and cobaloxime catalysts, hydrogen-evolution dimerization of styrenes has been achieved without the use of oxidants or HAT reagents. This reaction proceeds smoothly under mild conditions, and the sole byproduct is hydrogen gas.

[19] V. Gudla, R. Balamurugan, *Chem. Asian J.,* **2013**, 8, 414–428.
[20] K. Wang, L. G. Meng, Q. Zhang, L. Wang, *Green Chem.,* **2016**, 18, 2864–2870.
[21] Y. L. Liu, M. F. Zhang, C. H. Tung, Y. F. Wang, *Acs Catal.,* **2016**, 6, 8389–8394.
[22] E. P. Farney, T. P. Yoon, *Angew. Chem. Int. Ed.,* **2014**, 53, 793–797.
[23] J. Liu, Q. Liu, H. Yi, C. Qin, R. P. Bai, X. T. Qi, Y. Lan, A. W. Lei. *Angew. Chem. Int. Ed.,* **2014**, 53, 502–506.
[24] S. M. Stevenson, M. P. Shores, E. M. Ferreira, *Angew. Chem. Int. Ed.,* **2015**, 54, 6506–6510.
[25] C. J. Wu, W. X. Cao, T. Lei, Z. H. Li, Q. Y. Meng, X. L. Yang, B. Chen, V. Ramamurthy, C. H. Tung, L. Z. Wu, *Chem. Commun.,* **2017**, 53, 8320–8323.
[26] P. K. Pei, F. Zhang, H. Yi, A. W. Lei, *Acta Chim. Sin.*, **2017**, 75, 15-21
[27] X. Y. Yu, F. Zhou, J. R. Chen, W. J. Xiao, *Acta Chim. Sin.*, **2017**, 75, 86–91.
[28] L. F. Wang, F. J. Wu, J. A. Chen, D. A. Nicewicz, Y. Huang, *Angew. Chem. Int. Ed.,* 2017, **56**, 6896–6900.
[29] D. L. Wei, Y. R. Li and F. S. Liang, *Adv. Synth. Catal.,* **2016**, 358, 3887–3896.
[30] S. Fukuzumi, H. Kotani, K. Ohkubo, S. Ogo, N. V. Tkachenko, H. Lemmetyinen. *J. Am. Chem. Soc.,* **2004**, 126, 1600–1601.
[31] H. Kotani, K. Ohkubo, S. Fukuzumi, *J. Am. Chem. Soc.,* **2004**, 126, 15999–16006.
[32] K. Ohkubo, K. Mizushima, R. Iwata, K. Souma, N. Suzuki, S. Fukuzumi, *Chem. Commun.,* **2010**, 46, 601–603.
[33] D. A. Nicewicz, T. Nguyen, *ACS Catal.,* **2014**, 4, 355–360.
[34] N. A. Romero, D. A. Nicewicz, *Chem. Rev.,* **2016**, 116, 10075–10166.
[35] J. L. Dempsey, B. S. Brunschwig, J. R. Winkler, H. B. Gray, *Acc. Chem. Res.,* **2009**, 42, 1995–2004.
[36] A. Bhattacharjee, M. Chavarot-Kerlidou, E. S. Andreiadis, M. Fontecave, M. J. Field, V. Artero, *Inorg. Chem,* **2012**, 51, 7087–7093.
[37] P. W. Du, R. Eisenberg, *Energy Environ. Sci.,* **2012**, 5, 6012–6021.
[38] Q. Y. Meng, J. J. Zhong, Q. Liu, X. W. Gao, H. H. Zhang, T. Lei, Z. J. Li, K. Feng, B. Chen, C. H. Tung, L. Z. Wu, *J. Am. Chem. Soc.,* **2013**, 135, 19052–19055.
[39] J. J. Zhong, Q. Y. Meng, B. Liu, X. B. Li, X. W. Gao, T. Lei, C. J. Wu, Z. J. Li, C. H. Tung, L. Z. Wu, *Org. Lett.,* **2014**, 16, 1988–1991.
[40] X. W. Gao, Q. Y. Meng, J. X. Li, J. J. Zhong, T. Lei, X. B. Li, C. H. Tung, L. Z. Wu, *ACS Catal.,* **2015**, 5, 2391–2396.
[41] M. Xiang, Q. Y. Meng, J. X. Li, Y. W. Zheng, C. Ye, Z. J. Li, B. Chen, C. H. Tung, L. Z. Wu, *Chem. Eur. J.*, **2015**, 21, 18080–18084.
[42] G. T. Zhang, C. Liu, H. Yi, Q. Y. Meng, C. L. Bian, H. Chen, J. X. Jian, L. Z. Wu, A. W. Lei, *J. Am. Chem. Soc.*, **2015**, 137, 9273–9280.
[43] C. J. Wu, Q. Y. Meng, T. Lei, J. J. Zhong, W. Q. Liu, L. M. Zhao, Z. J. Li, B. Chen, C. H. Tung, L. Z. Wu, *ACS Catal.,* **2016**, 6, 4635–4639.
[44] Y. W. Zheng, B. Chen, P. Ye, K. Feng, W. G. Wang, Q. Y. Meng, L. Z. Wu, C. H. Tung, *J. Am. Chem. Soc.,* **2016**, 138, 10080–10083.
[45] G. T. Zhang, X. Hu, C. W. Chiang, H. Yi, P. K. Pei, A. K. Singh, A. W. Lei, *J. Am. Chem. Soc.,* **2016**, 138, 12037–12040.
[46] G. T. Zhang, L. L. Zhang, H. Yi, Y. Luo, X. T. Qi, C. H. Tung, L. Z. Wu, A. W. Lei, *Chem. Commun.,* **2016**, 52, 10407–10410.
[47] L. B. Niu, H. Yi, S. C. Wang, T. Y. Liu, J. M. Liu, A. W. Lei, *Nat. Commun.*, **2017**, 8, 14226–16223.
[48] H. Yi, L. B. Niu, C. L. Song, Y. Y. Li, B. W. Dou, A. K. Singh, A. W. Lei, *Angew. Chem. Int. Ed.,* **2017**, 56, 1120–1124.
[49] X. Hu, G. T. Zhang, F. X. Bu, X. Luo, K. B. Yi, H. Zhang, A. W. Lei, *Chem. Sci.*, **2018**, 9, 1521–1526.
[50] X. Hu, G. T. Zhang, F. X. Bu, A. W. Lei, *Angew. Chem. Int. Ed.,* **2018**, 57, 1286–1290.
[51] P. W. Du, K. Knowles, R. Eisenberg, *J. Am. Chem. Soc.,* **2008**, 130, 12576–12577.
[52] N. A. Romero, D. A. Nicewicz, *J. Am. Chem. Soc.,* **2014**, 136, 17024–17035.
[53] P. A. Jacques, V. Artero, J. Pecaut, M. Fontecave, *Proc. Natl. Acad. Sci. USA,* **2009**, 106, 20627–20632.

吖啶和钴肟配合物协同光催化苯乙烯放氢二聚反应构筑 1,2-二氢-1-芳基萘

曹文晓[a,b], 吴成娟[a], 雷　涛[a], 杨修龙[a], 陈　彬[a,b,*], 佟振合[a,b], 吴骊珠[a,b,#]
[a]中国科学院理化技术研究所, 光化学转换与功能材料重点实验室, 北京 100190
[b]中国科学院大学, 北京 100049

摘要: 芳基二氢萘类衍生物是许多生物活性的天然产物以及药物的常见结构单元, 其合成一直都受到化学家们的关注. 传统的 1,2-二氢-1-芳基萘骨架化合物的构筑大都需要进行底物的预官能团化, 在高温条件下进行, 且产物的选择性较差, 因此发展一种简单温和的制备方法很有必要. 最近兴起的可见光催化因具有条件温和、环境友好等特点而成为了合成化学家的研究热点. 近期研究发现, 在可见光作用下利用吖啶光敏剂的强氧化能力, 可以实现苯乙烯的加成. 但此类反应需要当量的氧化剂或氢原子转移试剂, 容易导致苯乙烯的二聚环合产物的进一步氧化或还原. 我们在前期发展的“放氢交叉偶联”反应的基础上, 利用吖啶光催化和钴肟催化的协同作用, 实现了苯乙烯的放氢二聚反应, 在室温下高效构筑了 1,2-二氢-1-芳基萘骨架, 反应条件温和, 底物脱除的电子和质子在钴肟催化剂作用下以氢气的形式释放, 反应具有中等及以上的收率.

本文以苯乙烯为模型底物, 吖啶为光敏剂, 钴肟配合物为质子还原催化剂, 在乙腈溶剂中, 蓝色 LED 灯下光照 24 h 可以获得 56% 的产率, 对于其它的光敏剂如 *fac*-Ir(ppy)$_3$ 等则不能催化该反应. 通过催化剂种类及用量筛选表明, 7 mol% 的 Co(dmgH$_2$)pyCl 配合物具有最好的反应效果, 可以获得 72% 的收率. 控制实验表明, 光敏剂、钴肟催化剂和光照都是必须的. 通过底物拓展我们发现, 烷基、卤素等不同取代基的苯乙烯类化合物均可以获得较好的收率, 不同苯乙烯之间也可以发生交叉反应.

随后, 我们进一步通过光谱和中间体捕获实验对反应机理进行了研究. 自由基捕获实验说明反应过程可能涉及自由基历程; 光谱淬灭实验表明苯乙烯和 Co(dmgH$_2$)pyCl 均可淬灭吖啶的发光, 但苯乙烯淬灭吖啶的程度远大于

$Co(dmgH_2)pyCl$ 淬灭吖啶的程度. 在反应时苯乙烯的浓度远大于催化剂的溶度, 因此, 我们认为激发态吖啶首先与苯乙烯发生反应; 可见光照射反应体系 1 min 后在 440–500 和 550–650 nm 处观察到明显的 Co^{II} 和 Co^{I} 的吸收峰. 基于以上实验结果, 我们提出了可能的催化循环: 吖啶受光激发到达激发态后, 首先与底物苯乙烯发生单电子转移生成苯乙烯正离子自由基和吖啶阴离子自由基 $Acr^{\bullet}$-Mes, $Acr^{\bullet}$-Mes 还原 $Co(dmgH_2)pyCl$ 生成 Co^{II} 中间体, 从而回到基态完成光催化循环. 苯乙烯正离子自由基与另一分子苯乙烯加成环合, 进而通过芳构化生成自由基中间体, 再与 Co^{II} 作用生成目标产物 1,2-二氢-1-芳基萘和 Co^{I}, Co^{I} 通过结合体系中的质子进而释放出氢气回到 Co^{III} 从而完成钴肟催化循环.

关键词: 放氢二聚; 苯乙烯; 1,2-二氢-1-芳基萘; 光催化; 钴肟催化剂

收稿日期: 2018-04-20. 接受日期: 2018-04-27. 出版日期: 2018-07-05.

*通讯联系人. 电话/传真: (010)82543576; 电子信箱: chenbin@mail.ipc.ac.cn

#通讯联系人. 电话/传真: (010)82543580; 电子信箱: lzwu@mail.ipc.ac.cn

基金来源: 中国科技部 (2014CB239402, 2017YFA0206903); 国家自然科学基金 (21390404); 中科院战略性先导科技专项（B类）项目 (XDB17000000); 中科院前沿科学重点研究计划项目 (QYZDY-SSW-JSC029).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(http://www.sciencedirect.com/science/journal/18722067).