三(三甲硅基)硅烷/氧气促进和可见光加速烷基碘向醇的转化

李健羽 曾金龙 陈剑锋* 赵宝国*

(上海师范大学化学与材料科学学院 资源化学教育部重点实验室和上海市稀土功能材料重点实验室 上海 200234)

摘要 发展了一种由烷基碘向醇转化的温和方法. 该反应的发生需要三(三甲硅基)硅烷/氧气存在, 同时可以通过可见光照射加速. 不同类型的烷基碘化物, 如一级、二级和三级烷基碘化物都能顺利发生反应, 以 38%~99% 的收率得到相应的醇化合物.

关键词 三(三甲硅基)硅烷; 光催化; 碳自由基; 烷基碘; 醇

Tris(trimethylsilyl)silane/O₂-Promoted and Photo-accelerated Conversion of Alkyl Iodides to Alcohols

Li, Jianyu Zeng, Jinlong Chen, Jianfeng* Zhao, Baoguo*

(Key Laboratory of Resource Chemistry of Ministry of Education and Shanghai Key Laboratory of Rare Earth Functional Materials, College of Chemistry and Materials Science, Shanghai Normal University, Shanghai 200234)

Abstract A mild method for the conversion of alkyl iodides to alcohols was developed. The transformation was promoted by tris(trimethylsilyl)silane/O₂ and accelerated by photoredox catalysis under visible light irradiation conditions. Various alkyl iodides, including primary, secondary and tertiary iodides, can be smoothly converted to the corresponding alcohols in 38%~99% yields.

Keywords tris(trimethylsilyl)silane; photoredox catalysis; carbon radical; alkyl iodide; alcohol

1 Introduction

The conversion of alkyl halides to alcohols is an important transformation in organic synthesis.^[1] The conversion can be achieved by direct hydroxylation of alkyl halides with hydroxyl anion or nucleophilic substitution with oxygenated reagents such as acetate or formate via two-step processes.^[1-2] However, these traditional approaches are mainly applied to primary alkyl halides and often suffer from β -elimination side reactions. The C—X bonds undergo heterolytic cleavage during the replacement of the halogen atoms. On the other hand, homolysis of the C—X bonds to generate carbon radicals followed by oxygenated with appropriate O-reagents may provide an alternative method for the transformation from alkyl halides to alcohols.^[3-5] For example, Nakamura *et al.*^[3] found that Bu₃SnH/O₂ could promote the conversion of alkyl bromides and iodides to alcohols (Scheme 1, a). Reductive cleavage of the carbon-halogen bond by the tin hydride

generated carbon radical intermediates, which were trapped with O₂ and then reduced by Bu₃SnH to form alcohol products. Under UV light irradiation conditions, the transformation can be realized without the toxic tin hydride reagent (Scheme 1, b).^[4] In the presence of a photoredox catalyst,^[6] visible light irradiation also promoted the transformation from benzyl halides to alcohols (Scheme 1, c).^[5] Recently, we found that alkyl iodides can be smoothly converted to the corresponding alcohols in moderate to good yields in the presence of (SiMe₃)₃SiH^[7] and air under photoredox catalyzed visible light irradiation conditions (Scheme 1, d). The reaction worked well for primary, secondary as well as tertiary iodides. Herein, we report the preliminary results on this project.

2 Results and discussion

Initial investigation was carried out with alkyl iodide **1a** as the standard substrate due to its high fluorescence

* Corresponding authors. E-mail: jfchen@shnu.edu.cn; zhaobg2006@shnu.edu.cn

Received June 26, 2020; revised August 5, 2020; published online August 18, 2020.

Dedicated to the 40th anniversary of Chinese Journal of Organic Chemistry.

Project supported by the National Natural Science Foundation of China (No. 21672148), the Shanghai Municipal Education Commission (No. 2019-01-07-00-02-E00029) and the Shanghai Engineering Research Center of Green Energy Chemical Engineering.

国家自然科学基金(No. 21672148)、上海市教育委员会(No. 2019-01-07-00-02-E00029)和上海市绿色能源化工工程研究中心资助项目.

(a) Bu₃SnH/O₂ promoted conversion of alkyl halides to alcohols

(b) UV light-induced conversion of alkyl halides to alcohols

(c) Visible light-induced conversion of arylmethyl bromides to alcohols

(d) This work: TTMSS/O₂-promoted and photo-accelerated alkyl iodides to alcohols

Scheme 1 Strategies for the conversion of alkyl halides to alcohols via carbon radical processes

intensity for thin-layer chromatography (TLC) analysis (Table 1). In the presence of 1 mol% of [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ as the photoredox catalyst,^[8,9] compound **1a** was treated with tris(trimethylsilyl)silane (TTMSS) in *N,N*-dimethylformamide (DMF) under air atmosphere and blue LED light irradiation to produce alcohol **2a** in 94% yield with a trace amount of reduction by-product **3a** (Table, Entry 1). Change of the solvent from DMF to dimethylacetamide (DMA) or dimethyl sulfoxide (DMSO) resulted in decreased yields of **2a** (Table 1, Entries 2 and 3 vs 1). Silyl reagent TTMSS and O₂ both are crucial for the reaction. Without TTMSS or O₂, no or a trace amount of alcohol product **2a** was detected under otherwise the same conditions (Table 1, Entries 4 and 5). The absence of photoredox catalyst or/and LED light led to much lower yields of **2a** (Table 1, Entries 6~8), indicating the photoredox catalyzed irradiation can efficiently accelerate the transformation. In the absence of Na₂CO₃, the reaction became very messy, leading to an obvious decrease of the yield of **2a** (Table 1, Entry 9).

Under the optimal conditions, substrate scope was investigated for the transformation from alkyl halides to alcohols (Table 2). Various primary (for **2a**~**2k**), secondary (for **2l**~**2p**) and tertiary (for **2q** and **2r**) alkyl iodides were all effective substrates for the reaction, to give the corresponding alcohols in 38%~99% yields. Heteroaromatic rings such as thiophene (for **2j**) and heteroatomic groups such as ether (for **2h**) and piperine cycles (for **2o** and **2p**) were all well tolerated. Cyclic iodides could be smoothly converted to the alcohol products (for **2m**, **2s**, and **2t**) but with low *trans/cis* selectivity, likely due to the nature of the radical process. Under the reaction conditions, only a trace amount of benzylic alcohol was obtained from benzylic iodide. Alkyl bromides such as (3-bromobutyl)benzene and alkyl chlorides such as (3-chloropropyl)benzene are both ineffective for the reaction.

Table 1 Investigation of the impact of reaction conditions on the TTMSS/O₂ promoted conversion of alkyl iodides to alcohols^a

Entry	Conditions	Yield ^b /%		Recovered 1a ^b /%
		2a	3a	
1	As shown	94	Trace	0
2	DMA instead of DMF	86	Trace	7
3	DMSO instead of DMF	24	6	31
4	No TTMSS	4	0	95
5	Under N ₂ atmosphere	0	99	0
6	No photoredox catalyst	33	2	63
7	No blue LEDs	39	0	57
8	No photocatalyst and no blue LED	32	0	65
9	No Na ₂ CO ₃	32	6	15

^a The reaction was carried out with **1a** (0.10 mmol), TTMSS (0.22 mmol), Na₂CO₃ (0.10 mmol), [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (0.0010 mmol) in DMF (1.0 mL) under 8 W blue LED light irradiation at room temperature for 24 h unless otherwise stated. ^b The NMR yields of **2a** and **3a** and the recovery percentage of **1a** were determined by ¹H NMR analysis of the crude reaction mixture.

Introducing a radical-trapping reagent, 2,2,6,6-tetramethylpiperidine 1-oxyl free radical (2,2,6,6-Tetramethylpiperidinoxy, TEMPO) (**4**), to the reaction system resulted in the formation of a trace amount of alcohol product **2a** along with compound **5** in 14% yield (Scheme 2), demonstrating that a carbon radical related to alkyl iodide **1a** was involved in the reaction.

3 Conclusions

In summary, we have developed an interesting method for the transformation from alkyl iodides to alcohols with a wide substrate scope. Various types of alkyl iodides were efficiently converted to alcohols in 38%~99% yields by TTMSS/O₂ under mild conditions. The visible light photoredox catalysis condition can accelerate the transformation greatly.

4 Experimental section

4.1 General method

All commercially available reagents were used without further purification unless otherwise stated. Column chromatography was performed on silica gel (200~300 mesh).

Table 2 Substrate scope investigation for the transformation from alkyl iodides to alcohols^a

^a All the reactions were carried out with **1** (0.20 mmol), TTMSS (0.44 mmol), Na₂CO₃ (0.20 mmol), [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (0.0020 mmol) in DMF (2.0 mL) under 8 W blue LED light irradiation at room temperature for 24 h. The isolated yields of **2** were based on **1**. ^b The *cis/trans* ratio was determined as 1 : 1.1 by ¹H NMR analysis of the crude reaction mixture. ^c The *dr* value (epicholesterol/cholesterol) was determined as 1 : 1.3 by ¹H NMR analysis of the crude reaction mixture. ^d The *dr* value was determined as 2.5 : 1 by ¹H NMR analysis of the crude reaction mixture.

Scheme 2 Carbon radical capturing with TEMPO

¹H NMR spectra were recorded on a 400 MHz NMR spectrometer and ¹³C NMR spectra were recorded on a 100 MHz NMR spectrometer. ¹H NMR and ¹³C NMR shifts were referenced to CDCl₃ (δ_H 7.26, δ_C 77.16).

The photoredox catalyst [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ was prepared according to literature method^[19a].

The alkyl iodides **1a**~**1g**, **1i**~**1p** and **1s**~**1t** were synthesized by the reaction of the corresponding alcohols with I₂, PPh₃ and imidazole according to the literature procedure.^[10a] **1q**~**1r** were prepared from the corresponding alcohols via the reaction with KI and methanesulfonic acid in acetonitrile according to the literature procedure.^[10b] **1h** was prepared from methylparaben via the reaction with diiodopropane according to the literature procedure.^[10c]

4.2 Representative produce for the conversion of alkyl iodides to alcohols (Table 2, for **2a**)

To a 10 mL vial equipped with a magnetic stirrer were added [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (2.5 mg, 0.0020 mmol), Na₂CO₃ (21.2 mg, 0.20 mmol), 4-(3-iodopropyl)-1,1'-biphenyl (**1a**) (64 mg, 0.20 mmol) and DMF (2.0 mL). To the mixture was added tris(trimethylsilyl)silane (TTMSS) (110 mg, 0.44 mmol). The reaction vial was opened to the air, irradiated with 8W blue LEDs from 13 cm away, and cooled with an electronic fan. After stirring at room temperature for 24 h, ethyl acetate (20 mL) and

brine (20 mL) were added to the mixture. The organic layer was separated, washed with brine (20 mL × 2), dried over Na₂SO₄, filtered, concentrated, and purified by chromatography on silica gel [*V*(petroleum ether) : *V*(ethyl acetate) = 10 : 1] to give 3-([1,1'-biphenyl]-4-yl)propan-1-ol (**2a**)^[11a] (39.8 mg, 94%) as a white solid. m.p. 72~74 °C (Lit.^[11b] 60~63 °C); ¹H NMR (400 MHz, CDCl₃) δ: 7.59 (d, *J*=7.2 Hz, 2H), 7.53 (d, *J*=8.0 Hz, 2H), 7.44 (t, *J*=7.2 Hz, 2H), 7.34 (t, *J*=7.2 Hz, 1H), 7.29 (d, *J*=8.0 Hz, 2H), 3.72 (t, *J*=6.4 Hz, 2H), 2.77 (t, *J*=7.6 Hz, 2H), 1.99~1.90 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 141.2, 141.1, 139.0, 129.0, 128.8, 127.3, 127.2, 127.1, 62.4, 34.3, 31.8.

Compounds **2b**~**2t** were prepared according to the synthetic method of compound **2a**.

2-Phenylethan-1-ol (**2b**):^[11c] Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ: 7.36~7.30 (m, 2H), 7.27~7.21 (m, 3H), 3.87 (t, *J*=6.8 Hz, 2H), 2.88 (t, *J*=6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 138.6, 129.1, 128.7, 126.6, 63.8, 39.3.

3-Phenylpropan-1-ol (**2c**):^[11c] Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ: 7.32~7.26 (m, 2H), 7.23~7.16 (m, 3H), 3.68 (t, *J*=6.4 Hz, 2H), 2.72 (t, *J*=7.6 Hz, 2H), 1.95~1.85 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 141.9, 128.55, 128.53, 126.0, 62.4, 34.3, 32.2.

5-Phenylbutan-1-ol (**2d**):^[11d] Colorless oil. ¹H NMR

(400 MHz, CDCl₃) δ : 7.31~7.26 (m, 2H), 7.21~7.16 (m, 3H), 3.66 (t, J =6.4 Hz, 2H), 2.65 (t, J =7.2 Hz, 2H), 1.76~1.66 (m, 2H), 1.66~1.57 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 142.5, 128.5, 128.4, 125.9, 63.0, 35.8, 32.5, 27.7.

5-Phenylpentan-1-ol (**2e**):^[11e] Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ : 7.31~7.25 (m, 2H), 7.21~7.16 (m, 3H), 3.64 (t, J =6.8 Hz, 2H), 2.63 (t, J =7.6 Hz, 2H), 1.71~1.56 (m, 4H), 1.47~1.36 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 142.7, 128.5, 128.4, 125.8, 63.0, 36.0, 32.7, 31.4, 25.5.

2-Phenylpropan-1-ol (**2f**):^[11f] Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ : 7.38~7.31 (m, 2H), 7.27~7.22 (m, 3H), 3.71 (d, J =6.8 Hz, 2H), 3.01~2.91 (m, 1H), 1.28 (d, J =6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 143.8, 128.8, 127.6, 126.8, 68.9, 42.6, 17.7.

Methyl 4-(3-hydroxypropyl)benzoate (**2g**):^[11g] Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ : 7.95 (d, J =8.0 Hz, 2H), 7.27 (d, J =8.0 Hz, 2H), 3.90 (s, 3H), 3.67 (t, J =6.4 Hz, 2H), 2.77 (t, J =8.0 Hz, 2H), 1.95~1.85 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 167.3, 147.6, 129.8, 128.6, 62.0, 52.1, 33.9, 32.2.

Methyl 4-(3-hydroxypropoxy)benzoate (**2h**):^[11h] White solid, m.p. 52~53 °C (Lit.^[11i] 54 °C); ¹H NMR (400 MHz, CDCl₃) δ : 7.97 (d, J =9.2 Hz, 2H), 6.91 (d, J =9.2 Hz, 2H), 4.16 (t, J =6.0 Hz, 2H), 3.87 (s, 3H), 3.86 (t, J =6.0 Hz, 2H), 2.10~2.02 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 167.0, 162.7, 131.7, 122.7, 114.2, 65.6, 59.9, 52.0, 32.0.

2-(Naphthalen-1-yl)ethan-1-ol (**2i**):^[11i] White solid, m.p. 59~61 °C (Lit.^[11j] 63~65 °C); ¹H NMR (400 MHz, CDCl₃) δ : 8.06 (d, J =8.0 Hz, 1H), 7.87 (d, J =8.0 Hz, 1H), 7.77 (d, J =8.0 Hz, 1H), 7.57~7.46 (m, 2H), 7.46~7.34 (m, 2H), 4.00 (t, J =6.8 Hz, 2H), 3.36 (t, J =6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 134.5, 134.1, 132.2, 129.0, 127.5, 127.3, 126.2, 125.8, 125.6, 123.8, 63.2, 36.4.

2-(Thiophen-2-yl)ethan-1-ol (**2j**):^[11k] Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ : 7.18 (d, J =5.2 Hz, 1H), 6.96 (dd, J =5.2, 3.2 Hz, 1H), 6.88 (d, J =3.2 Hz, 1H), 3.86 (t, J =6.4 Hz, 2H), 3.09 (t, J =6.4 Hz, 2H), 1.68 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ : 140.9, 127.1, 125.7, 124.1, 63.6, 33.4.

6-((*Tert*-butyldiphenylsilyloxy)hexan-1-ol (**2k**):^[11l] Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ : 7.69~7.64 (m, 4H), 7.45~7.35 (m, 6H), 3.69~3.59 (m, 4H), 1.63~1.50 (m, 4H), 1.44~1.28 (m, 4H), 1.05 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ : 135.7, 134.3, 129.6, 127.7, 64.0, 63.1, 32.9, 32.6, 27.0, 25.7, 25.6, 19.4.

4-Phenylbutan-2-ol (**2l**):^[11m] Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ : 7.32~7.26 (m, 2H), 7.23~7.17 (m, 3H), 3.89~3.78 (m, 1H), 2.82~2.62 (m, 2H), 1.87~1.71 (m, 2H), 1.24 (d, J =6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 142.2, 128.5, 125.9, 67.6, 41.0, 32.3, 23.8.

4-Phenylcyclohexan-1-ol (**2m**):^[11n-11q] *cis*-**2m**: White solid, m.p. 97~100 °C (Lit.^[11r] 76~77 °C); ¹H NMR (400 MHz, CDCl₃) δ : 7.33~7.27 (m, 2H), 7.27~7.22 (m, 2H), 7.22~7.15 (m, 1H), 4.16~4.10 (m, 1H), 2.60~2.47

(m, 1H), 1.97~1.82 (m, 4H), 1.74~1.62 (m, 4H); ¹³C NMR (150 MHz, CDCl₃) δ : 147.5, 128.5, 127.0, 126.1, 65.8, 44.0, 33.2, 27.9. *trans*-**2m**: White solid, m.p. 109~113 °C (Lit.^[11r] 118~118.5 °C); ¹H NMR (400 MHz, CDCl₃) δ : 7.33~7.27 (m, 2H), 7.24~7.17 (m, 3H), 3.75~3.65 (m, 1H), 2.55~2.45 (m, 1H), 2.17~1.88 (m, 4H), 1.65~1.38 (m, 5H); ¹³C NMR (150 MHz, CDCl₃) δ : 146.7, 128.5, 126.9, 126.2, 70.8, 43.6, 36.1, 32.6.

2,3-Dihydro-1*H*-inden-2-ol (**2n**):^[11s] White solid, m.p. 62~63 °C (Lit.^[11t] 67~69 °C); ¹H NMR (400 MHz, CDCl₃) δ : 7.28~7.22 (m, 2H), 7.21~7.16 (m, 2H), 4.73~4.67 (m, 1H), 3.22 (dd, J =16.4, 6.0 Hz, 2H), 2.92 (dd, J =16.0, 3.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 140.9, 126.8, 125.1, 73.4, 42.8.

1-Tosylpiperidin-4-ol (**2o**):^[11p] Yellow solid, m.p. 126~128 °C (Lit.^[11u] 130~132 °C); ¹H NMR (400 MHz, CDCl₃) δ : 7.64 (d, J =8.0 Hz, 2H), 7.32 (d, J =8.0 Hz, 2H), 3.80~3.70 (m, 1H), 3.35~3.25 (m, 2H), 2.88~2.78 (m, 2H), 2.43 (s, 3H), 1.98~1.88 (m, 2H), 1.70~1.60 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 143.7, 133.3, 129.8, 127.7, 66.0, 43.3, 33.3, 21.6.

(4-Hydroxypiperidin-1-yl)(phenyl)methanone (**2p**):^[11p] White solid, m.p. 83~86 °C (Lit.^[11v] 82~84 °C); ¹H NMR (400 MHz, CDCl₃) δ : 7.43~7.35 (m, 5H), 4.35~4.08 (m, 1H), 4.00~3.92 (m, 1H), 3.80~3.57 (m, 1H), 3.50~3.28 (m, 1H), 3.28~3.08 (m, 1H), 2.06~1.90 (m, 1H), 1.90~1.73 (m, 2H), 1.70~1.40 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ : 170.5, 136.1, 129.7, 128.6, 126.8, 67.0, 45.0, 39.5, 34.6, 33.9.

2-Methyl-4-phenylbutan-2-ol (**2q**):^[11w] Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ : 7.32~7.25 (m, 2H), 7.23~7.15 (m, 3H), 2.75~2.67 (m, 2H), 1.84~1.75 (m, 2H), 1.30 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ : 142.7, 128.5, 128.4, 125.9, 71.1, 45.9, 30.9, 29.5.

Adamantan-1-ol (**2r**):^[11s] White solid, m.p. 210~211 °C (Lit.^[11x] 220 °C sublimes); ¹H NMR (400 MHz, CDCl₃) δ : 2.18~2.09 (m, 3H), 1.71 (d, J =2.8 Hz, 6H), 1.67~1.55 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ : 68.3, 45.4, 36.2, 30.8.

Compound **2s**: White solid. epicholesterol-**2s**:^[11y] m.p. 119~120 °C (Lit.^[11y] 135~136 °C); ¹H NMR (400 MHz, CDCl₃) δ : 5.43~5.38 (m, 1H), 4.04~3.97 (m, 1H), 2.62~2.52 (m, 1H), 2.10~0.95 (m, 30H), 0.91 (d, J =6.4 Hz, 3H), 0.86 (d, J =6.4 Hz, 6H), 0.68 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ : 138.7, 124.2, 67.3, 56.9, 56.3, 50.5, 42.5, 40.0, 39.9, 39.7, 37.5, 36.3, 36.0, 33.4, 32.1, 32.0, 29.1, 28.4, 28.2, 24.4, 24.0, 23.0, 22.7, 21.0, 18.9, 18.8, 12.0. cholesterol-**2s**:^[11z] m.p. 141~143 °C (Lit.^[11aa] 147~152 °C); ¹H NMR (400 MHz, CDCl₃) δ : 5.37~5.32 (m, 1H), 3.58~3.46 (m, 1H), 2.35~2.17 (m, 2H), 2.05~0.95 (m, 29H), 0.91 (d, J =5.6, 1.6 Hz, 3H), 0.86 (d, J =6.4 Hz, 6H), 0.67 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ : 140.9, 121.9, 72.0, 56.9, 56.3, 50.3, 42.48, 42.46, 39.9, 39.7, 37.4, 36.7, 36.4, 35.9, 32.07, 32.06, 31.8, 28.4, 28.2, 24.5, 24.0, 23.0, 22.7, 21.2, 19.6, 18.9, 12.0.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexan-1-ol (**2t**):^[11ab] White solid. m.p. 40~41 °C (Lit.^[11ac] 38~

40 °C); ^1H NMR (400 MHz, CDCl_3) δ : 3.41 (td, $J=10.4$, 4.4 Hz, 1H), 2.23~2.10 (m, 1H), 2.00~1.92 (m, 1H), 1.70~1.55 (m, 2H), 1.48~1.34 (m, 2H), 1.15~1.06 (m, 1H), 1.02~0.84 (m, 9H), 0.80 (d, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 71.7, 50.3, 45.2, 34.7, 31.8, 26.0, 23.3, 22.4, 21.1, 16.3.

Supporting Information Procedure for radical capturing experiment with TEMPO and the characterization data for compound **5**. ^1H NMR and ^{13}C NMR spectra copies for alcohols **2**. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn/>.

References

- [1] (a) Larock, R. C. *Comprehensive Organic Transformations*, 2nd ed., Wiley-VCH, New York, **1999**, p. 890.
(b) Smith, M. D.; March, J. *Advanced Organic Chemistry*, 6th ed., Wiley-Interscience, New York, **2007**, p. 425.
- [2] (a) Harris, M.; Bull, M. J. *Synth. Commun.* **1985**, *15*, 1225.
(b) Alexander, J.; Renyer, M. L.; Veerapanane, H. *Synth. Commun.* **1995**, *25*, 3875.
(c) Ruddick, C. L.; Hodge, P.; Houghton, M. P. *Synthesis* **1996**, 1359.
(d) Abad, A.; Agulló, C.; Cuñat, A. C.; Navarro, I. *Synthesis* **2005**, 3355.
(e) Chougala, B. M.; Samundeeswari, S.; Holiyachi, M.; Shastri, L. A. *ChemistrySelect* **2017**, *2*, 1290.
(f) Liu, H.; Liu, J.; Cheng, X.; Jia, X.; Yu, L.; Xu, Q. *ChemSusChem* **2019**, *12*, 2994.
- [3] (a) Nakamura, E.; Inubushi, T.; Aoki, S.; Machii, D. *J. Am. Chem. Soc.* **1991**, *113*, 8980.
(b) Nakamura, E.; Sato, K.; Imanishi, Y. *Synlett* **1995**, 525.
(c) Sawamura, M.; Kawaguchi, Y.; Nakamura, E. *Synlett* **1997**, 801.
(d) Sawamura, M.; Kawaguchi, Y.; Sato, K.; Nakamura, E. *Chem. Lett.* **1997**, 26, 705.
- [4] Cai, Y.-M.; Xu, Y.-T.; Zhang, X.; Gao, W.-X.; Huang, X.-B.; Zhou, Y.-B.; Liu, M.-C.; Wu, H.-Y. *Org. Lett.* **2019**, *21*, 8479.
- [5] (a) Itoh, A.; Kodama, T.; Inagaki, S.; Masaki, Y. *Org. Lett.* **2001**, *3*, 2653.
(b) Li, J.; Wang, H.; Liu, L.; Sun, J. *RSC Adv.* **2014**, *4*, 49974.
(c) Xu, J.; Liu, N.; Zou, L.; Cheng, F.; Shen, X.; Liu, T.; Lv, H.; Khan, R.; Fan, B. *Asian J. Org. Chem.* **2019**, *8*, 261.
- [6] (a) Xuan, J.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2012**, *51*, 6828.
(b) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322.
(c) Dai X.; Xu, X.; Li, X. *Chin. J. Org. Chem.* **2013**, *33*, 2046 (in Chinese).
(戴小军, 许孝良, 李小年, 有机化学, **2013**, *33*, 2046.)
(d) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. *J. Org. Chem.* **2016**, *81*, 6898.
(e) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075.
(f) Matsui, J. K.; Lang, S. B.; Heitz, D. R.; Molander, G. A. *ACS Catal.* **2017**, *7*, 2563.
- [7] (a) Chatgililoglu, C. *Acc. Chem. Res.* **1992**, *25*, 188.
(b) Chatgililoglu, C.; Ferreri, C.; Landais, Y.; Timokhin, V. I. *Chem. Rev.* **2018**, *118*, 6516.
- [8] Mills, I. N.; Porras, J. A.; Bernhard, S. *Acc. Chem. Res.* **2018**, *51*, 352.
- [9] (a) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A. Jr.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* **2005**, *17*, 5712.
(b) Nguyen, J. D.; Tucker, J. W.; Konieczynska, M. D.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2011**, *133*, 4160.
(c) Wallentin, C.-J.; Nguyen, J. D.; Finkbeiner, P.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2012**, *134*, 8875.
- [10] (a) Stien, D.; Gastaldi, S. *J. Org. Chem.* **2004**, *69*, 4464.
(b) Damont, A.; Médran-Navarrete, V.; Cacheux, F.; Kuhnast, B.; Pottier, G.; Bernards, N.; Marguet, F.; Puech, F.; Boisgard, R.; Dolle, F. *J. Med. Chem.* **2015**, *58*, 7449.
(c) Dudnik, A. S.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 10693.
- [11] (a) Lee, K. C.; Lee, S.-Y.; Choe, Y. S.; Chi, D. Y. *Bull. Korean Chem. Soc.* **2004**, *25*, 1225.
(b) Nicholson, J. S.; Richards, H. C.; Adams, S. S. *GB 1030756*, **1966**.
(c) Osako, T.; Torii, K.; Hirata, S.; Uozumi, Y. *ACS Catal.* **2017**, 7371.
(d) Itami, K.; Kamei, T.; Mitsudo, K.; Nokami, T.; Yoshida, J. *J. Org. Chem.* **2001**, *66*, 397.
(e) Khan, S. N.; Zaman, M. K.; Li, R.; Sun, Z. *J. Org. Chem.* **2020**, *85*, 5019.
(f) Sakai, N.; Kawana, K.; Ikeda, R.; Nakaike, Y.; Konakahara, T. *Eur. J. Org. Chem.* **2011**, *2011*, 3178.
(g) Reddy, A. G. K.; Krishna, J.; Satyanarayana, G. *ChemistrySelect* **2016**, *1*, 1151.
(h) Cavedon, C.; Madani, A.; Seeberger, P. H.; Pieber, B. *Org. Lett.* **2019**, *21*, 5331.
(i) Ishibashi, M. *J. Polym. Sci. B Polym. Lett.* **1964**, *2*, 789.
(j) Reddy, M. V.; Kang, S. M.; Yoo, S.; Woo, S. S.; Kim, D. W. *RSC Adv.* **2019**, *9*, 9435.
(k) Rysak, V.; Descamps-Mandine, A.; Simon, P.; Blanchard, F.; Burylo, L.; Trentesaux, M.; Vandewalle, M.; Collière, V.; Agbossou-Niedercorn, F.; Michon, C. *Catal. Sci. Technol.* **2018**, *8*, 3504.
(l) Green, R. A.; Jolley, K. E.; Al-Hadedi, A. A. M.; Pletcher, D.; Harrowven, D. C.; De Frutos, O.; Mateos, C.; Klauber, D. J.; Rincón, J. A.; Brown, R. C. D. *Org. Lett.* **2017**, *19*, 2050.
(m) Xu, G.; Leloux, S.; Zhang, P.; Mejjide Suárez, J.; Zhang, Y.; Derat, E.; Ménand, M.; Bistri-Aslanoff, O.; Roland, S.; Leyssens, T.; Riant, O.; Sollogoub, M. *Angew. Chem., Int. Ed.* **2020**, *59*, 7591.
(n) Ouali, A.; Majoral, J.-P.; Caminade, A.-M.; Taillefer, M. *ChemCatChem* **2009**, *1*, 504.
(o) Rösler, S.; Obenauf, J. Kempe, R. *J. Am. Chem. Soc.* **2015**, *137*, 7998.
(p) Soulard, V.; Villa, G.; Vollmar, D. P.; Renaud, P. *J. Am. Chem. Soc.* **2018**, *140*, 155.
(q) Zhong, R.; Wei, Z.; Zhang, W.; Liu, S.; Liu, Q. *Chem* **2019**, *5*, 1552.
(r) Ungnade, H. E. *J. Org. Chem.* **1948**, *13*, 361.
(s) Weng, W.-Z.; Liang, H.; Zhang, B. *Org. Lett.* **2018**, *20*, 4979.
(t) Polidano, K.; Williams, J. M. J.; Morrill, L. C. *ACS Catal.* **2019**, *9*, 8575.
(u) Tohma, H.; Maegawa, T.; Takizawa, S.; Kita, Y. *Adv. Synth. Catal.* **2002**, *344*, 328.
(v) Parshikov, I. A.; Modyanova, L. V.; Dovgilevich, E. V.; Terent'ev, P. B.; Vorob'eva, L. I.; Grishina, G. V. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1992**, *28*, 159.
(w) Aguilar Troyano, F. J.; Ballaschk, F.; Jaschinski, M.; Özkaya, Y.; Gómez-Suárez, A. *Chem. Eur. J.* **2019**, *25*, 14054.
(x) Bach, R. D.; Taafée, T. H.; Holubka, J. W. *J. Org. Chem.* **1980**, *45*, 3439.
(y) Boonyarattanakalin, S.; Martin, S. E.; Dykstra, S. A.; Peterson, B. R. *J. Am. Chem. Soc.* **2004**, *126*, 16379.
(z) Matt, C.; Kern, C.; Streuff, J. *ACS Catal.* **2020**, *10*, 6409.
(aa) Pujari, N. S.; Kulkarni, M. R.; Large, M. C. J.; Bassett, I. M.; Ponrathnam, S. *J. Appl. Polym. Sci.* **2005**, *98*, 58.
(ab) Toogood, H. S.; Cheallaigh, A. N.; Tait, S.; Mansell, D. J.; Jervis, A.; Lygidakis, A.; Humphreys, L.; Takano, E.; Gardiner, J. M.; Scrutton, N. S. *ACS Synth. Biol.* **2015**, *4*, 1112.
(ac) Zengin, G. *Chem. Nat. Compd.* **2011**, *47*, 550.

(Cheng, F.)