Journal of Saudi Chemical Society (2016) **xxx**, xxx–xxx

King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Bromo-catalyzed photo esterification of benzylsilanes with alcohols under aerobic conditions

Aishun Ding [c], Ruixia Xie [a], Guangxin Gu [b,*], Jing Sun [a,*]

[a] *School of Chemistry and Materials Science, Liaoning Shihua University, Dandong Road 1, Fushun 113001, PR China*
[b] *Department of Materials Science, Fudan University, 220 Handan Road, Shanghai 200433, PR China*
[c] *Department of Macromolecular Science, Fudan University, 220 Handan Road, Shanghai 200433, PR China*

Received 20 August 2016; revised 29 September 2016; accepted 1 October 2016

KEYWORDS

Photochemistry;
Esterification;
Bromo;
Benzylsilane;
Ester

Abstract A photoinduced esterification reaction has been developed. In this reaction, benzylsilane shows very nice reactivity and selectivity, affording the corresponding esters as the only products. Under photo irradiation, the highly active bromo radical can be generated from the pre-catalyst CBr_4, which would promote the initial C—Si bond cleavage of benzylsilane via single electron transfer and the final transformation of acetal into ester via proton transfer. The existence of oxygen can not only oxidize the *in situ* generated benzyl radical into aldehyde intermediate, but also assist to regenerate bromo radical from bromine anion.

1. Introduction

Esterification is a kind of important reaction which plays a key role in modern organic chemistry both in academia and industry [1–3]. Traditionally, esterification was commonly performed using carboxylic acids [4] or aldehydes [5] as starting materials to react with alcohols. Recently, the aerobic oxidative direct esterification of alcohols or aldehydes with alcohols using transition metal catalysts under mild conditions has attracted great attention. Esters can also be prepared via the direct esterification of alcohols with silanes. Silicon chemistry has a rich history [6]. Owing to their unique properties and reactivities, transformations from silanes into various complex molecules are a widely used method in organic synthesis [7]. It is assumed that the esterification of alcohols with silanes can be beneficial, since the isolation of aldehyde from silanes can be avoided. Nevertheless, comparing to the well-established esterification of alcohols with carboxylic acids or aldehydes, direct esterification of alcohols with silanes are less developed [8]. Moran et. al. have reported iron(III) and nitrate ions mediated esterification of acylsilanes with alcohols, yielding the corresponding esters in moderate to excellent yields [9]. To the best of our knowledge, this is the only report regarding the direct esterification of alcohols with silanes. So far the photo-induced esterification of alcohols with silanes has not yet been reported. Photoinduced reactions have been receiving lot of attention in recent years [10], since such a transformation can be a constituent of the concept of green chemistry.

---

[*] Corresponding authors. Fax: +86 24 56863837 (J. Sun), +86 21 65648837 (G. Gu).

E-mail addresses: guangxingu@fudan.edu.cn (G. Gu), sunjing@lnpu.edu.cn (J. Sun).

Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jscs.2016.10.001
1319-6103 © 2016 King Saud University. Production and hosting by Elsevier B.V.

To realize the above mentioned direct esterification, the highly efficient and selective break of the C—Si bond is very important. Recently, Guo et al. have reported the Br-catalyzed photo-cleavage of C—Si bond under aerobic conditions [11]. In such a photo-reaction, the bromo radical shows very nice catalytic activity in C–Si bond cleavage and the *in situ* generated aldehyde intermediates could be efficiently oxidized into benzoic acid derivatives yielding highly efficiently (Scheme 1). Based on this previous work, we hypothesized that one-pot synthesis from benzylsilanes into esters via aldehyde species under similar photo-oxidative conditions might be possible and did research in the field of photo-induced direct esterification of alcohols with silanes (Scheme 1). Herein, we would like to report our recent observation on the bromo-catalyzed photoinduced direct esterification of benzylsilanes with alcohols under aerobic conditions.

2. Experimental

2.1. General consideration

^{1}H (400 MHz) NMR spectra of samples in $CDCl_3$ (unless stated otherwise) were recorded on an AVANCE III 400 spectrometer.

2.2. General procedure for the photoreaction

Benzyltrimethylsilanes (0.20 mmol), CBr_4 (0.06 mmol) and alcohols (5 mL) were added to a dry Pyrex reaction flask which was equipped with a magnetic stirrer. The mixture was irradiated by a Xe lamp (300 W) at rt under oxygen atmosphere. After completion of the reaction (monitored by TLC, eluent: petroleum ether:ethyl acetate = 10:1), the solvent was removed and the residue was purified by flash chromatography on silica gel (eluent:petroleum ether:ethyl acetate = 10:1) to afford the corresponding products.

Methyl 4-methoxybenzoate (3aa) [12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.8 Hz, 2 H), 6.91 (d, J = 8.4 Hz, 2 H), 3.88 (s, 3 H), 3.85 (s, 3 H).

Methyl 4-ethoxybenzoate (3ba) [13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2 H), 6.89 (d, J = 8.4 Hz, 2 H), 4.08 (q, J = 6.8 Hz, 2 H), 3.88 (s, 3 H), 1.34 (t, J = 6.9 Hz, 3 H).

Methyl 4-(tert-butyl)benzoate (3ca) [14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2 H), 7.45 (d, J = 8.4 Hz, 2 H), 3.90 (s, 3 H), 1.34 (s, 9 H).

Methyl 4-phenylbenzoate (3da) [15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.8 Hz, 2 H), 7.68–7.58 (m, 4 H), 7.48–7.42 (m, 2H), 7.41–7.35 (m, 1H), 3.93 (s, 3 H).

Methyl benzoate (3ea) [12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–8.02 (m, 2 H), 7.58–7.51 (m, 1 H), 7.46–7.42 (m, 2 H), 3.92 (s, 3 H).

Methyl 4-fluorobenzoate (3fa) [16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.8, 5.2 Hz, 2 H), 7.11 (dd, J = 8.8, 5.2 Hz, 2 H), 3.91 (s, 3 H).

Methyl 4-chlorobenzoate (3ga) [12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2 H), 7.41 (d, J = 8.4 Hz, 2 H), 3.92 (s, 3 H).

Methyl 4-bromobenzoate (3ha) [12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2 H), 7.58 (d, J = 8.4 Hz, 2 H), 3.91 (s, 3 H).

Methyl 4-(trifluoromethyl)benzoate (3ia) [17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 2 H), 7.71 (d, J = 8.4 Hz, 2 H), 3.96 (s, 3 H).

Methyl 1-naphthoate (3ja) [14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, J = 8.8 Hz, 1 H), 8.17 (d, J = 7.2 Hz, 1 H), 8.00 (d, J = 8.0 Hz, 1 H), 7.87 (d, J = 8.0 Hz, 1 H), 7.87 (d, J = 8.0 Hz, 1 H), 7.64–7.58 (m, 1 H), 7.56–7.45 (m, 2 H), 4.00 (s, 3 H).

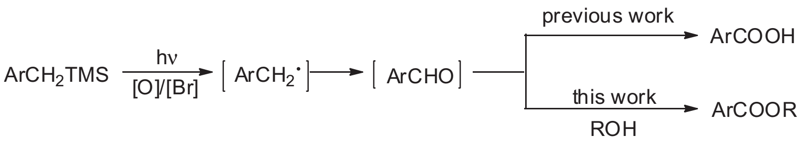
Methyl 2-naphthoate (3ka) [12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1 H), 8.08–8.02 (m, 1 H), 7.93 (d, J = 8.0 Hz, 1 H), 7.87 (d, J = 8.8 Hz, 2 H), 7.60–7.50 (m, 2 H), 3.97 (s, 3 H).

Ethyl 4-methoxybenzoate (3ab) [18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.8 Hz, 2 H), 6.91 (d, J = 8.8 Hz, 2 H), 4.35 (q, J = 7.2 Hz, 2 H), 3.86 (s, 3 H) 1.38 (t, J = 7.2 Hz, 3 H).

Propyl 4-methoxybenzoate (3ac) [19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.8 Hz, 2 H), 6.92 (d, J = 8.8 Hz, 2 H), 4.25 (t, J = 6.4 Hz, 2 H), 3.86 (s, 3 H) 1.78 (m, 2 H), 1.02 (t, J = 7.2 Hz, 3 H).

3. Results and discussion

To explore the feasibility of this reaction, (4-methoxybenzyl)trimethylsilane **1a** and methanol **2a** were chosen as the model substrates for the following studies. Firstly, HBr (aq. 40%) was used as the pre-catalyst under photo-oxidative conditions. It is satisfactory to see that the side reaction-oxidation of aldehyde into carboxylic acid was totally inhibited. However, only 3% of the desired ester was formed (entry 1, Table 1). To improve the yield of ester, other inorganic bromides were tested. Disappointingly, no desired product was afforded at all (entries 2–4, Table 1). Next, organic bromine sources NBS and CBr_4 were applied in the reaction system. To our delight, 85% and 95% of the corresponding esters could be obtained, respectively (entries 5 and 6, Table 1). CBr_4 was then chosen as the pre-catalyst for further studies. When reducing the amount of CBr_4 from 30 to 10 mol%, both the yield and selectivity were decreased however (entries 7 and 8, Table 1). Without the introduction of pre-catalyst, no ester was afforded (entry 9, Table 1). The control experiments indicated that light (entry 10, Table 1) and oxygen (entry 11, Table 1) were also necessary for this reaction. Finally, the reaction was conducted under air atmosphere, affording **3aa** in 78% yield (entry 12,



Scheme 1 Transformations of arylsilanes under photo-oxidative condition.

Please cite this article in press as: A. Ding et al., Bromo-catalyzed photo esterification of benzylsilanes with alcohols under aerobic conditions, Journal of Saudi Chemical Society (2016), http://dx.doi.org/10.1016/j.jscs.2016.10.001