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p-Toluenesulfonic acid a useful and selective reagent for the oxidation of benzoins to benziles under solvent-free condition

Nader Noroozi-Pesyan [*,a], Abdul Hossein Dabbagh [b]

[a] *Department of Chemistry, Faculty of Science, Urmia University, Urmia, Iran*
[b] *College of Chemistry, Isfahan University of Technology, Isfahan, Iran*

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Abstract

Oxidation of some benzoins to benziles is reported by using *p*-toluenesulfonic acid as a selective oxidation catalyst under solvent-free condition in high yield. The adjacent carbonyl group is necessary for the oxidation of hydroxyl group in these compounds. The reaction is carried out in a sand-bath at 100 °C with minimum by-products.

Keywords: Benzoins, Benziles, α-Diketones, *p*-Toluenesulfonic acid (PTSA), Solvent-free

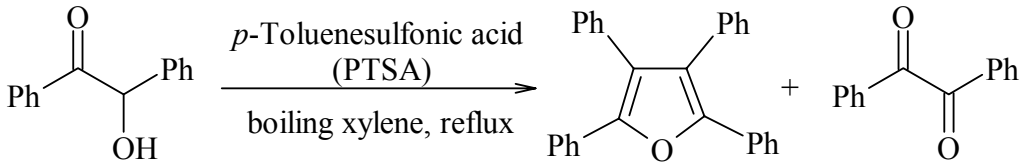
1. Introduction

Several biological compounds are obtained from α-diketones such as: 5,5-diphenylhydantoin [1], pyrazine derivatives [2, 3] and other related biological compounds, are important in organic synthesis. α-Diketones can also be utilized for the preparation of a variety of organic compounds [4]. Methyl or methylene groups which are located at the α position of a carbonyl can be oxidized with selenium dioxide to give, respectively, α-keto aldehyde and α-diketones [5]. These compounds can also be prepared straightforward by oxidation of α-hydroxy ketones in the presence of dinitrogentetraoxide complex of iron (III) and cupper(II) [6], cupper(II) in alkaline [7], dimethyl sulfoxide (DMSO)-$SbCl_5$ (1:1) complexes [8], thallium (III) nitrate (TTN) [9], polyvinylpyridinium dichromate [10], cupper (II) acetate, ammonium nitrate or pyridiniumchlorochromate as an oxidant with microwave assisted [11], nickel acetate [12] and etc. Selective oxidation of benzylic alcohol to corresponding carbonyl compounds under solvent-free conditions [13], and also solid phase oxidation of organic compounds with benzyltriphenylphosphonium dichromate [14] and 1,4-dibenzyl-1,4-diazoniabicyclo [2.2.2] octane chlorochormate (DBDABOCC) [15] are reported. Recently, we reported the selectively oxidation of benzoins to benziles on the surface of alumina and/or silica gel with heating under solvent-free condition in excellent yield [16].

p-Toluenesulfonyl chloride, *p*-toluenesulfonic anhydride, methansulfonic anhydride with dimethyl sulfide in hexamethylphosphoramide (HMPA) at –20 ^{o}C oxidize secondary alcohols to ketones in high yield [17]. Benzoin as an α-hydroxy ketone is known to undergo an interesting transformation tetraphenylfuran (**7**) when refluxed in the presence of catalytic amount of *p*-toluenesulfonic acid in dry xylene with azeotropic removal of water (Scheme 1). In this reaction, the benzil is yielded 45% as by-product [18]. *p*-Toluenesulfonic acid also is used for reaction

* Corresponding author. Tel.: +98 4412780952; fax: +98 4412776707.
E-mail address: n.noroozi@mail.urmia.ac.ir and pesyan@gmail.com (N. Noroozi-Pesyan)

under solid state conditions for the conversion of diphenylcarbinol to bis (diphenylmethyl) ether by Toda *et al* [19].



1a **7** (major product) **1b** (45%)

Scheme 1 Synthesis of tetraphenylfuran from benzoin [18]

2. Experimental

2.1. General

The IR spectra were obtained on a Shimadzu IR-470, ^{1}H-NMR spectra were recorded at Varian EM 390 (90 MHz). The melting points were taken by the Gallenkamp melting point apparatus (uncorrected). The reaction progress monitored by TLC. The apparatus used for the oxidation was a mortar equipped in sand-bath. All of reactants are synthesized in laboratory based on reported literature [20] and all of products are characterized by comparison of their spectral (IR, ^{1}H NMR and TLC) and physical data (melting point) with those of authentic samples [6, 16, 20, 21].

2.2. Typical procedure: Oxidation of benzoins to benziles in the presence of PTSA under solvent-free condition

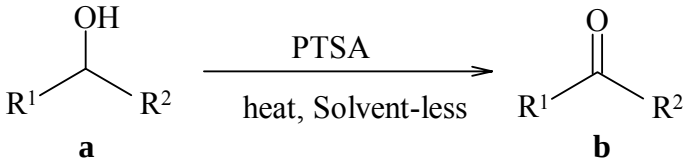
p-Toluenesulfonic acid (2.36 mmol) and benzoin (2.36 mmol) are mixed, grinded in a mortar homogenized, and heated in a sand-bath at 100 °C. The mixture is liquefied and changed perturbed to be dark brown colored. The reaction progress was monitored with TLC and checked every 10 minutes (the solvent of TLC was cyclohexane:ethyl acetate /80:20). The mixture was dissolved in 5 mL CH_2Cl_2 and extracted with the mixture of 5 mL H_2O and few mL dilute $NaHCO_3$ solution in two times (2×5 mL) then washed with brine. The organic layer was dried with $MgSO_4$. The product was pured after isolation by column chromatography and the yield of products are presented in Table 1. The spectroscopic and physical data of two products, **1b** and **3b**, are given in below as representative examples.

Benzil (**1b**). Light green needle-like crystals, mp 95 °C (lit. [6,16,20,21] 95 °C); IR (KBr): 3100 (C–H, ar), 1680 (C=O), 1595 (C=C); ^{1}H-NMR (90 MHz, CCl_4), δ 7.3 – 7.9 (m, 3H, *m* and *p*-PhH), 8.0 – 8.3 (m, 2H, *o*-PhH). 4,4'-Dimethoxybenzil (**3b**). Green solid, mp 133 °C (lit. [6,16,20,21] 132-134 °C); IR (KBr): 3050 (C–H, ar.), 2900, 2800 (C–H, aliph.), 1670 (C=O), 1595 (C=C), 1160 (C–O); ^{1}H-NMR (90 MHz, $CDCl_3$, CCl_4), δ 4.0 (s, 3H, CH_3), 7.2 (d, J = 9 Hz, 2H), 8.2 (d, J = 9 Hz, 2H).

3. Results and discussion

We used *p*-toluenesulfonic acid as a selective oxidation catalyst for the oxidation of some benzoins into benziles under solvent-free condition in high yield (Scheme 2). The conversion of benzoins (**1a-4a**) to benziles (**1b-4b**) in the presence of PTSA under solvent-free condition is summarized in Table 1. The compounds diphenylcarbinol **5a** and benzyl alcohol **6a** were oxidized to bis (diphenylmethyl) ether and dibenzyl ether, respectively (Table 1). It seems the adjacent carbonyl group is necessary for the oxidation of hydroxyl group in benzoins in the presence of *p*-toluenesulfonic acid according based to references [16, 18]. Neither **5a** nor **6a**

oxidized to corresponding carbonyl compounds **5b** and **6b** (benzophenone and benzaldehyde, respectively) at the same condition in the presence of *p*-toluenesulfonic acid based on our observation.

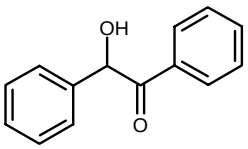
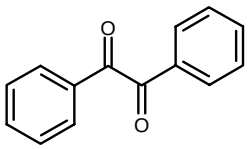
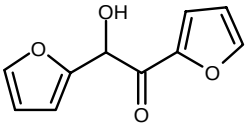
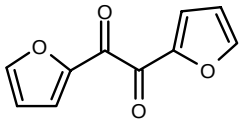
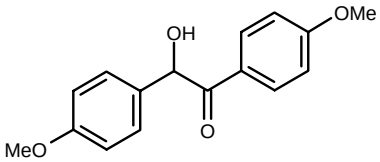
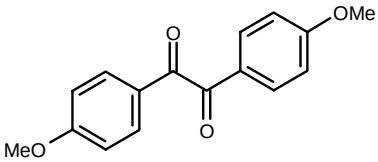
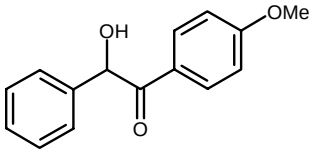
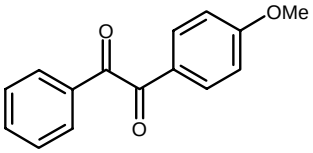
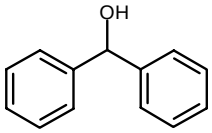
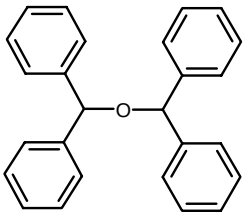
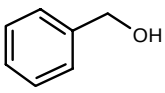
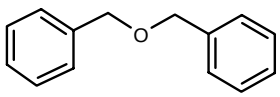


a **b**

Scheme 2 Selectively conversion of benzoins into benziles in the presence of PTSA

These results are good evidences for selective oxidation of benzoins (as α-hydroxy ketones) to benziles in the presence of PTSA. Also, it is the best reason that the oxygen molecule from air is not interfered on this oxidation process. The reaction time and isolated yields depend to mole ratio of catalyst and reactant (acid: benzoin). The isolated yield was 100% when mole ratio of acid: benzoin became 2:1 during 15 minutes and all results are summarized in Table 2.

Table 1
Oxidation of benzoins to benziles in the presence of PTSA under solvent-free condition at 100 °C and 15 minutes [a]

Entry	Reactant (**a**)	Product (**b**)	Isolated Yield / % [b]
1			90
2			90
3			70
4			90
5			c
6			d

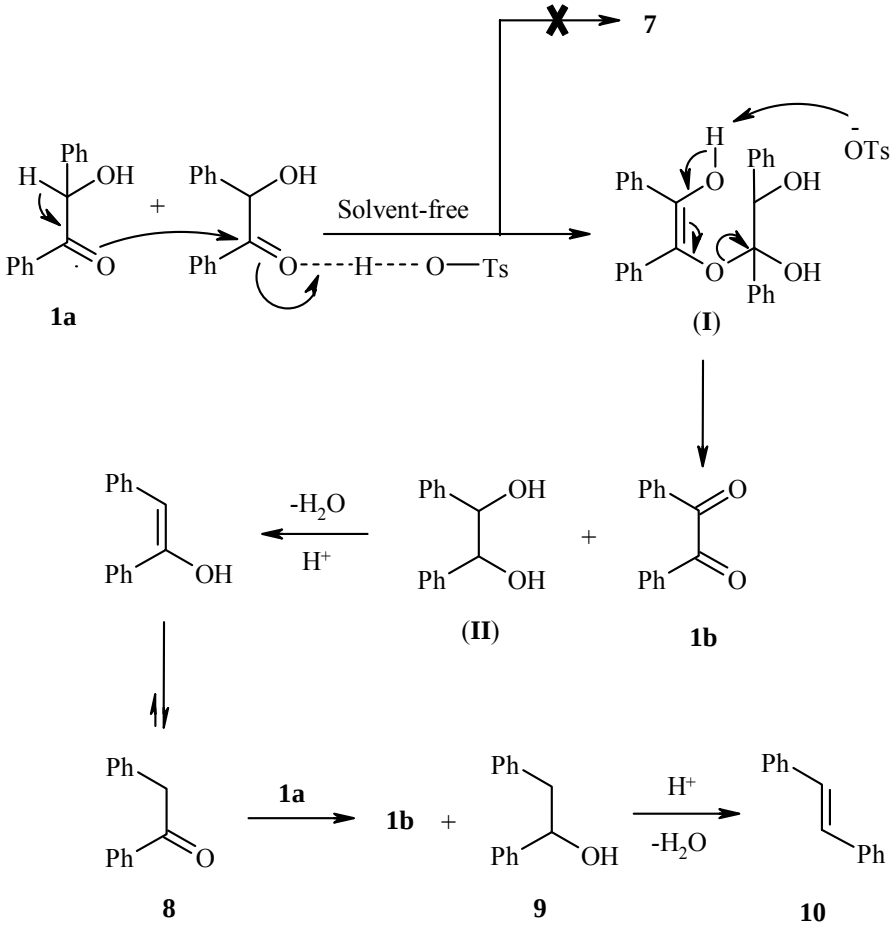
a) Mole ratio of PTSA: benzoin = 1:1
b) Based on separated by silica gel column chromatography (cyclohexane/ethyl acetate: 90/10)
c) The product is bis(diphenylmethyl) ether [19]
d) The product is dibenzyl ether [19]

Table 2
The effect of mole ratio of PTSA: benzoin (**1a**) in oxidation on sand-bath [a]

Entry	PTSA:Benzoin	Time /min	Isolated Yield / %
1	2:1	15	100
2	1:1	40	90
3	0.5:1	50	90

[a] Temperature of sand bath is 100 °C

Transformation of benzoin to tetraphenylfuran, **7** is still the best method for the making **7** [22,23]. Kar *et al* [18] reported a mechanism for the transformation of benzoin to tetraphenylfuran and also to benzil (yielded 45%) as by-product in the presence of catalytic amount of *p*-toluenesulfonic acid as an oxidation catalyst in boiling xylene (solvent case). In the presence of PTSA, benzoin (**1a**) undergoes a self-condensation reaction giving rise to form benzil (**1b**) and other by-products through intermediates under solvent case (Scheme 1) [18]. On the other hand, in this research, benziles are of major products with high yield (up to 80%) and no **7** was observed under solvent-free condition. A suitable proposed mechanism for the oxidation of benzoin into benzile is described in Scheme 3. Initially, **1a** undergoes a self-condensation reaction giving rise to intermediate **I** in the presence of PTSA. *p*-Toluenesulfonate captured proton from intermediate **I** and its intramolecularly cleavage produced **1b** and intermediate **II**. The removing of water from intermediate **II** formed deoxybenzoin (**8**) in acidic condition then condensed with **1a**, regenerated **1b** and 1,2-diphenylethanol (**9**). The removing of water from **9** in acidic condition converted to stilbene (**10**) (Scheme 3).



Scheme 3 Proposed mechanism for the conversion of benzoin into benzil under solvent-free condition in the presence of PTSA

Therefore, the oxidation of some benzoins without of any acid sensitive substituents to benziles straightforward carried out by *p*-toluenesulfonic acid under solvent-free condition. Limitation of this reaction is that no benzoins consisting of acid sensitive substituents (e.g. amino groups) are used for the oxidation in this process.In comparison, this method has some advantages such as; (i) Recoverable oxidant (PTSA) after working up. (ii) Solvent-free condition and low cost. (iii) An environmentally friendly chemical process and not environmental pollution. (iv) A clean reaction with minimum by-products. (v) No necessity for the purification of *p*-toluenesulfonic acid in reaction condition.

4. Conclusions

We concluded the oxidation of benzoins to benziles in the presence of *p*-toluenesulfonic acid under solvent-free is more convenient than solvent condition. All products obtained in high yield and with minimum by-product in this method. The adjacent carbonyl group is necessary in this oxidation reaction similar to solvent case.

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