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A first example of a reaction under viscous conditions: oxidation of solid benzoins with manganese dioxide

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Abstract A new, general, and efficient technique for the reaction of solid substrates under viscous conditions with shaking at room temperature is described, which can overcome some of the problems existing in common solvent-free reactions solids as the starting materials. In this manuscript we present as a first example of this method the oxidation of solid benzoins into the corresponding benzils using an environmentally friendly and inexpensive oxidant, manganese dioxide.

Keywords Viscous conditions; Solid substrate; Solvent-free reactions; Oxidation; Solid benzoins.

Introduction

Considerable attention has been paid to solvent-free reactions, which have attracted interest not only from an ecological point of view, but in many cases also offer considerable synthetic advantages in terms of yield, selectivity, simplicity of the procedure, and operation at room temperature [1–3]. These factors are especially important in industry. Unfortunately, under solvent-free conditions, it is in most cases not possible to performed reaction at room temperature because both the reacting molecules, substrates and reagents, are in crystal forms that makes it difficult for reach collision for reaction. Consequently, such reactions are normally carried out at a temperature near or over the substrate melting point by either heating or other methods in order to dissolve the solid substrates into liquid forms to increase the reaction rate. Therefore, some of the reported solvent-free reactions, especially for those solid substrates, require modification to improve their profile.

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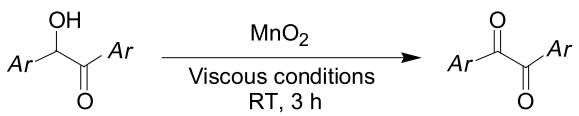
Results and discussion

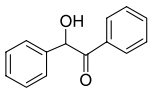
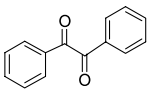
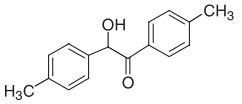
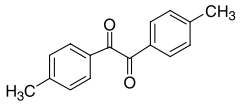
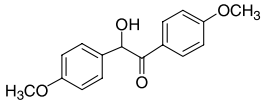
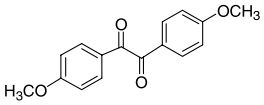
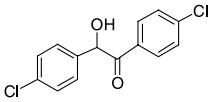
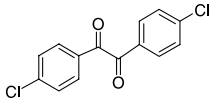
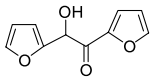
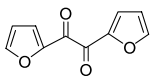
In continuation of our ongoing program related to developing new oxidation methods we wish to report here a novel, general, and more efficient procedure for solid substrate reactions under viscous conditions with shaking at room temperature. As a first example of this approach we report here the oxidation of solid benzoins **1** into the corresponding benzils **2** using an environmentally friendly and inexpensive oxidant, manganese dioxide (MnO_2).



92–96%

1 **2**

Table 1 Oxidation of solid benzoins under viscous conditions with MnO_2

Substrate	Product[a]	Reaction time/h	Yield[b]/%	m.p./°C	
				Found	Reported [17]
		3	96	94–95	95
		3	93	102–103	104–105
		3	95	133–134	131–133
		3	92	197–199	197–199
		3	95	161–163	162

[a] All the products are known compounds and were identified by comparison of their spectra with the literature values
[b] Yield of isolated product

The oxidation of benzoins into benzils is an important synthetic reaction in organic chemistry [4–6]. Benzils are versatile compounds which can be used for the preparation of a variety of molecules, many of which show a diversity of interesting biologically activities [7–12]. To the best of our knowledge, there are only few reports about the use of MnO_2 for the oxidation of benzoins to benzils, for instance, with solid MnO_2 [13, 14], and with supported MnO_2 reagent [15], all of which are carried out under heterogeneous conditions at reflux.

In our case, active MnO_2 is prepared from potassium permanganate ($KMnO_4$) under basic conditions according to literature [16]. The molar ratio of substrate to MnO_2 is 1:2. The oxidation is very simple: first the solid substrate is dissolved with a very minimum amount of dichloromethane to form a viscous liquid, and then the oxidant is added in one portion. The mixture is shaken magnetically at room temperature until TLC analysis indicates complete conversion. All the reactions are completed within 3 h. Finally the residue is washed, and the product is then purified by preparative TLC. The results, which are shown in Table 1, show that this method is an efficient oxidation method for solid benzoins and gives the corresponding benzils in high yields.

The main advantage of the present procedure is that under viscous conditions the oxidation of the solid substrates can be carried out very efficiently using a shaking machine under mild conditions. Compared to previous heterogeneous MnO_2 oxidations [13–15], for example, the yields of the products are higher, the oxidations can be performed at room temperature without any heating, the supported reagents are no need of preparation, and the work-up is easier. On the other hand, owing to the reaction using a very minimum amount of solvents, combustion, toxicity, and environmental pollution of the solvents are quite reduced.

In summary, a new, general and efficient technique for solid substrate reactions under viscous conditions with shaking at room temperature is described, which can overcome problems known for common solvent-free solid reactions.

Experimental

Oxidation of benzoin to benzil: typical procedure

Benzoin (212 mg, 1 mmol) is dissolved in a minimum amount of dichloromethane (0.22 cm^3) to form a viscous liquid, to which active MnO_2 (174 mg; 2 mmol) [16] is added in a normal test tube. This mixture is shaken mechanically (Horizontal oscillator; Model: HY-2, Zhengji Instrument Co. Ltd.) at room temperature for 3 h. The progress of the reaction is monitored by TLC (plates: aluminum-backed silica gel Merck 60 GF_{254}) using *n*-hexane:ethyl acetate (7:3) as eluent. The reaction mixture is then washed with dichloromethane

($3 \times 5\,cm^3$). The combined filtrates are evaporated to give crude product, which is purified by preparative TLC with hexane:ethyl acetate (7:3) to afford benzil (202 mg; 96%).

With tetrahydrofuran (*THF*) as a different solvent for the oxidation of benzoin the corresponding benzil was obtained in 93% yield.

References

1. Metzger JD (1998) Angew Chem Int Ed 37:2975
2. Tanaka K, Toda F (2000) Chem Rev 100:1025
3. Sineriz F, Thomassigny C, Lou J-D (2004) Curr Org Synth 1:137
4. Tymonko SA, Nattier BA, Mohan RS (1999) Tetrahedron Lett 40:7657
5. Kirihara M, Ochiai Y, Takizawa S, Takahata H, Nemoto H (1999) Chem Commun:1387
6. Skobridis K, Theodorou V, Weber E (2006) Arkivoc:102 and references cited therein
7. Morrison H, Danishefsky S, Yates P (1961) J Org Chem 26:2617
8. a) (1981) Matsushita Electric Industrial Co. Ltd., Jpn Kokai Tokkyo Koho 8198203; b) Chem Abstr 95:188163v
9. Vollhardt KPC, Schore NE (1994) Organic Chemistry, 2nd edn. Freeman, New York, p 924
10. Mitra AK, De A, Karchaudhuri NJ (1999) Chem Res (S):246
11. Vogel A (1978) Textbook of Practical Organic Chemistry including Qualitative Organic Analysis, 4th edn. Longman, New York, p 883
12. Joul JA, Mills K, Smith GF (1995) Heterocyclic Chemistry, 3rd edn. Chapman & Hall, London
13. Pratt EF, Van de Castle JF (1961) J Org Chem 26:2973
14. Papadopoulos EP, Jarrar A, Issidorides CH (1966) J Org Chem 31:615
15. Khandekar AC, Paul AM, Khadilkar BM (2002) Synth Commun 32:2931
16. Attenburrow J, Cameron AFB, Chapman JH, Evans RM, Hems BA, Jansen ABA, Walker T (1952) J Chem Soc:1094
17. Okimoto M, Takahashi Y, Nagata Y, Sasaki G, Numata K (2005) Synthesis:705