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The solid-phase catalytic oxydation of 2-hydroxy-3,5-di-*tert*-butylbenzyl alcohol

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The solid-phase catalytic oxidation in the 2-hydroxy-3,5-di-*tert*-butylbenzyl alcohol—MnO_2—NaOH system to yield 2-hydroxy-3,5-di-*tert*-butylbenzaldehyde was carried out. Gaseous oxygen participates in the regeneration of the active form of the oxidant.

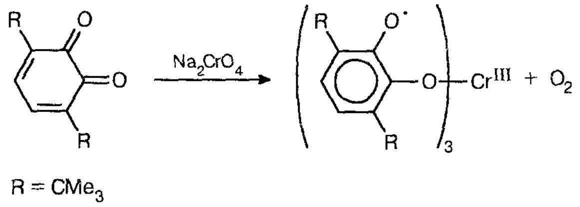
Key words: oxidation, benzyl alcohol, salicylic aldehyde, catalysis, synthesis, solid phase, liquid phase.

In a search for methods for the synthesis of 3,5-di-*tert*-butylsalicylic aldehyde (SA) we carried out the catalytic oxidation of 2-hydroxy-3,5-di-*tert*-butylbenzyl alcohol (BA) with equivalent amounts of inorganic oxidizing agents under various conditions, including the solid-phase version of the process.[1] It was found that benzyl oxidation can be used as the basis for a solid-phase synthesis of SA. However, taking into account the practical demand for SA and the real possibilities of its industrial production, we studied the possibility of using oxygen as the oxidant in the catalytic oxidation of BA.

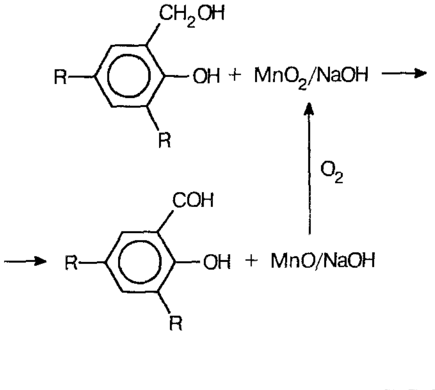
No plausible data on the solid-phase catalytic oxidation of organic compounds are present in the literature. Our attempts to carry out such oxidation of BA and a number of other derivatives of sterically hindered phenols in the presence of various coordination compounds of Mn, Co, *etc.* that are traditionally used in liquid-phase homogeneous catalytic oxidation were unsuccessful. The foregoing, together with the data on the mechanochemical instability of oxo and peroxo compounds of metals that liberate oxygen under the action of pressure and shear stresses,[2] created an unfavorable outlook for the possibility of the solid-phase version of this catalytic oxidation. Furthermore, organic compounds capable of coordination with a metal may even promote the solid-phase deoxygenation of oxygen-containing metal compounds.[3] For example, this effect is observed in the solid-phase reactions of ortho-quinones with chromates, tungstenates, and transition metal oxides (Scheme 1).

Therefore, it may be suggested that the formation of an "organic substrate — metal-containing catalyst — O_2" complex is of little significance in the solid-phase process. However, an alternative possibility exists, namely, catalysis may be achieved by the participation of oxygen in the regeneration of the active form of the oxidant.

Scheme 1



In the case of BA, we managed to carry out this version of solid-phase oxidation in the BA—MnO_2—NaOH system. The amount of the oxidizing agent, MnO_2/NaOH, taken for this reaction was no more than 0.01 equivalent.



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Complete BA→SA conversion is achieved after a period of several minutes, and the product is separated from the catalyst by vacuum distillation. After this, the catalyst can be recycled. It is likely that this is the first example of solid-phase catalytic oxidation that may be called perfect, since none of its steps requires the use of a solvent.

Experimental

BA was prepared by the previously described procedure.[4] A mechanical mixture of BA (5.7 g, $2 \cdot 10^{-4}$ mol) with the oxidant was passed through a previously described[5] worm conveyer for 10 min at room temperature. The product was distilled off *in vacuo* at 10—20 Torr, the distillate crystallized on cooling. Its melting point of 62 °C corresponds to the value reported for SA.[1] The product was identical to the authentic sample of SA prepared by oxidation of BA with $Mn(OAc)_3$ in MeCOOH.

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Electrochemical co-oxidation of C—H acids and methanol as a new route to functionalized cyclopropanes

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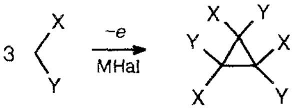
Electrolysis of dimethyl malonate or methyl cyanoacetate in methanol in the presence of LiCl in an undivided cell leads to formation of 1,1,2,2-cyclopropanetetracarboxylic derivatives.

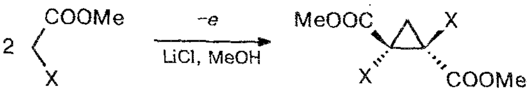
Key words: electrochemical oxidation, malonic ester, cyanoacetyc ester, 1,1,2,2-cyclopropanecarboxylic acid.

We discovered previously the reaction of electrochemical cyclotrimerization of malonic ester in methanol[1] and cyanoacetic ester in acetone[2] during electrolysis in an undivided cell in the presence of bromides and iodides of alkali metals as a mediators.



X, Y = COOMe, COOEt; M = Li, Na, K; Hal = Br, I

In this paper we established that electrolysis of malonic or cyanoacetyc esters (**1a,b**) in methanol in the presence of lithium chloride leads to formation of 1,1,2,2-cyclopropanetetracarboxylic acid derivatives (**2a,b**).



1a,b **2a,b**

a: X = COOMe; **b**: X = CN

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