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Synthesis of peroxyesters in tri-liquid system using quaternary onium salts and polyethylene glycols as phase-transfer catalysts

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ABSTRACT

A mild and efficient method for the synthesis of organic peroxyesters from acid chlorides and tertiary alkyl hydroperoxides in the presence of aqueous solution of inorganic base is described. The process was conducted in a tri-liquid system using quaternary onium salts and polyethylene glycols as phase-transfer catalysts. A model reaction of cumyl hydroperoxide (CHP) with butyryl chloride was investigated under a wide range of conditions. Selected peroxyesters were obtained in moderate to high yields (62–93%).

1. Introduction

Organic peroxyesters are used in a broad spectrum of applications, mainly in the polymer industry [1,2]. They have a labile oxygen—oxygen bond, which under the influence of various factors such as temperature or ultraviolet radiation can undergo decomposition to generate free radicals. Peroxyesters offer the broadest range of temperature activity of any of the peroxide compounds. Thus, they are willingly used as initiators in free radical polymerization reactions and as cross-linking compounds. They can be also used in the organic reactions, for example, the epoxidation of olefins.

The most commonly employed industrial method for the preparation of peroxyesters is the reaction of alkyl hydroperoxides with acid chlorides, usually under basic conditions. In this process can be used either organic bases e.g. pyridine, or aqueous solutions of alkali. The synthesis of peroxyesters in the presence of inorganic bases can be carried out with phase-transfer catalysts, which role is to facilitate the contact between reagents located in the organic and aqueous phases. The advantages of this technique are: high reaction rate, high yield and selectivity, mild conditions and simple procedure of the process. One type of phase-transfer catalysis is a liquid–liquid–liquid catalysis (L–L–L PTC) in which catalyst forms a third insoluble liquid phase in the reaction system between the inorganic and organic phase [3–18]. This method is especially noteworthy because of the ease of the catalyst separation from the reaction mixture, which allows its reuse in the process. The reactions carried out in this system are characterized by greater reaction rate, efficiency and selectivity than those occurring in the two-phase system. We have successfully applied a triphase system to the synthesis of dialkyl peroxides [17–19].

Herein, we reported results obtained for a model reaction of butyryl chloride with cumyl hydroperoxide in the presence of aqueous solutions of mild inorganic base as K_2CO_3. The reaction was carried out in a tri-liquid system using quaternary onium salts and polyethylene glycols as phase-transfer catalysts. The effect of various experimental parameters on the reaction course was studied. Then, selected peroxyesters were obtained under optimized conditions.

2. Experimental

2.1. Chemicals and catalysts

Cumyl hydroperoxide (CHP, 1-methyl-phenylethyl hydroperoxide, 88% pure) from Aldrich was purified according to a procedure described in the literature [20]. *Tert*-butyl hydroperoxide (TBHP, 5.5 M solution in decane, from Aldrich), butyryl chloride (Acros Organics) and benzoyl chloride (Fluka) were distilled prior to use. Tetrabutylammonium bromide and chloride (TBAB, TBAC), tetrabutylphosphonium bromide (TBPB), polyethylene glycols monomethyl ether of molecular weights from 350 to 2000 (PEG MM 350, 550, 1100 and 2000), polyethylene glycols dimethyl ether (PEG DM 500) and polyethylene glycol (PEG 600) were obtained from Fluka Chemie AG. Benzyltributylammonium chloride (BTBAC), tributylmethylammonium chloride (TBMAC) and

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