Letters to the Editor

Synthesis of benzofurans by phase transfer catalysis. Intramolecular cyclization of α-aryl-substituted 1,3-dicarbonyl compounds

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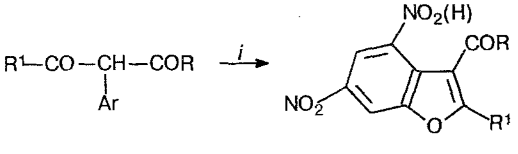
Intramolecular cyclization of polyfunctional organic compounds is a classical synthetic route to heterocyclic compounds, *inter alia*, benzofurans.[1] α-Aryl substituted carbonyl compounds containing an easily leaving group at the *ortho*-position of the benzene ring are routinely used as substrates for the preparation of benzofurans. Usually, the cyclization is carried out in dipolar aprotic solvents in the presence of strong bases.[2,3]

To develop a straightforward and convenient synthesis of benzofurans, we studied the possibility of an intramolecular cyclization of α-aryl-1,3-dicarbonyl compounds under conditions of basic phase transfer.

As convenient models for the studies, we choose a set of well-known[3,4] α-arylated 1,3-diketones and ketoesters containing an easily leaving *o*-nitro group in the *ortho*-position of the aromatic ring. It is known that such diketones containing two or more nitro groups in the aromatic ring exist in solutions exclusively in the enol form and have the high acidity (pK = 11—13).[5,6] Hence, one can expect that under conditions of basic phase-transfer catalysis, these substrates would readily give an alkaline salt of enol form of the carbonyl compound, which is required for the cyclization. In fact, after introduction of the carbonyl compounds of this type into the reaction system, consisting of potassium carbonate, 18-crown-6, and an aromatic hydrocarbon, we observed a rapid appearance of a specific coloration of the corresponding anion,[7] which disappeared at refluxing of the solution. After elution of the reaction mixture through a layer of alumina and evaporation of the solution, practically pure benzofurans were obtained in the residues. The general scheme of the process can be depicted as follows:



R = Me, Ph, OEt, OMe;

R¹ = Me, Pr^i, Ph;

Ar = 2,4-dinitrophenyl, 2,4,6-trinitrophenyl.

i. K_2CO_3, 18-crown-6, Δ, in toluene or xylene.

The cyclization of picryl derivatives of 1,3-dicarbonyl compounds proceeds especially smoothly. Heating of the reagents in toluene at 110 °C for 30 min is enough for the complete conversion of the parent compounds. Attempted cyclization of substrates containing 2,4-dinitroaryl substituents in toluene was inefficient. Only replacement of toluene by a mixture of xylenes having higher b.p. allowed us to achieve the success. In

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our opinion, such tendency in the reactivity of the substrates results from stronger activation of the *o*-nitro group being substituted in the case of picryl derivatives *vs.* 2,4-dinitroaryl derivatives.

Thus, the method proposed allows one to avoid dipolar aprotic solvents and strong bases and to simplify significantly the synthesis and isolation of benzofurans.

General Procedure. Ethyl α-picrylacetoacetate (10 mmol), potassium carbonate (10 mmol), and 18-crown-6 (1 mmol) were placed into a one-necked flask (50 mL) equipped with a reflux condenser, and the mixture was refluxed for 30 min in 50 mL of toluene or xylene. The reaction was monitored by TLC. After disappearance of the color of the starting substrate anion, the reaction mixture was cooled and passed through a layer of alumina. The solution obtained was evaporated, and the residue was crystallized from hexane. The yield of 2-methyl-3-carbethoxy-5,7-dinitrobenzofuran was 60 %, m.p. 62—64 °C. 2-Methyl-3-acetyl-5,7-dinitrobenzofuran (64 %), 2-phenyl-3-benzoyl-5,7-dinitrobenzofuran (62 %), 2-isopropyl-3-carbethoxy-5,7-dinitrobenzofuran (68 %), 2-phenyl-3-carbethoxy-5,7-dinitrobenzofuran (58 %), and 2-methyl-3-carbethoxy-7-nitrobenzofuran (40 %) were prepared similarly. The data on elemental and physicochemical analyses of benzofurans are in accord with those published in the literature.[7]

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Chemiluminescence during decomposition of dimethyldioxirane

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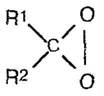
Chemiluminescence in the visible spectral region during decomposition of dimethyldioxirane in a cumene-acetone mixture at 22—52 °C has been detected. Arrhenius parameters of this process have been obtained.

Key words: organic peroxides, dimethyldioxirane, chemiluminescence, reaction mechanism.

Information on the mechanism of decomposition of dioxiranes **1** is scarce and controversial. Chemiluminescence (CL) during decomposition of one of these compounds, *viz.*, dimethyldioxirane **1a**, was observed in this work for the first time.



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We put 12 g of sodium hydrogencarbonate, 13 g of acetone, and 12 ml of water into the reaction flask in order to obtain a 0.07 mol L^{-1} solution of dimethyldioxyrane in acetone. Then 25 g of $KHSO_4$ was added. The reaction was performed in an argon atmosphere at pH = 7 with vigorous stirring. The dioxirane produced was distilled off under reduced pressure. Dioxirane and acetone vapors were trapped at −80 °C in a special trap. Compound **1a** was identified by the ^{13}C NMR (a characteristic signal of a carbon atom bonded to the peroxide group was observed at 101.35 ppm) and spectropho-

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