

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-di-

nitrobenzofuran (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

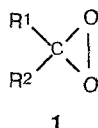
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Chemiluminescence in the visible spectral region during decomposition of dimethyldioxirane in a cumene-acetone mixture at 22–52 °C has been detected. Arrhenius parameters of this process have been obtained.

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.



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 dimethyldioxirane in acetone. Then 25 g of KHSO₄ 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 ¹³C NMR (a characteristic signal of a carbon atom bonded to the peroxide group was observed at 101.35 ppm) and spectrophoto-

tometrically ($\lambda_{\max} = 335$ nm), quantitative determination being similar to that described recently.¹ Chemiluminescence (CL) from a reaction vessel containing a solvent (1 mL of cumene) and 0.06 mol L⁻¹ of **1a** solution (0.8 mL) in an oxygen atmosphere was detected using a setup equipped with an FEU-140 photomultiplier. The temperature was varied within the range 22 to 52 °C. With thermal decomposition of the **1a** in cumene CL in the visible spectra region was observed. The luminescence decay was of the first order in the whole temperature range. The effective activation

energy of the process in cumene was $E_1 = (9.0 \pm 1.6)$ kcal/mol and $\log A = (4.0 \pm 1.1)$ [s⁻¹]. Apparently, the CL observed is due to the recombination of the peroxide radicals formed in this process. Detection of free radicals by the ESR technique during **1a** decomposition and decrease in the CL yield after the system had been purged with argon verified this suggestion.

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(S)-1-(2,4-Dinitrophenyl)prolyl chloride — a novel reagent for kinetic optical resolution of diaziridines

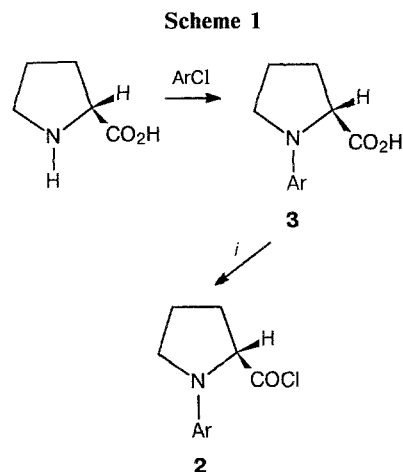
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The following chiral reagents for kinetic optical resolution of diaziridines are used: (*S*)- α -phenylethylisocyanate,^{1,2} *d*-(+)-10-camphorsulfonyl chloride,³ and more efficient (*S*)-*N*-tosylprolyl chloride (TPC).^{2,4-6} The action of 0.5 eq. of (*S*)-TPC or (*R*)-TPC on 1-methyl-3,3-pentamethylenediaziridine gives both enantiomers, (1*R*,2*R*)-(+)- or (1*S*,2*S*)-(-),^{2,5} respectively, in an optical yield up to 60%.⁶ In the case of (-)-1-(3-oxobutyl)-3,3-dimethyldiaziridine (**1**), the action of (*S*)-TPC gives (+)-**1** in a significantly lower optical yield (11%). We propose a novel chiral reagent for kinetic resolution of NH-diaziridines, viz., (*S*)-1-(2,4-dinitrophenyl)prolyl chloride (**2**) (Scheme 1).

Using (*S*)-**2**, diaziridine (-)-**1** was prepared in 35.4 % optical yield, which is 3.2 times higher than that with (*S*)-TPC in a similar procedure.⁶ It is important that the enrichment with the opposite enantiomer also occurs. Thus, starting from readily available *S*-proline, using (*S*)-TPC and (*S*)-**2**, the samples of **1** considerably enriched with either (+)- or (-)-enantiomers may be prepared (Scheme 2).

Compound (*S*)-**3** was obtained using a modified procedure⁷ in 42% yield, m.p. 142–144 °C, $[\alpha]_D^{12} -619.6^\circ$ (c 2.1, ethanol). Reagent (*S*)-**2** was obtained as shown in Scheme 1; after evaporation of the mixture, extraction with anhydrous ether and drying *in vacuo* its yield was 48 %.



i. SOCl₂, DMF, CH₂Cl₂; 20 °C, 18 h

