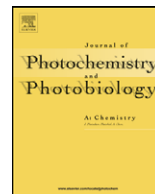




Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

The effect of fluorine as leaving group in the photolysis of 2-fluoro-1,2-diphenylethanone: Preparative and mechanistic investigation

Berta Košmrj^a, Hassen Boudebous^b, Boris Šket^{a,*}^a University of Ljubljana, Aškerčeva 5, SI-1000 Ljubljana, Slovenia^b Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

ARTICLE INFO

Article history:

Received 21 January 2008

Received in revised form 24 April 2008

Accepted 5 May 2008

Available online 24 May 2008

Keywords:

Cyclization

Fluoroethanone

Benzoin

Benzofuran

ABSTRACT

Photolysis of 2-fluoro-1,2-diphenylethanone (**1**) in MeCN or MeOH produces mainly 2-phenylbenzofuran. In MeOH some traces of solvent addition to the benzoyl radical formed by α -cleavage were detected. In trifluoroethanol several products are due to direct α -cleavage. Only 3% of 2-phenylbenzofuran and 13% of the α -ketocation solvent adduct are formed. The triplet state of **1** observed in nanosecond experiment at low temperature has been confirmed in femtosecond experiment. The triplet is formed quite fast at 370 nm (rise time 4.5 ps in acetonitrile and 22 ps in trifluoroethanol) and is stable up to 1.9 ns (a lifetime of 20 ns has been determined by quenching experiments with naphthalene).

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Benzoin is an important representative of “caged compounds”, which are inert in the dark but, upon exposure to light, are converted to active species that are able to participate in a chemical or biochemical process. Benzoin is an attractive alternative to the widely used 2-nitrobenzyl caging groups for a number of reasons. First of all, the syntheses of benzoin-caged derivatives are accomplished in good yield by easy procedures. Benzoin properties fulfill most of the criteria required for the design of a good photoremovable protecting group. The main advantages of benzoin are the high quantum yields and rates of release. The photochemical by-product accompanying the released reagent is an inert benzofuran.

The first study about the photolysis of benzoin compounds was made by Sheehan and Wilson in 1964 [1]. They observed that benzoin acetate undergoes photolytic cyclization to form 2-phenylbenzofuran. They also studied the photolysis of many derivatives for which they determined the reaction yield. They used a high-pressure mercury-vapour lamp with a Pyrex filter and isolated 2-phenylbenzofuran as the major product. Factors which should influence the cyclization reaction were investigated. The benzofuran chemical yields are to a small extent solvent dependent (from 15% in benzene to 8 and 10% in dioxane and propan-2-ol, respectively). Another important discovery is the effect of the leav-

ing group. By replacing acetate by chloride as a leaving group, a reduction from 15 to 1% of the chemical yield is observed in benzene.

Givens et al. [2] studied benzoin phosphate. Benzoin-caged phosphates are capable of rapid release of nucleotides and other biologically active phosphates, which are used to study the kinetics of muscle action by ATP, or calcium channel activation by GTP, for example. Photolysis at 350 nm of solutions of γ -*o*-desyl glutamate and *o*-desyl GABA in 1:1 H₂O:acetonitrile releases glutamate and GABA, respectively, with rate constants of ca. 10^7 s⁻¹ to give 2-phenylbenzofuran as the only by-product.

Wirz et al. [3] have studied the kinetics and the mechanism of diethyl phosphate photorelease from the benzoin ester by ns and ps laser flash photolysis. Steady-state irradiation of benzoin diethylphosphate gives 2-phenylbenzofuran as a main product with a quantum yield of 0.26 in benzene. In trifluoroethanol, only 25% of 2-phenylbenzofuran was formed, the major product being a solvent adduct.

Nanosecond laser flash photolysis of benzoin diethyl phosphate in degassed acetonitrile at 248, 308 or 351 nm gave a permanent absorbance around 300 nm that was formed in less than 25 ns (laser pulse width). In water or trifluoroethanol, a second absorption band was observed at $\lambda = 570$ nm, that was also formed within the duration of the laser pulse and decayed with a rate constant of $k = (2.3 \pm 0.2) \times 10^6$ s⁻¹ in degassed aqueous solution. Addition of sodium azide accelerates the decay rate of the 570 nm transient with a quenching coefficient $k_q = (9.9 \pm 0.4) \times 10^9$ M⁻¹ s⁻¹ and reduced the amplitude of the signal.

* Corresponding author. Tel.: +386 1 241 9240; fax: +386 1 241 9273.
E-mail address: sket.boris@email.si (B. Šket).

In acetonitrile, dichloromethane, chloroform, tetrahydrofuran, diethyl ether, methanol, ethanol, propan-2-ol and ethyl acetate no transient was observed at 570 nm. The permanent product observed at 300 nm was identified as 2-phenylbenzofuran by comparison of its fluorescence with that of an authentic sample. The lifetime of the triplet state of the diethyl phosphate benzoin was determined by energy transfer experiments with naphthalene ($\tau = (24 \pm 2)$ ns in trifluoroethanol).

Picosecond laser flash photolysis in acetonitrile at room temperature gave a large transient at 340 nm with a rise time of 2–4 ps and a lifetime of at least 5 ns.

The triplet of the starting molecule was assigned as the reactive excited state, the lifetime of which has been estimated to be between 10 and 25 ns, depending on the solvent.

Quenching experiments have allowed Wirz et al. to prove that the triplet-excited state of benzoin diethyl phosphate is the common precursor of 2-phenylbenzofuran and the transient at 570 nm. Radicals and carbenes were ruled out as candidates to describe this intermediate because of their incompatible reactivity, solvent dependency and absorption spectra. Wirz et al. also gave arguments to explain the role of the solvent. In principle a polar solvent should favour heterolytic dissociation, but no cation transient has been observed in the case of acetonitrile. The difference of conformation in the different solvents may explain the different reactivity.

The photolysis of many benzoin derivatives shows that the nature of leaving group being bonded at C2 position has substantial effect on the transient kinetics. To determine what is more important: bond energy between carbon atom and leaving group or nucleofugacity of leaving group, we chose 2-fluoro-1,2-diphenylethanone as substrate from several reasons:

- C–F bond is the strongest single bond and homolysis under the conditions used in photolytic experiments is not possible;

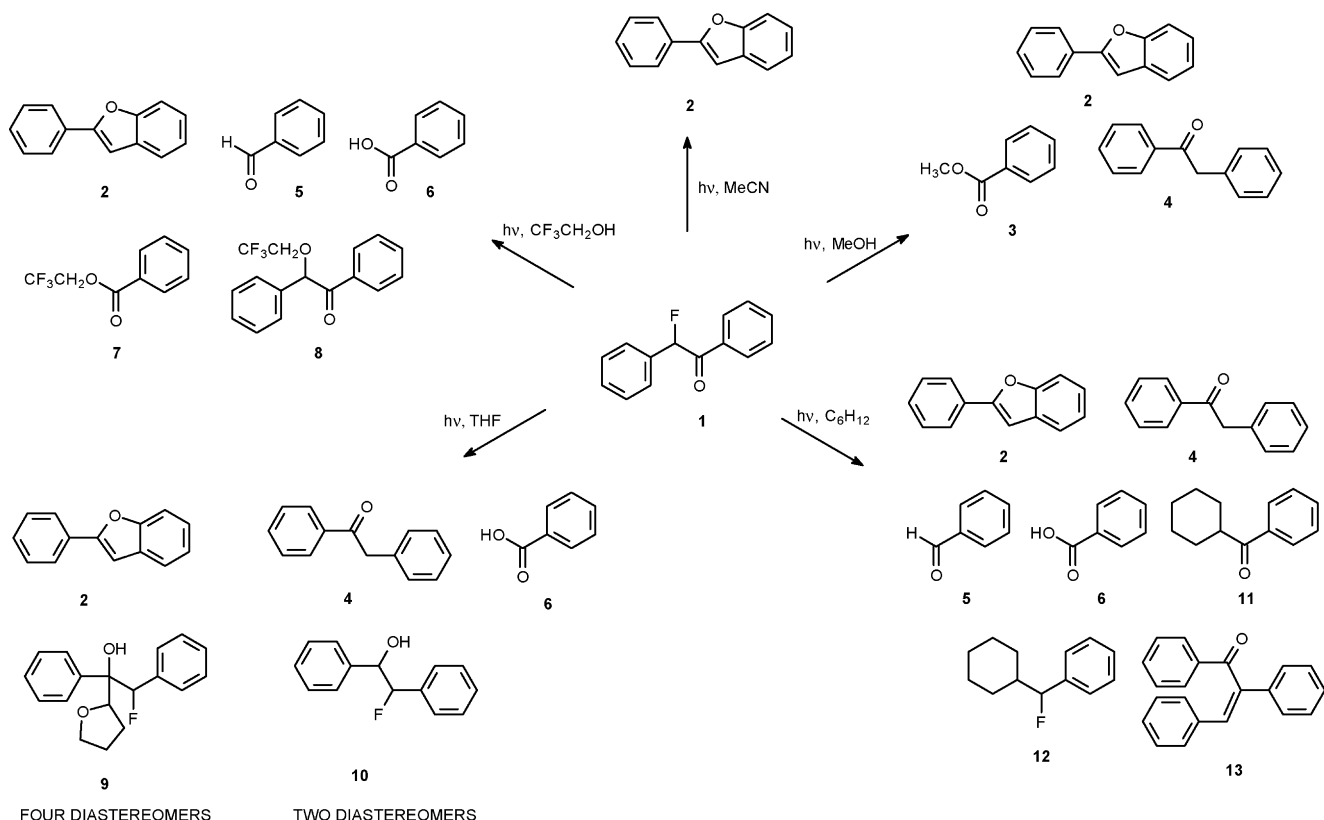
- acidity constant of HF ($pK_a = 3.17$) is very close to diethylphosphate ($pK_a = 1.39$) and acetic acid ($pK_a = 4.76$), quite different to that of HCl ($pK_a = -7$);
- fluorine atom stabilized the intermediates in many cases;
- fluorine atom can serve as a marker in different reactions.

2. Experimental

The photochemical reactions were performed in PhotoReactors Ltd MLU 18, equipped with light source of 350 nm. The reaction mixture were analyzed by GC Hewlett Packard HP 6890 equipped with flame ionization detector using 30 m capillary column HP5 and HP1 and temperature program: $T_{\text{start}} = 150^\circ\text{C}$ (3 min); rise $20^\circ\text{C}/\text{min}$; $T_{\text{end}} = 280^\circ\text{C}$ (10 min). The NMR spectra were recorded in CDCl_3 at 302 K with Bruker Avance DPX 300 spectrophotometer. Chemical shifts are given on the δ scale (ppm) and are referenced to internal TMS for ^1H and ^{13}C spectra and to CCl_3F for ^{19}F spectra. IR spectra were determined on a PerkinElmer 1310 spectrometer. Melting points were measured on Kofler microscope and are uncorrected. The reaction mixtures were analyzed by GC and GC/MS and by comparison of the spectral data of products to those of the authentic samples: 2-phenylbenzofuran (**2**), methyl benzoate (**3**), deoxybenzoin (**4**), benzaldehyde (**5**), benzoic acid (**6**), 2,2,2-trifluoroethyl benzoate (**7**) [4], 2-(2,2,2-trifluoroethoxy)-1,2-diphenylethanone (**8**) [3], 2-fluoro-1,2-diphenylethanone (**10**) [5], cyclohexyl phenyl ketone (**11**), 1,2,3-triphenylprop-2-en-1-one (**13**) [6].

2.1. 1,2-Diphenyl-2-fluoroethanone (**1**) [7]

To dichloromethane (20 mL) solution of 4.03 g (19 mmol) of benzoin at room temperature was dropwise added 2.5 mL (19 mmol) of (diethylamino)sulfur trifluoride (DAST). Stirring was continued for



Scheme 1. Products formed in photolysis of 2-fluorobenzoin (**1**) in different solvents.

Download English Version:

<https://daneshyari.com/en/article/27942>

Download Persian Version:

<https://daneshyari.com/article/27942>

[Daneshyari.com](https://daneshyari.com)