

Short communication

# Notable solvent effects on the regioselectivity in the Paternò–Büchi reaction of 1,3-dimethylthymine with 4-methoxybenzophenone

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## Abstract

Notable solvent effects on the regioselectivity and the photochemical efficiency were observed in the Paternò–Büchi (PB) reaction of 1,3-dimethylthymine (DMT) with 4-methoxybenzophenone (MBP). As a comparison, photochemical reactions of 4,4'-difluorobenzophenone (DFBP) and benzophenone (BP) with DMT were performed under the same condition. With increasing the proportion of water in the solution, besides the PB reaction, an electron-transfer reaction was observed in the DFBP–DMT system. The PB reaction of BP–DMT system revealed similar effects on the regioselectivity and the efficiency with that of MBP–DMT system, but the latter is more remarkable. The notable solvent effects may be responsible for a strongly solvent-dependent properties of the excited triplet MBP.

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**Keywords:** Paternò–Büchi reaction; Regioselectivity; Solvent effect; Excited triplet state; Benzophenones

## 1. Introduction

The regioselectivity and stereoselectivity in the Paternò–Büchi (PB) reaction, which is a photochemical [2 + 2] cycloaddition of a carbonyl compound with an alkene, have attracted considerable attention [1–4]. From the mechanistic points of view, recent researches focus on factors that influence the regioselectivity and the stereoselectivity [4–9]. For most cases, the predominant isomer formed can be correctly predicted from consideration of the more stable diradical (in triplet) intermediate formed by addition of the carbonyl oxygen to the carbon–carbon double bond. This is one of reasons why studies on the regioselectivity are relatively scarce comparing to the stereoselectivity. However, the regioselectivity is not always simply predicted from the stability of the intermediate diradicals. When two regioisomeric diradicals possess similar stability, other factors must play important roles in determining the regioselectivity. For example, in the PB systems with regioisomeric diradicals of similar stability, notable substituent and temperature effects on the regioselectivity have been observed in the photochemical reactions of substituted furans [6,7],

1,3-dimethylthymine (DMT) [9–11] and 1,3-dimethyluracil (DMU) [10,11] with aromatic carbonyl compounds.

Using benzene and acetonitrile/methanol as solvents, solvent effects on the regio- and diastereoselectivity in PB reactions were discussed, focusing on whether a photoinduced electron transfer occurred [5,12,13] or a hydrogen-bonding exciplex formed [14].

The nature and energy level of the lowest triplet state ( $T_1$ ) for 4-methoxybenzophenone (MBP) are strongly solvent-dependent,  $n, \pi^*$  character, 288 kJ mol<sup>-1</sup> in organic solvent and  $\pi, \pi^*$ , 275 kJ mol<sup>-1</sup> in water [15]. Hence, the photochemical reaction of MBP with DMT in acetonitrile–water binary solvents would allow to investigate the effect of the nature and energy level of the lowest triplet state on the PB reaction. In this paper, we reported a notable solvent effect on the regioselectivity of PB reaction of 1,3-dimethylthymine and 4-methoxybenzophenone through measuring product ratio crude product mixture of reaction in acetonitrile–water binary solvents.

## 2. Materials and methods

### 2.1. Materials

1,3-Dimethylthymine (DMT) was prepared from thymine. Acetonitrile-*d*<sub>3</sub> and water-*d*<sub>2</sub> was purchased from Beijing

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Chongxi High-Tech Incubator Co., Ltd. and benzene- $d_6$  from Aldrich Chemical Co., Inc. Other materials were obtained from commercial suppliers and used as received without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured with a Bruker AV 300 spectrometer operating at 300 MHz and 75 MHz, respectively. Mass spectra were obtained with a Micromass GCF TOF mass spectrometer.

## 2.2. Characterization for photoproducts of PB reaction of DMT and MBP

### 2.2.1. (*exo*- and *endo*-) (Z)-2,4,6-Trimethyl-8-phenyl-8-*p*-methoxyphenyl-7-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (**1**)

$^1\text{H}$  NMR (300 MHz, acetone- $d_6$ , TMS):  $\delta$  = (1.66, 1.69) (s, 3H,  $\text{CH}_3$ ), (2.76, 2.85) (s, 3H,  $\text{NCH}_3$ ), (3.08, 3.09) (s, 3H,  $\text{NCH}_3$ ), (3.76, 3.80) (s, 3H,  $\text{OCH}_3$ ), (4.87, 4.91) (s, 1H, CH), 6.87–7.45 (m, 9H,  $\text{H}_{\text{benzene}}$ ).  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ ):  $\delta$  = (170.5, 170.3) (NCOC), 160.1, 152.2 (2C), 146.0, 140.9, 137.6, 132.5, 129.2, 128.8, 128.4 (2C), 128.0, 127.7, 126.7, 126.1, 114.5, 114.2, 92.1, 92.0, 77.3 (2C), 66.5, 66.4, (55.6, 55.5) ( $\text{OCH}_3$ ), (35.7, 35.6) ( $\text{NCH}_3$ ), (27.5, 27.4) ( $\text{NCH}_3$ ), (24.1, 24.0) ( $\text{CH}_3$ ).  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  = 1714s, 1674s, 748m. TOFMS (EI) calcd. for  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4$  ( $M$ ) $^+$ : 366.1580, found: 366.1585.

### 2.2.2. (*exo*- and *endo*-) (Z)-2,4,6-Trimethyl-7-phenyl-7-*p*-methoxyphenyl-8-oxa-2,4-diazabicyclo[4.2.0]octane-3,5-dione (**2**)

$^1\text{H}$  NMR (300 MHz, acetone- $d_6$ , TMS):  $\delta$  = (1.42, 1.43) (s, 3H,  $\text{CH}_3$ ), (2.65, 2.72) (s, 3H,  $\text{NCH}_3$ ), (3.10, 3.11) (s, 3H,  $\text{NCH}_3$ ), (3.71, 3.77) (s, 3H,  $\text{OCH}_3$ ), (5.39, 5.41) (s, 1H, CH), 6.81–7.51 (m, 9H,  $\text{H}_{\text{benzene}}$ ).  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ ):  $\delta$  = 170.1 (NCOC), (159.9, 159.7), 152.5, 144.0, 143.0, 135.5, 134.5, 131.8, 130.2, 128.9, 128.4, 128.0 (2C), (127.6, 127.3), 126.1, 125.8, 125.0, 114.4, 113.9, 90.4 (2C), (88.7, 88.6), (55.5, 55.4), (53.6, 53.3) ( $\text{OCH}_3$ ), 32.9 ( $\text{NCH}_3$ ), 27.7 ( $\text{NCH}_3$ ), (20.2, 19.9) ( $\text{CH}_3$ ). TOFMS (EI) calcd. for  $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4$  ( $M$ ) $^+$ : 366.1580, found: 366.1587.

## 2.3. Photoproduct assay

The solution of reactants was placed in a Pyrex NMR tube (>290 nm), bubbled with high purity  $\text{N}_2$  for 10 min, and irradiated with 125 or 300 W high-pressure Hg lamp. The yields of photoproducts were assessed by  $^1\text{H}$  NMR spectroscopy (300 MHz) directly on the crude product mixture, using the sum of the aromatic signals as internal standard. The ratios of two regioisomeric oxetanes were obtained from their peak area of

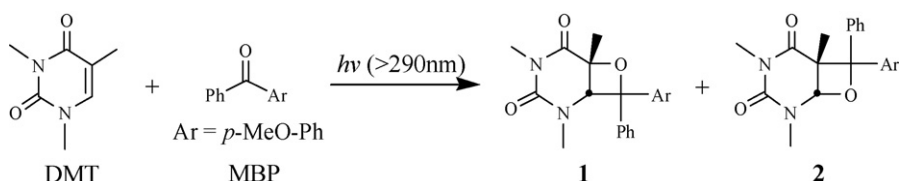
H-1 on the  $^1\text{H}$  NMR spectra, and the experimental was error within  $\pm 5\%$ .

## 3. Results and discussion

The photochemical reaction of DMT with MBP gives two regioisomers, A-type oxetane (**1**) and B-type oxetane (**2**) as shown in Scheme 1. The PB reaction is initiated by pure triplet MBP undergoing two diradical intermediates, which possess similar stability to give two regioisomeric oxetanes like other benzophenone derivatives (BPs) [9,10]. Both **1** and **2** have two possible diastereomers, *endo*-form and *exo*-form. The *endo* form is that phenyl group and 6-methyl group are at the same side (*cis*), and *trans* for the *exo* form. Very low diastereoselectivities for **1** and **2** were observed from  $^1\text{H}$  NMR spectra, two isomer ratios near to 1:1. Similar to the regioisomeric oxetanes formed from other BPs [9,10] their chemical shift of the proton H-1 ( $\delta_{\text{H-1}}$ ) are in the range 4–6, and less  $\delta_{\text{H-1}}$  for A-type oxetanes than B-type oxetanes. To investigate the effect of solvent on the regioselectivity, the photochemical reactions of DMT with MBP or other BPs were performed, and then measured by  $^1\text{H}$  NMR spectroscopy directly on the crude product mixture in deuterated solvents.

The PB reaction of DMT and MBP has been performed in deuterated acetonitrile-water binary solvents in various ratios, and the regioselectivity (A-type/B-type) and the yield were listed in Table 1. Data show that the regioselectivity is strongly dependent on the ratio of two solvents. With increasing the proportion of water in solution, the proportion of B-type product fast increases, such as A:B = 44:56 for neat acetonitrile, and 7:93 for 1:3 (v/v) acetonitrile–water. As a comparison, using 4,4'-difluorobenzophenone (DFBP) and benzophenone (BP) instead of MBP, the experiments were also performed under the same condition. In contrast to large changes of the regioselectivity in the DMT–MBP system, small changes were observed, as 66:34 to 49:51 for DFBP–DMT system and 56:44 to 41:59 for BP–DMT system. This may relate to strong solvent effects of the lowest triplet of MBP [15].

Besides the decrease in the regioselectivity (A:B) for these three PB systems, the photochemical yields decrease largely especially in DFBP system, but only mass balance of DFBP system decrease remarkably, with increasing proportion of water in the binary solutions. Obvious side products, which may be formed via an electron transfer reaction from DMT to triplet DFBP, were observed in the solution containing high proportion of water, beginning at 3:2 acetonitrile–water, and increased with raising the proportion of water. The photoinduced electron-transfer reaction was observed in photochemical reaction of 4,4'-dicyanobenzophenone with DMT in acetonitrile [10].



Scheme 1.

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