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Photochemical oxidation of *N*,*N*-bis-(*tert*-butoxycarbonyl)-1,4-dihydropyrazine derivatives

Abstract: The photochemical oxidation of *N*,*N*-Bis-(*tert*-butoxycarbonyl)-1,4-dihydropyrazines was investigated by irradiation using a medium-pressure mercury lamp. The main products were isolated, and their structures were determined by spectral methods and single crystal X-ray diffraction analysis. Photooxygenation is suggested to be a [2+2] cycloaddition reaction of oxygen to the double bond.

Keywords: 1,4-dihydropyrazines; cycloaddition; photooxygenation; singlet oxygen.

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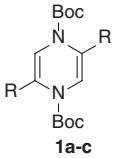
Introduction

The 1,4-dihydropyrazine moiety is a component of flavin coenzymes and several marine luciferins [1, 2]. The 1,4-dihydropyrazine system, with an 8π-electron structure and two enamine functions, has attracted much interest. Its antiaromatic character, electron-charge distribution in the molecule, properties of charge-transfer complexes, and role in redox-active biological molecules have been investigated [3–5]. Although the chemical properties of 1,4-dihydropyrazines have been studied for many years, their photochemical properties have received little attention. Here, a series of substituted 1,4-dihydropyrazines **1** were synthesized by the reported method [6, 7], and their photochemical oxidation properties were investigated. This work is a continuation of our studies of the photochemical properties of heterocyclic compounds, such as photodimerization and photochemical ring contraction [8–11]. The photochemical reactions involving oxygen were found to result in the oxygenation of nitrogen heterocycles [12–14]. The photochemical oxidation properties of *N*,*N*-bis-(*tert*-butoxycarbonyl)-1,4-dihydropyrazines **1** were investigated by irradiation with a medium-pressure mercury lamp under an oxygen atmosphere. Control experiments were designed to study the mechanisms of the photooxygenation of compounds **1**.



1a-c

a: R = H
b: R = Ph
c: R = COOMe

Results and discussion

The photooxygenation of a solution of **1** in acetone in the presence of oxygen was investigated by irradiation with a 450-W medium-pressure mercury lamp. Acetone is a photosensitizer that enhances the photochemical reaction rate of the 1,4-dihydropyrazines [15–18]. After the reaction was completed, as judged by thin-layer chromatography (TLC) analysis, the solvent was removed under reduced pressure, and the residue was subjected to chromatography on silica gel using a mixed solvent of petroleum ether and ethyl acetate (20:3 v/v).

In the photooxygenation of **1a** for 6 h, product **2a** was obtained with a yield of 34% (Scheme 1). The formation of the methylated diol may involve a methyl radical that is generated by the irradiation of acetone via a Norrish type I reaction [19]. The initial diol structure is apparently the product derived from an intermediate dioxetane by reaction with H_2O as postulated in similar reports by Adam et al. [20, 21]. It can be suggested that H_2O and methyl radical in the system undergo a reaction with the dioxetane to yield **2a**. This suggestion was substantiated by control experiments, in which the formation of **2a** was accelerated with the addition of several drops of H_2O. When conventional solvents such as CH_2Cl_2 were used in the photooxygenation of **1a**, the diol was not found.

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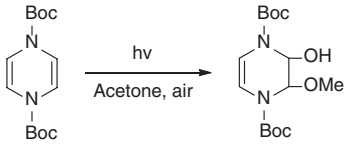
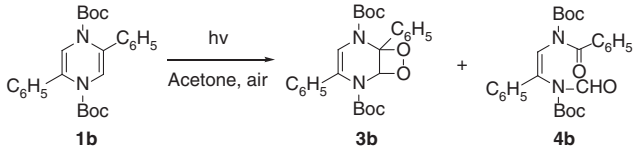


Scheme 1

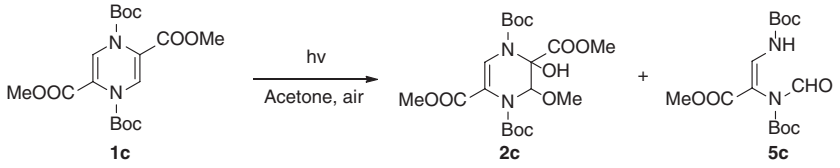


Scheme 2

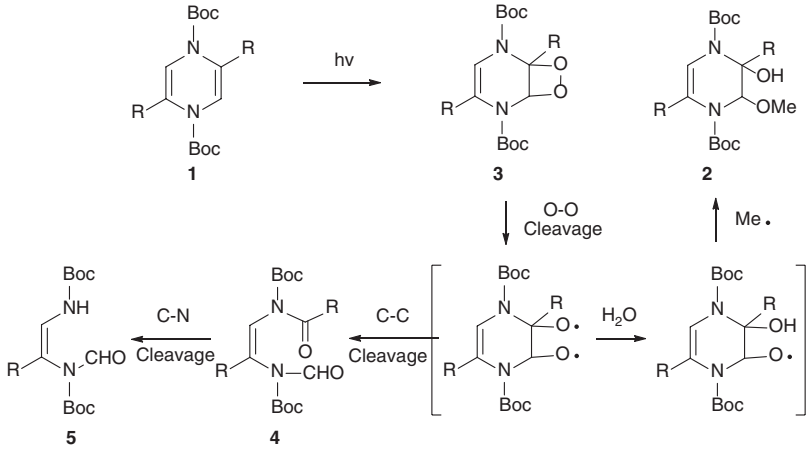
In the photooxygenation of **1b** for 10 h, products **3b** and **4b** were obtained with yields of 22% and 24%, respectively (Scheme 2). The dioxetane **3b** is apparently the product of the reaction of **1b** with O_2 by [2+2] cycloaddition, as referred to by Adam et al. [22]. It can be suggested that the dioxetane is unstable and undergoes decomposition to the carbonyl compound **4b** by cleavage of the O-O and C-C bonds. Similar chemistry has been described [23–25]. In addition, it was observed that **3b** is formed first, and product **4b** is gradually formed as the reaction progresses. It was also observed that the isolated compound **3b** is smoothly transformed to **4b** with a yield of 55% upon further irradiation.

In the photooxygenation of **1c** for 18 h, products **2c** and **5c** were obtained with the respective yields of 22% and 23% (Scheme 3). The formation of **2c** can be understood in terms of a similar process as the formation of **2a**, and the formation of **5c** is analogous to the formation of **4b** [26].

These findings form a basis for the suggested unified mechanism for the photooxygenation of **1** (Scheme 4). In the first step, substrate **1** undergoes a reaction with singlet oxygen by [2+2] cycloaddition that yields dioxetane **3**. Singlet oxygen is generated when triplet oxygen in air absorbs UV light (wavelengths <320 nm) [27–31]. The low energy gap between triplet and singlet oxygen allows for a sensitized excitation that can be achieved by UV light irradiation. The suggestion that singlet oxygen as a critical intermediate in the photooxygenation reaction of **1** was verified by flushing the reaction mixture with air or nitrogen. When air was continuously bubbled through the solution, the formation of **3** was accelerated, and the formation of **3** was abated under a nitrogen atmosphere. The role of singlet oxygen in this reaction was demonstrated by the addition of a quencher, which can capture the singlet oxygen, or a photosensitizer, which can convert the oxygen molecule to singlet oxygen. The quencher used



Scheme 3



Scheme 4 Proposed mechanism for the photooxygenation of **1**.

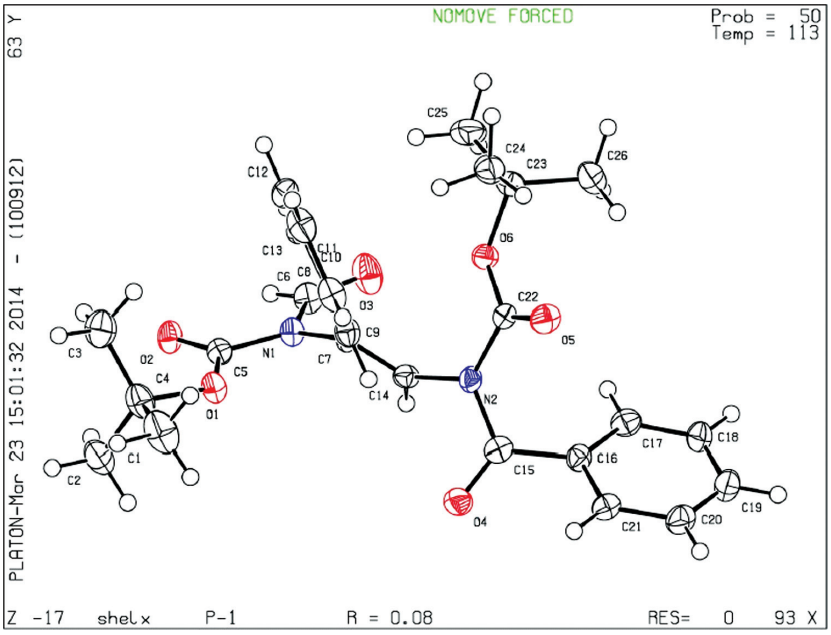


Figure 1: ORTEP diagrams of the crystal structure of **4b**.

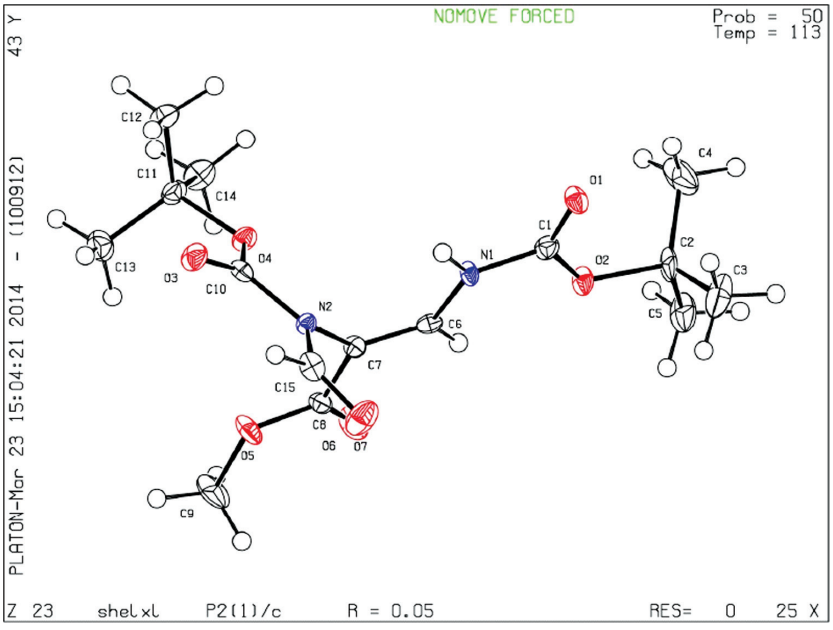


Figure 2: ORTEP diagrams of the crystal structure of **5c**.

was 1,4-diazabicyclo[2.2.2]octane, and the formation of **3** was dramatically suppressed in its presence. By contrast, in the presence of rubrene, a known photosensitizer, the formation of **3** was considerably accelerated.

The formation of **2** from dioxetane **3** is proposed to be an intramolecular electron transfer–mediated cleavage of the peroxide. Because the O-O bond is weaker than the C-C bond, compound **3** is decomposed by a stepwise process involving the homolysis of the peroxide bond to form a biradical intermediate, which then undergoes a reaction with H_2O to form a hydroxyl compound [32, 33]. The hydroxyl compound is methylated to give **2**. This methylation involves the methyl radical that is generated by irradiation of acetone (Norrish type I) [19]. The formation of **4** is proposed to originate from dioxetane **3** by a stepwise process that involves the

homolysis of the peroxide bond to form a biradical intermediate and a subsequent C-C bond cleavage [32, 34]. Compound **4** is directly converted to product **5** via a C-N bond cleavage, which is similar to the cleavage of N-boc oxamates, giving N-boc carbamates [26, 35]. Note that compound **4c** is unstable and is converted to the final product **5c** via a C-N bond cleavage. The three-dimensional structures of **4b** as *E*-isomer and **5c** as *Z*-isomer reflect the stability of **4** by the steric hindrance effect of the groups on the nitrogen atom. The increased steric interactions between the benzoyl and the phenyl groups lead to the *E*-isomer of **4b** being much more stable than the *Z*-isomer of **4b**.

Conclusions

Products of the photooxygenation of *N*,*N*-bis-(*tert*-butoxycarbonyl)-1,4-dihydropyrazines were isolated, and their structures were determined by ^{1}H NMR, ^{13}C NMR, high-resolution mass spectral (HRMS), and single crystal X-ray diffraction analysis. The photooxygenation is suggested to proceed via the intermediary 1,2-dioxetane derived by [2+2] cycloaddition of singlet oxygen to the double bond.

Experimental

All chemicals were purchased from commercial sources and used without further purification. TLC was conducted on silica gel 60 F254 plates (Merck KGaA). Melting points were determined on a XT-5A digital melting point apparatus and are uncorrected. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 and 100 MHz, respectively, in $CDCl_3$ or DMSO-d_6. HRMS analyses were conducted using a VG 70SE mass spectrometer operating in electrospray ionization mode. Irradiation for photochemical reactions was conducted using an Osram HBO 450W medium-pressure mercury lamp. The samples were irradiated in quartz cuvettes.

Preparation of *N*,*N*-bis-(*tert*-butoxycarbonyl)-1,4-dihydropyrazine derivatives 1

Compound **1a** was synthesized by the treatment of 1,4-dihydropyrazine bis(vinyl phosphate) with triethylammonium formate, palladium acetate, and triphenylphosphine in THF [6]. Compound **1b** was synthesized by a Pd-catalyzed Suzuki-Miyaura coupling reaction of 1,4-dihydropyrazine bis(vinyl phosphate) [6]. Compound **1c** was synthesized by the treatment of methyl ester of *N*-(4-toluenesulfonyl)-*N*-(*tert*-butoxycarbonyl)-α,β-didehydroalanine with DMAP and K_2CO_3 [7].

***N*,*N*-Bis-(*tert*-butoxycarbonyl)-1,4-dihydropyrazine (1a)** White solid isolated in 43% yield (lit. yield 45% [6]); mp 105–106°C (lit. mp 105–106°C [6]); ^{1}H NMR ($CDCl_3$): δ 1.45 (s, 18H), 5.77 (s, 2H), 5.89 (br s, 2H), 5.94 (br s, 2H), 6.04 (s, 2H).

***N*,*N*-Bis-(*tert*-butoxycarbonyl)-2,5-diphenyl-1,4-dihydropyrazine (1b)** White solid isolated in 69% yield (lit. yield 72% [6]); mp 188–189°C (lit. mp 188–189°C [6]); ^{1}H NMR ($CDCl_3$): δ 1.07 (s, 18H), 6.46 (s, 2H), 7.20–7.35 (m, 10H).

***N*,*N*-Bis-(*tert*-butoxycarbonyl)-2,5-bismethoxycarbonyl-1,4-dihydropyrazine (1c)** White solid isolated in 85% yield (lit. yield 89% [7]); mp 155–156°C (lit. mp 155–156°C [7]); ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 18H), 3.80 (s, 6H), 7.09 (s, 2H).

General procedure for the photooxygenation of *N*,*N*-Bis-(*tert*-butoxycarbonyl)-1,4-dihydropyrazines 1

A solution of **1** (0.32 mmol) in 200 mL of acetone in a quartz vessel was irradiated using a 450-W medium-pressure mercury lamp. The progress of the reaction was monitored by TLC. After completion, the solvent was removed under reduced pressure, and the residue was subjected to chromatography on silica gel using a mixed solvent of petroleum ether and ethyl acetate (20:3 v/v) as an eluent to provide products **2–5**.

Di-*tert*-butyl 2-hydroxy-3-methoxy-2,3-dihydropyrazine-1,4-dicarboxylate (2a) Colorless needles; mp 147–148°C; ^{1}H NMR (DMSO-d_6): δ 6.31–6.46 (m, 1H, -OH), 5.94–6.14 (m, 2H, =CH), 5.17–5.55 (m, 2H, -CH), 3.20 (d, 3H, -OCH_3), 1.46 (s, 9H, -$OC(CH_3)_3$), 1.45 (s, 9H,-$OC(CH_3)_3$); ^{13}C NMR (DMSO-d_6): δ 174.5, 152.5, 151.4, 73.0, 71.5, 55.1, 28.3, 28.2. HRMS (ESI). Calcd for $C_{15}H_{26}N_2O_6$ ($M+Na^+$): *m/z* 353.36651. Found: *m/z* 353.36619.

1,4-Di-*tert*-butyl 2,5-dimethyl-2-hydroxy-3-methoxy-2,3-dihydropyrazine-1,2,4,5-tetracarboxylate (2c) Colorless needles; mp 155–156°C; ^{1}H NMR ($CDCl_3$): δ 7.41 (s, 1H, =CH), 5.42 (s, 1H, -CH), 4.48 (s, 1H, -OH), 3.84 (s, 3H, -OCH_3), 3.80 (s, 3H, -OCH_3), 3.37 (s, 3H, -OCH_3), 1.50 (s, 9H, -$OC(CH_3)_3$), 1.47 (s, 9H,-$OC(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ169.3, 164.3, 152.8, 150.7, 122.2, 109.5, 55.3, 53.7, 51.8, 27.9**.** HRMS (ESI). Calcd for $C_{19}H_{30}N_2O_{10}$ ($M+Na^+$): *m/z* 469.43867. Found: *m/z* 469.43429.

Di-*tert*-butyl 1,4-diphenyl-7,8-dioxa-2,5-diazabicyclo[4.2.0]oct-3-ene-2,5-dicarboxylate (3b) White needles; mp 153–155°C; ^{1}H NMR ($CDCl_3$): δ 9.13 (s, 1H, =CH), 7.28–7.75 (m, 10H, Ar-H), 6.96 (s, 1H, -CH), 1.31 (s, 9H,-$OC(CH_3)_3$), 1.23 (s, 9H,-$OC(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 170.5, 161.0, 151.6, 151.2, 136.1, 135.5, 132.5, 129.1, 128.5, 128.4, 128.2, 125.3, 125.2, 123.7, 84.3, 27.5, 27.4. HRMS (ESI). Calcd for $C_{26}H_{30}N_2O_6$ ($M+Na^+$): *m/z* 489.20016. Found: *m/z* 489.19871.

***tert*-Butyl (*E*)-benzoyl(2-(*N*-(*tert*-butoxycarbonyl)formamido)-2-phenylvinyl)carbamate (4b)** Colorless needles; mp 135–136°C; ^{1}H NMR ($CDCl_3$): δ 9.44 (s, 1H, -CHO), 7.24–7.53 (m, 10H, Ar-H), 6.52 (s, 1H, =CH), 1.36 (s, 9H,-$OC(CH_3)_3$), 1.10 (s, 9H,-$OC(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 171.3, 162.8, 152.1, 151.3, 135.4, 134.7, 131.8, 130.1, 128.7, 128.5, 128.3, 128.0, 127.9, 127.1, 27.7, 27.2. HRMS (ESI). Calcd for $C_{26}H_{30}N_2O_6$ ($M+Na^+$): *m/z* 489.20039. Found: *m/z* 489.19871. Single crystal X-ray diffraction of **4b**: deposition CCDC-995232 (see next section).

Methyl (*Z*)-3-[(*tert*-butoxycarbonyl)amino]-2-[*N*-(*tert*-butoxycarbonyl)formamido]acrylate (5c) Colorless needles; mp 169–170°C; ^{1}H NMR ($CDCl_3$): δ 9.26 (s, 1H, -CHO), 8.01 (s, 1H, =CH), 6.61 (s, 1H, -NH), 3.77 (s, 3H, $-OCH_3$), 1.52 (s, 18H, $-OC(CH_3)_3$); ^{13}C NMR ($CDCl_3$): δ 164.0, 162.0, 151.5, 150.8, 85.0, 83.3, 52.0, 29.7, 28.0, 27.8. HRMS (ESI). Calcd for $C_{15}H_{24}N_2O_7$ (M+Na$^+$): *m/z* 367.35003. Found: *m/z* 367.34968. Single crystal X-ray diffraction of **5c**: deposition CCDC-995231 (see next section).

X-ray diffraction analysis of 4b and 5c

Crystals of **4b** and **5c** suitable for X-ray diffraction analysis were obtained by slow evaporation of an ethyl acetate solution of **4b** and **5c** at room temperature. The single crystal X-ray diffraction measurement was conducted on a Rigaku Saturn CCD area-detector diffractometer at 113(2) K using graphite monochromated Mo Kα radiation (λ=0.71070 Å) in the ω and φ scanning mode (Figures 1 and 2). An empirical absorption correction was applied using the ABSCOR program. All structures were solved by direct methods using the SHELXS-97 program and refined by full matrix least squares on F^2 using the SHELXL-97 program. All hydrogen atoms were geometrically fixed using the riding model. Files CCDC-995231 and CCDC-995232 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html.

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