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Photolysis of dibenzocycloocta-1,4-diene-6-diazo-3,7-dione in methanol. Intramolecular trapping of the Wolff rearranged product by photochemically formed hydroxyl group

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Abstract

Irradiation ($\lambda > 300$ nm) of dibenzocycloocta-1,4-diene-6-diazo-3,7-dione in methanol gave a bicyclic lactone as the sole isolable product. This can be explained in terms of intramolecular lactonization by attack of the hydroxyl group (produced as a result of the photoaddition of methanol on the excited carbonyl group at the 3 position) on the methoxycarbonyl group (formed by Wolff rearrangement followed by nucleophilic attack of the solvent).

Keywords: Intramolecular lactonization; Photoaddition of methanol; Decarbonylation; Keto-ketene

1. Introduction

The photolysis or thermolysis of α-diazoketones generating ketenes, generally known as the Wolff rearrangement, has attracted much attention since its discovery, and much mechanistic and preparative work has been accumulated [1]. This is mainly due to the large variety of products which can be obtained from ketenes as a result of their reactions with nucleophiles, unsaturated bonds and other functional groups. Intramolecular trapping of ketenes is often feasible leading to a highly functionalized product. For instance, the intramolecular [2+2] cycloaddition of ketenes with alkenes is a generally useful method for the synthesis of bridged and fused bicyclic compounds containing cyclobutanone [2]. During the course of our studies on the chemistry of functionalized ketocarbene [3], we synthesized and photolysed dibenzocycloocta-1,4-diene-6-diazo-3,7-dione (**1**) incorporated into a seven-membered ring bearing an additional carbonyl group at the transannular position in methanol. Compound **1** underwent multiple reactions involving Wolff rearrangement, methanol trapping of the resulting ketene and electronically excited ketone and transannular interaction between the ester and photochemically formed hydroxyl group to form a bicyclic lactone.

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2. Results and discussion

2.1. Synthesis of the diazodione (1)

Compound **1** was prepared by diazo transfer reaction to the corresponding ketone (**5**) with *p*-tosyl azide using $KF-Al_2O_3$ as base. While tertiary amines were found to be completely ineffective as a base in this reaction, more conventional strong bases, i.e. KOt-Bu (t-Bu, tert-butyl), were found to be unsatisfactory, although effective, and the diazo transfer using $KF-Al_2O_3$ usually gave superior results. Compound **1** was obtained as a rather stable gummy solid, which was purified by chromatography on deactivated alumina at low temperature and stored in a refrigerator for months without appreciable decomposition. It should be noted that no bis(diazo) ketone was detected in the reaction mixture even after prolonged stirring. This is in sharp contrast with that observed for an analogous reaction with 1,2,3,4-di(benzo)cyclohepta-1,3-diene-6-one, a seven-membered analogue of **1**, where an initially formed monodiazoketone was further diazotized to form 5,7-bis(diazo)-1,3-diene-6-one under essentially the same reaction conditions [4].

2.2. Irradiation of 1 in methanol

Irradiation of **1** was carried out in degassed methanol in a Pyrex tube using a 300 W high-pressure Hg lamp

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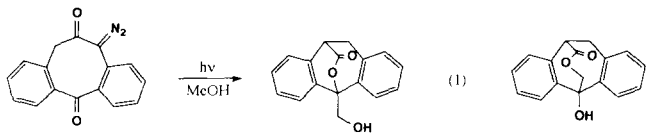
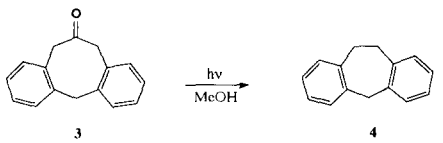
at 0 °C until thin layer chromatography (TLC) monitoring showed that all the starting compounds had been consumed. Separation of the photomixture by TLC resulted in one major component. The proton nuclear magnetic resonance (^{1}H NMR) spectrum of the product showed an AB quartet at 4.80 and 4.76 ppm and an ABC pattern at 4.08, 3.65 and 3.18 ppm in $CDCl_3$. These data coupled with the mass spectrum suggest that a bicyclic lactone, either **2** or **2′**, is the most probable structure for the photoproduct (Eq. (1)).



(1)

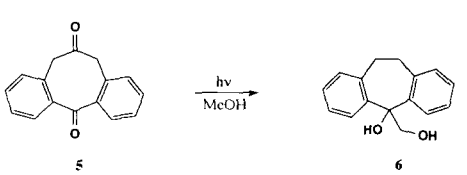
Crucial data for differentiating between the two alternatives were obtained in the ^{1}H NMR spectrum measured in dimethylsulphoxide-d_6 (DMSO-d_6), where coupling between the CH_2 protons and OH was observed (see Section 3). This is better explained in terms of lactone **2** bearing a CH_2OH side chain. The formation of lactone **2** is rather unexpected, and indicates that the initial product expected from simple Wolff rearrangement followed by reaction with the solvent, which was not isolated under these conditions, must undergo subsequent reaction very efficiently.

In order to obtain insight into the mechanism of formation of the lactone, the following control experiments were carried out. First, irradiation of 1,2,4,5-dibenzocycloocta-1,4-diene-3-one (**3**) in methanol under similar conditions ($\lambda > 300$ nm at 20 °C) produced dibenzocycloheptadiene (**4**) almost exclusively (Eq. (2))



(2)

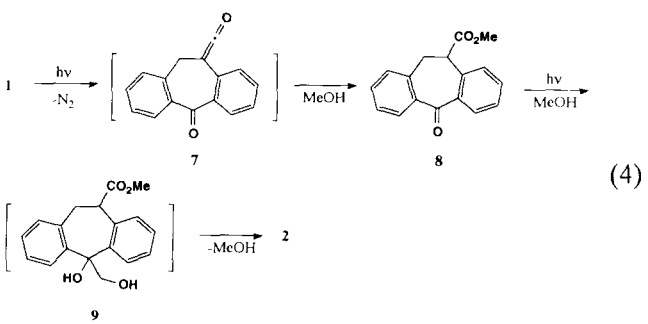
suggesting that photodecarbonylation of this ketone is very efficient. This is not surprising since dibenzyl ketone also undergoes efficient photodecarbonylation in solution [5]. Second, the similar irradiation of dibenzocycloocta-1,4-diene-3,7-dione (**5**) gave 3-hydroxy-3-hydroxymethyldibenzocycloheptadiene (**6**) in high yield (Eq. (3)).



(3)

This can be interpreted as indicating that the dione undergoes photodecarbonylation to produce dibenzocycloheptadienone, which subsequently abstracts a hydrogen atom from the C–H bonds of methanol on further excitation, and that both processes occur very efficiently. These observations indicate that the 3-carbonyl group in the dibenzocycloheptadienone structure is highly susceptible to hydrogen abstraction on photoexcitation. The reason for the almost exclusive formation of the alcohol adduct, i.e. **6**, during irradiation is partly because of the difficulty in the coupling of ketyl radicals, forming pinacols, due to steric hindrance.

From these observations, a plausible mechanism for the formation of **2** during the photolysis of **1** in methanol is proposed in Eq. (4).



(4)

Thus irradiation of **1** must result in the formation of ketene (**7**) which is trapped by the solvent to form 6-(methoxycarbonyl)dibenzocyclooctadienone (**8**). Subsequent photoexcitation of **8** generates the excited state of the carbonyl group, which abstracts hydrogen from the solvent to afford the solvent adduct (**9**).

Intramolecular transannular attack of the hydroxyl group on the methoxycarbonyl group must produce the lactone (**2**). Support for this explanation comes from the observation that the thermolysis of **1** in methanol produces the ester (**8**), which was "elusive" in the photolytic runs, and subsequent photoexcitation of the ester in methanol produces the final lactone (**2**) almost instantaneously.

The almost exclusive formation of the lactone without the accumulation of **9** is worthy of comment with respect to the vicinity of both the functional groups and the stereoselectivity of the addition of methanol to the excited ketone. Inspection of a molecular model for **9** reveals that both hydroxyl groups in **9** must lie close to the methoxycarbonyl group to undergo intramolecular lactonization. However, conformational analysis of each transition state leading to **2** and **2′** indicates that, for the CO_2Me group to interact effectively with the CH_2OH group forming **2′**, the C–CO_2Me bond should be located in the eclipsed conformation with respect to the adjacent methylene group, whereas the bond can remain in a more stable staggered conformation in the state leading to **2**. This explains the exclusive formation of **2** rather than **2′**. Ab initio calculations (STO-3G) of **2** and **2′** indicate that **2** is some 12 kcal mol^{-1} more stable than **2′**. It has been well documented [6] that lactonization

occurs very easily in many hydroxy-esters where the appropriate distance and orientation between the functional groups are retained, and therefore it plays a key factor in enzyme catalysis. Failure to isolate **9** in the photomixture suggests that the hydroxy-ester meets the requirement for lactonization. On the other hand, the almost exclusive formation of **2** might suggest that the photoaddition of methanol proceeds rather stereoselectively to form the diastereomer of **9** leading to **2**. If we accept that the addition takes place through hydrogen abstraction by an n,π^* excited carbonyl group, followed by the coupling of the resulting ketyl and hydroxymethyl radicals [7], the approach of the methyl radical anti to the methoxycarbonyl group is sterically favoured. This may explain the observed stereoselectivity. However, it should be pointed out that the lactone is isolated in only 35% yield. ^{1}H NMR analysis of the fresh photomixture indicates that **2** is already present as the major product and that no prominent signals which can be ascribed to other products are observed. It may be that the isomers are formed but lost due to other reactions, since photolysis of the ester **8** in methanol produces **2** in about 50% yield. Further experiments are in progress to support the proposed mechanism. Thus the present observations not only provide another example of the use of intramolecular quenching in the Wolff rearrangement for the synthesis of functionalized compounds, but also give some insight into the intramolecular control of the stereochemistry of photochemical addition of an alcohol to an excited carbonyl compound.

3. Experimental details

3.1. General method

IR spectra were measured on a JASCO A-100 recording spectrometer, and mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer (70 eV). ^{1}H NMR spectra were determined with a JEOL JNM-EX 270 spectrophotometer with tetramethylsilane as internal standard. TLC was performed on Merck Kieselgel 60 PF_{254}. Gas–liquid chromatography (GLC) was carried out using a Yanagimoto G-80 gas chromatograph with OV-7 on Diasolid L (5.0 mm × 50 cm). Compounds **3** [8], **4** [9] and **5** [10] were prepared according to literature procedures.

3.2. Preparation of 1

To a solution of **5** (100 mg, 0.42 mmol) in anhydrous MeCN (10 cm^3) was added KF–Al_2O_3 [11] (76.2 mg, 1 equiv.) and tosyl azide (83.4 mg, 0.42 mmol), and the mixture was stirred for 3 h at room temperature. After filtration of KF–Al_2O_3 and evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and the solution was washed with 5% KOH (aqueous) and H_2O and dried over Na_2SO_4. The mixture, after concentration, was chromatographed on an alumina column at 0 °C eluted with $CHCl_3$–*n*-hexane (10 : 1) to give **1** as a yellowish gummy solid (43 mg, 39%); δ_H ($CDCl_3$): 8.12–8.06 (m, 2-H), 7.64–7.20 (m, 6-H), 3.78 (S, 2-H); ν_{max} (KBr) (cm^{-1}): 2100s.

3.3. Irradiation for analysis purposes

The irradiations were carried out in a Pyrex tube of 5.0 ml capacity below 10 °C. In order to avoid ambiguity of the yields due to oxidation, the solution was degassed by subjecting the sample to a minimum of three freeze–thaw cycles at a pressure of approximately 10^{-5} Torr before irradiation. Irradiation was carried out with a 300 W mercury lamp and was generally continued until all the starting material had been consumed. Product identifications were established by gas chromatography–mass spectrometry (GC–MS) as well as NMR comparisons with authentic samples.

3.4. Photolysis of 1

Irradiation of **1** (40 mg, 0.21 mmol) in anhydrous MeOH (25 cm^3) in a Pyrex tube was carried out using a Halos 300 W high-pressure Hg lamp until all the starting diazo compound had been consumed. After evaporation of the solvent, the mixtures were separated by preparative TLC (Merck Kieselgel 60 PF_{254}) eluted with CH_2Cl_2–*n*-hexane (9 : 1) to give **2** (16 mg, 35%) as a yellowish oil. δ_H ($CDCl_3$): 7.34–7.09 (m, 8-H), 4.80 (d, *J* 18.1, 1-H), 4.76 (d, *J* 12.2, 1-H), 4.08 (dd, *J* 4.0, 17.8, 1-H), 3.65 (dd, *J* 4.0, 17.8, 1-H), 3.18 (dd, *J* 4.0, 17.8, 1-H), 1.60 (bs, 1-H); δ_H (DMSO-d_6): 7.45 (d, *J* 7.32, 1-H), 7.41–7.24 (m, 5-H), 7.17 (t, *J* 7.32, 1-H), 7.10 (d, *J* 7.94 1-H), 4.69 (dd, *J* 12.20, 6.11, 1-H), 4.57 (dd, *J* 12.20, 5.49, 1-H), 4.13 (dd, *J* 4.27, 3.67, 1-H), 3.51 (dd, *J* 18.31, 1-H), 3.10 (dd, *J* 18.31, 4.27, 1-H), 2.50 (dd, *J* 6.11, 5.49, 1-H); *m/z* 266 (M^+, 7.1%), 220 (52.4%), 178 (100%).

3.5. Thermolysis of 1

A solution of **1** (40 mg, 0.21 mmol) in anhydrous MeOH (10 cm^3) was refluxed for 24 h. After evaporation of the solvent, the mixtures were separated by preparative TLC to afford **8** (30 mg, 75%) as an oil. δ_H ($CDCl_3$): 8.10 (d, *J* 7.92, 1-H), 8.01 (d, *J* 7.59, 1-H), 7.52–7.18 (m, 6-H), 4.26 (t, *J* 4.95, 1-H), 3.55 (d, *J* 4.95, 1-H), 3.50 (s, 3-H); *m/z* 266 (M^+, 51.8%), 251 (14.9%), 208 (46.0%), 207 (100%), 180 (29.8%), 179 (27.6%), 178 (58.1%), 152 (31.9%), 76 (26.6%).

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