Bull. Chem. Soc. Jpn., 61, 1437—1439 (1988)

The Photocyclization of *N*,*N*-Dialkyl *β*-Oxo Amides Adsorbed on Silica Gel

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(Received June 13, 1987)

Synopsis. *β*-Oxo amides 1 adsorbed on silica gel underwent photocyclization via *δ*-hydrogen abstraction to give the five-membered lactams **2**. No severe restrictions on the molecular motion could be observed in the photoreaction on the silica-gel surface. However, the relative photoreactivity of *N*,*N*-dibenzyl-2-benzoylacetamide (**1a**) to *N*,*N*-dibenzyl-2-benzoylpropionamide (**1b**) increased greatly on the silica-gel surface compared to that in solution, probably because of the greater keto content on the surface.

The photochemistry and photophysics of organic molecules adsorbed on silica gel have been studied well and compared with their solution counterparts.[1–5] The mobility of excited molecules or radical pair intermediates has received particularly much attention because they are unique surface probes.[3d] Most of the photochemical studies have, however, been concerned with photodecompositions via radical-pair intermediates, and much less attention has been focussed on the intramolecular photoreactions of organic molecules on the dry silica gel surface.[5] We will report here as the photocyclization of *N*,*N*-dialkyl *β*-oxo amides via intramolecular *δ*-hydrogen abstraction by the excited carbonyl group on a dry silica-gel surface.

Experimental

Materials. Silica gel (Merck Kiesel Gel 60, Art. #9385) was used as received. The *β*-oxo amides **1a—d** were prepared according to a previously described method.[6] Valerophenone was purified by fractional distillation with a Taika SM-NB spinning-band distilation apparatus. Phenanthrene (Tokyo Kasei Co.), a calibrant for the HPLC analysis, was recrystallized from ethanol. Hexadecane (Tokyo Kasei Co.), a calibrant for the GC analysis, was purified by passing it through silica gel.

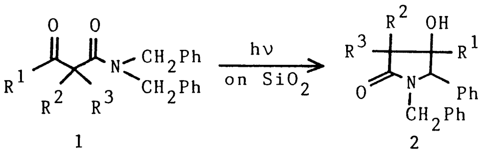
General Procedure. Preparative Irradiation of the *β*-Oxo Amides 1 on Dry Silica Gel: The *β*-oxo amide **1** (ca. 0.1 mmol) in 5 cm^3 of dichloromethane was added to 2 g of silica gel in a Pyrex tube (30×200 mm). The mixture was sonicated for 5 min, and then the solvent was evaporated under reduced pressure. The tube was rotated and irradiated for 10 h with a 100 W high-pressure mercury lamp (Taika Co.). Acetonitrile (10 cm^3) was then added to the mixture, the mixture was sonicated, and the adsorbed material was extracted with acetonitrile.[7] After the removal of the solvent, the residue was chromatographed on silica gel. Elution with a mixture of benzene-ethyl acetate (10/1 (v/v)) gave the unreacted *β*-oxo amide **1** and the lactam **2**. The structures of **2a—d** were determined by comparison with authentic samples.[6,8] The yields of the lactam **2** are summarized in Table 1.

The Quantitative Photolysis of the *β*-Oxo Amides 1 on Dry Silica Gel: The *β*-oxo amide **1** (ca. 0.03 mmol) in 1 cm^3 of dichloromethane was added to 0.5 g of silica gel in a Pyrex tube (18×180 mm). In the quenching experiments, appropriate amounts of 2,5-dimethyl-2,4-hexadiene in dichloromethane were added. The mixture was sonicated for 5 min, and then the solvent was evaporated under reduced pressure. The tubes were rotated and irradiated with a 100 W high-pressure mercury lamp. The adsorbed material was sonicated and extracted with acetonitrile. To the acetonitrile solution was added 1 cm^3 of an acetonitrile solution containing a known amount of phenanthrene (ca. 0.001 mmol) as a calibrant for the HPLC analyses. The analyses were performed using a Gasukuro Kogyo 570B high-pressure liquid chromatograph with a Model 511 single-wave UV detector (254 nm). A Unishil QC18 column (4×250 mm) was used, and a mixture of methanol-water (7/3 (v/v)) was employed as the moving phase at a flow rate of 0.7 ml min^{-1}.

Photolysis of Valerophenone on Dry Silica Gel: Valerophenone (ca. 0.03 mmol) in 1 cm^3 of dichloromethane was adsorbed on 0.5 g of silica gel and irradiated as has been described above. After the extraction with acetonitrile, 1 cm^3 of an acetonitrile solution containing a known amount of hexadecane (ca. 0.001 mmol) as a calibrant was added. The mixture was then analyzed using a Shimazu GC-4B gas chromatograph equipped with a flame ionization detector. Analysis was performed on a 2 m×4 mm column packed with 5% DCQF-1 and 1% EGS on Chromosorb P.

Results and Discussion

The irradiation of *N*,*N*-dibenzyl-2-benzoylacetamide (**1a**) adsorbed on silica gel with a 100 W high-pressure mercury lamp gave a five-membered lactam, 1-benzyl-



Scheme 1.

Table 1. Yields of the Photoproduct **2** and the Reaction Conditions

	Starting material			Yield of **2**/%	
	R^1	R^2	R^3	In benzene	On silica gel
1a	Ph	H	H	80[a)]	83
1b	Ph	Me	H	90[a)]	91
1c	Ph	Me	Me	65[a)]	63
1d	2-Naphthyl	H	H	50[b)]	7

a) Ref. 8, b) Ref. 6.

4-hydroxy-4,5-diphenyl-2-pyrrolidinone (**2a**), in an 83% yield. Similarly, the irradiation of two β-oxo amides, **1b** and **1c**, on dry silica gel gave the lactam **2b** and **2c** in 91 and 63% yield respectively. The yields of the lactams **2a—c** from photolyses of the β-oxo amides **1a—c** on silica gel are similar to those in photoreactions in solution[8] (Table 1). The formation of the lactams **2a—c** on silica gel can be explained in terms of the intramolecular δ-hydrogen shift to the carbonyl oxygen, as in photoreactions in solution.[6] The rates at which the β-oxo amides **1** adsorbed on silica gel undergo conformational change should be as fast as the rate at which they react chemically from their electronically excited states.

The β-oxo amide **1a** exhibits the keto-enol tautomerism. We have previously reported that the enol-form of the β-oxo amides 1 acted as an internal filter in solution photochemistry; the quantum yield for the production of the lactam from **1a** in benzene was 33 times lower than that from 1b ($\phi_{2a}/\phi_{2b}=0.03$).[6] The enol tautomer may reduce the photoreactivity of the β-oxo amides **1** on silica gel. However, the rate of the disappearance of the β-oxo amide **1a** on silica gel was equal to that of **1b** (Fig. 1). This result may be explained in two ways; the efficiency of the photoreaction of **1a** may be increased, or that of 1b may be decreased, by the steric effect of the 2-methyl group. However, it seems that the latter possibility can be excluded because the quantum yield for the production of **2b** from **1b**[6] is comparable to that for acetophenone formation from valerophenone[9] in solution photochemistry ($\Phi_{2b}/\Phi_{PhCOMe}=0.79$). The reaction rate for the production of **2b** from **1b** on the silica gel surface relative to that of acetophenone formation from valerophenone on the surface was also comparable ($\Phi_{2b}/\Phi_{PhCOMe}=0.56$). This result indicates that the photoreactivity of **1a** on the silica gel surface is increased to the same level as that of **1b**. The efficient photoreactivity of **1a** might indicate that the β-oxo amide **1a** exists nearly completely as in the keto form on the surface. The enol content of **1a** in a solution depends on the solvent polarity. The enol content of **1a** as well as other β-oxo amides[10] decreases with an increase in the solvent polarity.[8] The increment of the keto form of **1a** may be due to the polar property of the silica-gel surface. The surface of silica gel is presumed to be a suitable field for a photoreaction from only the keto tautomer of β-dicarbonyl compounds.

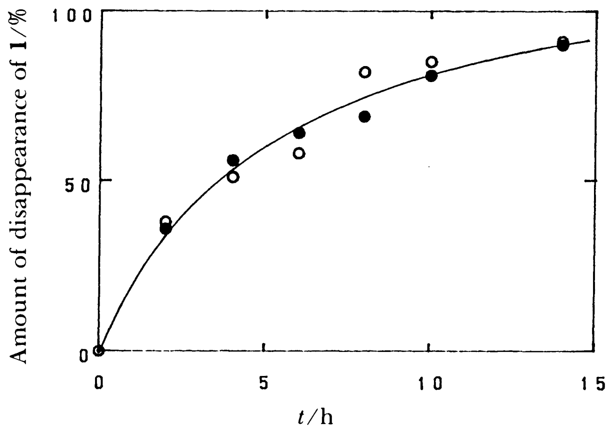


Fig. 1. Disappearance of the β-oxo amide **1a** (○) and **1b** (●) on silica gel. In each case 0.028 mmol of the oxo amides was used.

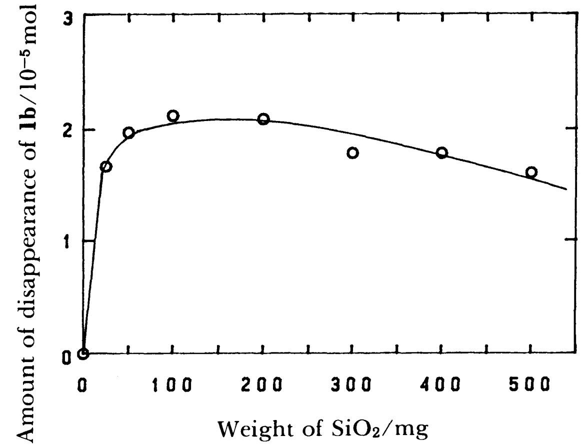


Fig. 2. Efficiency of the photoreaction of **1b** on silica gel. In each case 0.028 mmol of **1b** was used.

The rate of the disappearance of the β-oxo amides **1** on silica gel depended on the amounts of the β-oxo amides adsorbed on a unit gram of silica gel (Fig. 2). The amount of **1b** (0.028 mmol) which disappeared increased with the increase in the amounts of silica gel and reached its maximum at about 100 mg of silica gel. This suggests that 100% coverage is achieved with 0.028 mmol of **1b** per 100 mg of silica gel. This idea was supported by the following calculation. The surface area of silica gel (Merck Kiesel Gel 60, Art #9385) was 444 $m^2\ g^{-1}$. Consequently, the surface area occupied by one molecule can be calculated to be 2.6×10^{-18} m^2. The longest molecular chain of **1b** was calculated to be 15Å by using the values of bond lengths and bond angles.[11] From the experimental results described above, it was expected that the molecule of the β-oxo amides **1** on the silica gel surface could change its conformation within the lifetime of the excited state. Therefore, the surface area occupied by one molecule of the β-oxo amide **1b** can be approximated by the square model (15×15 $Å^2=2.3\times10^{-18}$ m^2). This value is almost entirely consistent with the experimental value. Therefore, 0.028 mmol of **1b** per 100 mg of silica gel corresponds to 100% monomolecular-layer coverage. When the ratio of the β-oxo amide **1b** to silica gel is over 0.028/100 mmol/mg, multiple layers might be formed. The molecules of the β-oxo amides on the monomolecular layer might act as filter for the β-oxo amide molecules in the layer.

The irradiation of **1b** in the solid state without silica gel under the same conditions resulted in the formation of a trace of the lactam **2b**, and more than 95% of the starting material was recovered.[12] The use of silica gel as an adsorbent effectively promotes the photoreaction of the β-oxo amides because silica gel has a wide surface area and because the β-oxo amide can be widespread on the silica-gel surface.

The quenching of the photoreaction of the β-oxo amides **1** on silica gel with 2,5-dimethyl-2,4-hexadiene was attempted. Scarecely no quenching was observed on **1a**, while the photoreaction of **1b** was remarkably quenched. These results are consistent with the photochemical behavior of the β-oxo amides in solution. The photoreaction of **1a** is presumed to occur through the charge-transfer intermediate. The $k_q\tau$ values could not be determined from the slopes in the Stern-Volmer plots because the diene was consumed during the irradiation.[13)]

The π,π^* excited state of ketones is generally not sensitive to direct hydrogen abstraction, while the n,π^* state is sensitive to it.[14)] The irradiation of the β-oxo amide **1d**, which is expected to have the π,π^* configuration in its lowest excited state, on silica gel also gave the lactam **2d** in a 7% yield. This result also suggests that electron transfer from nitrogen to the carbonyl group occurs prior to the hydrogen shift, even on silica gel, while the yield of **2d** is low.

The authors are grateful to Dr. Yoshimasa Inoue of the Central Research Laboratory, Sumitomo Metal Mining Co., for the surface-area determination.

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