JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 8, 31–34 (1995)

PHOTOISOMERIZATION OF 3-BENZOYLACRYLATES ON A SILICA GEL SURFACE: EFFECT OF REACTION ENVIRONMENT ON SELECTIVITY

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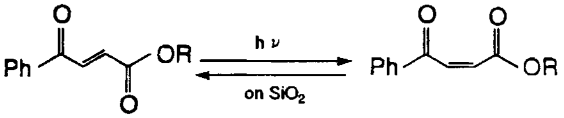
On irradiation on a dry silica gel surface, 2-(*N*, *N*-dialkylamino)ethyl 3-benzoylacrylates undergo selective E–Z isomerization. Competing processes, such as remote-hydrogen abstraction via a charge-transfer state, with the photoisomerization in solution are completely suppressed on the surface. The yield of the *Z*- from the *E*-isomer increases with increase in the coverage of the *E*-isomer on the surface, reaching a limiting value. Thermal isomerization of the *Z*- to the *E*-isomer occurs easily on the silica gel surface when the alkyl group on the nitrogen atom is small. Benzoylacrylates without any amino group also undergo selective photoisomerization.

1. INTRODUCTION

Selectivity in organic reactions is an important problem in synthetic and industrial chemistry and any general technique by which the course of a reaction may be modified is worthy of attention. Recently, photochemical processes in heterogeneous systems have attracted much interest because of their extensive applications in photography, photoresist technology, xerography, photopolymerization, chemical synthesis, and the storage and conversion of solar energy.[1–3] Solid surfaces may be divided into reactive and non-reactive surfaces.[1] Non-reactive surfaces, such as silica and alumina, provide an ordered two-dimensional environment for effecting and controlling photochemical processes more efficiently than can be attained in homogeneous solutions.[1] Dave *et al.*[4] have reported that photocycloaddition of allene to a steroidal enone, normally occurring from the less hindered α side, was directed in part to the more hindered β side by adsorption on the surface of silica gel. We have also reported that 2-benzoylcyclohexanones showed a different photochemical behaviour on a silica gel surface to that observed in solution.[5] However, the types of photoreactions observed on the surface are fundamentally the same as those seen in solution,[6] although large differences in the product distributions have been observed in some cases.[4,7] The *E–Z* photoisomerization of alkenes on surfaces[1,8] has been reported to occur as in solution, but with a low reaction rate and low *Z* percentage in the photostationary state.[8a] Recently, we have reported that 2-(*N*,*N*-dibenzylamino)ethyl (*E*)-3-benzoylacrylate [(*E*)-**1a**] underwent photoisomerization in solution to give the *Z*-isomer, which underwent a secondary photoreaction via remote hydrogen transfer to give a seven-membered azalactone.[9] The formation of the azalactone was not quenched with a diene because of the intervention of a charge-transfer intermediate, and the intervention facilitates the photocyclization.[9] Since the mobility of the adsorbed molecules is greatly



(E)-1 **(Z)-1**

a : R = $CH_2CH_2N(CH_2Ph)_2$
b : R = $CH_2CH_2N(CH_2Ph)CH_3$
c : R = $CH_2CH_2N(CH_3)_2$
d : R = $CH_2CH_2OCH_3$
e : R = CH_2CH_3

Scheme 1

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CCC 0894–3230/95/010031–04

Received 17 June 1994
Revised 10 September 1994

restricted in the adsorbed state,[10] photochemical processes which require comparatively much more conformational mobility may be completely suppressed on the surface. The remote hydrogen transfer in (*Z*)-**1a** requires the approach of a remote hydrogen to a carbonyl oxygen being governed by conformational flexibility and, therefore, is expected to be suppressed on the silica gel surface. In this work we studied the photochemical behaviour of 3-benzoylacrylates on a silica gel surface and we report here on the selective photoisomerization of benzoylacrylates on the surface (see Scheme 1).

EXPERIMENTAL

Silica gel (Merck Kieselgel 60, 70–230 mesh) was used as received. 3-Benzoylacrylates (*E*)-**1a–e** were prepared according to literature methods.[9,11] A Taika 100 W high-pressure mercury lamp was used as an irradiation source.

General procedure for preparative photolysis of (*E*)-1a–e on a dry silica gel surface

Compound **1** (*ca* 0·1–0·3 mmol; *ca* 60% coverage) in 5 cm^3 of dichloromethane was added to 1 g of silica gel in a 50 cm^3 round-bottomed flask. The mixture was sonicated for 5 min and the solvent was evaporated under reduced pressure. The coated silica gel was placed in a Pyrex tube (18 × 180 mm). The tube was rotated and irradiated for 5 h with a 100 W high-pressure mercury lamp. Acetonitrile (20 cm^3) was added for extraction of organic components and the mixture was sonicated for 10 min. The silica gel was separated by filtration and washed with 10 cm^3 of acetonitrile. The filtrate and washings were collected and then the solvent was removed under reduced pressure. Most of organic material was recovered by this method (more than 95% based on the weight of starting material used). The residue was chromatographed on silica gel. Elution with benzene–ethyl acetate (for **1a**, **b** and **d**), acetone (**1c**) or hexane–acetone (**1e**) gave the corresponding *Z*-isomer and the unreacted starting material. The yields are summarized in Table 1. The structures of the *Z*-isomers were determined by direct comparison with authentic samples[9,11] or on the basis of spectral data. However, complete purification of the *Z*-isomers, (*Z*)-**1b** and (*Z*)-**1d**, by distillation for elemental analyses could not be achieved because of thermal isomerization back to the corresponding starting *E*-isomers by heating. Pretreatment of the silica gel by drying at 200 °C for 3 h and use of different kinds of silica gel (Merck Kieselgel 60, 230–400 mesh) did not affect the photoreaction.

Photolysis of (E)-1a on a dry silica gel surface at different coverages and determination of production of (Z)-1a as a function of irradiation time

An appropriate amount (*ca* 0·12 mmol was used for rate determination) of (*E*)-**1a** was dissolved in 5 cm^3 of dichloromethane and the solution was added to 1 g of silica gel in a Pyrex tube (18 × 180 mm). The mixture was sonicated for 5 min, then the solvent was evaporated under reduced pressure. The tubes were rotated and irradiated for 2 h or an appropriate time with a 100 W

Table 1. Yields of photoproducts from **1**

Starting compounds	Reaction medium	Recovered starting compound (%)	Yields[a] of photoproducts (%)		
			Isomer	Others	Ref.
(*E*)-**1a**	On SiO_2	23[b]	~100[c]		
	In benzene	23	63[c]	1[e]	9
(*Z*)-**1a**	On SiO_2	80[b]	~100[d]		
	In benzene	45	17[d]	14[e]	9
(*E*)-**1b**	On SiO_2	63[b]	~100[c]		
	In benzene	36	—	9[f], 27[g]	9
(*E*)-**1c**	On SiO_2	100[b]	0[c]		
(*E*)-**1d**	On SiO_2	12[b]	~100[c]		
	In benzene	6	9[c]		
(*E*)-**1e**	On SiO_2	11[b]	~100[c]		
	In benzene	3	43[c]		

[a] Conversion yields.
[b] Percentage at photostationary state.
[c] (*Z*)-**1**.
[d] (*Z*)-**1**.
[e] 4-Benzyl-2-phenacyl-3-phenyl-4-aza-6-hexanolide.
[f] 4-Methyl-2-phenacyl-3-phenyl-4-aza-6-hexanolide.
[g] 2-(*N*-Benzyl-*N*-methyl)ethyl-3-benzoylpropionate.

high-pressure mercury lamp. The adsorbed material was sonicated and extracted with 5 cm^3 of acetonitrile. To the acetonitrile solution was added 1 cm^3 of an acetonitrile solution containing a known amount of phenanthrene (*ca* 0·005 mmol) as a calibrant for high-performance liquid chromatographic (HPLC) analysis. The analyses were performed using a Gasukuro Kogyo 570B HPLC system with a Model 511 fixed-wavelength UV detector (254 nm). An Inersil ODS-2 column was used with acetonitrile-water (7:3, v/v) as the mobile phase at a flow-rate of 0·8 cm^3 min^{-1}.

RESULTS AND DISCUSSION

Irradiation of (*E*)-**1a** on a dry silica gel surface with a 100 W high-pressure mercury lamp gave the isomer (Z)-**1a**. No photoproducts other than (Z)-**1a** could be detected, although a small portion of (*E*)- and (Z)-**1a** was hydrolysed when they were kept on a dry silica gel for a long period under light or even in the dark. The Z-isomer was isolated by silica gel column chromatography and its structure was determined by direct comparison with an authentic sample.[9] Similarly, irradiation of (Z)-**1a** gave (*E*)-**1a** as a sole photoproduct. Figure 1 shows the production of (Z)-**1a** in the photoreaction on the silica gel surface as a function of irradiation time. The photoreaction reached a photostationary state where *Z* to *E* ratio was *ca* 4. In contrast to the photochemical reaction of (*E*)-**1a** in solution, the surface photoreaction was clean (see Table 1). Photochemical processes such as remote-hydrogen transfer in the *Z*-isomer to give a medium-sized azalactone as observed in solution was completely suppressed on the surface. On the other hand, irradiation of (*E*)-**1a** spread over a glass plate in a thin layer, prepared by evaporation of the solvent from dichloromethane solution or by melting (*E*)-**1a** on a glass plate, gave a complex mixture involving the *Z*-isomer. These results strongly indicate that molecules only adsorbed on the dry silica gel surface undergo selective photoisomerization. The interaction between the surface and the acrylate molecules must be important for controlling the photochemical behaviour of the molecules. The silanol and the siloxane groups on the silica gel surface are known to be responsible for this interaction and the hydrogen bond between silanol and lone pair electrons or π-systems is considered to play the most important role in controlling the reaction.[12] The selective *E* to *Z* photoisomerization of **1** on the surface might be due to a decrease in conformational flexibility of the acrylate molecules on the surface.

The coverage of the molecules on the surface is an important factor for the reaction. The effect of surface coverage on the production of (*Z*)-**1a** was studied using samples loading different amounts of (*E*)-**1a** on 1 g of silica gel (Kieselgel 60, 70–230 mesh). The results obtained are shown in Figure 2. The production of (*Z*)-**1a** increased with increase in the amount of (*E*)-**1a** when the amounts loaded were below *ca* 0·25 mmol. Above this level, the amount of (Z)-**1a** produced was nearly constant. The surface area of the silica gel was 494 m^2 g^{-1}. Using Dreiding molecular models, the area per molecule of (*E*)-**1a** can be estimated to be *ca* $3{\cdot}8 \times 10^{-18}$ m^2, when the molecular coverage may be estimated on the basis of space-filling models as *ca* 0·22 mmol per gram of silica gel. When the amount of (*E*)-**1a** loaded on the silica gel is over *ca* 0·25 mmol g^{-1}, multiple layers may be formed.

Irradiation of 2-(*N*-benzyl-*N*-methyl)ethyl 3-benzoylacrylate [(*E*)-**1b**] on the silica gel surface also gave the *Z*-isomer as the sole photoproduct. However, the *Z*-isomer could not be isolated because it changed

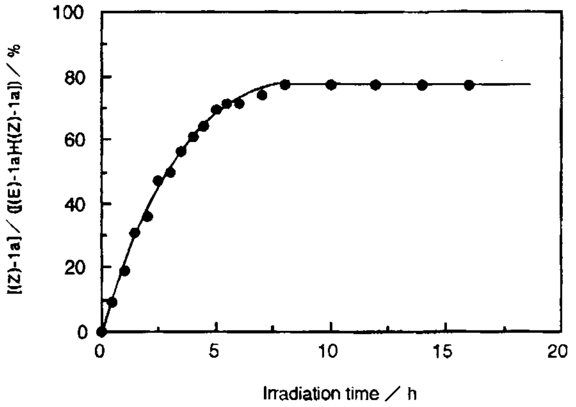

Figure 1. Production of (Z)-**1a** as a function of irradiation time on the surface photoreaction of (*E*)-**1a**. A 1 g amount of silica gel was used in all runs

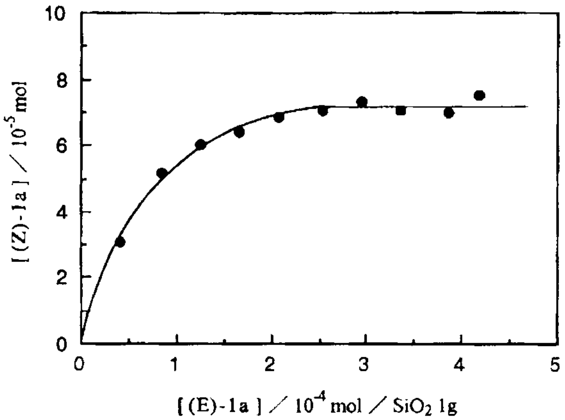

Figure 2. Dependence of product formation on the amount of starting material in the surface photoreaction of (*E*)-**1a** on silica gel. A 1 g amount of silica gel was used in all runs

completely into the *E*-isomer on passage through the silica gel column. The percentages of (*Z*)- and (*E*)-**1b** in the photostationary state shown in Table 1 were determined by NMR analysis. On the other hand, irradiation of 2-(*N*,*N*-dimethylamino)ethyl 3-benzoylacrylate [(*E*)-**1c**] on the surface gave no photoproducts. Irradiation of this compound in benzene gave an intractable mixture.[9] NMR analysis showed no evidences of the existence of (*Z*)-**1c** in the intractable mixture. When 3-benzoylacrylates without any amino group, (*E*)-**1d** and (*E*)-**1e**, were irradiated on the surface, the corresponding *Z*-isomers were formed as the sole photoproducts and could be isolated by column chromatography. Although side-reactions occurred on irradiation of these compounds in benzene, the reactions were almost completely suppressed on the surface. The *E* to *Z* ratios of **1a**, **d** and **e** before and after passage through the silica gel column were the same. Therefore, the amino group in the *Z*-form of the 3-benzoylacrylates (*Z*)-**1b** and (*Z*)-**1c** seems to facilitate the thermal isomerization of the Z to E form. The thermal isomerization occurred easily when the dialkylamino group was comparatively small, but the isomerization process was negligible in the case of (*Z*)-**1a**. Therefore, anchimeric assistance of the thermal isomerization by an amino group may occur.

In conclusion, a silica gel surface is a good reaction environment for controlling reactions. Photochemical processes via remote hydrogen transfer, which requires comparatively high conformational flexibility, were completely suppressed on the surface and the *E* to *Z* isomerization took place as the sole photochemical process.

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