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Photochemical Reaction of Ethyl 3-Methyl-3-phenylglycidate in Methanol and Ether Solvents

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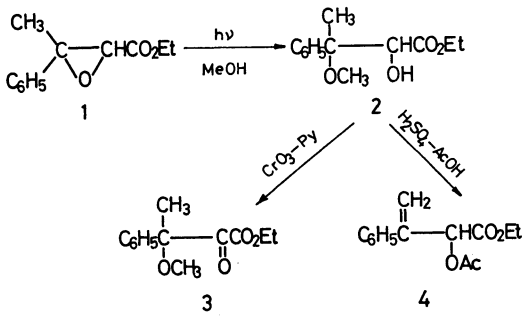
Synopsis. Irradiation of ethyl 3-methyl-3-phenylglycidate (**1**) in methanol gave an ionic addition product of the solvent, whereas in ether solvent different reaction paths leading to β-keto esters and carbene were observed.

It was previously reported that irradiation of aliphatic α,β-epoxy esters in an aprotic solvent gave corresponding β-keto esters,[1] while in a protic solvent completely different types of products were obtained.[2] In this note, we wish to report that the photochemical reaction of α,β-epoxy ester with a β-phenyl substituent in methanol gave an ionic addition product, but in ether solvent the reaction occurred with two competing pathway: a fragmentation to carbene and ketone and a rearrangement to β-keto ester. The photochemical fragmentation of aryl-substituted oxiranes to arylcarbenes has been studied extensively by Griffin and his co-workers.[3] The present work provides an additional example to the few reported ones where fragmentation occurs in the absence of vicinal diaryl substitution on the oxirane ring.[4]

Results and Discussion

Irradiation of ethyl 3-methyl-3-phenylglycidate (**1**) in methanol with 253.7 nm light for 45 hr gave a diastereoisomeric mixture of ethyl 2-hydroxy-3-methoxy-3-phenylbutyrate (**2**). The structure of **2** was determined by spectral data and by the following chemical transformations. Oxidation of **2** with chromium trioxide-pyridine complex gave α-keto ester (**3**), while treatment with warm sulfuric acid–acetic acid solution gave ethyl 2-acetoxy-3-phenyl-3-butenoate (**4**). Furthermore, a thermal reaction of **1** in methanol with a small amount of hydrochloric acid also gave **2** and its methyl ester in 45% and 19% yields, respectively.



Scheme 1.

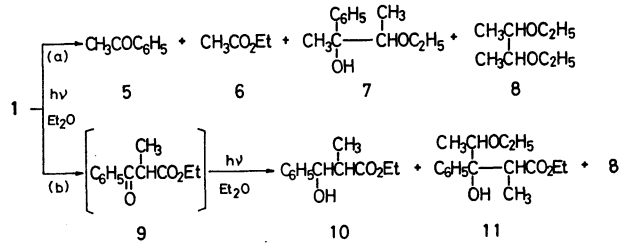
The results obtained under various conditions are summarized in Table 1. When the irradiation was carried out in the presence of hydrochloric acid or under oxygen atmosphere, an increased amount of **2** was obtained. The dark reaction of **1** in methanol did not give a detectable amount of **2**. In addition, it was also established that irradiation of **1** in methanol involving a small amount of alkali did not give **2**. These results demonstrate that this photochemical ionic reaction probably proceeds *via* a protonation of α,β-epoxy ester under irradiation. Photolysis of methanol in the presence of oxygen was reported to produce an acidic substance, which initiated the ionic reaction.[5] However, irradiation of degassed solution of **1** gave a 10% yield of **2**. Moreover, in a similar photochemical reaction of ethyl 1-oxaspiro[2,4]heptane-2-carboxylate, it was reported that the presence or absence of oxygen did not affect the yield of the ionic addition product of methanol.[2] Accordingly, although it is unknown what the nature of the acidic substance is, these results indicate that some acidic substances produced photochemically from the starting epoxy ester or solvent probably play an important role in these reactions.[5c]

Table 1. IRRADIATION OF **1** IN METHANOL UNDER VARIOUS CONDITIONS

Irradiation condition[a]	Yield of **2** (%)	Conversion of **1** (%)
N_2	20	97
N_2[b]	37	100
O_2	36	88
Degassed (1×10^{-4} mmHg)	10	65
Degassed, dark	0	58
Dark, in air	0	67
Dark, in air[b]	7	100

a) Irradiations were carried out with a 15 W low pressure mercury vapor lamp for 45 hr and dark reactions for 45 hr. b) A small amount of HCl was added.

The photochemical reaction of **1** in an aprotic solvent gave the following products mainly *via* two types of reaction paths, namely, a photolytic path leading to acetophenone and carbethoxycarbene (*a*)[3a] and a rearrangement to β-keto ester (*b*).[1] Irradiation of **1** in ether with a high pressure mercury vapor lamp for 90 hr gave acetophenone (**5**, 13%), ethyl acetate (**6**, 3%), 3-ethoxy-2-phenyl-2-butanol (**7**, 7%), 2,3-diethoxybutane (**8**, 40%), ethyl 3-hydroxy-2-methyl-3-phenylpropionate (**10**, 11%), and ethyl 4-ethoxy-3-hydroxy-2-methyl-3-phenylpentanoate (**11**, 32%) in a 95% conversion. Products **7**, **8**, **10**, and **11** involved an almost



Scheme 2

equal amount of diastereoisomers.

The formation of **5**, **7**, and **6** indicates that a photochemical cleavage of **1** occurred mainly at the C_α–O and C_α–C_β bonds. Products **7** and **8** have been shown to be produced by the photochemical reaction of acetophenone in ether,[6] while **6** may result from carbethoxycarbene. Ethyl acetate was shown to be produced by photolysis of ethyl diazoacetate in ether. The photolytic path to **10**, **11**, and **8** through β-keto ester (**9**) was confirmed by the fact that irradiation of **9** under the same conditions gave a mixture of **10**, **11**, and **8**. It was shown that β-methyl substituent migrates to α-carbon in preference to the phenyl group.[1,7]

Experimental

Ethyl 3-methyl-3-phenylglycidate (**1**) was prepared by the procedure of the Darzens synthesis.[8] Ethyl 2-methyl-3-oxo-3-phenylpropionate (**9**) was prepared according to the procedure of Marvel.[9] Quantitative glpc analyses were carried out with the internal standard.

Photochemistry of **1** *in Methanol.* A mixture of **1** and methanol (0.08 M) in a quartz tube was cooled in water and externally irradiated with a 15W low pressure mercury vapor lamp for 45 hr. Nitrogen gas was allowed to pass through the mixture during the irradiation. Distillation and a preparative glpc of the irradiation mixture gave diastereoisomeric ethyl 2-hydroxy-3-methoxy-3-phenylbutyrate (**2**): bp 250 °C; n_D^{23} 1.5050; IR (CCl_4) 3540, 1735 cm^{-1}; NMR (CCl_4) τ 9.02 and 8.92 (t, 3H), 8.42 and 8.40 (s, 3H), 6.85 and 6.90 (s, 3H), 7.42 (s, 1H, OH), 5.98 (s, 1H), 6.10 (q, 2H); *m/e* 238 (M^+), 135, 103. Found: C, 65.32; H, 7.89%. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61%.

Oxidation of **2** with chromium trioxide and pyridine[10] produced ethyl 3-methoxy-2-oxo-3-phenylbutyrate (**3**): n_D^{20} 1.4980; IR (CCl_4) 1740, 1725 cm^{-1}; NMR (CCl_4) τ 8.82 (t, 3H), 8.37 (s, 3H), 6.80 (s, 3H), 5.87 (q, 2H), 2.7 (s, 5H); *m/e* 135 (M^+–$COCO_2Et$), 104, 73. Found: C, 65.68; H, 7.02%. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%.

Treatment of **2** with freshly prepared warm sulfuric acid–acetic acid solution[11] gave ethyl 2-acetoxy-3-phenyl-3-butenoate (**4**): n_D^{20} 1.5115; IR (CCl_4) 1750, 865 cm^{-1}; NMR (CCl_4) τ 8.90 (t, 3H), 7.90 (s, 3H), 5.92 (q, 2H), 4.56 (s, 1H), 4.46 (s, 1H), 4.25 (s, 1H), 2.72 (m, 5H); *m/e* 248 (M^+), 189, 175, 145. Found: C, 67.87; H, 6.59%. Calcd for $C_{14}H_{16}O_4$: C, 67.73, H, 6.50%.

Thermal reaction of **1** in methanol in the presence of a small amount of HCl for 2 hr gave **2** and diastereoisomeric methyl 2-hydroxy-3-methoxy-3-phenylbutyrate: bp 230 °C, n_D^{23} 1.5160.

Photochemistry of **1** *in Ether.* An etheral solution of **1** (0.08 M) was irradiated with a 500 W high pressure mercury vapor lamp for 90 hr. Distillation and a preparative glpc gave **5**, **6**, **7**, **8**, **10**, and **11**. The identities of **7**, **8**, and **10** were established by comparison of IR, NMR, and mass spectr awith those of authentic samples.[6] β-Hydroxy ester **10** was prepared by a reduction of ethyl 2-methyl-3-oxo-3-phenylpropionate (**9**) with sodium borohydride in ethanol: bp 148—150 °C/11 mmHg (lit,[12] 109—110 °C/0.5 mmHg), n_D^{20} 1.5085 (lit,[12] n_D^{23} 1.5007). The spectral data of **11** were completely identical to those of the product obtained by the irradiation of **9** in ether: IR (CCl_4) 3475, 1735 cm^{-1}; *m/e* 207 (M^+–$CH(OC_2H_5)CH_3$), 105, 77. Found: C, 68.53; H, 8.47%. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63%.

Photochemistry of **9** *in Ether.* An etheral solution of **9** (0.08 M) was irradiated with a 500 W high pressure mercury vapor lamp for 25 hr. Distillation and a preparative glpc gave **10**, **11**, and **8**. The spectral data of the former two were completely identical to those of **10** and **11** obtained by the irradiation of **1** in ether.

Photochemistry of Ethyl Diazoacetate in Ether. An etheral solution of ethyl diazoacetate (0.3 M) was irradiated with a 500 W high pressure mercury vapor lamp for 15 hr. Distillation and a preparative glpc gave ethyl acetate (**6**), diethyl maleate, diethyl fumarate, ethyl 2-ethoxyacetate, and ethyl 3-ethoxybutanoate. The structure of ethyl 3-ethoxybutanoate was identified by comparison with an authentic sample[13]: n_D^{20} 1.4125 (lit,[13] n_D^{19} 1.4092); IR (CCl_4) 1735, 1200, 1100 cm^{-1}; NMR (CCl_4) τ 8.87 (t, 3H), 8.74 (t, 3H), 8.84 (d, 2H), 7.57 and 7.73 (d, 2H), 6.56 (q, 2H), 5.92 (q, 2H), 6.23 (sex, 1H); *m/e* 160 (M^+), 145, 131, 85, 73.

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