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PHOTOCHEMICAL REACTION OF ALIPHATIC α,β-EPOXY ESTER

M. Tokuda, M. Hataya, J. Imai, M. Itoh and A. Suzuki

Department of Chemical Process Engineering, Hokkaido
University, Sapporo, Japan

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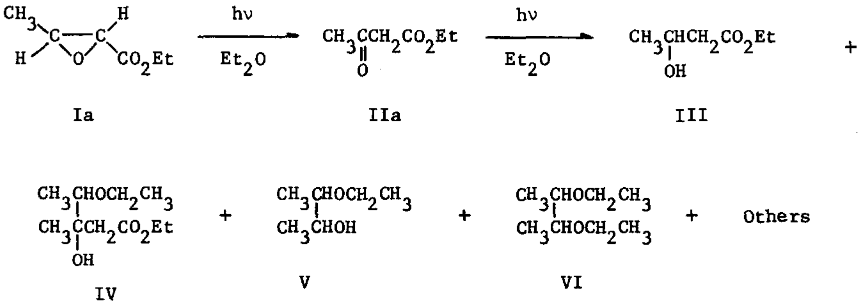
Although photochemical transformations of α,β-epoxy ketones have been studied[1)], only a few reports are available on the photochemical transformation of α,β-epoxy esters[2)], in spite of the expectation that the carbonyl group of ester would give a different photochemical reactivity and reaction path from that of ketone carbonyl[3)]. The photochemical reactions of α,β-epoxy ketones were described to give two types of reaction products; 1,3-diketone through migration of the β-substituent, and α-hydroxy ketone through abstraction of the γ-hydrogen[1c)], although studies on simple acyclic α,β-epoxy ketone with no aromatic substituents were almost ignored, probably because the product formed was subjected to secondary photolysis.

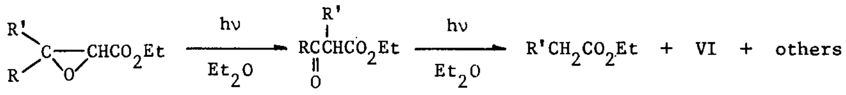
In the present paper, we wish to report the photochemical reaction of α,β-epoxy esters with simple alkyl substituents. The reaction path observed was only that to β-keto ester, and products resulting from hydrogen abstraction[1c)] and photolysis to carbene[4)] were not detected.

Irradiation[5)] of trans-ethyl β-methyl glycidate (Ia) in ether for 20hr produced ethyl 3-hydroxy butyrate (III), diastereoisomeric ethyl 3-methyl-3-hydroxy-4-ethoxy valerates (IV, IV'), 2,3-diethoxy butane (VI)[6)], a small amount of diastereoisomeric 2-hydroxy-3-ethoxy butane (V, V')[6)] and others in a 67% conversion. IV: bp 225°; n^{13} 1.4313; ir(CCl_4) 3500, 1713, 1195



1113cm^{-1}; nmr(CCl$_4$) τ8.90(d,3), 8.91(s,3), 8.72(t,3), 7.56(s,2), 6.5(m,3), 5.85(q,2); mass spectrum m/e 189(M$^+$-15), 131, 117, 73. IV': bp 223.5°; n^{13} 1.4324. The ir, nmr and mass spectra of IV' were almost identical with those of IV. Diastereoisomeric V and V' were also determined by comparison with the irradiated product of acetaldehyde in ether.

Ethyl β,β-dimethyl glycidate (Ib), ethyl β-methyl-β-ethyl glycidate (Ic) and ethyl β,β-diethyl glycidate (Id) also proceed through the same reaction path to give photolysed products, such as VII, VI and others. These products are probably yielded from the radical $\mathrm{R'\dot{C}HCO_2Et}$ which should result from a homolysis of α,β-bond of the corresponding β-keto esters (II). This is suggested from the fact that the photochemical reaction of both α,β-epoxy ester and β-keto ester were strongly retarded in the presence of DPPH. Irradiation of



Ib, R=R'=CH$_3$ IIb, c, d VII

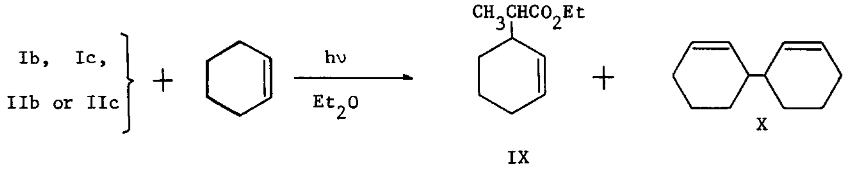
c, R=C$_2$H$_5$, R'=CH$_3$

d, R=R'=C$_2$H$_5$

α,β-epoxy ester (Ib) gave ethyl propionate (VII, R'=CH$_3$), ethanol, acetaldehyde, V, VI and others in a 63% conversion, Ic in a 61% conversion to ethyl propionate (VII), VI and others, and Id in a 56% conversion to ethyl butyrate (VII, R'=C$_2$H$_5$), 3-amyl alcohol, ethyl 2-ethyl-3-ethoxy butyrate (VIII)[6], VI and others.

That α,β-epoxy ester (I) was photolysed to various decomposition products through β-keto ester (II) was confirmed by the following results. When the corresponding β-keto esters which were separately prepared were irradiated under the same conditions, they completely disappeared and gas chromatograms of the resulting products were almost the same as those from I. Secondly, when α,β-epoxy esters, Ib and Ic, were independently irradiated in the presence of cyclohexene, with the expectation to trap the enol forms of keto esters[7], the same products, ethyl 2-(3-cyclohexenyl) propionate (IX)[6] and 3,3'-bicyclohexenyl (X), were obtained in both cases. Moreover, the irradiation of the β-keto esters, IIb or IIc, under the same conditions gave the same mixture of products[8]. The product IX in the above four reactions may have resulted from the reaction of the identical radical

$R'\dot{C}HCO_2Et$ $(R'=CH_3)$ and cyclohexene, which indicates the presence of intermediate, β-keto ester in the photochemical reaction of α,β-epoxy ester. That in the case of Ia, the decomposition of an intermediate IIa is restrained, and the keto ester is converted into III and IV, is probably due to the instability of the radical $R'\dot{C}HCO_2Et$ $(R'=H)$ and the larger amount of enol form in ethyl acetoacetate (IIa)[9].



Migration of methyl or ethyl substituent in α,β-epoxy ester Ic may well produce β-keto ester IIc $(R=C_2H_5,\ R'=CH_3)$ or IIc' $(R=CH_3,\ R'=C_2H_5)$, respectively. When IIc and IIc' were irradiated for 6hr, 79% of IIc and 95% of IIc' were converted to give ethyl propionate and ethyl butyrate, respectively. Irradiation of Ic was found to give ethyl propionate and others without ethyl butyrate. Moreover, a gas chromatogram of the resulting product was very much alike that of IIc, indicating the preferential migration of the methyl group. Consequently, it was shown that a hydrogen atom migrates to α-carbon in preference to methyl group in Ia and the methyl group moves preferentially to the ethyl group in Ic. Migrational aptitude in these results, hydrogen ⟩ methyl ⟩ ethyl, is somewhat different from that reported by Reusch et. al[1d], hydrogen ⟩ methylene ⟩ methyl ⟫ phenyl, in the case of epoxy ketones. However, since the "methylene" employed by the above workers was not a simple alkyl substituent but a ring methylene, the position of ethyl substituent in the order of the present work appears to be not unreasonable.

Although the photochemical transformation of α,β-epoxy ketones to β-diketone was reported to proceed <u>via</u> a singlet excited state[1d], that of α,β-epoxy esters to β-keto esters seems to proceed <u>via</u> a triplet excited state, because it was shown that the reaction was quenched by piperylene, benzene and naphthalene, and that the photochemical decomposition of β-keto ester was not affected by piperylene.

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5. Ether solution of α,β-epoxy ester (0.3M) in a quartz tube was externally irradiated with a 500 watt high pressure mercury vapor lamp under nitrogen atmosphere. Irradiated samples were cooled with running water throughout the irradiation.
6. These products were identified from the spectral data. Those will be published elsewhere.
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8. On irradiation of a mixture of Ib or Ic (1mmol), cyclohexene (2.5ml) and ether (7.5ml) with a 500 watt high pressure mercury vapor lamp, irradiation time, conversion and yield of IX and X were as follows: Ib, 60hr, 81, 7, 10%; Ic, 60hr, 77, 6, 12%; IIb, 10hr, 81, 20, 16%; IIc, 10hr, 75, 13, 15%.
9. The enol form involved in Ia, Ib, Ic and Id in CCl_4 was estimated to be 24, 9, 6 and 10% from nmr spectra.