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THE PHOTOCHEMICAL 1,3-CYCLOADDITION OF CARBONYL COMPOUNDS WITH OXIRANES: A COMPETITIVE CLEAVAGE OF CARBON-CARBON AND CARBON-OXYGEN BONDS IN ETHYL 2-METHYL-3-PHENYLGLYCIDATE

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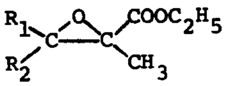
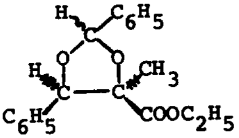
When a benzene solution of either *cis* (**1**-*c*) or *trans* 2-methyl-3-phenylglycidate (**1**-*t*) was irradiated in benzene under N_2 at 254 nm for 48 hrs., about 20% conversion to a complex mixture was observed. Silica gel chromatography afforded only one crystalline product m.p. 103-104°, (for example, 30 mg from 3.8 g **1**-*t* in 200 ml C_6H_6). It had M.W. 312 (mass spec.) and its nmr in CCl showed two phenyls at 8.2-7.3 (m), one methyl at 1.80 (s), one ethoxycarbonyl at 1.17 (tr) and 4.13 (q),[1] and two singlet protons at 4.81 and 5.92 ppm. Its acid-catalyzed hydrolysis yielded ethyl *erythro*-2-methyl-3-phenylglycerate (**3**) and benzaldehyde (**4**), and the structure **2** which satisfies these observations was confirmed by a standard ketal synthesis from **3** and **4** in the presence of an acid catalyst. The configuration at C-2 in **2** is still unknown.



1-*t*, R_1=H, R_2=C_6H_5
1-*c*, R_1=C_6H_5, R_2=H



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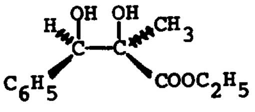

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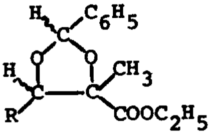


5, R=CH_3
6, R=H

The formation of **2** from **1** formally required the participation of one additional molecule of **4**, which necessarily came from **1**, perhaps cleaving into carbonyl and carbene fragments.[2-3] Although we failed in our attempts to trap the presumed carbene intermediate with cyclohexene, possibly because of its rapid conversion into ethyl acrylate followed by polymerization, we tested the hypothesis by photolyzing **1** in the presence of one equivalent of **4**. The yield was not appreciably increased, but the formation of polymeric by-products was reduced.

In order to assign the origin of the phenyl group at either C-2 or C-4 to the newly added 4 in structure 2, an equimolar mixture of 1-*t* and $C_6H_5{}^{14}CHO$ (4*) was photolyzed in benzene. A radioactive dioxolane (2*) with high specific activity was obtained (Table 1). It was hydrolyzed to 3* and 4* which were *both* radioactive, containing 14 and 86% of the activity of 2* respectively.[4]

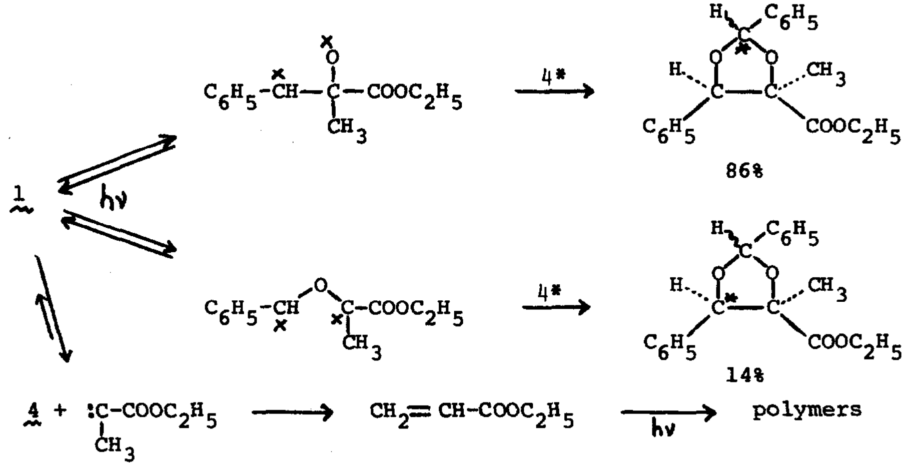
	Specific Activity (DPM/mole x 10^{-8})	%
Benzaldehyde-(C-14) (4*)	6.41	100
Dioxolane 2*	6.08	94.9
Recovered Glycidic Ester 1*	<0.12	<1.9
Glyceric Ester 3*	0.84	13.1

Table 1. The Irradiation of 1 in the Presence of 4*

The presence of label at both benzylic positions in 2* could have been the result of any reversible reaction of 1, competing with the formation of 2. Thus, the cleavage of 1 into 4 and carboethoxyl methyl carbene, followed by recombination with 4* would give 1*, from which a doubly labelled 2* would result from the subsequent addition of 4*. This pathway probably operated, but was not very significant as shown by the low activity of the recovered starting material (Table 1).

Since a mixture of 1 and 4 had been irradiated, with both compounds absorbing strongly at 254 nm, it was conceivable that two different photochemical reactions operated, each one involving the excited state of a different molecule. The observation that no 2 was formed in conditions where 4 was in a tenfold excess over 1 suggested that the photochemistry described herein proceeded from an excited state of 1.

The photochemical ring opening of oxiranes was previously reported to occur either with carbon-carbon bond cleavage to carbonyl ylides,[5] or with carbon-oxygen bond cleavage as in the conversion of epoxystyrene to phenylacetaldehyde[6] or α,β-epoxyketones to β-diketones.[7] Here, our observations demonstrate that both processes occur competitively in going from 1 to 2*, as shown in Scheme 1.



Scheme 1. The photolysis of 1 in the presence of 4*. (No assumption is made about the homolytic or heterolytic nature of the oxirane bond cleavages.)

The photolysis of 1 in the presence of acetaldehyde or formaldehyde yielded the dioxolanes 5 and 6 in 40 and 75% yield respectively. These were formed by trapping of the carbonyl ylide, and no dioxolane derived from carbon-oxygen bond breaking in 1 was detected by nmr. This difference with the outcome of the photolysis of 1 in the presence of benzaldehyde, and the very low quantum yield of the cycloaddition reactions suggested that while both types of bond breaking can occur upon irradiation of the oxirane, they are reversible, and the efficiency of trapping of each intermediate depends upon the trapping agent, and/or the conditions.

Acknowledgments. The partial financial support of this work by the National Science Foundation is gratefully acknowledged.

References

1. The spectrum actually showed that the methylene protons were diastereotopic and the ethyl group signals were typical for an ABX_3 pattern. We are indebted to Dr. U. Bürger, University of Geneva, for the nmr analysis at 100 MHz.

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3. This type of fragmentation was substantiated with other glycidic esters: T. I. Temnikova and I. P. Stepanov, *Zh. Org. Khim.*, **3**, 2253 (1967); P. C. Petrellis and G. W. Griffin, *Chem. Commun.*, 691 (1967).

4. The radioactivity measurements were performed with a Nuclear-Chicago 6081 liquid scintillation counter. The sample of 2* was recrystallized to constant specific activity. The sample of 1* was saponified, the sodium salt recrystallized and further converted into its phenacyl ester. The amount of product and activity were too low for accurate measurements. The sample of 3* was purified chromatographically and was spectroscopically pure.

   In another experiment, 3* was converted back into crystalline 1* by BF_3-catalyzed reaction with 4. Its specific activity was found to be 15% of that of 2*.

   The activity of 4* was not measured since the acid treatment of ethyl 3-phenylglycerates was found to result in a retroaldol cleavage (J. Kagan and D. A. Agdeppa, Jr., unpublished results). Therefore the measured activity of 4* would have included contributions from both C-4 and C-2.

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6. H. Kristinsson and G. W. Griffin, *Ibid.*, **88**, 1579 (1966); R. S. Becker, R. O. Bost, J. Kolc, N. R. Bertoniere, R. L. Smith, and G. W. Griffin, *Ibid.*, **92**, 1302 (1970).

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