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EPOXIDE FORMATION BY THE PHOTOLYSIS OF CYCLIC OXALATE ESTERS

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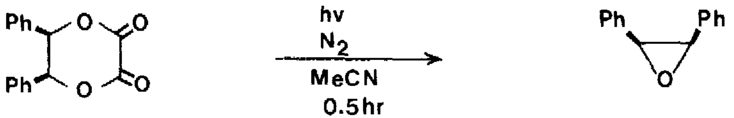
Abstract: The cyclic oxalate esters from *meso*- and *d,l*-hydrobenzoin were prepared and photolyzed. *Meso*-hydrobenzoin oxalate gave only *cis*-stilbene oxide upon photolysis while the *d,l* isomer gave *trans*-stilbene oxide.

The photolysis of oxalate esters is a field of growing interest. Acyclic aryl oxalates undergo the photo-Fries rearrangement with simultaneous phenol formation[1]. Photolysis of dibenzyl oxalate in cyclohexane solution gives products derived from benzyl radicals[2]. However, the photolysis of cyclic oxalates has received scant attention. A recent report on the photolysis of catechol oxalate showed the primary process was decarbonylation to produce catechol carbonate in high yield[3]. The bis decarboxylation product, benzyne, was not detected although effort was made to determine its presence.

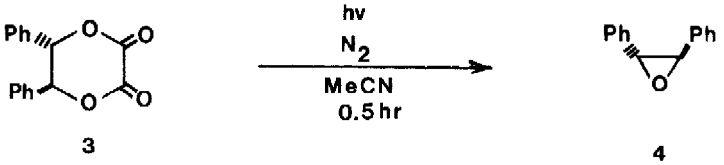
In order to gain more information on the photochemical reactions of cyclic oxalates, the cyclic oxalate esters of *meso*-[4] and *d,l*-hydrobenzoin[5] were prepared[6] and irradiated. Despite the presence of benzyl substituents which could facilitate the bis decarboxylation to stilbene, the Vycor filtered irradiation[7] of *meso*-hydrobenzoin oxalate (1) led to disappearance of the starting material and the formation of only *cis*-stilbene oxide (2) isolated in 68% yield. Longer irradiation times resulted in the formation of minor amounts of *trans*-stilbene oxide (4) presumably via a secondary photoreaction of the initially formed *cis*-stilbene oxide[8].



1

2

Similarly, irradiation of *d,l*-hydrobenzoin oxalate (3) under the same conditions[7] resulted in the formation of only *trans*-stilbene (4)[9] in 73% yield.



The fact that the stereochemistry of the phenyl groups is maintained throughout the reaction is suggestive of either a concerted process or the ultimate formation of a 1,3-diradical in which ring closure competes effectively with carbon-carbon bond rotation. A mechanistic study is beginning. It is also of interest to note that the above reactions do not resemble those of the closely related meso- and d,l-hydrobenzoin carbonates[5] in which benzaldehyde and phenyl carbene are formed to the exclusion of any epoxides.

(1) T. Inoue, Y. Shigemitsu and Y. Odaira, Chem. Comm., 668 (1978).

(2) S. Icli, V. J. Nowlan, P. M. Rahimi and T. T. Tidwell, Can. J. Chem., 55, 3349 (1977).

(3) S. P. Schmidt and G. B. Schuster, J. Org. Chem., 43, 1823 (1978).

(4) L. F. Fieser, "Organic Experiments", D. C. Heath, Boston, MA, 1960, p. 216

(5) G. W. Griffin, R. L. Smith and A. Manmade, J. Org. Chem., 41, 338 (1976).

(6) The cyclic oxalates were formed from the corresponding hydrobenzoin with oxalyl chloride and triethylamine as described in reference 3.

(7) Irradiations were carried out on 1.25×10^{-2} M solutions of the corresponding oxalate ester in purified acetonitrile which were purged with nitrogen for one hour prior to photolysis. The products were isolated by chromatography over silica gel using hexane as the eluent.

(8) G. A. Lee, J. Org. Chem., 41, 2656 (1976).

(9) The cis- and trans-stilbene oxides were identified by comparison of their nmr and ir spectra with those of authentic samples prepared by the m-chloroperbenzoic acid oxidation of the corresponding stilbene.

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