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PHOTOLYSIS OF OZONIDES

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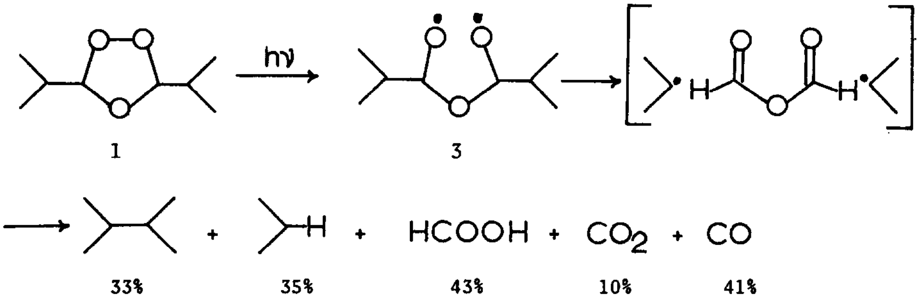
We report herein preliminary results from the first study of the photochemistry of ozonides. Although ozonides have been known for some time as intermediates in ozonolysis reactions *(1)*, it has only been recently that systematic studies of their chemistry and properties has become feasible. *(2)* The purpose of this communication is to call attention to the several noteworthy mechanistic and synthetic aspects of the investigation. In essence, utilization of the procedures described here provides a means, via ozonolysis, of removing from a molecule the elements of a double bond. Cyclopentene ozonide, for example, gives cyclopropane in good yield.

For the purposes of our initial investigations we have focused on two relatively simple ozonides, diisopropyl ozonide(1)[a *cis, trans* mixture from ozonolysis of *cis*-diisopropylethylene*(2c)*] and cyclopentene ozonide (2)*(3)*. Simple ozonides of this type have been found to exhibit ultraviolet absorption very similar to that of the corresponding alkyl peroxides*(4)* and, therefore, permit photolysis in Pyrex. On the basis of the similarity in absorption spectra, the electronic transition in ozonides (in Pyrex) is quite likely to be the same as that assumed for alkyl peroxides, $\pi^* \rightarrow \sigma^*$. *(4)*

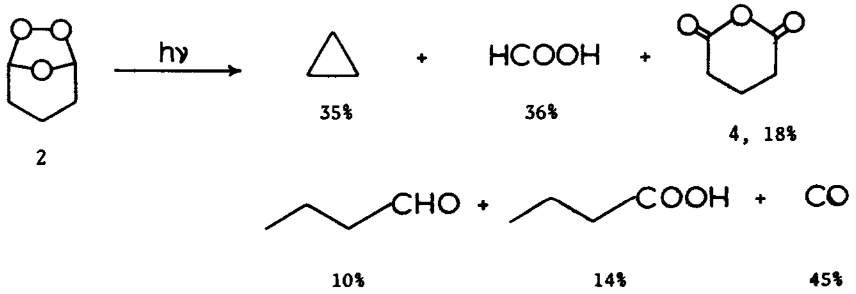
In a typical experiment, a degassed solution of 1 in pentane [1.013 g of 1 in 320 ml of pentane] was irradiated for 150 minutes in a standard Pyrex Hanovia apparatus employing a 450 watt (#679A) lamp; 97% of the ozonide was depleted in this time. Analysis of the crude product mixture by glpc revealed, in addition to isobutyraldehyde(14%) and isobutyric acid (7%), the products shown in the reaction scheme.*(5)*

By analogy to alkyl peroxides, the expected primary photochemical process for ozonides would be homolytic cleavage of the oxygen-oxygen bond to yield the intermediate, 3.*(4,6)* Accordingly, propane and the dimer, 2,3-dimethylbutane, can be accounted for by β-cleavage of 3 to give isopropyl radicals. A solvent cage recombination of isopropyl radicals formed in simultaneous or near-simultaneous double β-cleavages to give the dimer is suggested by the results of two experiments. (1) Photolysis of 1 in methanol gives a reduced but still

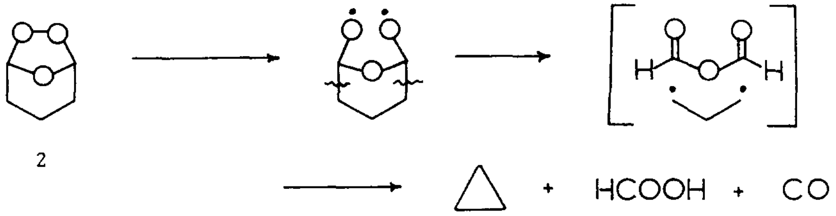


relatively high yield (20%) of dimer and a comparable yield (54%) of methyl formate, probably arising directly from formic anhydride. (2) In addition, photolysis of the unsymmetrical ethyl isopropyl ozonide in pentane was found to yield as the only hydrocarbon dimer, 2-methylbutane (12%). We are unable to choose, at this point, between several possible reaction paths which may lead to isobutyric acid and isobutyraldehyde.

Photolysis of the bicyclic cyclopentene ozonide, 2, proved to be particularly instructive, differing from that of 1 in several important respects. Using the previously described conditions, photolysis of 2 in pentane gave butyraldehyde, butyric acid, formic acid, cyclopropane, glutaric anhydride, carbon monoxide, and only trace amounts of carbon dioxide and propane; carbon monoxide and formic acid probably arise, at least in part, from decomposition of formic anhydride.*(7)*



As in the case of the diisopropyl ozonide(1), the predominant photochemical process in irradiation of 2 appears to be homolytic cleavage of the oxygen-oxygen bond followed by a double β-scission. It is quite clear from the presence of only a trace of carbon dioxide in photolysis of 2 that the intermediate formic anhydride does not in itself thermally or photochemically generate carbon dioxide.*(7)* From the present data, it would appear that formation of carbon dioxide in photolysis of 1 may result from hydrogen abstraction from formic anhydride by isopropyl radical within the solvent cage. The absence of a significant amount of propane in this case is not likely due simply to a solvent cage effect. The yield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of cyclopropane is undiminished in methanol and, again, only a trace of propane is formed. The efficient formation of a spin-paired 1,3-propane diradical from the double β-scission is indicated.

The yield of cyclopropane obtained on photolysis of 2 suggested that the reaction could have merit for the synthesis of cyclopropanes and, perhaps, via cyclohexene ozonide*(3)*, cyclobutanes. However, since the yield of cyclopentene ozonide from ozonolysis of cyclopentene is at best about 20%, we undertook the photolysis of the crude cyclopentene ozonolysis mixture and found that cyclopropane, under these conditions, is produced in 50% yield, based on cyclopentene. Surprisingly, the "polymeric ozonides" *(3)* give a higher yield of cyclopropane than does the pure ozonide. This suggests that formation of the monomeric ozonide need not necessarily be a prerequisite for use of this procedure. Photolysis of 1,2-dimethylcyclopentene ozonide has also been found to yield cyclopropane (30%) along with acetic anhydride. Preliminary results also show that photolysis of cyclohexene ozonide and cyclohexene ozonolysis mixture produces cyclobutane and butane, each in about 10% yield.

On the assumption that glutaric anhydride(4) was more likely formed non-photolytically through hydrogen abstraction from 2 by radicals produced during the reaction, we have treated 2 with N-bromosuccinimide, benzoyl peroxide, and with t-butyl hypochlorite but find the ozonide to be essentially inert. Treatment of 2 with azobis-(isobutyronitrile) served to decompose the ozonide but glutaric anhydride was not formed.

Recently, Ullman and Henderson*(8)* have demonstrated that the ozonide of 2,2-diphenylindenone undergoes photorearrangement to a keto anhydride. More than likely, the reaction proceeds ionically in Baeyer-Villiger style *(9,6)*, not an unreasonable possibility in light of the similarity between an ozonide and the Criegee intermediate for the Baeyer-Villiger reaction.*(9)* We have observed similar photorearrangements on irradiation of some cyclobutene ozonides. Ozonides rearrange quite readily in Baeyer-Villiger fashion in the presence of acids.*(10)*

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