

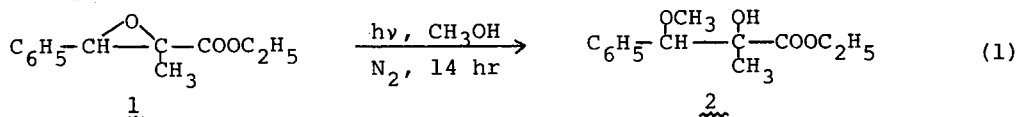
CATALYSIS OF THE IONIC-LIKE PHOTOADDITION OF METHANOL TO EPOXIDES BY Fe(III)

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The photochemical ionic addition of alcohols to epoxides has been attributed to adventitious acid catalysis,¹ brought about by air oxidation of the solvent. We now demonstrate one other alternative, which involves metal ion catalysis.

Over the years, we found the yield of photoreaction 1 to be quite variable.



However, when the solvent was distilled from disodium ethylenediaminetetracetate (EDTA), the addition of MeOH to 1 was no longer observed, even when O₂ was bubbled during the photolyses. Furthermore, deliberate addition of as much as 1 eq. of formic acid had an almost negligible effect. This dramatic effect of EDTA suggested that metal ions were capable of catalyzing the photoreaction 1. This has now been confirmed, as described with Fe(III).

Control experiments proved that (Z)-1 reacted quantitatively with EDTA-purified MeOH in the dark in the presence of FeCl₃, but that (E)-1 was inert. The latter, when irradiated in the presence of FeCl₃, yielded ca. 10% of 2. No (E)-(Z) isomerization of 1 was detected, and no reaction took place with FeCl₂ instead of FeCl₃.

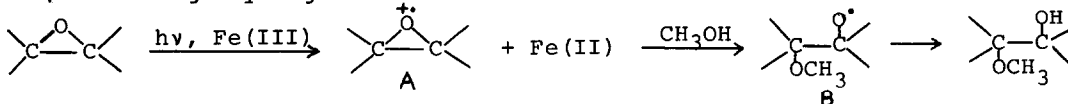
A solution of (E), (Z)-1 in EDTA-purified MeOH was also photolyzed in the presence of Fe₂O₃ powder. The yields of 2 varied between 20 and 100%, depending on factors such as the presence or absence of air, and the rate of stirring. When the photolysis was in Fe₂O₃-saturated MeOH without excess of oxide, the yield was very low in the presence of N₂, but high in the presence of air.

A rational explanation for these results calls for the active catalyst in the photoaddition of MeOH to be Fe(III). Its competing facile photoreduction by MeOH² depletes the very dilute solution, so that under N₂ very little solvent addition may proceed. In the presence of O₂, however, the oxidation of Fe(II) continually regenerates the catalytically active Fe(III).

The Fe(III)-catalyzed ionic photoaddition of EDTA-purified MeOH was also observed with 1-methylcyclohexene oxide (3). After 6h of photolysis in the presence of air with excess Fe₂O₃, essentially complete solvent addition had taken place, but no more than a few percent was detected by glc in a blank kept in the dark, or in a solution photolyzed in the absence of Fe₂O₃.

Basic reagents had been shown to repress the photochemically induced ionic addition of MeOH to organic substrates including 3, a powerful argument in favor of adventitious acid catalysis.¹ However, after confirming that the photolysis of 3 in EDTA-purified MeOH gave no solvent addition in the presence of Na₂CO₃, we observed that its photolysis in the presence of an excess of both Na₂CO₃ and Fe₂O₃ did lead to addition, forcefully demonstrating the catalytical activity of Fe(III).

The ionic photoaddition of MeOH to epoxides is readily understood in terms of the known charge-transfer photochemistry of Fe(III) complexes, giving Fe(II) and a radical derived from the ligand. Here the conversion of Fe(III) into Fe(II) would be coupled to the formation of a radical-cation A, which would then undergo nucleophilic attack by the solvent, yielding B. The conversion of the latter into the neutral product could occur either through reduction by Fe(II), followed by protonation, or through hydrogen radical abstraction from the solvent.



Finally, contrary to the claim that 3 underwent fairly rapid uncatalyzed MeOH addition in the dark,³ we found this epoxide to be stable in EDTA-purified MeOH, so that the dramatic effect of metal ions noted with dioxetanes in the dark⁴ must now be extended to epoxides as well, both in the presence and in the absence of light.⁵ These results also suggest that the removal of metal ions from alcohols commonly used as solvents should become a routine procedure.⁶

References

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5. Extended standing of the purified MeOH in the presence of air generated a solvent capable of reacting with 3 in the dark. Whether this effect was due to the glassware or to air oxidation has not been established.
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