PHOTOCHEMICAL CYCLIZATION OF EPOXY-ALCOHOL
A NEW SYNTHESIS OF SUGIRESINOL DIMETHYL ETHER

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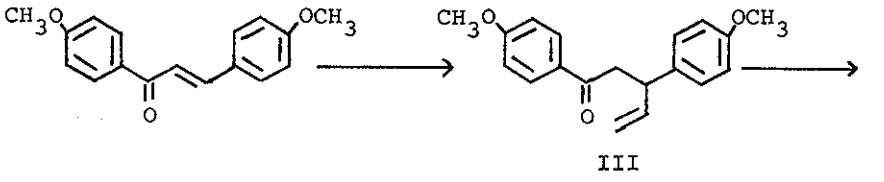
Photochemical cyclization of 1,3-bis(4-methoxyphenyl)-4,5-epoxy-1-pentanol gave sugiresinol dimethyl ether in good yield.

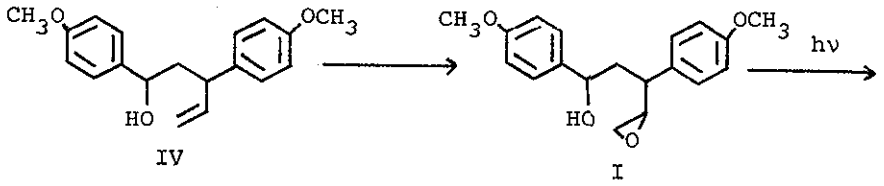
It is known that the photochemical alcoholysis of oxiranes gives alkoxy-alcohols in good yield.[1,2] Tokumaru[1] reported that the photochemical alcoholysis of cyclohexene oxide was initiated by the photoexcitation of the oxirane group. In the photolysis of propylene oxide, Gritter and his co-workers[3] reported the C-1-O to C-2-O cleavage ratio is about 25:1. In order to find a new synthetic route to 3-hydroxytetrahydropyran, the photochemical cyclization of epoxy-alcohol[4], 1,3-bis(4-methoxyphenyl)-4,5-epoxy-1-pentanol (I), was examined. This paper discribes a new synthesis of sugiresinol dimethyl ether (II)[5] via photochemical cyclization.

Reaction of 4,4'-dimethoxychalcone with vinylmagnesium bromide in

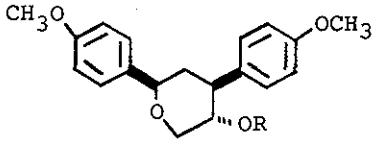
the presence of cuprous chloride gave 1,3-bis(4-methoxyphenyl)-4-penten-1-one (III)[6] in 91% yield, which was reduced with sodium borohydride to give a stereoisomeric mixture of 1,3-bis(4-methoxyphenyl)-4-penten-1-ol (IV) in 85% yield. Treatment of IV with m-chloroperbenzoic acid gave a stereoisomeric mixture of I in 61% yield. Irradiation of I in Pyrex tube without solvent with a 450 W high pressure mercury lamp at 35-40° for 15 hr gave a crude material (II), which was treated with acetic anhydride and pyridine to give the acetate (V), mp 120.5-121.5°, in 51% yield (from I). Reduction of V with lithium aluminum hydride gave II, mp 121-122°, in 62% yield. This product (II) was identified by comparison with the natural sugiresinol dimethyl ether.



III



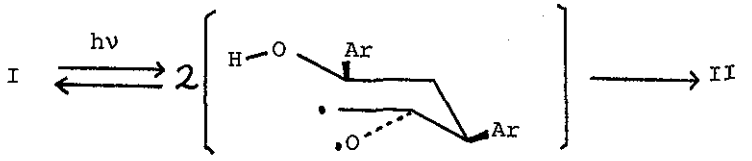
IV I



V: R = CH_3CO

II: R = H

In the photolysis of I in a solvent (benzene, chloroform, acetone and methanol), cyclization product (II) was not obtained. The reaction process was assumed in the following scheme:



Further works on the mechanism of this photochemical cyclization reaction are in progress.

ACKNOWLEDGEMENT The authors would like to express their sincere thankness to Professor Y. Kai of Shizuoka University for providing the sample of sugiresinol dimethyl ether.

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6. Satisfactory analytical and spectral data were obtained for new compounds.

Received, 4th March, 1977