

PHOTOCHEMICAL TRANSFORMATION OF UNSATURATED SULTONES INTO FURANS

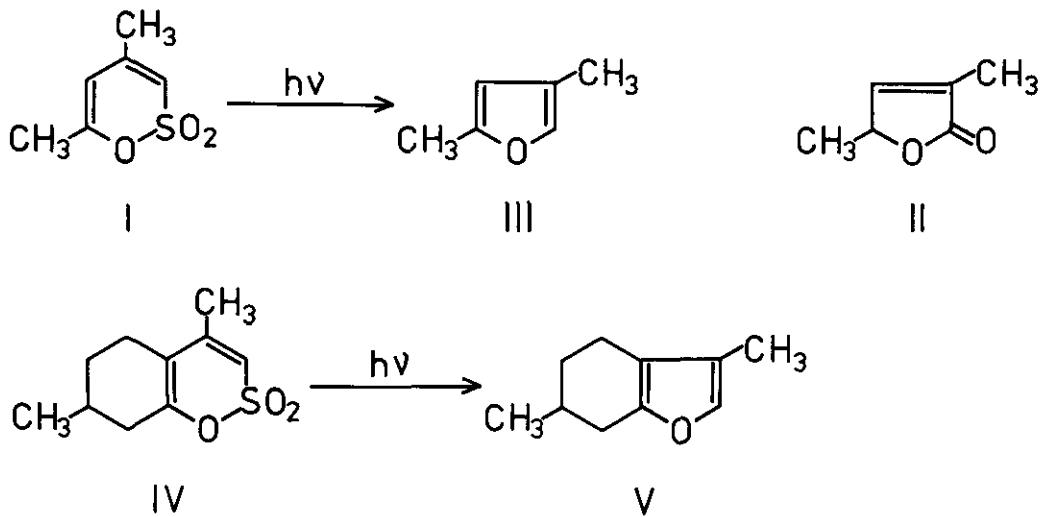
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Abstract Photolysis of unsaturated sultones I and IV afforded 2,4-dimethylfuran(III) and menthofuran(V), respectively.

Recently, Gorewit and Rosenblum have reported the photochemical conversion of sultones to γ -butyrolactones¹⁾. We reexamined this reaction in order to use in syntheses of some bioactive lactones, and found the formation of furans instead of the products expected.

By using the similar reaction conditions to those described by them except the solvent, we carried out photolysis of sultone I²⁾, which has been shown to give 4-hydroxy-2-methyl-2-pentenoic acid lactone(II). A *n*-pentane solution of I was cooled to 0° in an ice-bath, and irradiated with a 100W high pressure mercury lamp(Ushio: UM-102) through a quartz filter for 10 minutes while introducing a stream of nitrogen. After evaporation of the solvent, the residue was separated



by silica gel chromatography to afford only one product in 18 % yield, which was identified with a synthetic specimen of 2,4-dimethylfuran(III)³⁾. The expected lactone(II) could not be detected by any chromatographic analysis. Sultone IV⁴⁾ was also irradiated in a benzene solution under ice-cooling for 30 minutes. An oily product obtained in 43 % yield was identified as menthofuran(V)⁵⁾, which is known as a naturally occurring monoterpane isolated from Mentha piperita⁶⁾.

We can not explain the apparent discrepancy between the foregoing observation and ours. However it is worth noting that the elimination of sulfur dioxide during irradiation of I in a hot diglyme solution and the photochemical formation of a pyrrole from a sultam have been reported, although no detailed description has been given⁷⁾.

The mechanistic consideration of the photolysis of unsaturated sultones has already been described by de Mayo and his co-workers as follows⁸⁾. The irradiation of unsaturated sultones in the presence of methanol has been shown to give methyl ketosulfonates, and the corresponding thermal reaction of sultones is known to lead to sulfonic acid derivatives. It was proposed that this reaction yield sulfenes as the intermediates, which react with the medium. Not long after, however, they have concluded from the flash photolysis study that the transients in methanol are not the sulfenes and that if sulfenes are intermediates, their lifetime are exceedingly short⁷⁾.

On the basis of our result, a mechanism passing through the sulfene intermediates is conceivable again. The sulfenes are known to be easily decomposed to sulfur dioxide and carbenes⁹⁾. The resulting carbenes might be cyclized to give furan derivatives.

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