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THE Hg SENSITIZED VAPOR PHASE PHOTOLYSIS OF γ-CROTONOLACTONE AND SIMPLE BUTENOLIDES

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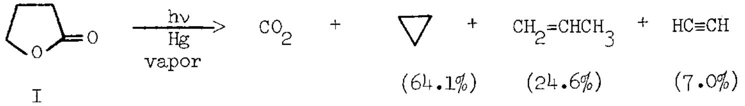
As part of our effort to define the synthetic utility of mercury photosensitized reactions, we wish to present some results on the vapor phase photolysis of γ-butyrolactone (I), γ-crotonolactone (II), and β-methyl-$\Delta^{\alpha,\beta}$-butenolide (III), all of which lose carbon dioxide as the primary process.[**] Simple aliphatic esters have been found to undergo all three possible bond cleavages of the ester moiety (2).

In our experiments we have used a low pressure flow system, a quartz reactor tube (300 mm x 45 mm), and a circular array of 8 watt low-pressure mercury lamps having a high output at 2537 Å. Separation of gaseous photoproducts was accomplished utilizing two separate vacuum traps (Dry-Ice-acetone and liquid nitrogen). The products were identified by standard analytical procedures: nmr, ir, vpc,[***] and mass spectrometry.

Redistilled γ-butyrolactone (I) was photolyzed so that the pressure of unreacted vapor and gaseous photoproducts was kept low (~ 200 μ). Under these conditions, about 60% of the starting material reacted to give a 60% yield of volatile photoproducts.[****] The vpc showed the presence of three main products, indicated below with their percent compositions. Carbon dioxide was analyzed by ir.



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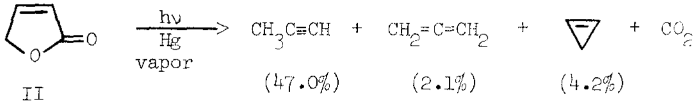
[**] The liquid phase photolysis of γ-butyrolactone has recently been reported to yield allyl formate, succinaldehyde, cyclopropane, carbon dioxide, and small amounts of ethylene, propylene, and carbon monoxide (1).

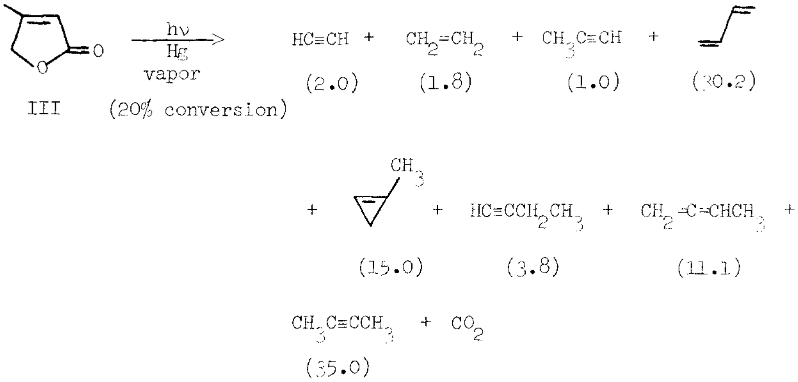
[***] Vpc analyses were performed on: 1) 5% propylene carbonate on Porasil A (100-150 mesh), 6' x 1/8" column at 75°; 2) Porapak S, 6' x 1/4" column at 100°; and 3) Porapak Q, 6' x 1/4" column at 75° (flow = 50 ml/min).

[****] Some polymer formed on the walls of the quartz reactor in this and all other cases described.

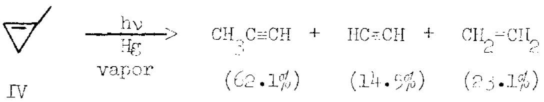
The simple butenolide γ-crotonolactone (3), II, was photolyzed as above to 80% conversion, and yielded methylacetylene, allene, and cyclopropene (4), as indicated below with their absolute yields. In contrast, β-methyl-$\Delta^{\alpha,\beta}$-butenolide (5) (III) gave a complex mixture



of primary and secondary photoproducts, shown below along with percent compositions.



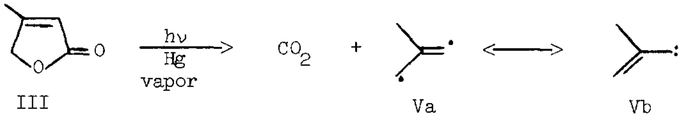
Photolysis of 1-methylcyclopropene (6) (IV) under our conditions leads in about a 10% conversion to the products indicated below (percent compositions). No 2-butyne or other



C_4H_6 isomers were apparent in the vpc.

Photolysis of 1,2-butadiene (7) under our conditions leads to the formation of 1-butyne and 1,3-butadiene, as well as other secondary products. Frey has observed the unimolecular decomposition of vibrationally excited methylenecyclopropane, generated by the addition of methylene to allene (8). The products were: acetylene, ethylene, 1,3-butadiene, 1,2-butadiene, 2-butyne, and 1-butyne, the same products observed in the photolysis of III. We thus initially assign the formation of 1-butyne and 1,2-butadiene to secondary reactions of either 1-methylcyclopropene or methylenecyclopropane. However, we cannot exclude the possibility that some 1-butyne and/or 1,2-butadiene is formed via a 1,2-methyl migration in the proposed intermediate V. This intermediate has been discussed before by Closs in the photolysis of 3H-pyrazoles (9), and in the study of alkenylcarbenes leading to cyclopropenes (4,10).

We cannot at present indicate which is the better representation for V, the diradical, Va, or the alkenylcarbene structure, Vb.



The Hg sensitized vapor phase photolysis of butenolides and butyrolactones represents a new and potentially useful method for generating cyclopropene and cyclopropane derivatives, since various precursor structures are readily obtained (11,12). We are currently attempting a number of these syntheses, as well as finding methods for eliminating undesirable secondary photo- and/or thermal reactions of the primary photoproducts.

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