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MERCURY PHOTOSENSITIZED EXTRUSION REACTIONS FOR THE PREPARATION OF HETEROCYCLES

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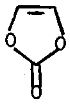
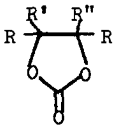
Mercury photosensitized extrusion of carbon monoxide and/or carbon dioxide from cyclic ketones,[1] lactones,[2] and cyclic anhydrides[3] is a general reaction, useful for the synthesis of small ring hydrocarbons.[4] This reaction has now been extended to the synthesis of heterocyclic systems. In addition, the diradical or dipolar intermediates in these reactions are of theoretical interest.[5]

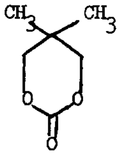
We have studied the mercury photosensitized, vapor phase irradiation of cyclic carbonates (I-III), pyrrolidinone (IV), 2-oxazolidinones (Va-d), diglycolic anhydride (VI), and 6-hydroxytetrahydropyran-2-carboxylic acid lactone (VII). Not all of these compounds are sensitive to these conditions. In those cases where products are obtained, they can be accounted for by reaction (closure, fragmentation, or hydrogen migration) of the hetero-residuum resulting from extrusion of carbon monoxide and/or carbon dioxide and, in some cases, further reaction of these products. The results are summarized in the Table.



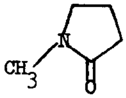
I



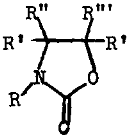
IIa (R=R'=R"=H)
b (R=R'=H, R"=CH_3)
c (R=R'=R"=CH_3)



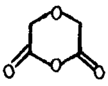
III



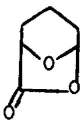
IV



Va (R=R'=R"=R'"=H)
b (R=C_6H_5, R'=R"=R'"=H)
c (R=C_6H_5, R'=R'"=H, R"=CH_3)
d (R=C_6H_5, R'=R"=H, R'"=CH_3)



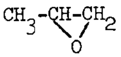
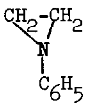
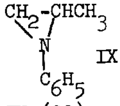
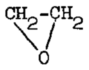
VI



VII

The apparatus and technique for carrying out these reactions were similar to that reported previously.[2,3] In a typical experiment, 1 gm of purified reactant was irradiated in a low pressure (50-200 μ) flow system consisting of a quartz vessel (300 mm x 45 mm) surrounded by an array of sixteen, 8 watt, low-pressure mercury lamps. In some cases it was necessary to warm the starting material reservoir to achieve the desired pressure. The unreacted starting material and the volatile products were separated in traps kept at Dry-ice acetone and liquid nitrogen temperature, respectively. The products were identified by standard analytical procedures (nmr, ir, vpc, and mass spectrometry), and were compared with authentic material. The pereent yields and conversions were determined by calibrated vpc and/or nmr using internal standards. No effort was made to optimize the yields. Control experiments attested to the requirement for mercury vapor in these reactions.[6]

TABLE

Reactant	Percent Conversion	Products (Percent Yield)
I	-	No reaction detected
IIa	-	No reaction detected
IIb	1	CH_3CH_2CHO (80), C_2H_4, C_2H_2, HCHO, CH_3CHO, $(CH_3)_2CO$, 
IIc	$<$ 1	$(CH_3)_2CO$, CH_2CHCH_3, C_2H_4, C_2H_2
III	$\sim$ 100	$(CH_3)_2CCH_2$ (14), HCHO (11), C_2H_2
IV	-	No reaction detected
Va	$\sim$ 100	C_2H_4, C_2H_2, HCN
Vb	$\sim$ 100	 (40), polymer of VIII VIII
Vc	$\sim$ 100	 (95) IX
Vd	$\sim$ 100	IX (90)
VI	95	 (57), CH_3CHO (32), C_2H_4, C_2H_2
VII	1	CH_2CHCHO (40),  (7), C_2H_4 (37), C_2H_2 (14)

The extrusion of carbon dioxide from the cyclic carbonates studied was inefficient. This is in contrast to the recent report of the direct irradiation of benzpinacol carbonate (II $R=R'=R''=C_6H_5$) in solution where benzophenone and diphenylcarbene (isolated as benzhydrylmethyl ether) were formed efficiently; no tetraphenyloxirane was detected.[8] Similarily no tetramethyloxirane was detected upon irradiation of IIc while acetone and propylene, products of carbon-carbon bond cleavage, were obtained. With IIb the carbon-carbon bond remains intact in the major product, propionaldehyde; the oxide was also detected. The predominance of propionaldehyde over acetone may reflect the preference for a secondary versus a primary radical formed in the intermediate.

N-methylpyrrolidinone, which might have extruded either carbon monoxide or methyl isocyanate, was stable to these conditions. However, the 2-oxazolidinones (V) extrude carbon dioxide efficiently and azirines can be obtained in high yields. With 2-oxazolidinone the unsubstituted azirine, if formed, was too unstable to survive. The mercury photosensitized decomposition of azirine to ethylene, hydrogen and nitrogen has been observed previously.[9] The mechanism for formation of hydrogen cyanide is not clear; however, it is known to be a product of the reaction of hydrogen atoms with azirine.[10] The mercury photosensitized decomposition of succinimide has been studied and carbon monoxide, ethylene, and isocyanic acid are among the products.[7]

The extrusion of carbon dioxide and carbon monoxide from VI is analogous to the extrusion of carbon monoxide from ketooxetanes[11] and nitrogen from Δ^3-1,3,4-oxadiazoline-3[12] upon direct irradiation in solution. Here a fair yield of the oxirane is obtained. The acetaldehyde may be the result of decomposition of the oxirane either before loss of excess thermal energy or by further irradiation.[13]

The products obtained from 6-hydroxytetrahydropyran-2-carboxylic acid lactone (VII) were unexpected. None of the cyclopentene epoxide was detected; instead the products can be accounted for by extrusion of carbon dioxide followed by hydrogen migration (1-4).[14] The resulting dihydropyran is known to decompose under these conditions to acrolein and ethylene.[15]

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(6) The requirement for mercury is not always clear. In most cases the same reaction can be brought about by direct irradiation of the vapor (Ref. 1b, c, and 7); however, the reactant may have a low extinction coefficient at 2537 Å and thus higher pressure would be required for efficient light utilization.

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