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LIQUID PHASE PHOTOLYSIS OF γ-BUTYROLACTONE

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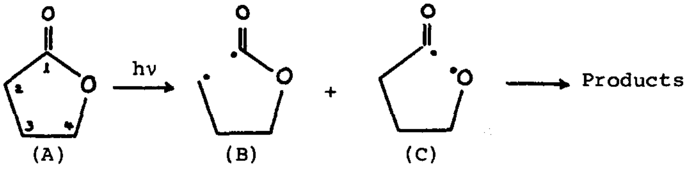
In view of the variety of interesting photochemical reactions reported for saturated cyclic ketones (1) and acyclic esters (2) and the lack of similar studies on lactones, we have photolysed representatives of the latter class of compounds and report here preliminary results with γ-butyrolactone.

Vacuum degassed butyrolactone (absorbs < 2600 Å) was irradiated in a quartz cell (9 ml) with a Hanovia medium pressure SH lamp, and gaseous products were separated by conventional high-vacuum techniques. The major products, carbon monoxide, carbon dioxide, cyclopropane and ethylene (relative amounts 2.5 : 0.9 : 0.9 : 1.0), were identified by comparison of gas chromatographic retention times (Hexadecane, 25°) and mass spectra with those of authentic materials. In addition, traces of ethane, propane and propylene were characterised by gas chromatographic comparisons.

Butyrolactone (9 ml) was irradiated in a quartz cell with a Hanovia SH lamp. A stream of pure nitrogen bubbled through the liquid removed volatile products, which were collected in a cold trap (-196°). G.l.c. analysis of the condensate (Cyanosilicone XF-1150, 55°) showed the following products: allyl formate, cyclopropanol, propionaldehyde and acetaldehyde (relative amounts 9.0 : 1.8 : 0.7 : 5.4 based on cyclopropane 0.9).

In order to obtain sufficient quantities of the photolysis products for characterisation, butyrolactone (150 ml) was irradiated in an annular quartz vessel with a Hanovia medium pressure lamp (type A). A nitrogen stream through the liquid removed 3 ml of volatile products into a cold trap in 12 h. Subsequent distillation of the discoloured butyrolactone left 4 g of a dark tar. The condensed photolysis products were separated by preparative g.l.c. Propionaldehyde and acetaldehyde were identified by g.l.c. and infrared comparison with authentic materials. Allyl formate (3) and cyclopropanol (4) had infrared absorption spectra identical with those reported in the literature; furthermore, the g.l.c. retention time of allyl formate was identical with that of an authentic sample, and cyclopropanol gave a phenylurethane, colourless needles from light petroleum, m.p. 102.5 - 103.5°; lit. (5) 101.5 - 102.5°. Under these conditions of photolysis allyl formate was a minor product (0.1 of propionaldehyde); probably the less efficient flushing of the larger reaction volume and the much more intense emission by the type A lamp could cause photoaddition of the allyl ester to butyrolactone, cf. (6).

Unless we accept a multiplicity of concerted decomposition pathways from an electronically excited butyrolactone, we can best account for the various photolysis products in terms of intramolecular hydrogen atom abstraction or other simple rearrangement and fragmentation of intermediate biradicals (B) or (C).



The isomerisation of (A) to allyl formate is analogous to the formation of 4-pentenal in the liquid phase photolysis (1) and radiolysis (7) of cyclopentanone. Similarly, propionaldehyde from (A) is analogous to 1-butene by radiolysis of cyclopentanone (7) or to 1-pentene by photolysis of cyclohexanone (1). The formation of cyclopropanol from (A) bears comparison with the photochemical ring contraction of cyclohexanone to 2-methylcyclopentanone (8).

Allyl formate, propionaldehyde and carbon monoxide, as well as cyclopropane and carbon dioxide can arise from biradical (B). Cyclopropanol and carbon dioxide can, however, arise from (B) or (C); whereas, acetaldehyde probably arises only from (C), although the complementary fragment, ketene, has not been detected. Oxetane, another possible product from butyrolactone, analogous to cyclobutane from cyclopentanone (1), was also not found.

The origin of ethylene is obscure, although it apparently comprises the 2,3-carbon atoms of (A), since photolysis of 4-methylbutyrolactone gave ethylene rather than propylene. Photolysis of butyrolactone in the presence of cis-2-butene resulted in partial isomerisation of the latter to the trans olefin and quenching of the cyclopropane and ethylene formation. These products therefore probably arise from triplet precursor(s) (9). We have not yet investigated the effect of cis-2-butene on the formation of other products. We are engaged in further studies to elucidate the mechanism of lactone photolysis (10).

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