Photochemistry of Matrix-isolated *o*-Phthalaldehyde

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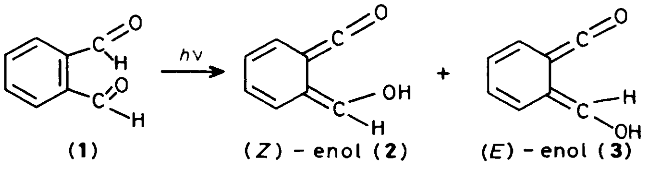
The (*E*)-enol (**3**), produced by photolysis of *o*-phthalaldehyde (**1**) in nitrogen matrix, has been characterized by i.r. spectroscopy.

Photochemical transformations of *o*-phthalaldehyde (**1**) have been studied in several laboratories,[1—5] and the important role of transient photoenols has been suggested in the reaction mechanism. Here we present direct evidence for the stabilization of the photoenol in a nitrogen matrix. Structural features, expected for the photoenol, are observed in the i.r. spectrum.

In principle, the irradiation of matrix-isolated (**1**) may lead to the two enol isomers, *i.e.* the (*Z*)-enol (**2**) and (*E*)-enol (**3**). Using the matrix-isolation technique[6,7] we have identified the key functional groups of the photoproduct.† Photolysis of (**1**) in the nitrogen matrix resulted in the formation of the new species, which gave intense absorptions at 3650, 2110, 2097, 2085, 1218, 1138 and 753 cm^{-1}. The signal at 3650 and the split signal in the vicinity of 2100 cm^{-1}, shown in Figure 1, can be assigned to the O–H and C=C=O stretching vibrations, respectively. The characteristic yellow colour of the photoproduct suggests the presence of an extended chromophore. The evidence given above contains all the typical features to be expected for the photoenol. The single band characteristic of free OH (ν 3650 cm^{-1}) points towards a single photoenol, *i.e.* (*E*)-enol (**3**). It is well known that the (*Z*)-enol (**2**) is considerably less stable to re-ketonization than is the (*E*)-form[5,8] and one may expect a very low barrier for this process.



(**1**) (*Z*) - enol (**2**) (*E*) - enol (**3**)

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† A Spectrim (Cryogenic Technology) cryostat and a Specord M-80 (Carl-Zeiss Jena) spectrophotometer were utilized in these studies. Photochemical reactions were carried out with a 200 W high pressure mercury lamp.

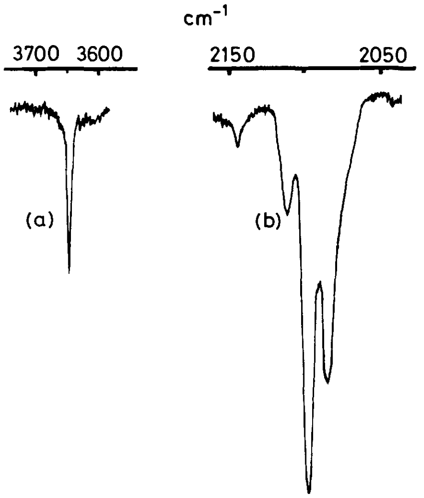

Figure 1. Expanded hydroxy (a) and ketene (b) stretching regions of the i.r. spectrum of *o*-phthalaldehyde isolated in a nitrogen matrix (T 15 K, estimated M/R 300). The sample was irradiated through a 313 nm interference filter for 5 min. Prior to irradiation no absorption was seen in these regions.

The evidence is consistent with the notion that the (Z)-enol (**2**) may be formed from (**1**) in the nitrogen matrix, but may rapidly revert to starting material perhaps *via* a tunnel reaction. A similar conclusion has been recently drawn from the studies of the *o*-tolualdehyde system.[8] The problems concerning secondary photochemistry, conformation, and matrix effects are under investigation.

This work was supported by the research programme CPBP 01.19.

Received, 20th May 1988; Com. 8/02007H

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