

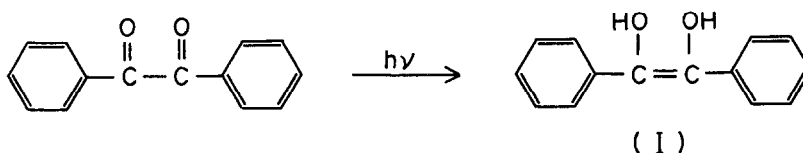
NOVEL PHOTOCHEMICAL REACTION OF BENZIL

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It has been known that photoirradiation of benzil in solution produces a variety of reaction products, i.e., benzaldehyde, benzoic acid, benzoin, benzil pinacol, and benzoin benzoate.¹⁻³⁾ However, the photochemical production of α,α' -dihydroxystilbene from benzil has been not reported hitherto, while it is produced by the electrolysis of benzil.⁴⁾ In this paper, the photochemical reaction of benzil in various solvents is studied.

The figure presented below shows the spectral change of the benzil solution in ethylene glycol ($4.1 \times 10^{-5} M$) on ultraviolet irradiation by means of a 70 W low pressure mercury arc lamp under N_2 . The absorption spectrum V in this figure can not be attributed to be due to the already known products described above. The reaction product having the 318 nm band is so sensitive to dissolved oxygen and heat that an attempt to isolate the product is unsuccessful. Nevertheless, the product in ethylene glycol could be identified as α,α' -dihydroxystilbene (I) according to the following findings.



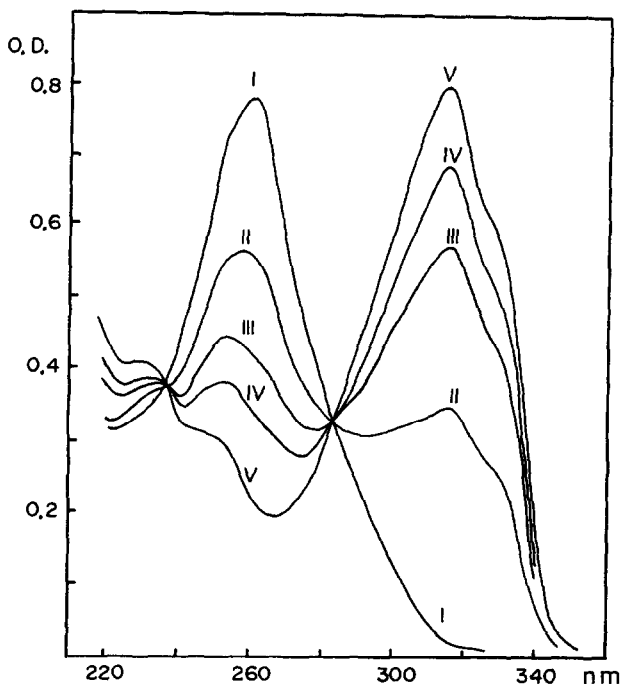


Fig. Spectral change of the ethylene glycol solution.
Irradiation time (sec) I:0, II:2, III:4, IV:6, V:12

1) The UV spectrum (Curve V) is identical with that of the electrolysis product of benzil which has been assigned to α, α' -dihydroxystilbene.⁴⁾

2) Acetylation of the reaction product with acetic anhydride produced the diacetylated compound. IR: 1620 cm^{-1} ($\nu_{\text{C}=\text{C}}$), 1210 cm^{-1} ($\nu_{\text{C}-\text{O}-\text{C}}$). The presence of the C=C bond in the acetylated compound is also indicated by the positive result of the permanganate test.⁵⁾

3) The 318 nm band shifts to the red (353 nm) on addition of NaOH or triethylamine. This indicates that the reaction product can ionize donating a proton to these bases. That is, the product takes an enol form.

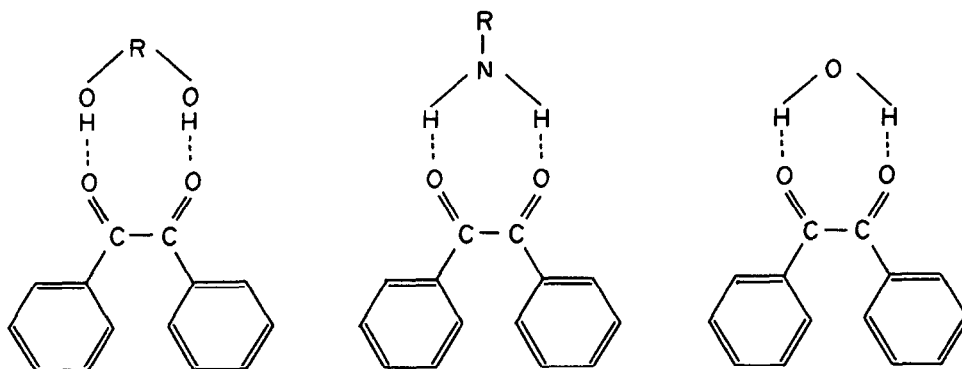
Whether α, α' -dihydroxystilbene is produced or not is dependent on solvent used. The following solvents and solvent systems were found to be suitable for the present reaction.

[Glycerine, Diols ($\text{HO}-(\text{CH}_2)_n-\text{OH}$, $n=2-5$), Formamide, n-Butylamine,]
[Ethanol containing water, glycine, or urea]

Although monohydric alcohols are usually employed as solvent and act as a hydrogen donor in the photoreductions of quinones, ketones, and azaaromatic compounds, monohydric alcohols are not suitable solvents in the present case. Therefore, besides being a hydrogen donor, a suitable solvent should have other advantage. It was found that a suitable solvent molecule possesses at least two hydroxyl groups or one amino group. This is clearly indicated from the fact that ethylene glycol, formamide, and n-butylamine are suitable solvents, whereas the corresponding alkylated compounds, e.g., ethylcellosolve, dimethylformamide, and di-n-butylamine are not suitable solvents. In the cases of the solvent systems, water, glycine, and urea are likely to play an essential roll in the reaction in a manner similar as a suitable solvent molecule. Especially, ethylene glycol and glycerine were found to be the most suitable solvents among the solvents used here. In solvents other than these, the photolysis also occurs simultaneously to fairly extent.

As an action of a solvent molecule, hydrogen bonding may be probable, since a suitable solvent is limited to be such one possessing two hydrogen atoms which are possible to form two hydrogen bonds with the carbonyl groups of benzil. However, such hydrogen bonds are not formed in the ground state of benzil owing to the skew structure in which the two carbonyl oxygen atoms are relatively far apart.^{6,7)} This is apparently indicated from the fact that the UV spectrum is almost independent of solvent used. If benzil takes nearly planar cisoid conformation bringing close the two carbonyl oxygen atoms, the above-mentioned hydrogen bondings even with an amino group and with water become feasible in spatial respect. With respect to this, it has been suggested by Evans and Leermaker⁸⁾ that the lowest triplet state of benzil has a planar structure. Accordingly, it can be said that benzil in the excited state, probably the lowest triplet state, is linked by the hydrogen bonds with solvent as illustrated below and such a hydrogen bonded species of benzil participates in the production of α,α' -dihydroxystilbene.

Studies on the detailed mechanism of the reaction is presently in progress.



References

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