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IRRADIATION OF o-PHTHALALDEHYDE IN DEUTERATED SOLVENTS

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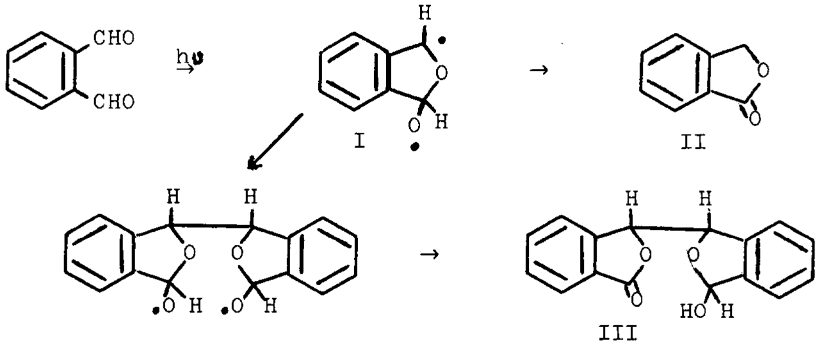
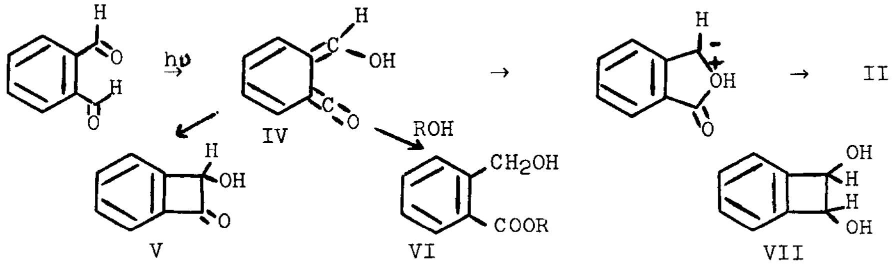
The results of a recent study(1) on the photochemistry of o-phthalaldehyde have been interpreted in terms of a solvent-dependent partitioning of biradical species I between phthalide (II) and dimer III formation, eq. 1.



(1)

Interested in light-induced hydrogen abstraction processes(2), we had envisioned that a reasonable pathway for formation of phthalide(3) would be intramolecular abstraction of aldehydic hydrogen by excited state carbonyl to produce ketene IV (directly or after intersystem crossing) which could, subsequently, undergo ionic intramolecular closure, as indicated in eq 2. Alternatively, cyclization to ketol V might occur. Unable to detect V,(4,5) we ini-



(2)

tiated irradiation studies in the presence of alcohols with the hope of isolating hydroxyester VI and/or diol VII, the product of intramolecular pinacol reduction. It was found that phthalide was a significant photoproduct, as determined by glc, even when the irradiation was conducted in neat isopropanol. Consequently, in order to differentiate between free radical, as in eq 1, and ionic hydrogen transfer to the benzylic position of phthalide, deuterium exchange studies were undertaken.

The pertinent results appear in Table I.(6) In each case the crude photoproduct was sublimed in vacuo at 100° to afford oily or crystalline material, rich in phthalide, which was further purified, when necessary, by recrystallization or preparative glc. The position (benzylic) and extent of deuterium incorporation were determined by nmr and mass spectrometry(7).

TABLE I

Irradiation of o-Phthalaldehyde[a] in Deuterated Solvents

Experiment	Solvent (v/v)	% Monodeuterophthalide[b]
1	benzene/CH_3OD (7/1)	80 (70)
2	chloroform/CH_3OD (7/1)	74 (64)
3	acetonitrile/D_2O (7/1)	86 (78)
4	benzene/$CDCl_3$ (7/1)	none
5[c]	benzene/CH_3OD (7/1)	none

[a] 0.5% solution. [b] See ref 7. [c] Control experiment: irradiation and quantitative recovery of phthalide.

Solvent effects on the course of photoreaction of o-phthalaldehyde are readily apparent both with regard to the overall rate, which, for example, is significantly faster in chloroform than in benzene, and the extent of phthalide formation, as previously noted(1), e.g. about 50% in benzene and almost quantitative in chloroform and carbon tetrachloride. On irradiation in benzene or chloroform in the presence of 12.5% methanol (or CH_3OD as in exp 1 and 2 of Table I), the rate of reaction and the yield of phthalide, although lower, remain characteristic of the neat solvent(8). This feature together with deuterium incorporation from D_2O (exp 3) appears to preclude free radical mechanisms of incorporation, e.g. by initial α-hydrogen abstraction from methanol. Experiments 4 and 5 demonstrate, respectively, the absence of deuterium incorporation from $CDCl_3$ and the stability of phthalide to deuterium exchange.

The results provide strong evidence for ionic hydrogen transfer and the intermediacy of ketene IV in the formation of phthalide. The ketene intermediate most likely results from intramolecular abstraction of aldehydic hydrogen by excited state carbonyl, analogously to photoenolization of *o*-benzylbenzophenone(9). In addition to the mechanism of eq 2, phthalide formation could reasonably occur by lactonization of intermediate VI (R = H or CH_3), although the presence of VI (R = CH_3) was not apparent in infrared spectra taken during the course of reaction. The observed, incomplete incorporation of deuterium (less than 100%) is readily explicable in terms of the mechanism of eq 2, e.g. as a result of protonation by the $CH_3\overset{+}{O}\begin{smallmatrix}\diagup H\\ \diagdown D\end{smallmatrix}$ species, produced at the reaction site, prior to dilution. Clearly, the intermediacy of biradical I is, at best, of minor importance in the formation of phthalide.

Abstraction of aldehydic hydrogen by both excited state carbonyl(10) and nitro(11) species has been discussed. In fact, the mechanism of eq 2 is entirely analogous to that proposed for the related photoredox reaction of *o*-nitrobenzaldehyde to afford *o*-nitrosobenzoic acid(11). It is of interest that the deuterium exchange experiments which demonstrated light-induced intramolecular hydrogen abstraction by the nitro group of *o*-nitrotoluene(12) together with the present results provide indirect experimental support for this early hypothesis.

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4. This work was carried out by Miss M. N. Amsden, National Science Foundation undergraduate research participant, summer of 1966.

5. Preliminary efforts to trap the ketene intermediate with maleic anhydride and dimethylacetylenedicarboxylate were equally unsuccessful.

6. A "Black Light" source (G.E. H100PSP38-4) was utilized. Nitrogen was passed through the solutions prior to and during the irradiations, which were carried out in Pyrex jacketed-beakers at about 20°.

7. The absence of a peak at m/e 136, after correction for isotopes of natural abundance, indicated no dideuteration. In determining deuterium incorporation, mass spectra were obtained under conditions (8 ev) in which phthalide does not exhibit an $(M-1)^+$ ion; however, a major fragment due to loss of the elements of CHO (CDO) could not be eliminated. Consequently, since this process might occur less readily with deuterophthalide, the upper and lower (in parenthesis) limits of deuterium incorporation (Table I) were estimated from the relative intensities of the molecular ions, m/e 134 and 135, assuming equal stabilities and an isotope effect of 0.2, respectively. In this regard, see J. K. McLeod and C. Djerassi, *Tetrahedron Letters*, 2183 (1966), in which isotope effects of 0.98 to 0.5 were observed for a variety of hydrogen transfer processes induced by electron impact.

8. As in the neat solvents, the rate of disappearance of *o*-phthalaldehyde is faster and the yield of phthalide is about twice as large in chloroform/methanol relative to benzene/methanol solution, although the phthalide yields are lowered (by about 60%) to 40 and 20%, respectively. Of possible significance, the yield of phthalide from *o*-phthalaldehyde on irradiation in acetonitrile/D_2O (exp 3) is lower than in neat acetonitrile by about 60%, as well.

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