Photochemical Behavior of Indane-1,2,3-trione in Degassed Alcoholic Solutions: Formation of 3-Substituted Phthalides

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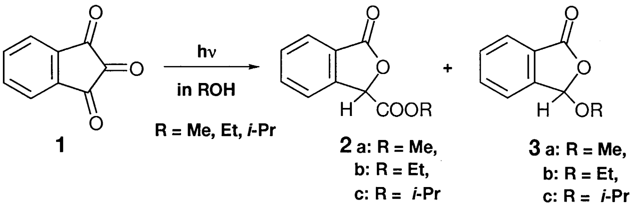
Irradiation of indane-1,2,3-trione in degassed alcoholic solutions affords 3-alkoxycarbonylphthalides as the major product together with 3-alkoxyphthalides. 3-Alkoxycarbonylphthalides may be derived from the reaction between alcohols and the spirooxiranone intermediate, generated photochemically by cleavage of the bond between two carbonyl groups of indane-1,2,3-trione *via* a cyclobutenone biradical derivative.

The photochemical behavior of the carbonyl groups of cyclic vicinal polyketones has received considerable attention in the last few years.[1] Furthermore, the photochemical reaction of cyclic vicinal triketone has also attracted interest from the viewpoint of the study of transient intermediate photochemistry in the photolysis of indane-1,2,3-trione.[2] The photochemical reaction of ninhydrin gave hydrindantin as the main product.[3] Recently, it has been reported that irradiation of indane-1,2,3-trione in acetonitrile or benzene - cyclohexa-1,4-diene (1:1) gave a small amount of a trans-biphthalyl and diisocoumarin-like compound and hydrindantin, respectively.[1b] In the course of examining the photochemical reactions of vicinal polyketones,[4] we found that irradiation of degassed alcoholic solutions of indane-1,2,3-trione or its hydrate ninhydrin gave the corresponding 3-alkoxycarbonylphthalides as the major product together with 3-alkoxyphthalides. Herein, we wish to report the first example of the photochemical formation of 3-substituted phthalides from indane-1,2,3-trione.

Irradiation of indane-1,2,3-trione **1**[5] in degassed alcoholic solutions[6] (3 mmol dm^{-3}, 5 ml) at 15 ℃ with a 300 W high-pressure mercury lamp gave a mixture of products which were analyzed by GC and GC-MS. The photoproducts[7] were also separated by column chromatography on silica gel and characterized by IR, ^{1}H- NMR, and Mass spectroscopies. The yields of the photoproducts were determined by GC analysis. The results of the photochemical reactions of **1** in alcoholic solutions

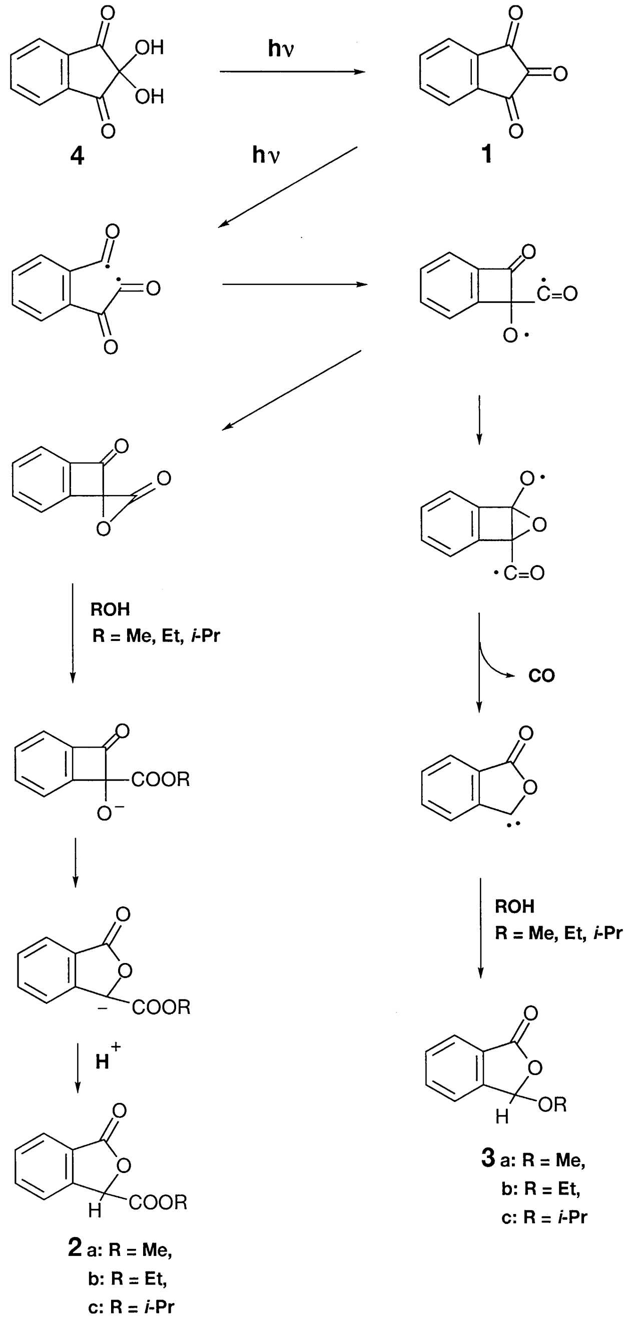


Scheme 1.

Table 1. Photochemical reactions of indane-1,2,3-trione in alcohols

Entry	Solvent	Irr.time / h	Conv / %	Products / %[a] 2		3	
1	MeOH	0.5	55	57	**2a**	21	**3a**
2	EtOH	1.0	31	54	**2b**	12	**3b**
3	*i*-PrOH	1.0	73	35	**2c**	5	**3c**

[a]Determined by GC analysis.



Scheme 2.

are summarized in Table 1. As can be seen from Table 1, photochemical reactions of **1** in degassed alcoholic solutions afforded 3-alkoxycarbonylphthalides **2** and 3-alkoxyphthalides **3**, Scheme 1. The photochemical reaction of ninhydrin **4** in degassed alcoholic solutions gave also similar results to that of **1**. Thus, it is possible to say that the photochemical reaction of **4** takes place *via* formation of **1** by a photochemical dehydration of **4**. The formation of **2** and **3** can be explained in terms of the possible pathways outlined in Scheme 2.[8] The first step in the photochemical processes of **4** in a degassed alcoholic solutions may be cleavage of the C-OH bond to form a semidione radical which subsequently undergoes decomposition to give **1** and hydrogen atom.[3b, 9] The photochemical process of **1** in a degassed solution may be cleavage of the C-C bond between the two vicinal carbonyl groups in **1** to form a diradical which subsequently converts to either spirooxiranone derivative or oxacarbene by the decarbonylation of the diradical. The spirooxiranone derivative then reacted with alcohol to give **2**. On the other hand, the oxacarbene reacted with alcohol to afford **3**.

In order to gain insight into information on the excitation energy on the carbonyl groups in **1**, phosphorescence spectra of **1**, indane-1,3-dione, and indan-2-one were measured, respectively.[10] The phosphorescence spectrum of **1** in butyronitrile - butyl acetate is similar to that of indane-1,3-dione. On the other hand, the emission spectrum of **1** is different in position and structure from the spectrum of indan-2-one. These results suggest that the excitation energy of **1** may be localized to the carbonyl group at its benzoyl moiety.

In conclusion, we have demonstrated that 3-alkoxycarbonylphthalides and 3-alkoxyphthalides can be obtained by photochemical reaction of indane-1,2,3-trione in degassed alcoholic solutions and 3-substituted phthalides seem to be produced *via* spirooxiranone for **2** and oxacarbene for **3**. Similar products were obtained from the irradiation of 5-bromo-, 5-chloro-, 5-methoxy-, 4,5-dimethoxyindane-1,2,3-triones and their hydrates in degassed alcoholic solutions.[11]

References and Notes

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5 Indane-1,2,3-trione was prepared from the dehydration of ninhydrin by heating at 120 ℃ for a few hours under reduced pressure.

6 Before irradiation, indane-1,2,3-trione in alcoholic solutions in Pyrex tubes were degassed by an ultrasonic generator under purging argon and cooled with ice-water for 30 minutes.

7 Selected spectroscopic data for **2a**: IR(KBr) 1775, 1750 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.80 (s, 3H, OMe), 5.87 (s, 1H, CH), 7.4 - 8.0 (m, 4H, ArH); MS: m/z 192 (relative intensity) (M$^+$, 7), 148 (7), 133 (100), 104 (15). **2b**: IR(KBr) 1775, 1740 cm^{-1}; δ (CDCl$_3$) 1.34 (t, 3H, J = 7.3 Hz, Me), 4.28 (q, 2H, J = 7.3 Hz, CH$_2$), 5.99 (s, 1H, CH), 7.5 - 8.1 (m, 4H, ArH); MS: m/z 206 (relative intensity) (M$^+$, 0.9), 162 (2.4), 134 (40), 133 (100), 105 (18). **2c**: IR(KBr) 1780, 1750 cm^{-1}; δ (CDCl$_3$) 1.28 (d, 6H, J = 7.2 Hz, Me), 5.07 (sep, 1H, J = 7.2 Hz, CH), 5.77 (s, 1H, CH), 7.4 - 8.0 (m, 4H, ArH); MS: m/z 220 (relative intensity) (M$^+$, 0.1), 205 (0.4), 134 (95), 133 (100), 104 (28). 3-Methoxyphthalide **3a**[1a] was prepared by the reaction of 3-bromophthalide with anhydrous methanol overnight at room temperature. 3-Ethoxyphthalide **3b**[12] and 3-isopropoxyphthalide **3c** were prepared by following a procedure similar to that described above. **3c**: MS: m/z 192 (relative intensity) (M$^+$, 0.2), 164 (1), 149 (100), 133 (33), 104 (26).

8 We thank a referee for his/her suggestion of this pathway.

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10 The phosphorscence emission spectra of **1** and indane-1,3-dione were observed at 546 and at 554 nm, respectively, on the other hand, that of indan-2-one was observed at 418 nm.

11 All new compounds were fully characterized.

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