

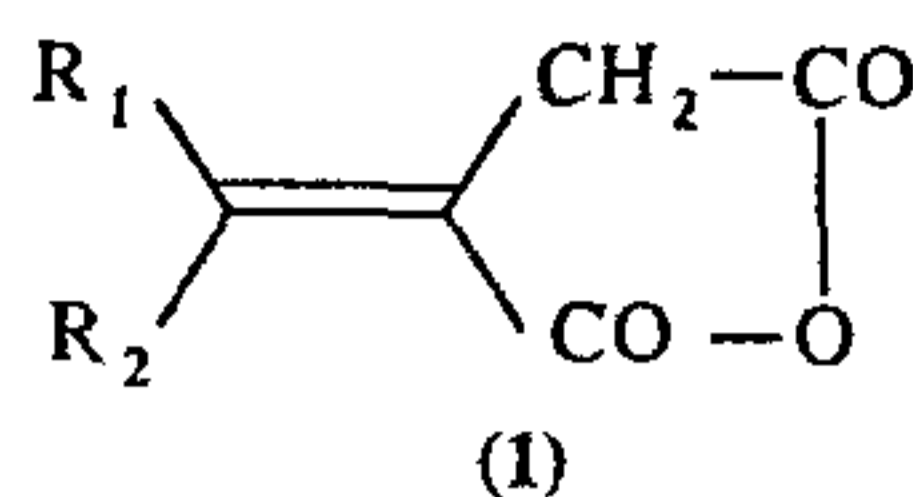
Photochromism in Stobbe condensation and cyclised products

Photochromism occurs in fulgides having either phenyl, substituted phenyl, furyl or styryl substituents and the mechanism of the photochemical change has been analysed¹.

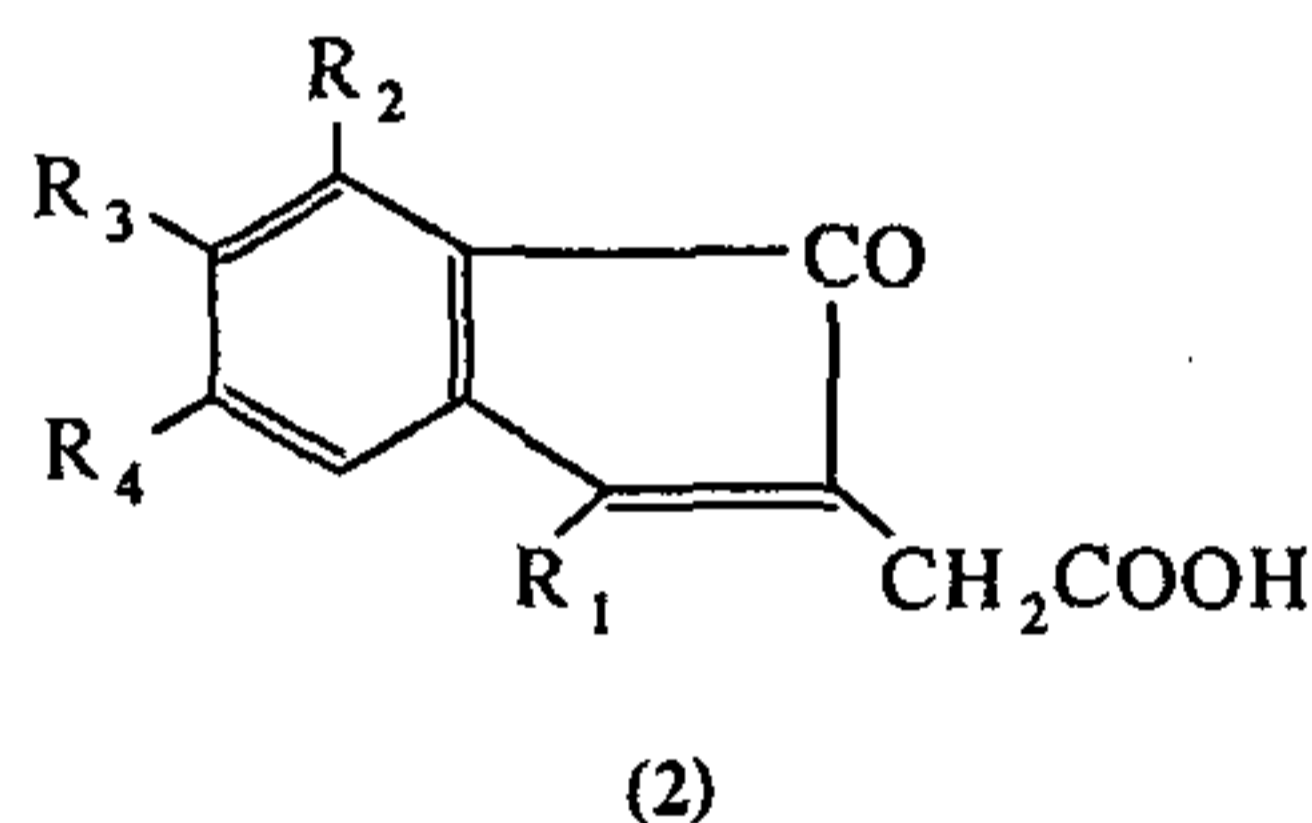
In the course of studies on structure and stereochemistry of Stobbe reaction products²⁻⁵, based on the mechanism suggested by Santiago and Becker¹, many anhydrides (prepared by Stobbe condensation of dimethylsuccinate and aldehyde or ketones and acetylchloride treatment to the diacid), fulgides (prepared by Stobbe condensation at both the methylenes with aldehyde and ketones and dehydration of the subsequent fulgenic acid) and indenones (prepared by cyclization of Stobbe reaction products with PPA, conc. H₂SO₄ or internal Friedel-Crafts reaction) were synthesized⁶⁻⁸ which were studied for their photochromic properties.

0.01 g of the compound in each case was dissolved in 10 ml benzene and exposed to light. After 5 h, experimental solution was compared with the colour of the instantly prepared solution of the same compound in 10 ml benzene and the results are noted.

Photochromic substances are useful as optical brighteners, in colour photography, in coloured polymers (and plastics with photochromic dye) as analytical reagents etc. In the present study, products had colours varying from yellow to orange which, on exposure to light, intensified with a *mild change* in colour for (1 a-d), *moderate change* for (1 e-g; 2 a-d, g; 3 a-c and 4 d, e) and *intense change* for (1 h, i; 2 e, f; 3 d-g and 4 a-c). The colour changes are irreversible*. The phenomenon is observed in the solutions. Many more systems have been studied⁹ in the



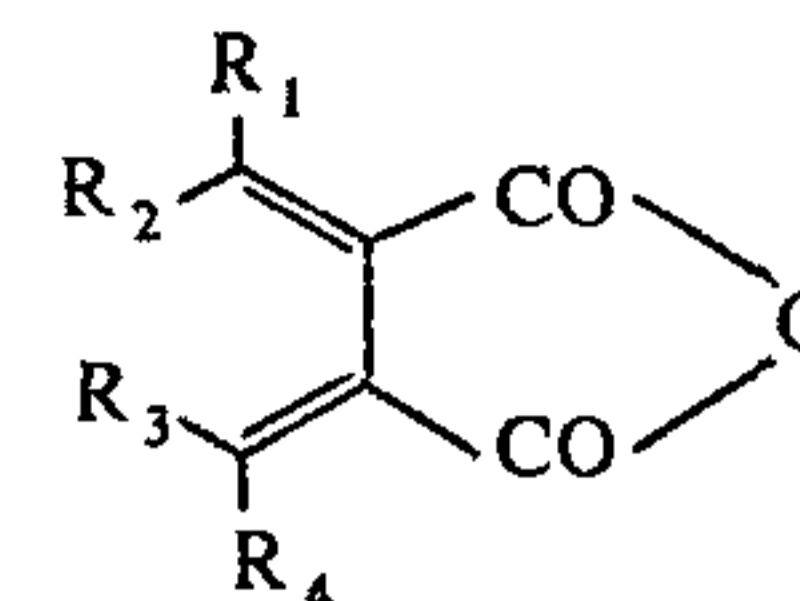
- (a) R₁ = p-OMePh, R₂ = H
- (b) R₁ = 2-C₁₀H₇, R₂ = H
- (c) R₁ = p-ClPh, R₂ = Ph
- (d) R₁ = Ph, R₂ = p-ClPh
- (e) R₁ = Ph, R₂ = H
- (f) R₁ = 3,4,5-tri OMePh, R₂ = H
- (g) R₁ = 2-furyl, R₂ = H
- (h) R₁ = R₂ = Ph
- (i) R₁ = Me, R₂ = Ph



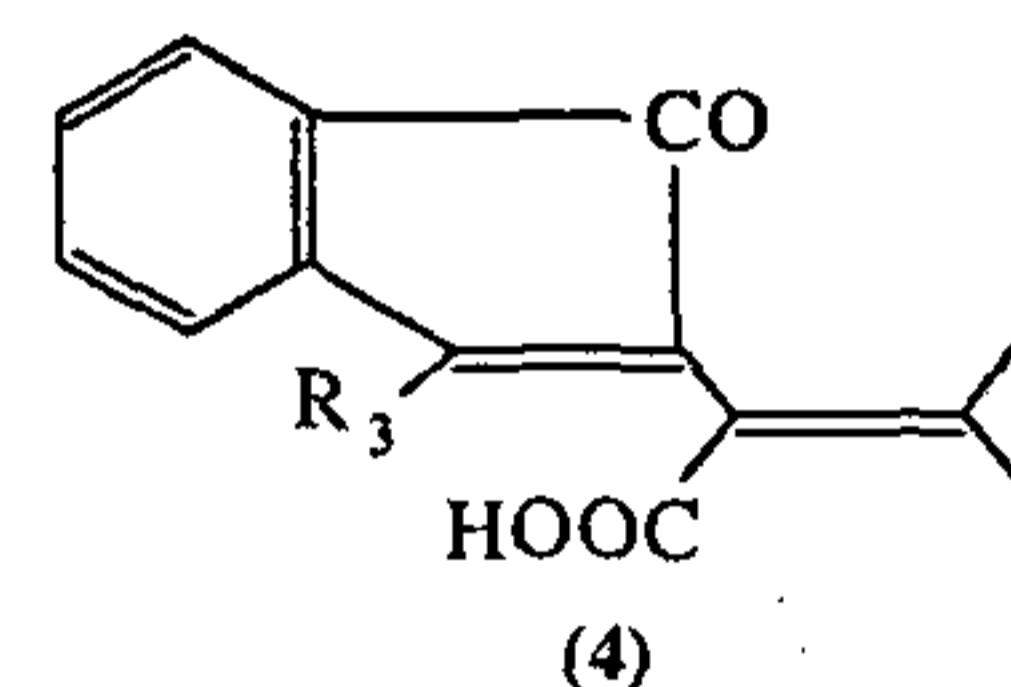
- (a) R₁ = R₂ = R₄ = H, R₃ = OMe
- (b) R₁ = H, R₂ = R₃ = R₄ = OMe
- (c) R₁ = p-ClPh, R₂ = R₃ = R₄ = H
- (d) R₁ = Me, R₂ = R₃ = R₄ = H
- (e) R₁ = R₂ = R₃ = R₄ = H
- (f) R₁ = Ph, R₂ = R₃ = R₄ = H
- (g) R₁ = H, R₂-R₃ = C₆H₄, R₄ = H

photochemical reactor by UV irradiation which is being published elsewhere.

1. Santiago, A. and Becker, R. S., *J. Am. Chem. Soc.*, 1968, **90**, 3654-3658.
2. Bagavant, G. and Banerjee, S., *Curr. Sci.*, 1976, **B15**, 487-489.



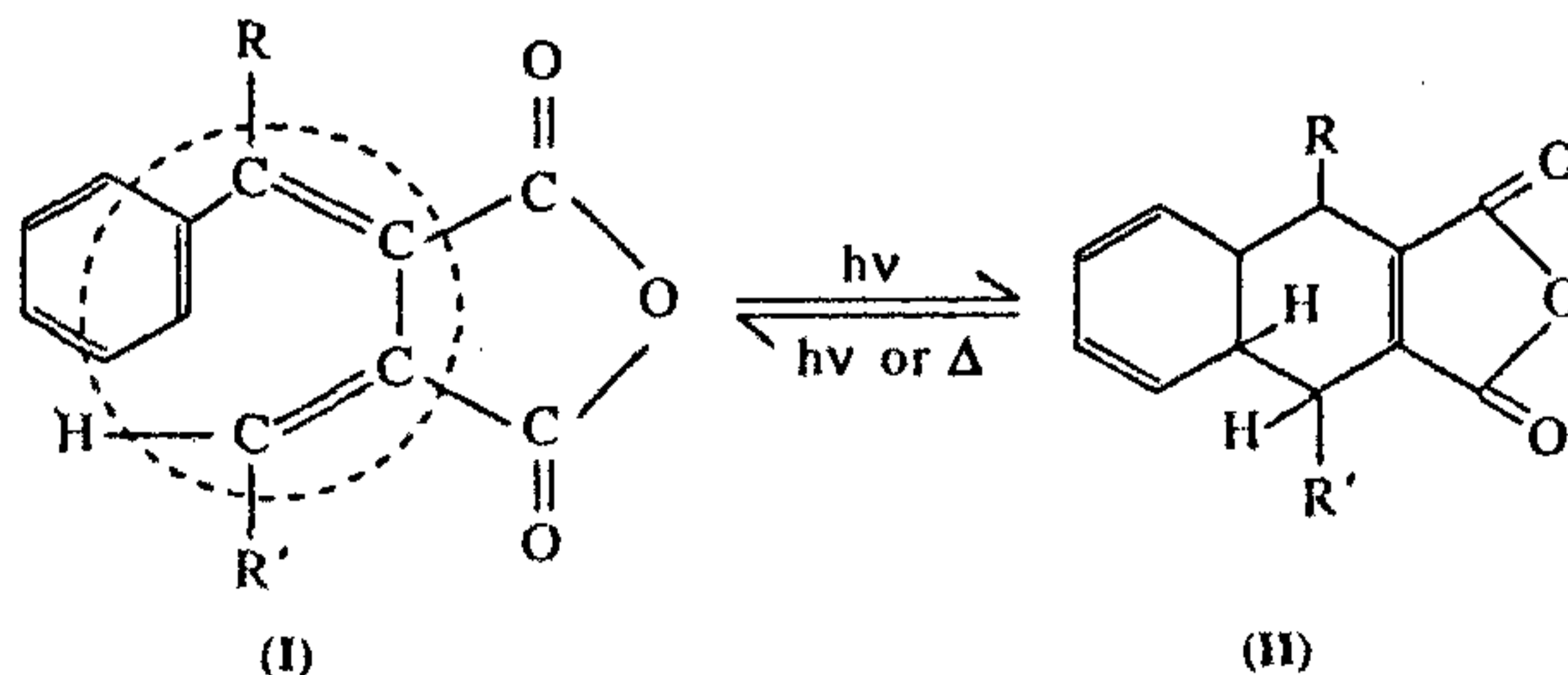
- (a) R₁ = R₄ = H, R₂ = R₃ = 2-C₁₀H₇
- (b) R₁ = R₂ = Ph, R₃ = 2-C₁₀H₇, R₄ = H
- (c) R₁ = Ph, R₂ = Me, R₃ = 2-C₁₀H₇
- (d) R₁ = R₄ = Ph, R₂ = R₃ = H
- (e) R₁ = R₂ = R₃ = R₄ = H
- (f) R₁ = R₄ = Ph, R₂ = R₃ = Me
- (g) R₁ = R₃ = Me, R₂ = R₄ = Ph



- (a) R₁ = H, R₂ = 2-C₁₀H₇, R₃ = Me
- (b) R₁ = H, R₂ = 2-C₁₀H₇, R₃ = Ph
- (c) R₁ = R₂ = R₃ = Ph
- (d) R₁ = R₃ = Me, R₂ = Ph
- (e) R₁ = Ph, R₂ = R₃ = Me

3. Bagavant, G. and Banerjee, S., *Chem.*, 1981, **B20**, 362-365.
4. Gupta, G. and Banerjee, S., *Indian J. Chem.*, 1990, **B29**, 787-790.
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*Santiago and Becker have suggested that photochromism was observed only if one of the substituted groups was an aromatic moiety as (I). This makes the fulgide a substituted 1,2,5-hexatriene in which an aromatic bond serves in place of one of the double bonds of the triene. The photogenerated valence tautomer is a dihydronaphthalene derivative (II) as illustrated below.



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