

Photochemical Conversion of Grisadiendiones into Dibenzofurans

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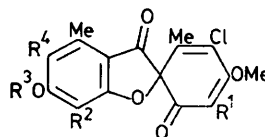
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Summary Appropriately substituted grisadiendiones on u.v. irradiation undergo rearrangement to dibenzofurans with loss of carbon dioxide; the mechanism of this reaction is discussed.

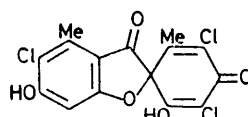
WE have reported¹ the synthesis of the grisadiendiones (1)–(5) and their rearrangements to depsidones under basic or thermal conditions. Their photochemical behaviour is quite different and involves excitation of the dienone chromophore.

On irradiation through borosilicate glass in dry benzene under dry nitrogen in a Rayonet apparatus with light centred at 350 nm the grisadienones (1)–(5) gave the dibenzofurans† (7)–(10) and (12) respectively, in good yield. The reaction of the grisadiendione (5) is slower than the others presumably because phototautomerism to (6) is necessary. The dibenzofuranoid nature of these products was apparent from their characteristic electronic spectra and their lack of i.r. carbonyl absorption. The benzyl ether (11), derived from (7) on saturation of the benzylic proton signal in its ¹H n.m.r. spectrum gave a 39% nuclear Overhauser effect at the aromatic proton signal, thus indicating that the aromatic proton is *ortho* to a hydroxy group in (7). Methylation and hydrogenolysis of (7) gave the dibenzofuran (13) identical with a specimen secured by rational synthesis.² The dibenzofuran (10) was also related to the known compound (14)³ by methylation and hydrogenolysis.

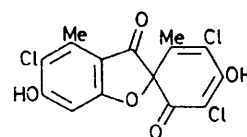
We have shown that the related depsidones¹ are not intermediates in these photochemical conversions. Hence we



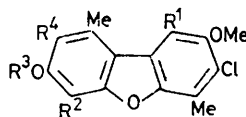
- (1) R¹ = R⁴ = Cl, R² = R³ = H
 (2) R¹ = R⁴ = Cl, R² = H, R³ = Me
 (3) R¹ = Me, R² = R³ = R⁴ = H
 (4) R¹ = R² = Me, R³ = R⁴ = H



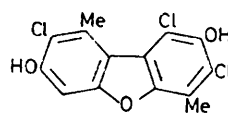
(5)



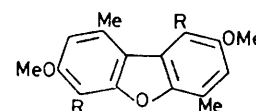
(6)



- (7) R¹ = R⁴ = Cl, R² = R³ = H
 (8) R¹ = R⁴ = Cl, R² = H, R³ = Me
 (9) R¹ = Me, R² = R³ = R⁴ = H
 (10) R¹ = R² = Me, R³ = R⁴ = H
 (11) R¹ = R⁴ = Cl, R² = H, R³ = CH₂Ph



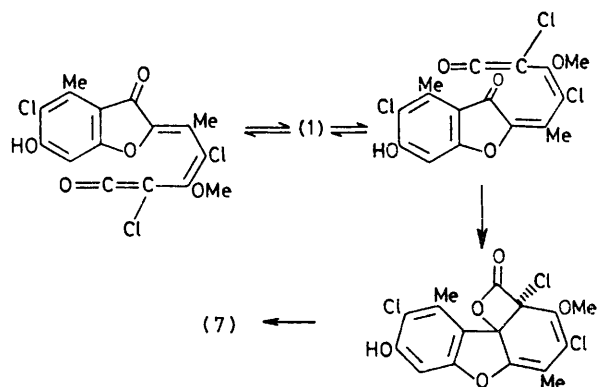
(12)



- (13) R = H
 (14) R = Me

† All new compounds gave satisfactory elementary analyses or high resolution mass spectral molecular ion peaks.

propose that excitation of the dienone chromophore of the grisadienones (1)–(5) causes either concerted or radical ring opening to pairs of stereoisomeric dienylketens.



SCHEME

Only one member of each pair is able, because of its stereochemistry, to undergo an intramolecular $2\pi_a + 2\pi_s$ cyclization yielding a β -lactone. Loss of carbon dioxide would then yield the products. This mechanism is illustrated for the conversion (1) \rightarrow (7) (Scheme). Linearly conjugated cyclohexadienones are known to yield dienylketens on u.v. irradiation,⁴ and cyclizations of ketens similar to the above, which yield thermally unstable β -lactones, are also known.⁵ The novelty of the present reactions is the consecutive occurrence of these processes. The dienylketens were not trapped by conducting the photoreaction of (4) in methanol; this suggests that the intramolecular cyclization is more rapid than nucleophilic attack by methanol.

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¹ T. Sala and M. V. Sargent, preceding communication.

² J. MacMillan, T. P. C. Mulholland, A. W. Dawkins, and G. Ward, *J. Chem. Soc.*, 1954, 429.

³ J. A. Elix, D. P. H. Murphy, and M. V. Sargent, *Synth. Comm.*, 1972, 2, 427.

⁴ H. Staudinger and St. Bereza, *Annalen*, 1911, 380, 243.

⁵ G. Quinkert, *Angew. Chem.*, 1972, 84, 1157; 1975, 87, 851.