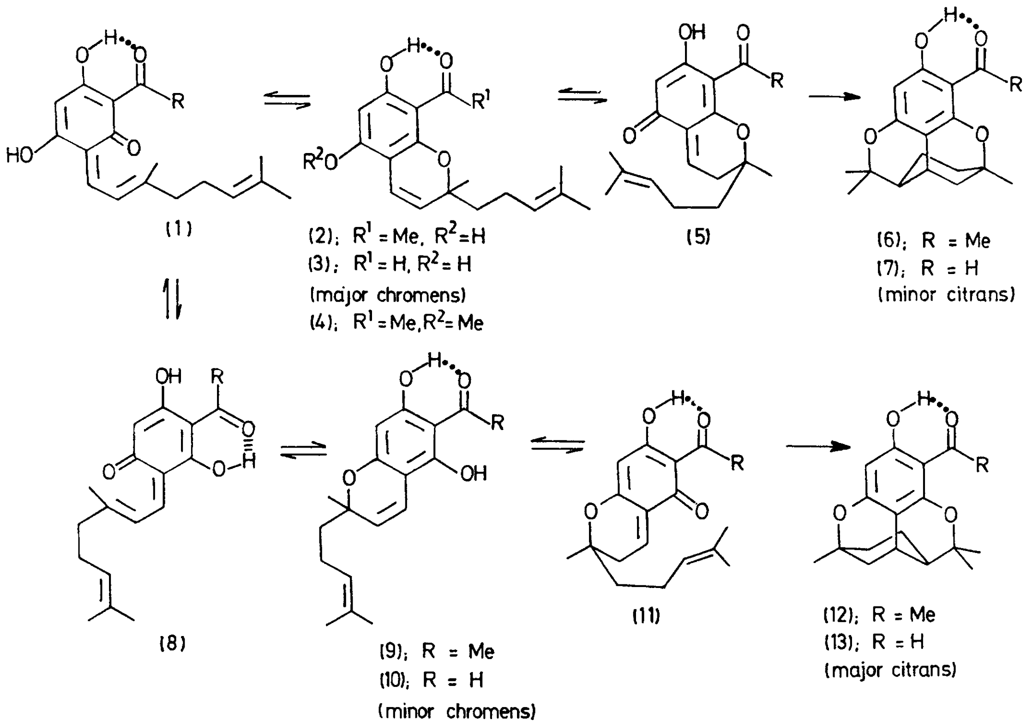
New Rearrangements Involving Dienone–Chromen Equilibration, in the Pyridine-catalysed Conversion of Chromens into Citrans

By Leslie Crombie,* David A. Slack, and Donald A. Whiting*
(*Department of Chemistry, The University, Nottingham* NG7 2RD)

Summary The chromens (**2**) and (**3**), at 110 °C in pyridine, are converted into citrans by a hitherto unexpected rearrangement involving thermal electrocyclic opening, (*E*)/(*Z*) isomerisation and tautomerism of the intermediate dienones, and reclosure to the alternative chromens; citran formation then proceeds from either of the equilibrating chromens.

Treatment of phloracetophenone, or phloroglucinaldehyde, with citral in pyridine at 110 °C leads in each case to a pair of isomeric citrans. From phloracetophenone the major citran is (**12**), and from phloroglucinaldehyde (**13**).[1] At lower temperatures the intermediate chromens can be isolated, and from phloracetophenone a chromen (**9**) is reported.[2] Its structure rests on n.m.r. data [*e.g.* τ ($CDCl_3$) $-3·80$ ($2 \times$ OH), separating on dilution], and conversion into (**12**) on heating in pyridine. We report that the reaction at 40 °C gave a single monochromen (31%)† and whilst most spectroscopic data matched those reported,[2] two phenolic OH resonances at τ 1·90 and $-3·78$ were noted. These, and a bathochromic base-shift of 38 nm in the u.v. spectrum were more appropriate to a 2,4-dihydroxyacetophenone (**2**) than a 2,6-dihydroxyacetophenone (**9**). To resolve the structure, the chromenylation was carried out with 2,6-dihydroxy-4-methoxyacetophenone,[3] [τ ($CDCl_3$), $-1·62$ (2 OH); 2,4-dihydroxy-6-methoxyacetophenone τ 0·55, $-3·88$]. The single monochromen product (**4**), of unambiguous structure, was identical with the monomethylation (diazomethane) product from (**2**) by ^{1}H and ^{13}C n.m.r., i.r., u.v. and t.l.c. Each specimen formed a *p*-nitrobenzoate (m.p. 90—91 °C and 89—91 °C; mixed m.p. 89—91 °C). In a similar way the single chromen formed from phloroglucinaldehyde by reaction with citral and pyridine at 40 °C for 16 h was formulated as (**3**) (τ 1·87 and $-1·94$, both OH).



Scheme

Heating chromens (**2**) and (**3**) in pyridine at 110 °C leads to the same citran products as were obtained directly at this temperature,[1] thus some unexpected rearrangement is obviously taking place. In hot pyridine, chromens (**2**) and (**3**) equilibrate with the ketonic form (**5**) from which, by intramolecular Diels-Alder reaction, the minor citrans (**6**) and (**7**) are formed. However, (**2**) and (**3**) also undergo reversible ring opening to (**1**) and (*E*)/(*Z*) isomerisation of the exocyclic double bond of the latter ensues to form (**8**). From (**8**), isomeric chromens (**9**) and (**10**) are formed and hence, *via* (**11**), citrans (**12**) and (**13**) (Scheme).

Since the Diels–Alder reactions (**5**) → (**7**) and (**11**) → (**13**) are irreversible,[1] the predominance of citrans (**12**) and (**13**)

---

† A bischromen and traces of citrans were also formed, but no other monochromen could be detected by t.l.c. or n.m.r. Yields have no preparative significance as conditions were chosen only to minimise product complexity.

appears to reflect the chelate stabilisation[4] of (**11**) relative to (**5**). The greater conjugation in (**1**) relative to (**8**) may be responsible for the preferred production of (**2**) and (**3**). The revision of the structure of chromen (**9**) to (**2**) indicates that the acid-catalysed conversion of (**2**) → (**6**) does not involve carbonium-ion rearrangements as has been discussed.[2]

We thank the S.R.C. for support.

(*Received*, *4th December* 1975; *Com.* 1350.)

---

[1] M. J. Begley, L. Crombie, R. W. King, D. A. Slack, and D. A. Whiting, preceding communication.

[2] G. Combes, J. L. Montero, and F. Winternitz, *Compt. rend.*, 1972, 1313; J. L. Montero and F. Winternitz, *Tetrahedron*, 1973, **29**, 1243.

[3] A. Sonn and W. Bülow, *Ber.*, 1925, **58**, 1691.

[4] W. M. Bandaranayake, M. J. Begley, B. O. Brown, D. G. Clarke, L. Crombie, and D. A. Whiting, *J.C.S. Perkin I*, 1974, 1007.