

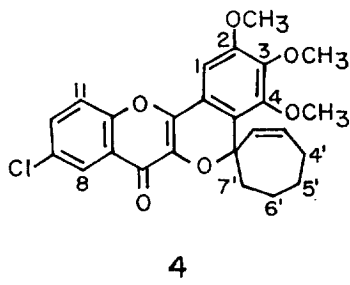
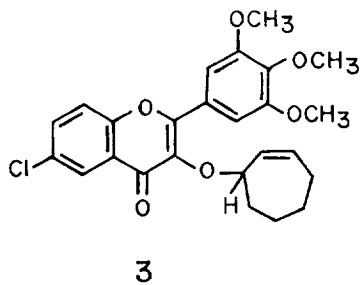
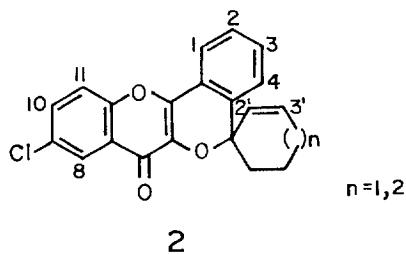
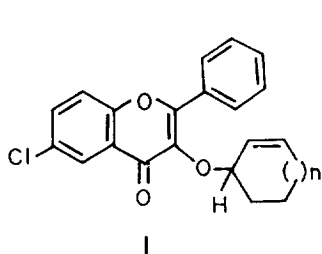
A Photochemical Synthesis of Spiropyrans

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Abstract : A direct photochemical route to the synthesis of some spirobenzopyranochromones via H-abstraction is reported.
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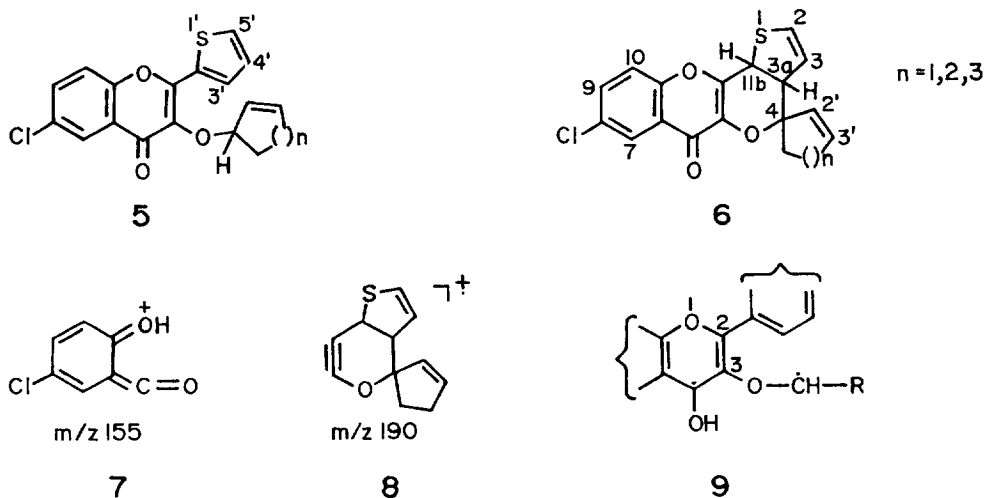
Spiropyrans find extensive use in Information storage technology¹ and the few methodologies developed for their synthesis are based upon (4+2) cycloadditions², reductive/thermal cyclisations³, enamine eliminations⁴, etc. These methods being specific are limited in their utility. Here, in this communication, we report a general and direct photochemical approach towards the synthesis of some complex spiropyrans which may extend their use as photochromic materials.



Photoirradiation of a MeOH/C₆H₆ solution of 3-cycloalkenyloxy chromone⁵ **1** with 450W Hanovia lamp through pyrex filter afforded after chromatographic workup **2** (n=1)⁶, yield 20%;

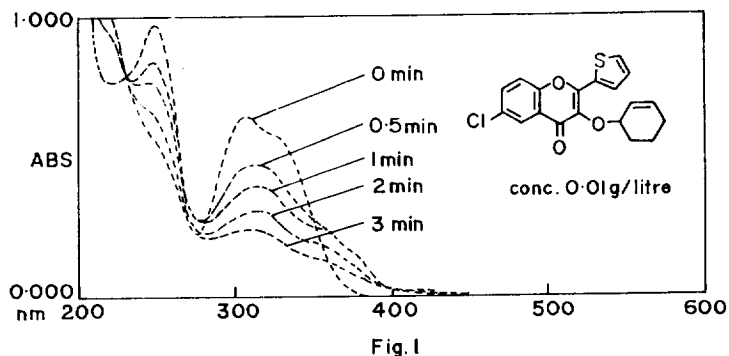
mp 235-236°; ν 1638 cm^{-1} ; λ_{max} 360, 320, 248 nm; δ (CDCl_3) 8.2 (d, $J = 2$ Hz, H-8), 7.7 (dd, $J = 8$ & 2 Hz, H-1)⁷, 7.45 (m, H-2, 3, 10, 11), 7.0 (dd, $J = 8$ & 1.5 Hz, H-4)⁷, 6.20 (m, H-3'), 5.85 (d, $J = 9$ Hz, H-2'), 2.18 (m, H-4'), 1.65 (m, H-5', 6'). The structure **2** ($n=1$) became further confirmed from M^+ 350 and two rDA fragments; m/z 155 and 196. Similarly the structures of **2** ($n=2$), yield 12%; mp 180-181° and **4** yield 15%; mp 164-166° were confirmed by their IR, PMR and mass spectra.

To assess the generality of this method, chromone **5** was photoirradiated to produce **6** ($n=1$), yield 50%; mp 170°; ν 1645 cm^{-1} ; λ_{max} 328, 292, 241 nm; δ (CDCl_3) 8.2 (d, $J = 2$ Hz, H-7), 7.5 (dd, $J = 9$ & 2 Hz, H-9), 7.4 (d, $J = 9$ Hz, H-10), 6.3 (dd, $J = 7$ & 3 Hz, H-2), 6.1 (d{t}, $J = 7\{1\}$ Hz, H-3'), 5.8 (d{m}, $J = 7\{1\}$ Hz, H-2'), 5.6 (dd, $J = 7$ & 3 Hz, H-3), 4.8 (d, $J=8$ Hz, H-11b), 3.6 (m, H-3a), 2.55 (m, H-4'), 2.1 (m, H-5'). The stirring of the resonances at δ 3.60 converted the signals at δ 6.3, 5.6 and 4.8 into doublets and singlet, respectively. The mass spectrum (M^+ 344) exhibited ions **7** and **8** at m/z 155 and 190 (rDA). The structures of **6** ($n=2$), yield 10%; mp 182° and **6** ($n=3$), yield 12%; mp 190-192° became evident from their spectral analysis.



In chromones **1** and **3**, formation of spirochromones **2** and **4** is attended by loss of two mass units but in conversion of **5** into **6**, it is simply a photoreorganisation⁸. The C/D ring fusion in **6** is *cis*, becomes evident from $J_{3a,11b} = 8$ Hz⁹.

Mechanistically these phototransformations (**1**, **3** & **5** to **2**, **4** & **6**) may be visualised as having occurred through an initial abstraction of O-methine H by the excited C=O of benzopyrone moiety^{8,9} leading to **9**. The easy abstractability of H is the result of the 6-membered transition state. The formation of only one product at low conversion rates is evident from the observance of isobestic points when changes in the UV spectrum of **1** ($n=1$) were studied (fig.1). Similar results were obtained with **5** ($n=1$).



Though the H-abstractions in the past have been utilised to obtain oxacyclobutanols¹⁰, benzofurans¹¹, spirobenzofurans¹², pyrans¹³ and benzoxepinols¹⁴ etc., but as far as we know this is the first example where H-abstractions could lead to the synthesis of spirobenzopyrans.

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- 1**, **3** and **5** were synthesised through the condensation of 5-chloro-2-hydroxyacetophenone and a benzaldehyde/thiophenecarboxaldehyde followed by H₂O₂/NaOH cyclisation and O-alkylation with 2-bromocycloalkene (K₂CO₃/CH₃COCH₃, RT).
- In photoreactions of **1** & **3** some 6-chloro-3-hydroxy-2-phenylchromone was also isolated.
- The lower field assignment of H-1 as compared to H-4 is based on the analogy from polynuclear hydrocarbons where protons in the bay region always appear at a lower field than other protons; Donekt, E.V.; Martin, R.H.; Evrard, F.G. *Tetrahedron*, **1964**, 20, 1495.

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