

# Synthesis of spiropyrans: H-abstractions in 3-cycloalkenyloxybenzopyrans

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## Full Research Paper

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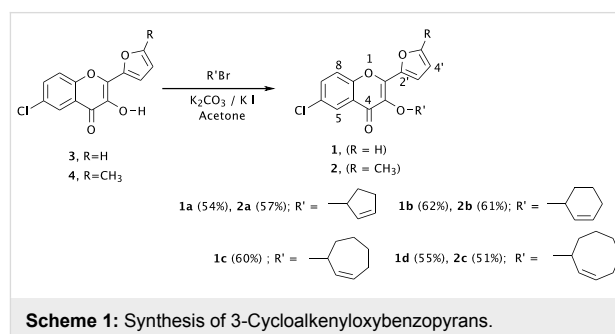
## Abstract

A photochemical route for the synthesis of some benzopyronspiropyrans from 2-furyl-3-cycloalkenyloxybenzopyrones involving H-abstraction is reported. How a methyl group on the furyl ring affects the product formation is also investigated.

## 1. Background

Spiropyrans exhibit photochromism due to the photoequilibrium with their open chain analogues merocyanins – a property that makes them a material of choice in digital storage technology. [1-5] Some spiropyrans have been found to have antiphlogistic, spasmolytic, antidiabetic and antifeedant activities amongst others. [6-10] The methods available for the synthesis of spiropyrans include enamine eliminations, reductive/thermal cyclisations and [4+2] cycloadditions. [11-16] These methods being specific in nature for a particular spirocyclic compound, offer limited synthetic utility. In the past, we have investigated the use of photochemical methods for the synthesis of organic molecules like vinyl ethers, [17] pyranopyrones [18,19] etc. and in continuation of that work we published a preliminary report on photochemical synthesis of spiropyrans. [20] To extend and

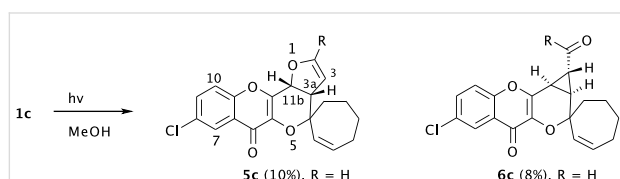
examine the scope of this methodology, in this communication, we report the synthesis of spiropyrans bearing dihydrofurlyls and acylcyclopropanes.



## 2. Results

The substrates **1** and **2** required for this study were obtained through the alkylation of 6-chloro-2-(2'-furyl)-3-hydroxy-4-oxo-4*H*-1-benzopyrans [21]**3** (R = H) and **4** (R = CH<sub>3</sub>) with an appropriate bromocycloalkene (R' Br).

The irradiation of **1c** in methanol with pyrex filtered light from a 125W Hg lamp produced two products **5c** and **6c** along with some **3**.

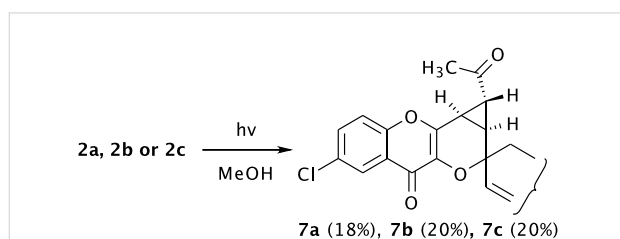


**Scheme 2:** Photolysis of 6-chloro-3-(1''-cyclohept-2''-enyloxy)-2-(2'-furyl)-4-oxo-4*H*-1-benzopyran.

## 3. Discussion

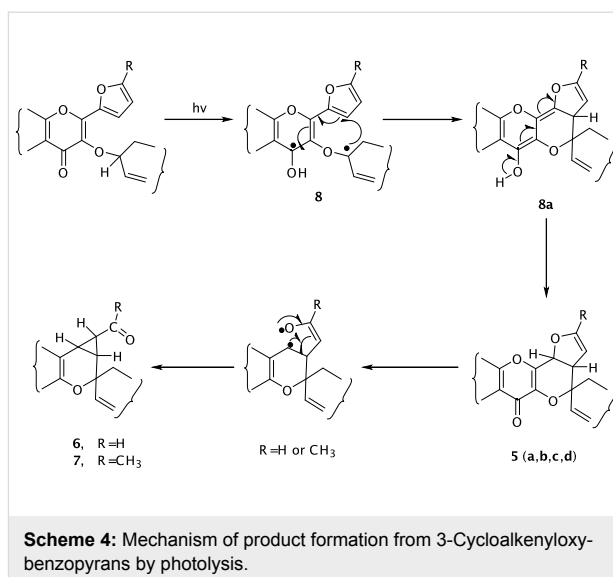
The structures of the photoproducts **5c** and **6c** were consistent with their spectral parameters [see Supporting Information File 1]; both the spiropyrans exhibited the presence of ions at *m/z* 155 and *m/z* 202 values in their mass spectra; these ions could very well be the result of rDA fragmentation of **5c** and **6c**. In the mass spectrum of **6c**, the base peak was at *m/z* 327 (M<sup>+</sup>-CHO).

The other chromones **1a**, **1b** and **1d** on photoirradiation rearranged to spirocyclic pyronopyrones **5a**, **5b**, **5d** and **6a**, **6b**, **6d**. The photoirradiation of **2a**, **2b** and **2c** yielded **7a**, **7b**, **7c** only and no photoproducts similar to **5** (R = CH<sub>3</sub>) could be isolated although the <sup>1</sup>H NMR of the crude photolysate of **2b** did show the presence of **5b** (R = CH<sub>3</sub>) in small proportions.



**Scheme 3:** Photolysis of 6-chloro-3-(1''-cycloalk-2''-enyloxy)-2-(2'-(5-methylfuryl))-4-oxo-4*H*-1-benzopyrans.

These photoconversions of the cycloalkenyloxy chromones (**1a**, **1b**, **1c**, **1d**, **2a**, **2b** and **2c**) to pyronospiropyranes can be visualized as having occurred through an initial abstraction of the *O*-methine proton of cycloalkenyl group by the excited carbonyl of the pyrone moiety to produce 1,4-biradical **8**. The photo-



product **5** (**a**, **b**, **c**, **d**), is then formed through bond formation between the alkoxy radical and furan (**8**), followed by 1,5-H migration in **8a**. [21]

The spiropyrans **6** (R = H) bearing cyclopropanes are the secondary photoproducts formed as a result of the further reorganization of **5** (R = H), through a ring contraction-ring expansion mechanism. [22,23] The formation of acetylcyclopropane compound **7** (R = CH<sub>3</sub>) from **2** (R = CH<sub>3</sub>) can be explained likewise. However, it is pertinent to mention here that when a large amount of **2b** was photolysed and the photolysate was carefully chromatographed, a very small amount (<3%) of photoproduct **5** (R = CH<sub>3</sub>) could be isolated (vide experimental). The reason for such behaviour of **2** (R = CH<sub>3</sub>) could be that the presence of -CH<sub>3</sub> group on dihydrofuryl moiety in the photoproduct **5** (R = CH<sub>3</sub>) makes the C-O bond easier to cleave. Thus as soon as **5** (R = CH<sub>3</sub>) is formed, it rearranges to **7** (R = CH<sub>3</sub>) or in other words the conversion of **5** (R = CH<sub>3</sub>) into **7** (R = CH<sub>3</sub>) is much faster than that of the formation of **5** (R = CH<sub>3</sub>) from **2** (R = CH<sub>3</sub>).

Regarding the stereochemical disposition of H-11b and H-3a in **5**, both of them are *cis* placed ( $J = 9.6\text{--}9.9$  Hz,  $\theta = 19.2^\circ$ ); in photoproducts bearing cyclopropanes [21]**6** (R = H) or **7** (R = CH<sub>3</sub>), H-1 is *trans* to H-2 and H-3 ( $J_{1,2} = 4.8$  Hz,  $J_{1,3} = 3.6$  Hz) and both H-2 and H-3 are *cis* ( $J_{2,3} = 9.0$  Hz).

## 4. Conclusion

In conclusion this photochemical method can be of utility for synthesizing a variety of pyronospiropyranes bearing both dihydrofuryls and acetylcyclopropanes. The substitution on the furan ring makes the primary photoproducts more amenable to cleavage.

## Supporting Information

### Supporting Information File 1

Experimental Data. The data provided represents the yield, melting point, IR, <sup>1</sup>H NMR and elemental analysis of the compounds.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-3-14-S1.doc>]

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