Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 104, No. 6, December 1992, pp. 753–757.
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Photochemical studies on 3,4-epoxy-3,4-dihydro-2H-1-benzopyrans

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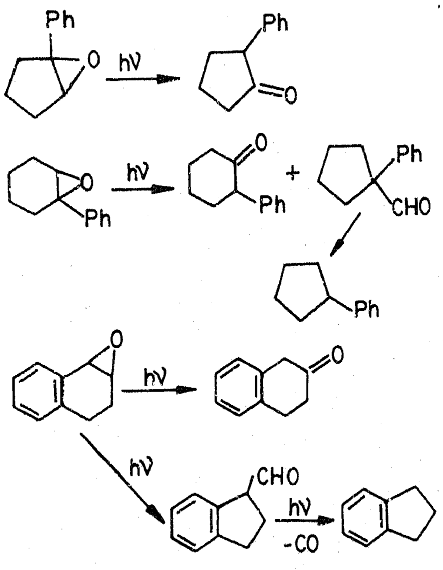
Abstract. Photochemical behaviour of 3,4-epoxy-3,4-dihydro-2H-1-benzopyrans, intermediates in the synthesis of pterocarpans, has been studied in various solvents. While ring contraction leading to 2,3-dihydrobenzofurans through a photodecarbonylation process was observed in cyclohexane, photoisomerisation leading to 3-chromanones was observed in acetone. This study has also been extended to antijuvenile hormone precocene(I) oxide.

Keywords. 3,4-Epoxy-3,4-dihydro-2H-1-benzopyran; pterocarpan; photodecarbonylative ring contraction; photoisomerisation; δ' hydrogen abstraction; precocene(I) oxide.

1. Introduction

The high degree of strain present in small ring heterocyclic systems, especially in oxiranes, results in unusual transformations both in the ground state as well as in their electronically excited states (Griffin and Padwa 1976). Considerable attention has been devoted to the area of aryl-substituted oxiranes (Griffin 1971). The photoreactions observed for this class of compounds include C–O bond cleavage and rearrangement, O–C bond cleavage accompanied by hydrogen migration, C–C bond cleavage and reversible zwitterion formation, cyclo elimination, deoxygenation and C–C and C–O bond cleavage accompanied by complex skeletal rearrangement. Some illustrative examples are shown in scheme 1.



Scheme 1.

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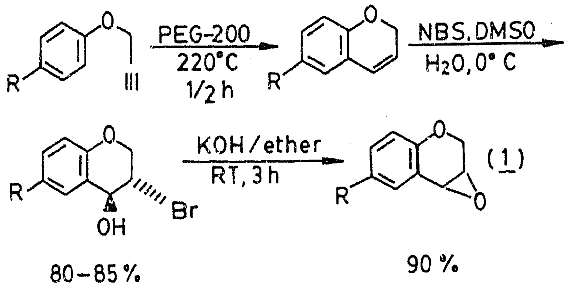
In view of these reports, we decided to study the photochemical behaviour of epoxychromans and epoxyprecocenes.

2. Synthesis

3,4-Epoxy-3,4-dihydro-2H-1-benzopyrans (epoxy chromans) and precocene(I) epoxide were prepared from phenyl propargyl ethers as described below (scheme 2).

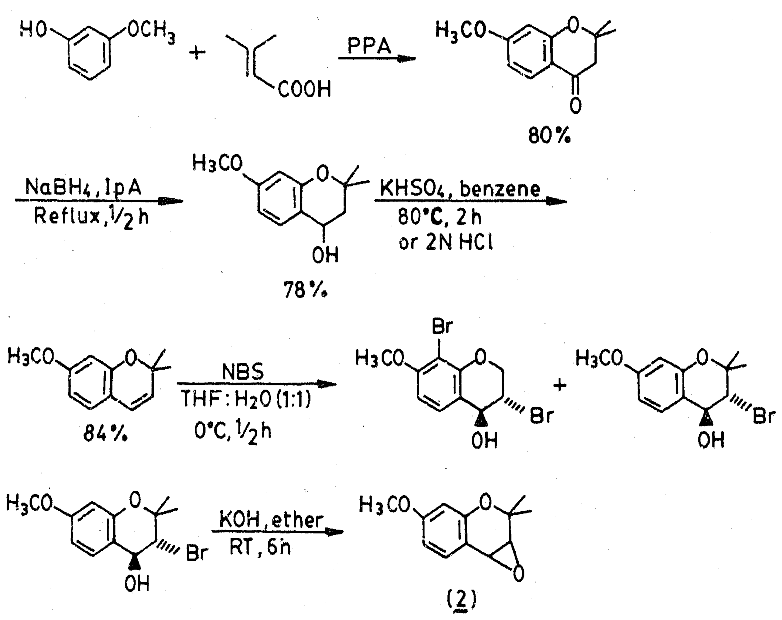


Scheme 2.

(i) Claisen rearrangement of phenyl propargyl ethers afforded the required 2H-1-benzopyrans (chromenes). (ii) Addition of N-bromosuccinimide and water in dimethylsulphoxide to the double bond of the chromenes yielded the *trans* bromohydrins.

(iii) Reaction of the bromohydrins with potassium hydroxide in ether furnished the epoxychromans (1) in good yield.

3,4-epoxy precocene (Jennings and Othridge 1979) was prepared from *m*-methoxyphenol in five steps as outlined in scheme 3.

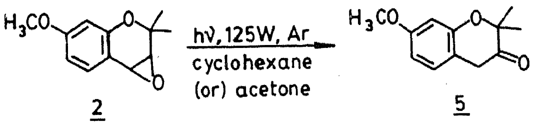


Scheme 3.

3. Results and discussion

3.1 *Photochemical studies on epoxyprecocene* (2)

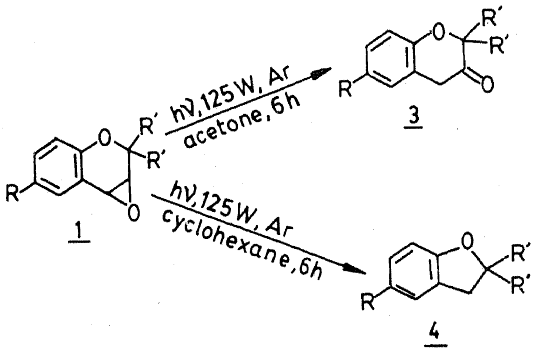
Irradiation of epoxyprecocene (2) in cyclohexane using a 125 W medium pressure mercury lamp under argon atmosphere for two hours yielded the 3-chromanone (5) in 64% yield (scheme 4). The structure of the product was established by spectral methods as well as by comparison with an authentic sample. Irradiation of the epoxyprecocene (2) in acetone also gave 3-chromanone, showing that solvent did not change the course of this photochemical reaction (scheme 4).



Scheme 4.

3.2 *Photochemical studies on 3,4-epoxy-3,4-dihydro-2H-1-benzopyrans (epoxychromans)*

In contrast to the results obtained in the photolysis of epoxyprecocene, epoxychromans (1) yielded different products in different solvents, showing that the course of the photochemical reaction is dependent upon the nature of the solvent employed (scheme 5).



Scheme 5.

Table 1. Photolysis of (1) (scheme 5) in cyclohexane and acetone with different substituents at positions R & R'.

R	R'	Yield (%) (4)	Yield (%) (5)
OCH_3	H	58	48
CH_3	H	56	60
Cl	H	48	50
H	H	36	40
OCH_3	CH_3	52	45

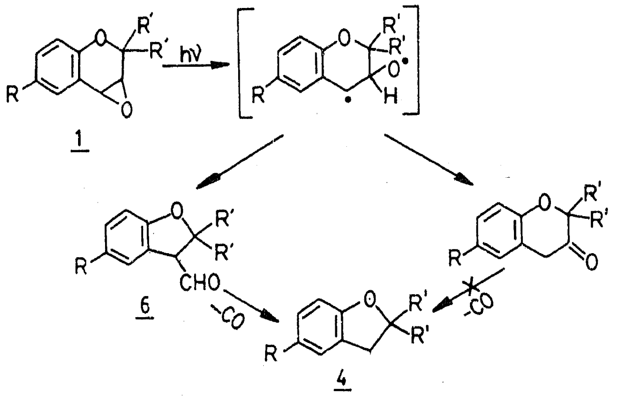
The structures of the products formed were established by spectroscopic techniques and confirmed by comparison with authentic samples. The transformation was extended to various substituted epoxychromans (table 1). Irradiation of (1) (scheme 5) in THF and diethylether under similar conditions afforded (4) in 45 and 48% yields, respectively. In benzene shorter duration photolysis resulted in recovery of starting material, while prolonged irradiation resulted in complex mixtures of products.

4. Mechanism

The formation of chroman-3-one may involve an excited triplet state (triplet energies of epoxides are close to that of acetone: 72–82 kcal (Murov 1973), while the formation of dihydrobenzofuran may proceed through the excited singlet state.

No photoreaction was observed in acetone in the presence of triplet quenchers. This indicates that the excited triplet state is involved. The excited triplet state species may collapse to give the zwitterionic species which may lead to the 3-chromanone (5). But irradiation of (2) in the presence of maleic anhydride or acrylonitrile did not lead to any characterisable product.

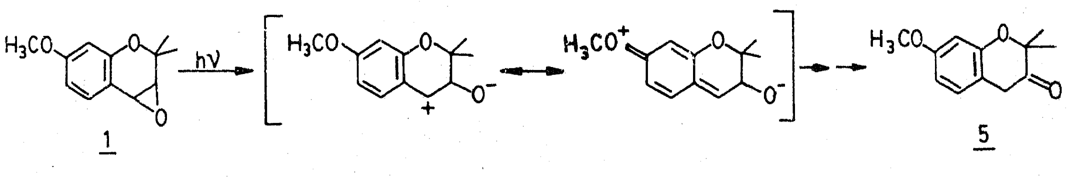
4-phenyl-3-chromanone is known to undergo photo-isomerisation to give 2-phenyl-3-chromanone (Padwa and Au 1975). However, photodecarbonylation of 3-chromanone or 4-chromanone has not been observed in any of the reported reactions. Hence, a probable route to 2,3-dihydrobenzofuran (4) may be through the intermediacy of 2,3-dihydrobenzofuran-3-carboxaldehyde (6), as depicted in scheme 6.



Scheme 6.

However, all efforts to detect the intermediate aldehyde (6) (scheme 6) by monitoring the photochemical reaction by HPLC, NMR and TLC were in vain.

The formation of chroman-3-one on irradiation of precocene epoxide in cyclohexane may be attributed to the influence of the methoxy group, which can facilitate the formation of the zwitterionic species, as the benzyl cation is stabilised by the methoxy group (scheme 7).



Scheme 7.

5. Conclusions

A systematic study of the photochemical behaviour of 3,4-epoxy-3,4-dihydro-2H-1-benzopyrans was undertaken. While a novel photo-decarbonylative ring concentration leading to the formation of 2,3-dihydrobenzofurans, via a secondary photoreaction of 2,3-dihydrobenzofuran-3-carboxaldehyde, was observed in cyclohexane, photo-isomerisation giving rise to 3-chromanone was encountered in acetone. In the case of epoxyprecocene, photoisomerisation was the only reaction path irrespective of the solvent employed.

Acknowledgements

Financial assistance from the Council of Scientific and Industrial Research, New Delhi is gratefully acknowledged. Thanks are due to Prof. G Schröder and Dr Röttle, Germany, the Regional Sophisticated Instrumentation Centre, IIT, Madras and Dr K Nagarajan, Searle (India), Bombay, for their help in obtaining spectral data. We thank M/s Badishe Anilin Soda Fabrik (BASF) for the gift of various propargyl alcohols.

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