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PHOTOCHEMICAL BEHAVIOUR OF 3,4-EPOXYPRECOCENE-I AND RELATED EPOXYCHROMANS

G. ARIAMALA and K.K. BALASUBRAMANIAN*

Department of Chemistry
Indian Institute of Technology
Madras-600 036, INDIA.

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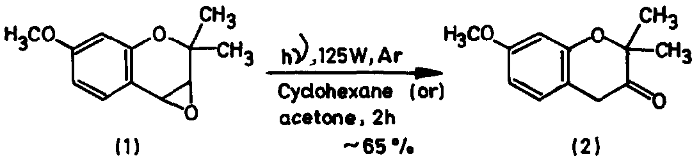
Abstract: A systematic study of photochemical behaviour of 3,4-epoxyprecocene-I and related epoxychromans was undertaken. Upon irradiation in acetone or cyclohexane, 3,4-epoxyprecocene-I 1 was found to undergo photoisomerisation to the corresponding 3-chromanone 2. In contrast, the photochemical behaviour of analogous 3,4-dihydro-3,4-epoxy-2H-1-benzopyrans 3 was found to be dependent upon the nature of solvent. Irradiation of 3 in cyclohexane led to photodecarbonylation leading to the formation of 2,3-dihydrobenzofurans 4, whereas irradiation in acetone resulted in the formation of chromanones 5.

The plant isolate precocene-I (7-methoxy-2,2-dimethyl-2H-1-benzopyran) shows marked growth regulatory effects on a range of insects[1] and causes necrosis of their corpora allata. The necrosis has been linked to covalent binding of the metabolically formed precocene 3,4-oxide[2] to cellular molecules[3]. The chemistry of precocene epoxides has attracted considerable attention in recent years. Camps et al[4] have reported the thermal and acid promoted dimerisation of 3,4-epoxyprecocenes. The reactivity of these epoxides with a variety of nucleophiles has been investigated by Bowers et al[5] with a view to understand their fate and action in living systems. However, there is no report on the photochemical behaviour of these biologically important epoxides. The photochemistry of oxiranes continues to attract attention [6] due to high degree of strain present in the system. In this publication, we report our findings from the study of photochemistry of the remarkably reactive procecene-I epoxide and its related analogues.

Photolysis of 3,4-epoxyprecocene-I: 1

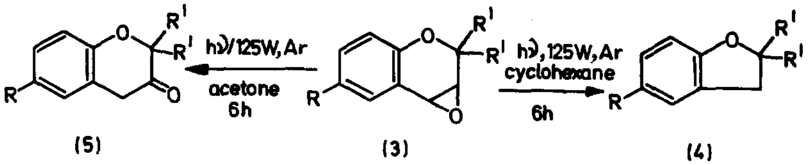
The 3,4-epoxyprecocene-I 1, required for the study was prepared from chroman-4-one following the literature[2] procedure and characterised thoroughly. Irradiation of 1 [λ_{max}^{nm} (cyclohexane) 290(9,000), 280(9,000)] in cyclohexane (10^{-3}M) using a 125W medium pressure mercury lamp in an argon atmosphere for 2 h at room temperature led to the disappearance of starting epoxide as revealed by the NMR spectrum. The NMR spectrum of the crude product displayed a singlet at ∂ 3.5 characteristic of 3-chromanone 2. This was confirmed by the presence of a carbonyl in the IR spectrum at 1720 cm^{-1}. Chromatographic purification afforded 2 in 64% yield. Varying the solvent to acetone did not alter the reaction course. This was found to be a genuine phototransformation, as there was no reaction in dark.



SCHEME - I

Photolysis of 3,4-epoxychroman 3

In contrast to the above observation, when epoxychromans 3 [7][λ_{max}^{nm} 290(6,000), 285(6,200), 260(3,000)] were irradiated, the reaction course was found to be dependent upon the solvent employed. Thus, when 3a was irradiated in cyclohexane under an argon atmosphere using 125W lamp for 6 h at room temperature, the product was found to be different, for the IR spectrum showed no carbonyl functionality. The product obtained in 58% yield after passing the crude mixture through short column of alumina showed a triplet at ∂ 3.0 (2H) and another triplet at ∂ 4.25 (2H) apart from the aromatic signals in its NMR spectrum. Based on literature reports and spectral data, the product was identified as 2,3-dihydrobenzofuran 4a(Scheme-II). Analysis of the NMR spectrum of the crude product did not indicate the presence of any reduction product or dimeric product. The transformation was found to be a general one by extending the same to other epoxides 3b-d (Table I).



SCHEME - II

The presence of gem dimethyl group in the pyran ring did not impede or alter the course of the reaction as evidenced in the case of isoprecocene-I epoxide 3e wherein 4e was isolated in 52% yield upon irradiation of 3e in cyclohexane. The effect of solvent on the photochemical reaction course was examined by carrying out the photolysis in various solvents.

Table - I

Photolysis of 3 in cyclohexane (and) acetone

Entry	R	R'	Yield of 4 %	Yield of 5 %
a	OCH$_3$	H	58	48
b	CH$_3$	H	56	60
c	Cl	H	48	50
d	H	H	36	40
e	OCH$_3$	CH$_3$	52	45

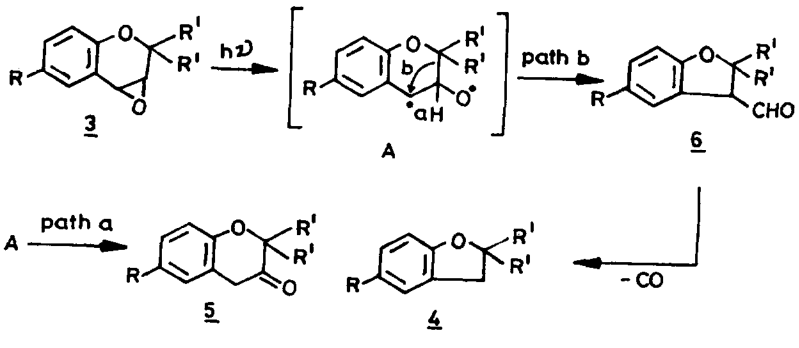
Irradiation of 3b in solvents like tetrahydrofuran (10^{-3} M), diethyl ether (10^{-3} M) for 5-6 h under an inert atmosphere afforded 4b, in 45% and 48% yield, respectively. Irradiation of 3b under identical conditions in benzene for shorter duration led to the recovery of starting epoxide and prolonged irradiation resulted in a complex mixture of products, as revealed by TLC and NMR spectrum. However, when 3b was irradiated in acetone (10^{-3} M) under an argon atmosphere using 125 W lamp for 6 h, the product obtained in 60% yield after column chromatographic purification was found to be chroman-3-one 5b, from its IR and NMR spectra. This was further confirmed by comparison with an authentic sample. Conversion of other epoxides 3a-e to the corresponding chroman-3-ones upon irradiation in acetone revealed this transformation to be a general one (Scheme-II and Table-I).

Mechanistic investigations:

While the triplet state energy of the epoxides 3 could not be measured, assuming that it would not be far different from that of anisole[8], one finds that it is close to that of acetone (E_T : 79-82 Kcal/mole), hence, the transformation of 3 to 5 may be a sensitised one. To check the same, the irradiation of 3 in acetone was carried out in the presence of triplet quenchers like oxygen (E_T : 22.5 Kcal/mole) and cyclohexadiene (5 equivalents) (E_T: 52.4 Kcal/mole). In the event, only the unreacted starting material was recovered in both the cases.

These observations indicate that the formation of chroman-3-one in acetone may involve the excited triplet state of 3 while the formation of dihydrobenzofuran in cyclohexane may proceed through the excited singlet state. The excited triplet may collapse to the zwitterion species and lead to the 3-chromanone. However, attempts to get some evidence for the intervention of the zwitterionic species by carrying out the irradiation in the presence of 1,3-dipolarophile like N-characterisable product. No evidence could be seen for the formation of the expected adduct from the NMR spectrum of the crude reaction product.

Formation of dihydrobenzofuran 4 could not be explained readily by a primary photoprocess. However, the mechanism of the transformation could be rationalised as depicted in Scheme-III, in analogy with literature reports for the aryl bicyclic oxides. Ring contraction involving alkyl migration will give rise to the intermediate 6.



Scheme III

While the photochemistry of 3-chromanone itself is not reported, 4-aryl or alkyl substituted 3-chromanones are known to undergo photoisomeristation [9] to the corresponding 2-

substituted 3-chromanones or to the products arising out of electrocyclic ring opening[10] depending upon the solvent employed. Photodecarbonylation of 3-chromanone leading to the ring contracted product is not reported.

This was further confirmed by irradiating 3-chromanone 5b in cyclohexane under similar conditions, wherein the starting ketone was recovered even after prolonged irradiation. Hence, the alternate pathway viz. path a, involving the intermediacy of 3-chromanone is eliminated. Formation of 4 from isomeric ketone viz. 4-chloromanone, was also ruled out on the basis of photostability of 4-chromanone under various conditions employed. Based on the above mentioned observations, the probable intermediate for this photodecarbonylation may be the 2,3-dihydrobenzofuran-3-carboxaldehyde 6. Schaffner et al have reported the photodecarbonylation of bicyclic aldehydes, wherein an intramolecular transfer of the aldehydic hydrogen takes place concomitant with the elimination of carbon monoxide[11].

Careful follow up of the photolysis of 3b in cyclohexane at different time intervals using NMR and HPLC did not show the presence of any intermediate species. Attempts to trap the intermediate zwitterion or biradical, in cyclohexane using dimethylacetylenedicarboxylate or dihydropyran did not afford anything tangible. Using acetonitrile as the solvent did not afford the expected trapped product, viz. 3a,9b-dihydro-2-methyl-4H-1-benzopyrano (4,3-d)-oxazole, but only led to the isolation of 2,3-dihydrobenzofuran.

In the case of precocene-I epoxide, the remarkable difference in the photobehaviour from that of its analogues 3 a-e may be attributed to facile electron transfer in the diradical species, may be due to the effect of methoxy group para to the benzylic epoxide carbon, leading to the Zwitterion, which rearranges to the 3-chromanone. However, no in depth study was undertaken to understand the photophysical process of this transformation.

Thus, the photochemistry of these aryl bicyclic oxides is found to be highly dependent upon the substituents present and the solvent employed.

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EXPERIMENTAL

General considerations:

Melting points are uncorrected. Infrared spectra were recorded on Perkin-Elmer 1310 instrument. NMR spectra were recorded on Varian EM-390 or Hitachi R-600 instruments with $CDCl_3$ as solvent and TMS as the internal standard. Photoreactions were carried out both in the Reyonet and immersion reactors (Applied Photophysics Inc., London). The solution of the photosubstrate was purged with Argon for 15-30 min prior to irradiation and irradiated under Ar atmosphere. The course of the reaction was monitored by TLC, HPLC and NMR spectra. Parallel dark reactions were performed for all the photoreactions.

Preparation of the photosubstrates:

The epoxides 3a-e required for the study were prepared as reported in literature[7] from the corresponding chromenes. The precocene-I epoxide 1 was prepared by following the reported methods from the corresponding chroman-4-one.

General procedure for irradiation of epoxides 3 and 1:

A 10^{-3} M solution of the respective epoxide in cyclohexane (or) acetone was purged with argon for 20 min. The solution was then irradiated in an immersion reactor using a 125 W medium pressure lamp for 6 h, under argon atmosphere. Then the solvent was removed under reduced pressure and the resulting viscous liquid was chromatographed over alumina for further purification.

Irradiation in cyclohexane

5-methoxy-2,3-dihydrobenzofuran: 4a : Yield : 58% ; IR : (neat) : cm^{-1}: 2800-3000(s), 1480(s), 1180-1200(s), 800(s), NMR : ∂ : 3.0 (t,J : 8Hz,2H), 3.7 (s,3H), 4.2 (t,J : 8Hz, 2H) and 6.6-6.9 (m, 3H).

5-methyl-2,3-dihydrobenzofuran : 4b : yield : 56% ; IR : (neat) : cm^{-1} : 3000-2800(s), 1480(s), 1200-1220(s), 820(s) ; NMR : ∂ : 2.1 (s, 3H), 3.05 (t, J : 8 Hz, 2H), 4.3 (t, J : 8 Hz, 2H) and 6.6-7.1 (m,3H).

5-chloro-2,3-dihydrobenzofuran : 4c : Yield : 48% : IR : (neat) : cm^{-1} : 3000- 2850(s), 1470-80(s), 1200(s), 800(s) ; NMR: ∂:2.8 (t,J : 8Hz, 2H), 4.2 (t,J : 8Hz, 2H) and 6.8-7.5 (m,3H).

2,3-dihydrogenzofuran : 4d : Yield : 36% : IR : (Neat) : cm^{-1} : 3000-2850(s), 1470-80(s), 1200(s), 800(s) : NMR : ∂ : 2.8 (t,J : 8 Hz, 2H), 4.2 (t, J : 8 Hz, 2H) and 6.8-7.2 (m,4H).

2,2-didmethyl-5-methoxy-2, 3-dihydrobenzofuran 4e : Yield : 52% : IR : cm^{-1} : 3000-2900(s), 1480(s) 1190-1250(s), 1020(s) : NMR : ∂ : 1.4 (s,6H), 3.0(s,2H), 3.7 (s,3H) and 6.6-6.9 (m,3H).

Irradiation in acetone

6-methoxychroman-3-one : 5a : Yield : 48% IR : cm^{-1} : 3000-2980(s) , 1730(s), 1520(s), 1200(s), 800(s) : NMR : ∂ : 3.5(s,2H), 3.8 (s,3H), 4.4 (s,2H), 2H) and 6.6-7.0 (m,3H).

6-methylchroman-3-one : 5b : Yield : 60% : IR : (CHCl$_3$) : cm^{-1} : 3000-2850(m), 1730(s), 1480(s), 1220(s), 900(s) : NMR : ∂: 2.3 (s, 3H), 3.6 (s,2H) 4.5 (s,2H) and 6.8-7.4 (m,3H).

6-Chlorochroman-3-one : 5c : Yield : 50% : IR : (CHCl$_3$) : cm^{-1} : 3000-2850(s), 1730(s), 1500(s), 1220-1200(s), 890(s), NMR : ∂ : 3.5(s,2H), 4.4(s,2H) and 6.8-7.6(m,3H).

Chroman-3-one : 5d : Yield : 40% : IR : (CHCl$_3$) : cm^{-1} : 3000-2800(s), 1730(s), 1520(s), 1200(s), 840(s) : NMR : ∂ : 3.6 (s,2H), 4.5(s,2H) and 6.7-7.2 (m,4H).

2,2-dimethyl-6-methoxychroman-3-one : 5e : Yield : 45% : IR : (CHCl$_3$) : cm^{-1} : 3000-2800(s), 1730(s), 1600(s), 1220(s), 1020(s), : NMR:∂:1.5(s,6H), 3.6 (s,2H), 3.8 (s,3H) and 6.4-6.9 (m,3H).

2,2-dimethyl-7- methoxychroman-3-one : 2 : Yield : 65% : IR : (CHCl$_3$) : cm^{-1} 2800-3000(s), 1720(s), 1600(s), 1420(s), 1200(s), 850(s) : NMR:∂: 1.5 (s,6H), 3.5 (s,2H), 3.75 (s,3H) and 6.2-6.9 (m.3H).

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