Chromones constitute one of the major classes of naturally occurring compounds, and the interests in their chemistry are alarming because of their worth as biologically active agents\(^1\). They also constitute an important part of the dietary materials for human beings due to their abundance in plants\(^2\).

**Figure 1: The chromone nucleus**

Some of the biological activities attributed to chromone derivatives include anticancer\(^3\)–\(^5\), neuroprotective\(^6\), HIV-inhibitory\(^7\), antimicrobial\(^8,9\), antifungal\(^10\), antioxidant\(^11\) etc. Genistein \(2.1\) and quercetin \(2.2\) inhibit protein tyrosine kinase, an enzyme known to be involved in cell proliferation\(^12\)–\(^14\).

Galangin \(2.3\), a flavonol has been reported to possess inhibitory actions against *Aspergillus tamarill*, *Aspergillus flavus*, *Cladosporium sphaerospermum*, *Pencillium digitatum* and *Penicillium italicum*\(^15\). Khellin\(^16\) \(2.4\) behaves as an antispasmodic agent and is also used in the treatment of anginapectoris. It also acts as an antidiabetic agent that improves peripheral insulin resistance in type-II diabetic patients.
Shariffer et al. reported that apigenin 2.5 and rutin 2.6 were found to be potent inhibitors of lipid peroxidation and oxidation of β-carotene.

\[
\text{R}=6-O-\alpha-L\text{-rhamnopyranosyl-D-glucoside}
\]

In addition, the chromones also have applications in dyeing technology, for example, a pentahydroxy chromone, quercetin 2.2 has been used as a yellow dye for long.

Flavone (2-phenyl-4-oxo-4\(H\)-1-benzopyran) 2.7 is known to act as a photodynamic transferring agent and has been shown to bring about \textit{cis-trans} isomerization\(^{19}\) in stilbenes. A similar isomerization, observed in \(\beta\)-D-glucosyl-\(\alpha\)-hydroxy cinnamic acid\(^{20}\) 2.8 present in leaves, has been rationalized on similar lines.

Chromones are known to exhibit photoreactions like photocycloadditions\(^{21,22}\), photorearrangements\(^{23}\), photodimerisations\(^{24,25}\), photooxidations\(^{26-29}\), photoreductions\(^{30}\) and photoisomerisations\(^{31-32}\) involving \(n\rightarrow\pi^*\) and \(\pi\rightarrow\pi^*\) transitions. The pyrone moiety in the chromones is non-aromatic like \(\gamma\)-pyrones. This makes the double bond and C=O group available to react in isolation or in conjugation in the photochemical reactions.

Photocycloaddition reactions of chromones with different olefins and related compounds are known to provide the products both through \([3+2]\pi\) and
[2+2]π cycloaddition reactions. The [2+2]π photocycloaddition reactions of chromones are extensively studied by Hannifin and Cohen. Irradiation of a solution of chromone 2.9 with 1,1-dimethoxyethylene 2.10 gave the photoproducts 2.11 and 2.12, the latter being a secondary photolysis Paterno-Buchi reaction product arising from 2.11 on interaction with 2.10.

In comparison, the substituted chromones, 2-cyanochromone 2.13 when reacted with ethylenes produced both [2+2]π and [3+2]π cycloadducts 2.15 and 2.16 respectively. These cycloadditions have been rationalized to occur through the involvement of an iminyl biradical 2.14.

A reaction between 3-alkoxychromones 2.17 and ethylene has found to give a tetracyclic compound 2.18. This photocycloaddition product is formed through a tandem cycloaddition and γ-hydrogen abstraction sequence.

3-Hydroxyflavone also undergo photorearrangement leading to the formation of indan-1,2-diones. Matsuura et al. have carried out a detailed study of 3-
hydroxy-2-arylchromones 2.19 which provided 3-aryl-1,2-indandiones 2.20 upon irradiation in 1:1 benzene-isopropyl alcohol with light of wavelength above 290 nm.

From our laboratory, a reaction on 2-methyl-3,5,7-trimethoxychromone\(^24\) 2.21 has been reported where H-abstraction coupled with dimerisation has lead to the formation of a dimeric oxetanol 2.22.

The irradiation of chromone-2-carboxylic esters\(^25\) resulted in the stereo- and regioselective formation of C\(_2\) chiral anti-HH dimers from the triplet excited state. On the contrary, their photolysis in the solid-state gave anti-HT dimers exclusively controlled by molecular arrangement in the crystal.

Chromones are also prone to undergo photo-oxidation that lead to a broad variety of products. Rotenone 2.26, a naturally occurring insecticide is a
modified flavonoid\textsuperscript{26} that on photooxygenation has been reported to give rotenonone \textsuperscript{2.27}. This provides an example of a biogenetic type of synthesis.

Chromones are also known to undergo photooxygenations\textsuperscript{27-28} and give a variety of products through reorganizations and degradations. In an unsensitized photooxygenation reaction, photochromic 3-benzoylchromone \textsuperscript{2.28} photoenolises to diene \textsuperscript{2.29} which on reaction with singlet O\textsubscript{2} provides \textsuperscript{2.30} whose decomposition gave 2,3-dibenzoylchromone\textsuperscript{29} \textsuperscript{2.31}.

Ohara\textsuperscript{30} et al. in their detailed investigation on the photochemical reduction of chromones obtained the products \textsuperscript{2.33} and \textsuperscript{2.34} by the photoreduction of 2,3-double bond and >C=O group respectively.

Under photolytic conditions, the chromones undergo rapid enolisation\textsuperscript{31}. Upon the irradiation of \textsuperscript{2.35} for 1-2 min, the orange photoenol \textsuperscript{2.36} was formed which displayed a $\lambda_{\text{max}}$ at 460 m$\mu$. But this orange color faded very quickly which led to the reformation of \textsuperscript{2.35}.
A 3-hydroxy flavone\textsuperscript{32} 2.37 photoisomerised to benzofuranone 2.38 in high yields upon photoirradiation. Such rearrangements are analogous to those exhibited by 2,6-dimethyl-\(\gamma\)-pyranone\textsuperscript{33}.

When an alkoxy instead of hydroxyl group is present at position-3 of the chromone then the photoreaction adopts a different route and the tetracyclic photoproducts 2.40 and 2.41 along with some other minor products are produced\textsuperscript{34}.

These photocyclisations have been rationalized through an initial abstraction of hydrogen from the 3-alkoxy group by the excited carbonyl group of pyrone moiety giving rise to a 1,4-biradical that gives cyclic products through cyclisation.
In the past, some work on the chromones bearing phenyl/35/furyl/36/thienyl/37 has been carried out in our laboratory as a part of our investigations pertaining to the photoreactions of 3-alkoxy-2-aryl/alkylchromones where the product obtained invariably depended upon the nature of substituent. Intramolecular H-abstraction/34-39 in 3-alkoxy-2-arylchromones is of considerable significance. These chromones on photoirradiation undergo cyclisation via γ-H abstraction to yield the angular tetracyclic products. For example, chromones 2.42, 2.43 and 2.44 under photolytic conditions gave 2.42a and 2.42b, 2.43a and 2.43b, 2.44a and 2.44b respectively.

The 3-alkoxy-2-thiophenyl-4H-chromen-4-ones on photoirradiation produced cyclized dihydro and dehydrogenated photoproducts/40 2.44a and 2.44b. From these, the cyclized dihydro photoproducts has been assumed to arise via 1,5-sigmatropic H-shift whereas the cyclized dehydrogenated products were formed by the expulsion of H2 during ketonisation directly. As a sequel to the above, in the present study, we have carried out investigations on the
photoreactions of 3-alkoxy-6-chloro-2-(3-methylthiophen-2-yl)-4H-chromen-4-ones.

![Chemical Structure](image)

2.48. \( R = \text{CH}_3 \)
2.49. \( = \text{CH}_2\text{C}=\text{CH} \)
2.50. \( = \text{CH}_2\text{CH}=\text{CH}_2 \)
2.51. \( = \text{CH}_2\text{CH}(\text{CH}_3)=\text{CH}_2 \)
2.52. \( = \text{CH}_2\text{C}_6\text{H}_5 \)

The main objectives are:

(i) how does the methyl group at 3'-position affect the product formation through its steric/inductive effect.

(ii) does the demethylation occurs leading to the formation of cyclized aromatic products or simple cyclisation occurs without its expulsion giving cyclized photoproducts analogous to dihydro-photoprotoduct having angular methyl group during photocyclisation and

(iii) to unravel the effect of different alkoxy groups at C-3 on the product formation/distribution.

**Results and Discussion:**

The targets, 2-(3-methylthiophen-2-yl)-4H-chromen-4-ones **2.48-2.52** needed for the photochemical studies were synthesized using the following sequence (Scheme-1) of reactions;
5-Chloro-2-hydroxyacetophenone 2.45 on condensation with 3-methylthiophene-2-carboxaldehyde in the presence of NaOH/EtOH\(^1\) gave 1-(5-chloro-2-hydroxyphenyl)-3-(3-methylthiophen-2-yl)prop-2-en-1-one 2.46 that under Algar Flynn Oyamada conditions\(^2\) (H\(_2\)O\(_2\)/OH) led to the formation of 6-chloro-3-hydroxy-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.47 in 70% yield. This 3-hydroxychromone was converted into its respective ethers 2.48 (R = -CH\(_3\), mp 136-138 °C), 2.49 (R = -CH\(_2\)C=CH, mp 156-158 °C), 2.50 (R = -CH\(_2\)CH=CH\(_2\), mp 130-132 °C), 2.51 (R = -CH\(_2\)(CH\(_3\))C=CH\(_2\), mp 98-100 °C) and 2.52 (R = -CH\(_2\)C\(_6\)H\(_5\), mp 132-134 °C) by reaction with suitable alkylating agents in the presence of dry acetone, freshly dried K\(_2\)CO\(_3\) and tetra-n-butylammonium iodide (TBAI) as catalyst.

The structures of these photo-labile substrates 2.48-2.52 were ascertained from their spectral parameters (IR, \(^1\)H NMR, \(^13\)C NMR, vide experimental).

6-Chloro-3-methoxy-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.48

The structure of compound 2.48 (mp 136-138 °C) was confirmed from its spectral parameters. The IR spectrum of 2.48 showed a strong absorption at 1643 cm\(^{-1}\) (C=O). In the \(^1\)H NMR spectrum (300MHz, CDCl\(_3\)) of 2.48, the thiophene protons H-5' and H-4' were seen at \(\delta\) 7.53 (d, \(J_{5',4'} = 5.1\) Hz) and \(\delta\)
7.00 (d, $J_{a', s'} = 5.1$ Hz) respectively. The benzenoid protons H-5, H-7 and H-8 showed themselves at $\delta$ 8.24 (d, $J_m = 2.4$ Hz), 7.62 (dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz) and 7.46 (d, $J_o = 9.0$ Hz) respectively. The -OCH$_3$ group gave a singlet integrating for three protons at $\delta$ 3.99. The 3'-CH$_3$ group protons resonated at $\delta$ 2.66 as a singlet. The compound gave two absorption maxima at 297 and 264 nm in methanol. The structure of compound 2.48 was further confirmed by proton decoupled $^{13}$C NMR spectrum (vide experimental).

**Photolysis of 6-chloro-3-methoxy-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.48:**

A deoxygenated methanolic solution of chromone 2.48 (1.0mM) contained in a pyrex glass vessel was purged with nitrogen for 30 min and then irradiated under nitrogen atmosphere with light from a 125 W Hg vapor lamp for 90 min. A tlc examination of the photolysate showed no more consumption of the starting substrate after 90 min and appearance of only one new spot was observed. The removal of solvent under reduced pressure left a gummy mass that was chromatographed over a column of silica gel (100-200 mesh). The column was eluted with increasing proportion of benzene in petroleum ether-benzene system yielding one new photoproduct (Scheme-2) 2.53.

![Scheme-2: Photolysis of compound 2.48.](image)

**Compound 2.53:**

The structure of the photoproduct 2.53 became evident from its spectral parameters. Its IR spectrum exhibited a strong absorption band at 1649 cm$^{-1}$ (C=O group). The $^1$H NMR spectrum of this showed a total of eleven protons consistent with the structure of product 2.53. The most downfield signal was located as a doublet at $\delta$ 8.25 ($J_m = 2.4$ Hz) which could be ascribed to H-7 (due to deshielding effect of C=O and Cl groups) while H-9 and H-10
produced signals at expected δ values: δ 7.60 (dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz) and δ 7.42 (d, $J_o = 9.0$ Hz). A comparison of the $^1$H NMR (300MHz) spectra of 2.48 and 2.53 showed that the resonance at δ 3.99 (-OCH$_3$) present in the former was found missing in the latter, thereby showing the involvement of the carbon to which these protons are attached in the photo-conversion. The protons H-2 and H-3 belonging to the modified thiophene moiety in 2.53 moved upfield as compared to H-5' and H-4' in 2.48 and appeared at δ 6.27 (d, $J_{2,3} = 6.6$ Hz) and δ 5.43 ($J_{3,2} = 6.6$ Hz) respectively, which indicated the loss of aromatic character of thiophene ring in 2.53. The ring junction proton H-11b gave a singlet at δ 4.44. The pyran protons H-4a and H-4b were observed as doublets at δ 4.08 ($J_{4a,4b} = 11.1$ Hz) and δ 3.88 ($J_{4b,4a} = 11.1$ Hz) respectively. A singlet integrating for three protons at δ 1.36 was assigned to 3a-CH$_3$ group protons. A proton decoupled $^{13}$C NMR spectrum showed a total of 15 carbons consistent to structure 2.53. The mass spectrum exhibits molecular ion peak at m/z = 307.

6-Chloro-2-(3-methylthiophen-2-yl)-3-propargyloxy-4H-chromen-4-one 2.49

The compound 2.49 (mp 156-158 °C) in its IR spectrum has C=O stretch at 1636 cm$^{-1}$. In the $^1$H NMR spectrum (300MHz, CDCl$_3$) of 2.49, the thiophene protons H-5' and H-4' were seen at δ 7.55 (d, $J_{5',4'} = 5.1$ Hz) and δ 7.00 (d, $J_{4',5'} = 5.1$ Hz) respectively. The benzenoid protons H-5, H-7 and H-8 showed themselves at δ 8.23 (d, $J_m = 2.7$ Hz), 7.63 (dd, $J_o = 9.0$ Hz, $J_m = 2.7$ Hz) and 7.48 (d, $J_o = 9.0$ Hz) respectively. The -OCH$_2$ group gave a doublet integrating to two protons at δ 5.07 ($J_{1'',3''} = 2.4$ Hz). The 3'-CH$_3$ group protons resonated at δ 2.65 as a singlet. The propargyl proton resonated at δ 2.40 ($J_{3'',1''} = 2.4$ Hz) as a triplet. The compound gave two absorption maxima at 294 and 263 nm in methanol. The mass spectrum exhibits molecular ion peak at m/z = 331.
Photolysis of 6-chloro-2-(3-methylthiophen-2-yl)-3-propargyloxy-4H-chromen-4-one 2.49:

A deoxygenated solution of compound 2.49 (1.0mM) in dry methanol was photolysed with a pyrex filtered light from 125 W mercury lamp under nitrogen atmosphere for 45 min. The progress of the reaction was monitored by tlc. The solvent was distilled off to obtain a red gummy viscous mass which was chromatographed over a column of silica-gel (100-200 mesh) packed in petroleum-ether. Elution of the column with increasing proportion of benzene in petroleum ether-benzene system gave a new compound 2.54 and some starting compound 2.49.

Scheme-3: Photolysis of compound 2.49.

Compound 2.54:
The structure of photoproduct 2.54 was identified by its spectral data. The IR spectrum of the compound 2.54 exhibited absorptions at 2114 cm\(^{-1}\) (C≡C) and at 1643 cm\(^{-1}\) (C=O). The 300MHz \(^1\)H NMR (CDCl\(_3\)) spectrum revealed that resonance at $\delta$ 5.07 due to OCH\(_2\)- of 2.49 was altogether missing in the spectrum of 2.54 thereby showing the involvement of the carbon to which these protons are attached in the photo-conversion. The benzenoid protons H-7, H-9 and H-10 were seen at usual positions at $\delta$ 8.25 (d, $J_m = 2.7$ Hz), 7.60 (dd, $J_m = 2.7$ Hz, $J_o = 9.0$ Hz) and 7.42 (d, $J_o = 9.0$ Hz) respectively. The protons H-2 and H-3 belonging to the thiophene moiety in 2.54 were located at $\delta$ 6.30 (d, $J_{2,3} = 6.0$ Hz) and $\delta$ 5.54 (d, $J_{3,2} = 6.0$ Hz) respectively which were upfield as compared to H-5' and H-4' in 2.49. Out of the rest of the six protons, the ring junction proton H-11b gave a singlet at $\delta$ 4.54. The pyran proton H-4 was observed as a doublet at $\delta$ 4.83 ($J_{4,2'} = 2.1$ Hz). A singlet integrating to three protons at $\delta$ 1.46 was assigned to 3a-CH\(_3\) group.
protons. The proton of -C≡CH group at C-4 resonated at δ 2.58 (d, $J_{2',4} = 2.1$ Hz). A proton decoupled $^{13}$C NMR showed 17 peaks corresponding to 17 carbons (vide experimental). The molecular ion afforded a peak at m/z = 331 in its mass spectrum.

3-Allyloxy-6-chloro-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.50

The IR spectrum of 2.50 showed two strong absorptions at 1643 (C=O) and 1605 cm$^{-1}$ (C=C). In the $^1$H NMR spectrum (300MHz, CDCl$_3$) of 2.50, the thiophene protons H-5' and H-4' were seen at δ 7.52 (d, $J_{5',4'} = 5.1$ Hz) and δ 7.00 (d, $J_{4',5'} = 5.1$ Hz) respectively. The benzenoid protons H-5, H-7 and H-8 showed themselves at δ 8.23 (d, $J_m = 2.4$ Hz), 7.61 (dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz) and 7.46 (d, $J_o = 9.0$ Hz) respectively. The protons of allyl group resonated at δ 6.07 (1H, ddt, $J_{2'',1''} = 6.6$ Hz, $J_{2'',3''a} = 17.4$ Hz, $J_{2'',3''b} = 10.8$ Hz, H-2''), δ 5.37 (1H, dd, $J_{3''a,1''} = 1.5$ Hz, $J_{3''a,2''} = 17.4$ Hz, H-3''a), δ 5.23 (1H, dd, $J_{3''b,2''} = 10.8$ Hz, $J_{3''b,1''} = 1.5$ Hz, H-3''b) and δ 4.76 (2H, d, $J_{1'',2''} = 6.6$ Hz, H-1''). The 3'-CH$_3$ group protons resonated at δ 2.64 as a singlet. The compound gave two absorption maxima at 296 and 266 nm in methanol.

Photolysis of 3-allyloxy-6-chloro-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.50:

The allyl ether 2.50 on photolysis in methanol with a pyrex filtered UV-light for 45 min gave one new photoproduct and some unreacted 2.50. An extensive column chromatographic workup using petroleum ether-benzene as an eluent produced one new compound 2.55.

![Scheme-4: Photolysis of compound 2.50.](image-url)
**Compound 2.55:**
The tetracyclic compound 2.55 (mp 176-178 °C) in its IR spectrum exhibited a strong absorption band at 1651 cm\(^{-1}\) which may be assigned to C=O of pyrone moiety. In its \(^1\)H NMR spectrum, the protons of ring A were found to be similarly placed as in 2.50. A comparison of the \(^1\)H NMR (300MHz) spectra of 2.50 and 2.55 showed that the resonance at δ 4.76 (-OCH\(_2\)-) present in the former was found missing in the latter, thereby showing the involvement of the carbon to which these protons are attached in the photoconversion. The protons H-2 and H-3 belonging to the modified thiophene moiety in 2.55 moved upfield and appeared as doublets at δ 6.37 (\(J_{2,3} = 6.0\) Hz) and δ 5.40 (\(J_{3,2} = 6.0\) Hz). The ring junction proton H-11b gave a singlet at δ 4.60. The pyran proton H-4 was observed as a doublet at δ 4.54 (\(J_{4,1'} = 6.6\) Hz). A singlet integrating to three protons at δ 1.26 was assigned to 3a-CH\(_3\) group protons. The protons of vinyl group at C-4 resonated between δ 5.99-5.35 with their usual coupling constants as in compound 2.50. A proton decoupled \(^{13}\)C NMR spectrum showed a total of 17 carbons consistent to structure 2.55. The molecular ion in its mass spectrum was observed at m/z 333.

**6-Chloro-3-(2-methylallyloxy)-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.51**
The IR spectrum of 2.51 showed two strong absorptions at 1636 (C=O) and 1605 cm\(^{-1}\) (C=C). In the \(^1\)H NMR spectrum (300MHz, CDCl\(_3\)) of 2.51, the thiophene protons H-5' and H-4' were seen at δ 7.52 (d, \(J_{5',4'} = 4.8\) Hz) and δ 6.98 (d, \(J_{4',5'} = 4.8\) Hz) respectively. The benzenoid protons H-5, H-7 and H-8 showed themselves at δ 8.19 (d, \(J_m = 2.7\) Hz), 7.62 (dd, \(J_o = 7.8\) Hz, \(J_m = 2.7\) Hz) and 7.46 (d, \(J_o = 7.8\) Hz) respectively. The protons H-3"a and H-3"b showed singlets at δ 5.03 and 5.09 respectively. The two protons at C-1" gave a singlet at δ 4.72. A singlet integrating to three protons appear at δ 1.80 corresponding to 2"-CH\(_3\) group. The 3'-CH\(_3\) group protons resonated at δ 1.58 as a singlet. The compound gave two absorption maxima at 297 and 263 nm in methanol.
Photolysis of 6-chloro-3-(2-methylallyloxy)-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.51:
Photolysis of a deoxygenated methanolic solution of compound 2.51 (1.0 mM) with a pyrex filtered light from 125 W mercury lamp under the nitrogen atmosphere for 45 min followed by the distillation provided a red gummy viscous mass which on chromatographic separation using petroleum ether-benzene as eluent system gave starting compound 2.51 and a new compound 2.56 (Scheme-5).

![Scheme-5: Photolysis of compound 2.51.](image)

**Compound 2.56:**
The structure of tetracyclic photoproduct 2.56 rests upon the following spectral parameters. The compound 2.56 in the functional group region of its IR spectrum had strong absorption band at 1659 cm\(^{-1}\), a characteristic of C=O of benzopyrone moiety. A comparison of the \(^1\)H NMR spectra of 2.51 and 2.56 showed that the resonance at \(\delta 4.72\) (-OCH\(_2\)-) present in the former was found missing in the latter, thereby showing the involvement of the carbon to which these protons are attached in the photo-conversion. The protons of ring A were found to be similarly placed in both the compounds. The protons H-2 and H-3 belonging to the modified thiophene moiety in 2.56 moved upfield as compared to H-5' and H-4' in 2.51, which indicated the loss of aromatic character of thiophenyl ring in 2.56. The protons H-2'a and H-2'b showed singlets at \(\delta 5.17\) and 5.14 respectively. The proton H-11b at ring junction gave a singlet at \(\delta 4.62\). The pyran proton H-4 was observed as a singlet at \(\delta 4.55\). The 1'-CH\(_3\) group protons resonated at \(\delta 1.94\) as a singlet. A singlet integrating to three protons at \(\delta 1.28\) was assigned to 3a-CH\(_3\) group protons. The structure of photoproduct 2.56 was further corroborated by
proton decoupled $^{13}$C NMR spectrum. The mass spectrum analysis showed the molecular ion peak at m/z = 347.

3-Benzylcyloxy-6-chloro-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.52

The ether 2.52 (mp 132-134 °C) in its IR spectrum showed C=O absorption at 1628 cm$^{-1}$. In the $^1$H NMR spectrum (300MHz, CDCl$_3$) of 2.52, the thiophene protons H-5' and H-4' were seen at δ 7.49 (d, $J_{5',4'} = 5.1$ Hz) and δ 6.96 (d, $J_{4',5'} = 5.1$ Hz) respectively. The benzenoid protons H-5 and H-7 showed themselves at δ 8.26 (d, $J_m = 2.4$ Hz), 7.62 (dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz). An unresolved multiplet corresponding to three protons i.e. H-8, 2'' and H-6'' was observed in the region δ 7.46-7.42. Other protons of phenyl ring H-3'', H-4'' and H-5'' appeared as a multiplet between δ 7.39-7.28. The -OCH$_2$ group gave a sharp singlet integrating to two protons at δ 5.22. The 3'-CH$_3$ group protons resonated at δ 2.55 as a singlet. The compound gave two absorption maxima at 297 and 263 nm in methanol.

Photolysis of 3-benzyloxy-6-chloro-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.52:

The chromone 2.52 (1.0mM) when photolyzed in methanol for 45 min under similar conditions as applied for the earlier compounds 2.48-2.51 and delivered a reaction mixture with one additional spot in tlc. A chromatographic separation gave starting compound 2.52 and a new photoprodut 2.57.

![Scheme-6](image)

Scheme-6: Photolysis of compound 2.57.

Compound 2.57:

The compound 2.57 (mp 186-188 °C) in its IR spectrum showed C=O absorption at 1651 cm$^{-1}$. The $^1$H NMR showed a total of eight protons in
aromatic region consistent with structure 2.57. The benzenoid protons were located at the same places as in 2.52. The two thiophenyl protons were found at $\delta$ 6.46 (1H, d, $J_{2,3} = 6.0$ Hz, H-2) and $\delta$ 5.16 (1H, d, $J_{3,2} = 6.0$ Hz, H-3) respectively. The ring junction proton H-11b gave a singlet at $\delta$ 4.74. The pyran proton H-4 was observed as a singlet at $\delta$ 5.12. A singlet integrating to three protons at $\delta$ 1.60 was assigned to 3a-CH$_3$ group protons. The protons of phenyl group and H-10 were found spreaded over $\delta$ 7.46-7.28. The structure of photoproduct 2.57 was further confirmed by proton decoupled $^{13}$C NMR spectrum. The mass spectrum exhibits molecular ion peak at $m/z =$ 383.

**Mechanistic Assumptions:**

These photoconversions of the 3-alkoxychromones 2.48-2.52 to angular cyclized dihydro type photoproducts may be visualized to occur through an initial H-abstraction from 3-alkoxy group by the excited carbonyl group of the pyrone moiety to produce 1,4-biradical intermediate that undergoes a bond formation by clipping of alkoxy radical with C-3 of 3-methylthienyl ring followed by ketonisation and H-migration to C-11b (1,5-H shift) to furnish the final product (Scheme 7). The thiophenyl moiety at C-2 possesses only 3'-carbon available for clipping of 1,4-biradical.
**Scheme-7:** *Mechanism of product formation from 3-alkoxybenzopyrans by photolysis.*

The thiophen-2-yl chromenones having same basic skeleton similar to 2.48-2.52 with no 3-CH₃ group at thiophenyl group furnished cyclised dihydro and cyclised dehydrogenated aromatic photoproducts⁴⁰. The cyclised dihydro photoproducts were formed via 1,5-sigmatropic H-shift whereas the cyclised dehydrogenated aromatic products were formed by the expulsion of H₂ during ketonisation directly. But in the present study, the thiophen-2-yl chromenones 2.48-2.52 having a -CH₃ group as a substituent at C-3 of thiophenyl, the formation of only cyclised dihydro type photoproducts 2.53-2.57 through 1,5-sigmatropic H-shift is favored. No demethylation leading to the formation of aromatic photoproducts was observed as the energy required to break C-C bond is higher than that of C-H bond.

Moreover, the yields of the photoproducts 2.53-2.57 formed depended upon the nature of the alkoxy group at C-3 position of the substrates 2.48-2.52. As the stability of the 1,4-biradicals generated *in situ* from 2.48 (R = -H) to 2.52 (R = -C₆H₅) increases (Scheme 7), yield of the corresponding photoproduct also increases (Table 1).
### Table 1: Yields of the photoproducts 2.53-2.57.

<table>
<thead>
<tr>
<th>Photoproduct</th>
<th>2.53</th>
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<tr>
<td>R</td>
<td>-H</td>
<td>-C≡CH</td>
<td>-CH=CH₂</td>
<td>-C(CH₃)=CH₂</td>
<td>-C₆H₅</td>
</tr>
<tr>
<td>Yield (%)</td>
<td>24</td>
<td>38</td>
<td>46</td>
<td>71</td>
<td>87</td>
</tr>
</tbody>
</table>

**Stereochemistry of Photoproducts**

In all these photoproducts, the ring C has half chair conformation and evidently the C/D ring fusion is cis. For example in 2.55, the trans-fusion of five-membered ring will result in higher conformational strain than the cis-fusion and this is in accordance with the earlier findings in case of the naturally occurring pterocarpans\(^43\)\(^{-45}\) and N-heterocycles\(^46\). Now assuming the C/D ring fusion as cis, the orientation of H-4 can be cis or trans with respect to -CH₃ at C-3a. So, four possible 3D conformations I, II (H-4 cis to CH₃-3a) and III, IV (H-4 trans to CH₃-3a) were derived from MM2 energy minimizations programme\(^47\) which are shown in figure 2.

![I and II conformations](image-url)

I

-CH=CH₂ \(\psi\)-equatorial

Ring C \(\psi\)-chair; Ring D exo

E(kcal/mol) = 13.86

II

-CH=CH₂ \(\psi\)-equatorial

Ring C \(\psi\)-chair; Ring D exo

E(kcal/mol) = 18.67
Figure-2: Possible energy minimized conformations of photoproduct 2.55.

From the above four conformations, the one which has minimum energy i.e. conformation I, could be the possible conformation for the photoproduct 2.55 in which H-4 is cis to 3a-CH₃ group and bulkier vinyl group is at ψ-equatorial position. Such a view is in conformity with the literature⁴⁸ where the heavier group at equatorial position in cyclohexane is always preferred.

Experimental

4-Chlorophenyl acetate

4-Chlorophenol (12.8g, 0.1mol) was stirred with acetic anhydride (11.2g, 0.11mol) in the presence of conc. H₂SO₄ (1.0ml) for 10-15 min. Reaction mixture was then poured into ice and organic layer was extracted with CCl₄. The product was collected by distillation.

Yield 14.5g (85%), liquid, bp 225-227 °C (Lit.⁴⁹ bp 226-228 °C).
5-Chloro-2-hydroxyacetophenone

4-Chlorophenyl acetate (8.5g, 0.05mol) was heated with anhydrous AlCl₃ (9.3g, 0.07mol) under the Fries rearrangement conditions. The crude product obtained was crystallized from ethanol.

Yield 6.0g (70%), white solid, mp 51-52 °C (Lit. mp 54 °C).

Synthesis of 1-(5-chloro-2-hydroxyphenyl)-3-(3-methylthiophen-2-yl)prop-2-en-1-one

To the well-stirred suspension of powered NaOH (0.8g, 0.02mol) in EtOH (10ml) at 0 °C were added 5-chloro-2-hydroxyacetophenone (1.70g, 0.01mol) and 3-methylthiophene-2-carboxaldehyde (1.38g, 0.011mol). The reaction mixture, which became deep red in color after 30 min, was stirred further for 3 hours. Thereafter, it was poured over ice and was neutralized with dil. HCl to obtain the product as yellow solid. It was further crystallized from ethanol.

Yield 1.90g (68.44%), yellow solid, mp 110-112 °C.

\[
\begin{align*}
\text{OH} & \\
\text{Cl} & \\
\text{CH}_3 & \\
\end{align*}
\]

2.45

\[
\begin{align*}
\text{OH} & \\
\text{Cl} & \\
\text{CH}_3 & \\
\end{align*}
\]

2.46

\[
\text{v}_{\text{max}} \text{ (cm}^{-1}\text{): } 3405 \text{ (OH), } 1628 \text{ (C}=\text{O)}.
\]

\[
\delta_H \text{ (CDCl}_3\text{): } \delta 12.90 \text{ (1H, s, -OH), } 8.19 \text{ (1H, d, } J_{3,2} = 15.0 \text{ Hz, H-3), } 7.84 \text{ (1H, d, } J_m = 2.4 \text{ Hz, H-6'}, \text{ 7.45 (1H, dd, } J_o = 9.0 \text{ Hz, } J_m = 2.4 \text{ Hz, H-4'}), \text{ 7.42 (1H, d, } J_{5',4'} = 5.4 \text{ Hz, H-5''}), \text{ 7.28 (1H, d, } J_{2,3} = 15.0 \text{ Hz, H-2), } 7.00 \text{ (1H, d, } J_o = 9.0 \text{ Hz, H-3'}), \text{ 6.97 (1H, d, } J_{4'',5''} = 5.4 \text{ Hz, H-4''}, \text{ 2.46 (3H, s, 3''-CH}_3\text{).}
\]
δ_{C} (CDCl$_3$): δ 192.24 (C-1), 162.02, 144.24, 137.26, 135.96, 134.25, 131.66, 128.75, 128.62, 123.47, 120.62, 120.17, 117.06, 114.38.

Anal. Calcd. for C$_{14}$H$_{11}$ClO$_2$S: C, 60.32; H, 3.98. Found: C, 60.30; H, 3.94.

**Synthesis of 6-chloro-3-hydroxy-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.47**

To the suspension of chalcone 2.46 (1.0g, 0.0036mol) in MeOH (15ml) was added aq. KOH (10ml, 20%) and cooled to 0 °C. To this dark red stirred solution was added H$_2$O$_2$ (30%) drop-wise till the color changed to yellow and the stirring was continued for 1h. The reaction mixture was neutralized with ice-HCl to give light yellow precipitates. This solid was filtered, dried and crystallized (CHCl$_3$-MeOH) to give light yellow crystals of benzopyrone 2.47.

Yield 0.74g (70%), light yellow solid, mp 190 °C.

\[ \nu_{\text{max}} (\text{cm}^{-1}): 3232 \text{ (OH)}, 1597 \text{ (C=O)}. \]

δ$_{H}$ (CDCl$_3$): 8.23 (1H, d, $J_m = 2.4$ Hz, H-5), 7.66 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz, H-7), 7.56 (1H, d, $J_{5',4'} = 5.1$ Hz, H-5'), 7.51 (1H, d, $J_o = 9.0$ Hz, H-8), 7.01 (1H, d, $J_{4',5'} = 5.1$ Hz, H-4'), 2.60 (3H, s, 3'-CH$_3$).

δ$_{C}$ (CDCl$_3$): δ 172.23 (C-4), 153.52, 144.02, 140.84, 137.12, 133.70, 131.44, 130.57, 129.44, 125.39, 124.72, 121.94, 119.73, 16.79.


**Synthesis of 6-chloro-3-methoxy-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.48**

To a suspension of 3-hydroxychromone, 2.47 (0.584g, 0.002mol) and freshly dried K$_2$CO$_3$ (0.5g) in dry acetone (15ml) was added dimethyl sulphate (0.252g, 0.002mol) and tetra-$n$-butylammonium iodide (50mg). The reaction
mixture was refluxed for 4h and the color of reaction mixture changed from reddish-orange to creamish. Filtration, evaporation of solvent and crystallization of the residue (EtOH) gave the product **2.48** as a creamish solid.

Yield 80%, creamish solid, mp 136-138 °C.

![Chemical structure](image)

**ν**<sub>max</sub> (cm<sup>-1</sup>): 1643 (C=O).

**λ**<sub>max</sub> (MeOH): 297, 264nm.

δ<sub>H</sub> (CDCl<sub>3</sub>): δ 8.24 (1H, d, <em>J</em><sub>m</sub> = 2.4 Hz, H-5), 7.62 (1H, dd, <em>J</em><sub>o</sub> = 9.0 Hz, <em>J</em><sub>m</sub> = 2.4 Hz, H-7), 7.53 (1H, d, <em>J</em><sub>5',4'</sub> = 5.1 Hz, H-5'), 7.46 (1H, d, <em>J</em><sub>o</sub> = 9.0 Hz, H-8), 7.00 (1H, d, <em>J</em><sub>4',5'</sub> = 5.1 Hz, H-4'), 3.99 (3H, s, -OCH<sub>3</sub>), 2.66 (3H, s, 3'-CH<sub>3</sub>).

δ<sub>C</sub> (CDCl<sub>3</sub>): δ 172.84 (C-4), 153.14, 141.83, 139.46, 133.46, 131.66, 130.74, 130.12, 125.33, 125.16, 124.57, 119.28, 77.19, 59.96, 17.33.

**Mass (m/z):** 307 (M+1, 88%).


**Photolysis of 6-chloro-3-methoxy-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.48**

A deoxygenated methanolic solution of chromone **2.48** (1.0mM) was irradiated in a pyrex glass vessel under nitrogen atmosphere for 90 min with a 125 W Hg vapor lamp. Progress of the reaction was monitored by tlc. A total of 500mg of compound **2.48** was photolysed in a number of batches to get the enough gummy mass that was chromatographed over a column of silica gel (100-200 mesh). The column was eluted with increasing proportion
of benzene in petroleum ether-benzene mixture as eluting system yielding photoproduct 2.53 along with some starting compound 2.48.

**Compound 2.53:**
Yield 24%, light yellow solid, mp 174-176 °C.

\[ \text{2.53} \]

$\nu_{\text{max}}$ (cm$^{-1}$): 1649 (C=O).

$\delta_H$ (CDCl$_3$): $\delta$ 8.25 (1H, d, $J_m = 2.4$ Hz, H-7), 7.60 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.4$ Hz, H-9), 7.42 (1H, d, $J_o = 9.0$ Hz, H-10), 6.27 (1H, d, $J_{2,3} = 6.6$ Hz, H-2), 5.43 (1H, d, $J_{3,2} = 6.6$ Hz, H-3), 4.44 (1H, s, H-11b), 4.08 (1H, d, $J_{4a,4b} = 11.1$ Hz, H-4a), 3.88 (1H, d, $J_{4b,4a} = 11.1$ Hz, H-4b), 1.36 (3H, s, 3a-CH$_3$).

$\delta_C$ (CDCl$_3$): $\delta$ 170.52 (C-6), 153.58, 151.94, 148.39, 138.83, 133.47, 130.57, 125.45, 124.73, 119.48, 100.60, 78.73, 65.88, 40.83, 17.90.

**Mass (m/z):** 307 (M+1, 3%).

Anal. Calcd. for C$_{15}$H$_{11}$ClO$_3$S: C, 58.73; H, 3.61. Found: C, 58.78; H, 3.64.

**Synthesis of 6-chloro-2-(3-methylthiophen-2-yl)-3-propargyloxy-4H-chromen-4-one 2.49**

A mixture of compound 2.47 (0.584g, 0.002mol) and K$_2$CO$_3$ (0.5g) in dry acetone (15ml) was refluxed for 15 minutes. After the salt formation, propargyl bromide (0.238g, 0.002mol) and tetra-$n$-butylammoniumiodide (50mg) were added to the reaction mixture. It was further refluxed for 4h (color changed from reddish-orange to light yellow). The reaction mixture was poured into ice-cold water. The solid obtained was filtered, washed with water and dried. It was crystallized from ethanol to get light yellow crystals of 2.49.

Yield 88%, light yellow solid, mp 156-158 °C.
$\nu_{\text{max}}$ (cm$^{-1}$): 1636 (C=O).

$\lambda_{\text{max}}$ (MeOH): 294, 263nm.

$\delta_{\text{H}}$ (CDCl$_3$): $\delta$ 8.23 (1H, d, $J_m = 2.7$ Hz, H-5), 7.63 (1H, dd, $J_o = 9.0$ Hz, $J_m = 2.7$ Hz, H-7), 7.55 (1H, d, $J_{5',4'} = 5.1$ Hz, H-5'), 7.48 (1H, d, $J_o = 9.0$ Hz, H-8), 7.00 (1H, d, $J_{4',5'} = 5.1$ Hz, H-4'), 5.07 (2H, d, $J_{1''',3''} = 2.4$ Hz, H-1''), 2.65 (3H, s, 3'-CH$_3$), 2.40 (1H, t, $J_{3''',1''} = 2.4$ Hz, H-3'').

$\delta_{\text{C}}$ (CDCl$_3$): $\delta$ 172.50 (C-4), 153.22, 152.10, 142.10, 141.00, 133.62, 131.47, 130.87, 130.27, 129.80, 125.15, 124.78, 119.36, 76.59, 76.33, 59.03, 17.39.

Mass (m/z): 331 (M+1, 36%).

Anal. Calcd. for C$_{17}$H$_{11}$ClO$_3$S: C, 61.73; H, 3.35. Found: C, 61.78; H, 3.37.

**Photolysis of 6-chloro-2-(3-methylthiophen-2-yl)-3-propargyloxy-4H-chromen-4-one 2.49**

A deoxygenated solution of 2.49 (1.0mM) in dry methanol was irradiated in a pyrex glass vessel under nitrogen atmosphere for 45 min with a 125 W Hg vapor lamp. A total of 500mg of compound 2.49 was photolyzed in a number of batches to get the enough photoproducts. In the tlc of reaction mixture, one new spot was seen. The solvent was distilled off under reduced pressure and the residue was chromatographed over a column of silica-gel (100-200 mesh). The column was eluted with increasing proportion of benzene in petroleum ether-benzene system gave photoproduct 2.54 along with some starting compound 2.49.

**Compound 2.54:**

Yield 38%, creamish white solid, mp 202-204 °C.
\( \nu_{\text{max}} (\text{cm}^{-1}) : 2114 \text{ (C=C)}, 1643 \text{ (C=O)}. \)

\( \delta_H (\text{CDCl}_3) : \delta 8.25 \text{ (1H, d, } J_m = 2.7 \text{ Hz, H-7)}, 7.60 \text{ (1H, dd, } J_o = 9.0 \text{ Hz, } J_m = 2.7 \text{ Hz, H-9)}, 7.42 \text{ (1H, d, } J_o = 9.0 \text{ Hz, H-10)}, 6.30 \text{ (1H, d, } J_{2,3} = 6.0 \text{ Hz, H-2)}, 5.54 \text{ (1H, d, } J_{3,2} = 6.0 \text{ Hz, H-3)}, 4.83 \text{ (1H, d, } J_{4,2'} = 2.1 \text{ Hz, H-4)}, 4.54 \text{ (1H, s, H-11b)}, 2.58 \text{ (1H, d, } J_{2',4} = 2.1 \text{ Hz, H-2'}), 1.46 \text{ (3H, s, 3a-CH\text{\textsubscript{3}})}. \)

\( \delta_C (\text{CDCl}_3) : \delta 170.39 \text{ (C-6)}, 153.66, 148.85, 137.21, 133.81, 130.67, 127.51, 127.11, 125.43, 124.55, 119.65, 76.63, 76.52, 68.40, 53.71, 51.54, 18.93. \)

**Mass (m/z):** 331 (M+1, 100%).

Anal. Calcd. for C\textsubscript{17}H\textsubscript{11}ClO\textsubscript{3}S: C, 61.73; H, 3.35. Found: C, 61.78; H, 3.31.

**Synthesis of 3-allyloxy-6-chloro-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.50**

To a solution of \( \text{2.47} \) (0.584g, 0.002mol) in dry acetone (15ml) was added 0.5g of freshly dried K\textsubscript{2}CO\textsubscript{3}, 0.240g (0.002mol) of 3-bromoprop-1-ene and and the phase transfer catalyst, \( n\)-Bu\textsubscript{4}N\textsuperscript{+}I\textsuperscript{-} (50mg). The reaction mixture was refluxed for 4h and reaction mixture became creamish color from reddish-orange. The resulting mixture was poured onto ice-HCl mixture. The solid obtained was filtered, washed with water and dried. It was crystallized from ethanol to get creamish crystals.

Yield 95%, creamish solid, mp 130-132 °C.

\( \nu_{\text{max}} (\text{cm}^{-1}) : 1643 \text{ (C=O)}, 1605 \text{ (C=C)}. \)
\( \lambda_{\text{max}} \) (MeOH): 296, 266 nm.

\( \delta_H \) (CDCl\(_3\)): \( \delta \) 8.23 (1H, d, \( J_m = 2.4 \) Hz, H-5), 7.61 (1H, dd, \( J_o = 9.0 \) Hz, \( J_m = 2.4 \) Hz, H-7), 7.52 (1H, d, \( J_{5',4'} = 5.1 \) Hz, H-5'), 7.46 (1H, d, \( J_o = 9.0 \) Hz, H-8), 7.00 (1H, d, \( J_{4',5'} = 5.1 \) Hz, H-4'), 6.07 (1H, ddt, \( J_{2'',1''} = 6.6 \) Hz, \( J_{2'',3''a} = 17.4 \) Hz, \( J_{2'',3''b} = 10.8 \) Hz, H-2''), 5.37 (1H, dd, \( J_{3''a,1''} = 1.5 \) Hz, \( J_{3''a,2''} = 17.4 \) Hz, H-3''a), 5.23 (1H, dd, \( J_{3''b,2''} = 10.8 \) Hz, \( J_{3''b,1''} = 1.5 \) Hz, H-3''b), 4.76 (2H, d, \( J_{1'',2''} = 6.6 \) Hz, H-1''), 2.64 (3H, s, 3'-CH\(_3\)).

\( \delta_C \) (CDCl\(_3\)): \( \delta \) 172.87 (C-4), 154.07, 153.12, 141.83, 137.87, 133.44, 133.21, 131.54, 130.69, 129.99, 125.20, 125.12, 124.76, 119.31, 119.18, 72.99, 17.36.

Mass (m/z): 333 (M+1, 3%).


**Photolysis of 3-allyloxy-6-chloro-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.50**

A methanolic solution of the compound 2.50 (500mg, 1.0mM) was photolysed with pyrex filtered light from 125 W Hg vapor lamp under nitrogen atm for 45 min. The photolysate was chromatographed over a column of silica-gel (100-200 mesh). Elution of the column with increasing proportion of benzene in petroleum ether-benzene system gave photoproduct 2.55 and some starting compound 2.50.

**Compound 2.55:**

Yield 46%, creamish solid, mp 176-178\(^\circ\)C.

\[ \nu_{\text{max}} \text{ (cm}^{-1}\text{)}: 1651 \text{ (C=O).} \]
δ_H (CDCl_3): δ 8.26 (1H, d, J_m = 2.4 Hz, H-7), 7.60 (1H, dd, J_o = 9.0 Hz, J_m = 2.4 Hz, H-9), 7.41 (1H, d, J_o = 9.0 Hz, H-10), 6.37 (1H, d, J_{2,3} = 6.0 Hz, H-2), 5.99 (1H, ddd, J_{1',2'} = 6.6 Hz, J_{1',2'a} = 17.4 Hz, J_{1',2'b} = 10.8 Hz, H-1'), 5.47 (1H, d, J_{2'a,1'} = 17.4 Hz, H-2'a), 5.35 (1H, d, J_{2'b,1'} = 10.8 Hz, H-2'b), 5.40 (1H, d, J_{3,2} = 6.0 Hz, H-3), 4.60 (1H, s, H-11b), 4.54 (1H, d, J_{4,1'} = 6.6 Hz, H-4), 1.26 (3H, s, 3a-CH_3).

δ_C (CDCl_3): δ 171.00 (C-6), 153.61, 148.15, 139.57, 138.47, 130.76, 128.59, 126.51, 125.79, 124.68, 119.67, 116.50, 78.7, 54.10, 52.06, 18.97.

Mass (m/z): 333 (M+1, 88%).

Anal. Calcd. for C_{17}H_{13}ClO_S: C, 61.35; H, 3.94. Found: C, 61.30; H, 3.91.

Synthesis of 6-chloro-2-(3-methylthiophen-2-yl)-3-(2-methylallyloxy)-4H-chromen-4-one 2.51

To a solution of 2.47 (0.584g, 0.002 mol) in dry acetone (15ml) was added 0.5g of freshly dried K_2CO_3, 0.246g (0.002mol) of iso-propylbromide and the phase transfer catalyst, n-Bu_4N^+I^- (50mg). The reaction mixture was refluxed for 4h and the reaction mixture became light yellow from reddish-orange. The resulting reaction mixture was poured onto ice-cold water. The solid obtained was filtered, washed with water and dried. It was crystallized from ethanol to obtain light yellow crystals.

Yield 95%, light yellow solid, mp 98-100 °C.

ν_{max} (cm^{-1}): 1636 (C=O), 1605 (C=C).

λ_{max} (MeOH): 297, 263nm.

δ_H (CDCl_3): δ 8.19 (1H, d, J_m = 2.7 Hz, H-5), 7.62 (1H, dd, J_o = 7.8 Hz, J_m = 2.7 Hz, H-7), 7.52 (1H, d, J_{5',4'} = 4.8 Hz, H-5'), 7.46 (1H, d, J_o = 7.8 Hz, H-
8), 6.98 (1H, d, J_{4',5'} = 4.8 Hz, H-4'), 5.09 (1H, s, H-3"b), 5.03 (1H, s, H-3"a), 4.72 (2H, s, H-1"), 1.80 (3H, s, 2"-CH_{3}), 1.58 (3H, s, 3'-CH_{3}).

\[ \delta_{C} (\text{CDCl}_3): \delta 172.88 (\text{C-4}), 154.02, 153.21, 141.76, 141.00, 138.46, 133.45, 131.33, 130.69, 129.87, 125.30, 125.15, 124.86, 119.35, 114.08, 75.67, 19.67, 17.10. \]

**Mass (m/z):** 347 (M+1, 8%).


**Photolysis of 6-chloro-2-(3-methylthiophen-2-yl)-3-(2-methylallyloxy)-4H-chromen-4-one 2.51**

Photolysis of a deoxygenated methanolic solution of compound 2.51 (500mg, 1.0mM) with a pyrex filtered light from 125 W medium pressure mercury lamp under the nitrogen atmosphere for 45 min followed by the distillation provided a red gummy viscous mass which on chromatographic separation gave photoproduct 2.56 and some starting compound 2.51.

**Compound 2.56:**

Yield 71%, creamish solid, mp 214 °C.

![Structure of compound 2.56](image)

\[ \nu_{max} (\text{cm}^{-1}): 1659 (\text{C}=\text{O}). \]

\[ \delta_{H} (\text{CDCl}_3): \delta 8.24 (1H, d, J_m = 2.7 Hz, H-7), 7.59 (1H, dd, J_o = 9.0 Hz, J_m = 2.7 Hz, H-9), 7.39 (1H, d, J_o = 9.0 Hz, H-10), 6.36 (1H, d, J_{2,3} = 6.0 Hz, H-2), 5.44 (1H, d, J_{2,3} = 6.0 Hz, H-3), 5.17 (1H, s, H-2'a), 5.14 (1H, s, H-2'b), 4.62 (1H, s, H-11b), 4.55 (1H, s, H-4), 1.94 (3H, s, 1'-CH_{3}), 1.28 (3H, s, 3a-CH_{3}). \]
\( \delta_c (\text{CDCl}_3) : \delta 170.51 (C-6), 153.62, 147.96, 139.87, 138.35, 133.61, 130.47, 128.56, 126.42, 125.39, 124.67, 119.62, 116.57, 78.34, 54.05, 52.01, 21.42, 18.78. \)

**Mass (m/z):** 347 (M+1, 27\\%).


**Synthesis of 3-benzyloxy-6-chloro-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.52**

To 0.584g (0.002mol) of 2.47 and 0.5g of freshly dried potassium carbonate in dry acetone was added 0.253g (0.002mol) of benzyl chloride and 50mg of tetra-\( n \)-butylammonium iodide and this reaction mixture was refluxed for 4h. The resulting reaction mixture was poured onto ice-cold water. The solid obtained was filtered, washed with water and dried. It was crystallized from ethanol to obtain light yellow crystals of 2.52.

Yield 95%, light yellow solid, mp 132-134°C.

\( \nu_{\text{max}} (\text{cm}^{-1}) : 1628 (\text{C}=\text{O}). \)

\( \lambda_{\text{max}} (\text{MeOH}) : 297, 263\text{nm}. \)

\( \delta_H (\text{CDCl}_3) : \delta 8.26 (1\text{H, d, } J_m = 2.4 \text{ Hz, H-5}), 7.62 (1\text{H, dd, } J_o = 9.0 \text{ Hz, } J_m = 2.4 \text{ Hz, H-7}), 7.46-7.42 (3\text{H, m, H-8, } 2''', 6'''), 7.49 (1\text{H, d, } J_{5',4'} = 5.1 \text{ Hz, H-5'}), 7.39-7.28 (3\text{H, m, H-3''', 4''', 5'''}, 6.96 (1\text{H, d, } J_{4',5'} = 5.1 \text{ Hz, H-4'}), 5.22 (2\text{H, s, -OCH}_2-), 2.55 (3\text{H, s, 3'-CH}_3). \)

\( \delta_C (\text{CDCl}_3) : \delta 172.95 (\text{C-4}), 154.14, 153.21, 141.82, 138.13, 136.40, 133.48, 131.32, 130.73, 129.91, 128.95, 128.22, 125.27, 125.12, 124.83, 119.38, 73.75, 17.11. \)

**Mass (m/z):** 383 (M+1, 4\\%).

**Photolysis of 3-benzyloxy-6-chloro-2-(3-methylthiophen-2-yl)-4H-chromen-4-one 2.52**

A deoxygenated solution of compound **2.52** (500mg, 1.0mM) in dry methanol was photolysed under nitrogen atm using pyrex filtered light from 125 W mercury vapor lamp for 45 min. Progress of the reaction was monitored by tlc. The chromatographic separation of photolysate over a column of silica gel provided photoproduct **2.57** and some starting compound **2.52**.

**Compound 2.57:**
Yield 87%, creamish solid, mp 186-188 °C.

![Chemical Structure](image)

$\nu_{\text{max}}$ (cm$^{-1}$): 1651 (C=O).

$\delta_H$ (CDCl$_3$): $\delta$ 8.28 (1H, d, $J_m = 2.1$ Hz, H-7), 7.62 (1H, dd, $J_o = 8.4$ Hz, $J_m = 2.1$ Hz, H-9), 7.46-7.28 (6H, m, H-10, 2'-6'), 6.46 (1H, d, $J_{2,3} = 6.0$ Hz, H-2), 5.16 (1H, d, $J_{3,2} = 6.0$ Hz, H-3), 5.12 (1H, s, H-4), 4.74 (1H, s, H-11b), 1.60 (3H, s, 3a-CH$_3$).

$\delta_C$ (CDCl$_3$): $\delta$ 170.51 (C-6), 153.68, 148.10, 138.72, 135.75, 133.70, 130.56, 128.23, 127.96, 127.85, 126.93, 125.48, 124.72, 119.64, 76.61, 53.57, 52.22, 17.77.

**Mass (m/z):** 383 (M+1, 44%).

References:


43. Minimize energy to Minimum RMS Gradient of 0.100 by MM2 incorporated in Chem office 8.0 Chem 3D ultra 8.0.


