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# Conformational and steric effects on the oxidation of some substituted tetrahydrothiopyran-4-ones and their 1,1-dioxides by pyridinium fluorochromate

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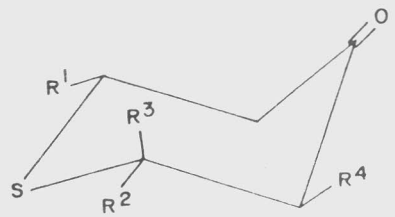
Kinetics of oxidation of the title compounds by pyridinium fluorochromate (PFC) in the presence of perchloric acid in aqueous acetic acid medium has been studied. The reactions show first order dependence each on [oxidant] and [substrate] and are observed to be acid-catalysed. An increase in polarity of the medium is found to decrease the rate and the variation in ionic strength of the medium has no significant influence on the rate of oxidation. All the reactions have been carried out at four different temperatures and various activation parameters are evaluated. The oxidation products have been isolated and characterised. Plausible mechanisms consistent with the observed kinetic results have been formulated. The relative reactivities of these compounds have also been rationalised based on their conformational differences and steric factors.

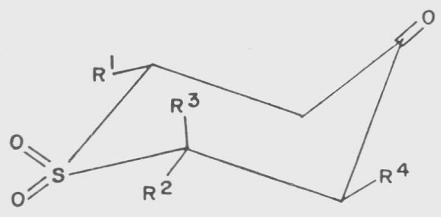
As the electronegativities of sulphur and carbon are almost similar, the chemical behaviour of the ketone derivatives of sulphur heterocyclics are expected to resemble other homocyclic ketones and to differ from those of nitrogen and oxygen analogues. Further, even a slight change in the nature of the sulphur end may alter the mechanism of oxidation itself. These objectives led to the choice of the above compounds as the substrates for oxidation. Although reports on the oxidation kinetics of organic sulphides by various oxidants[1-5] are numerous, similar studies involving tetrahydrothiopyran-4-ones (sulphide ketones) are very limited[6-8]. Literature survey has revealed that only the kinetics of oxidative bromination of tetrahydrothiopyran-4-one-1,1-dioxides (sulphone ketones) is in record and no other oxidant has been employed for the kinetic study of these compounds. Because of the growing interest in the use of pyridinium fluorochromate (PFC) in organic synthesis it was thought worthwhile to investigate the oxidation by PFC of these substrates. An attempt has been made to correlate conformation and reactivity and to throw light on the mechanism of oxidation of title compounds by PFC.




| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| 1 | Ph | Ph | H | H |
| 2 | Ph | H | Ph | H |
| 3 | Ph | H | Ph | $CH_3$ |
| 4 | Ph | H | Ph | $C_2H_5$ |

## Materials and Methods

All the chemicals and reagents used were of analytical grade. Triply-distilled water was used for the preparation of solutions. Acetic acid was purified by the standard procedure[9]. The various sulphide ketones **1-4** and sulphone ketones **5-9** were prepared by the literature methods [10-13]. PFC was prepared by the method of Chaudhuri and coworkers[14] and its purity was checked iodometrically. The acidity of all the solutions was adjusted using perchloric acid. Sodium perchlorate was used to maintain ionic strength.



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| 5 | Ph | Ph | H | H |
| 6 | Ph | Ph | H | $CH_3$ |
| 7 | Ph | H | Ph | H |
| 8 | Ph | H | Ph | $CH_3$ |
| 9 | Ph | H | Ph | $C_2H_5$ |

*Kinetic measurement*

The kinetic runs were carried out under pseudo-first order conditions using ten-fold excess of the [substrate] over the [oxidant]. The reactions were followed at constant temperatures (± 0.1K), by estimating the unconsumed oxidant iodometrically at different time intervals. The pseudo-first order rate constants ($k_1$), obtained from the linear plots ($r \geq 0.995$, $s \leq 0.021$) of log [PFC] versus time by the method of least squares, are reproducible within ±3%. The second order rate constants ($k_2$) were obtained by dividing $k_1$ by [substrate]. The error quoted in rate constant value is the 95% confidence limit of student's 't' test.

*Stoichiometry and product analysis*

Stoichiometric studies under kinetic conditions could not be carried out owing to the practical difficulty in measuring unreacted [substrate]. Hence, the stoichiometry of various oxidations studied herein was determined by the reaction of respective ketone with an excess of PFC followed by estimating the unreacted Cr (VI).

The oxidation products of sulphide ketones under 1:1 stoichiometry were found to be their corresponding sulphoxide ketones. For example, the product of oxidation of *cis*-2, 6- diphenyltetrahydrothiopyran-4-one **1** was identified to be *cis*-2, 6- diphenyltetrahydrothiopyran-4-one-1-oxide through TLC and spectral (IR and NMR) data. It was also confirmed by an undepressed mixed melting point with an authentic sample[12].

In the case of sulphone ketones the stoichiometric results gave a ratio of substrate and oxidant to be 1:3 and the products of oxidation are sulphone dicarboxylic acids. To quote an example, *cis*-2,6-diphenyltetrahydrothiopyran-4-one-1,1-dioxide **5** gave a sulphone dicarboxylic acid (m.p. 162°C). The products were characterised by TLC, IR and NMR spectral data and systematic qualitative tests.

**Results and Discussion**

Kinetics of oxidation of various sulphide ketones (**1-4**) and sulphone ketones (**5-9**) by PFC was investigated in aqueous acetic acid in the presence of perchloric acid under varied experimental conditions. The rate laws and other experimental data were obtained for all the substrates. Since the kinetic results are similar only representative data in each case are reproduced here.

Control experiments in the absence of substrate indicate that there is no self decomposition of PFC. The oxidation of both the sulphide and sulphone ketones are of first order in PFC as evidenced form the linearity ($r \geq 0.995$, $s \leq 0.015$) of log [PFC] versus time plots. However, the pseudo-first order rate constants decrease slightly with increasing initial [PFC] (Tables I and II). Similar observations have been made earlier in Cr (VI)[15] and PFC[16] oxidations. Inspection of kinetic data also shows that $k_1$ values increase markedly with the increase in [substrate]. The plots of log $k_1$ versus log [substrate] were linear ($r \geq 0.995$, $s \leq 0.014$) with a unit slope. Further, the second order rate constants, $k_2 = k_1$ [substrate], are found to be almost constant for various [substrate] confirming first order dependence on [substrate].

The rate measurements with varying [$HClO_4$] show that the order is one with respect to perchloric acid also. The observed hydrogen ion dependence may well be attributed to the involvement of protonated PFC in the rate-determining step. Being a better electrophile, the protonated form of PFC can function as a stronger oxidant and this accounts for the acid catalysis. Such protonated form of PFC has been indicated in earlier reports[17]

The rate data in Tables I and II also reveal that the values of $k_1$ increase with the increase in the proportions of acetic acid. The plots of log $k_1$ against the inverse of dielectric constant of the medium were linear ($r \geq 0.994$, $s \leq 0.037$) with positive slopes implying the occurrence of interaction between an ion and a dipole[18]. This provides convincing evidence that PFC is protonated. An increase in polarity of the solvent may enhance the solvation of pro-

Table 1— Rate data on the oxidation of *cis*-2,6- diphenyltetrahydrothiopyran-4-one by PFC in aqueous acetic acid medium {$\mu$ = 0.50 mol dm$^{-3}$; temp = 308K}

| $10^3$[PFC] (mol dm$^{-3}$) | $10^2$ [substrate] (mol dm$^{-3}$) | [$HClO_4$] (mol dm$^{-3}$) | Acetic acid (% v/v) | $10^4 k_1$ ($s^{-1}$) |
|---|---|---|---|---|
| 1.00 | 1.00 | 0.15 | 60 | 12.1 ± 0.29 |
| 1.00 | 1.25 | 0.15 | 60 | 16.1 ± 0.26 |
| 1.00 | 1.50 | 0.15 | 60 | 19.4 ± 0.78 |
| 1.00 | 2.00 | 0.15 | 60 | 24.5 ± 1.8 |
| 0.60 | 1.00 | 0.15 | 60 | 12.4 ± 0.00 |
| 0.80 | 1.00 | 0.15 | 60 | 12.3 ± 0.09 |
| 1.00 | 1.00 | 0.15 | 60 | 12.1 ± 0.29 |
| 1.50 | 1.00 | 0.15 | 60 | 12.0 ± 0.07 |
| 1.00 | 1.00 | 0.05 | 60 | 4.03 ± 0.00 |
| 1.00 | 1.00 | 0.10 | 60 | 8.07 ± 0.00 |
| 1.00 | 1.00 | 0.15 | 60 | 12.1 ± 0.29 |
| 1.00 | 1.00 | 0.15 | 60 | 16.3 ± 0.00 |
| 1.00 | 1.00 | 0.15 | 50 | 5.47 ± 0.37 |
| 1.00 | 1.00 | 0.15 | 60 | 12.1 ± 0.29 |
| 1.00 | 1.00 | 0.15 | 70 | 44.0 ± 1.7 |
| 1.00 | 1.00 | 0.15 | 75 | 98.0 ± 3.2 |

Table II — Rate data on the oxidation of *cis*-2,6- diphenyltetrahydrothiopyran-4-one-1,1-dioxide by PFC in aqueous acetic acid medium { $\mu$ = 1.00 mol dm$^{-3}$; temp = 308K}

| $10^3$[PFC] (mol dm$^{-3}$) | $10^2$ [substrate] (mol dm$^{-3}$) | [$HClO_4$] (mol dm$^{-3}$) | Acetic acid (% v/v) | $10^4 k_1$ ($s^{-1}$) |
|---|---|---|---|---|
| 0.60 | 1.50 | 0.75 | 70 | 3.35 ± 0.29 |
| 0.80 | 1.50 | 0.75 | 70 | 3.36 ± 0.06 |
| 1.00 | 1.50 | 0.75 | 70 | 3.34 ± 0.06 |
| 1.20 | 1.50 | 0.75 | 70 | 2.84 ± 0.13 |
| 1.50 | 1.50 | 0.75 | 70 | 2.69 ± 0.09 |
| 1.00 | 1.00 | 0.75 | 70 | 2.16 ± 0.14 |
| 1.00 | 1.20 | 0.75 | 70 | 2.53 ± 0.08 |
| 1.00 | 1.50 | 0.75 | 70 | 3.34 ± 0.06 |
| 1.00 | 1.80 | 0.75 | 70 | 3.80 ± 0.14 |
| 1.00 | 2.10 | 0.75 | 70 | 4.22 ± 0.18 |
| 1.00 | 1.50 | 0.25 | 70 | 1.10 ± 0.06 |
| 1.00 | 1.50 | 0.50 | 70 | 2.07 ± 0.10 |
| 1.00 | 1.50 | 0.75 | 70 | 3.34 ± 0.06 |
| 1.00 | 1.50 | 1.00 | 70 | 3.89 ± 0.20 |
| 1.00 | 1.50 | 0.75 | 50 | 1.52 ± 0.06 |
| 1.00 | 1.50 | 0.75 | 60 | 2.13 ± 0.06 |
| 1.00 | 1.50 | 0.75 | 70 | 3.34±0.06 |
| 1.00 | 1.50 | 0.75 | 80 | 4.88 ± 0.36 |
| 1.00 | 1.50 | 0.75 | 85 | 8.12 ± 0.29 |

Table III — Second order rate constants at various temperatures and activation parameters for the oxidation of sulphide ketones by PFC. [substrate] = $1.00 \times 10^{-2}$ mol $dm^{-3}$; [PFC] = $1.00 \times 10^{-3}$ mol $dm^{-1}$ [$HClO_4$] = 0.05 mol $dm^{-3}$; $\mu$ = 0.05 mol $dm^{-3}$; Solvent = 70%(v/v) aq. acetic acid

| Substrate | $10^2 k_2$(mol $dm^{-3}$ $s^{-1}$) | | | | $\Delta H^{\#}$ | $\Delta s^{\#}$ | $\Delta G^{\#}$ |
|---|---|---|---|---|---|---|---|
| | 308K | 313K | 323K | 328K | (KJ $mol^{-1}$) | JK $mol^{-1}$ | KJ $mol^{-1}$ |
| **1** | 12.2 ± 0.3 | 16.4 ± 0.7 | 28.2 ± 0.9 | 33.6 ± 0.9 | 40.6 ± 2.6 | 131 ± 8.8 | 80.9 |
| **2** | 20.4 ± 0.7 | 24.6 ± 0.9 | 41.6 ± 2.2 | 53.1 ± 2.6 | 38.4 ± 3.6 | 134 ± 12 | 79.6 |
| **3** | 15.3 ± 0.7 | 24.4 ± 0.7 | 39.6 ± 2.7 | 52.3 ± 1.7 | 46.9 ± 3.7 | 108 ± 12 | 80.3 |
| **4** | 13.9 ± 0.5 | 18.0 ± 0.0 | 28.7 ± 1.9 | 34.7 ± 6.5 | 36.1 ± 6.0 | 144 ± 20 | 80.6 |

Table IV — Second order rate constants at various temperatures and activation parameters for the oxidation of sulphone ketones by PFC. [substrate] = $1.00 \times 10^{-2}$ mol $dm^{-3}$; [PFC] = $1.00 \times 10^{-3}$ mol $dm^{-3}$ [$HClO_4$] = 0.75 mol $dm^{-3}$; $\mu$ = 1.00 mol $dm^{-3}$; Solvent = 70%(v/v) aq. acetic acid

| Substrate | $10^2 k_2$(mol $dm^{-3}$ $s^{-1}$) | | | | $\Delta H^{\#}$ | $\Delta s^{\#}$ | $\Delta G^{\#}$ |
|---|---|---|---|---|---|---|---|
| | 308K | 313K | 323K | 328K | (KJ $mol^{-1}$) | JK $mol^{-1}$ | KJ $mol^{-1}$ |
| **5** | 5.95 ± 0.32 | 13.3 ± 0.60 | 16.5 ± 0.70 | 26.4 ± 1.6 | 58.1 ± 4.2 | 99.1 ± 14 | 88.6 |
| **6** | 4.32 ± 0.16 | 10.3 ± 0.52 | 13.5 ± 0.75 | 23.6 ± 1.1 | 66.5 ± 3.9 | 74.5 ± 13 | 89.5 |
| **7** | 12.9 ± 0.29 | 24.6 ±0.28 | 33.2 ± 0.88 | 44.1 ±0.0 | 49.1 ± 2.4 | 12.2 ±8.1 | 86.7 |
| **8** | 50.0 ± 3.3 | 124 ± 6.0 | 196 ± 1.0 | 303 ± 13 | 73.1 ± 3.4 | 32.6 ± 11 | 83.2 |
| **9** | 22.1 ± 0.66 | 50.8 ± 2.9 | 82.9 ± 4.4 | 124 ± 4.6 | 70.2 ± 3.7 | 49.0 ± 12 | 85.3 |

tonated PFC and thus reducing its capacity to oxidise. Both sulphide and sulphone ketones are found to have only negligible salt effect on their rates of oxidation.

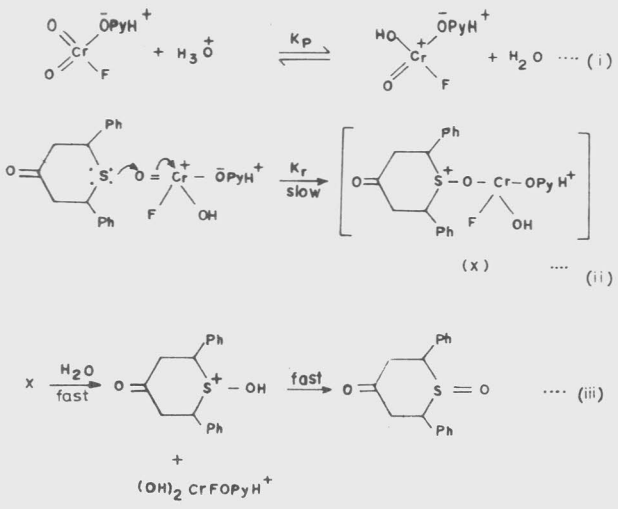
The oxidation of these compounds in an atmosphere of nitrogen failed to induce polymerisation of acrylonitrile indicating the absence of free radicals during the course of oxidation. All the reactions were studied at four different temperatures (308-328 K) and the various activation parameters computed are summarised in Tables III and IV. The precision of $\Delta H^{\#}$ and $\Delta s^{\#}$ was calculated by the method of Petersen *et al.*

## Mechanism, conformation and reactivities

It is interesting to note that eventhough sulphide and sulphone ketones have similar kinetic results, they show entirely different non-kinetic behaviour. It becomes essential, therefore, that their mechanisms and reactivities are to be dealt with independently.

### Sulphide ketones

The result of product analysis has indicated that oxidation of sulphide ketones **1-4** is essentially the oxidation of sulphur atom unlike their nitrogen[16] and oxygen[20] analogues wherein the ketone function is susceptible to oxidation by PFC. Earlier investigations on sulphide oxidations have indicated mainly two different mechanisms. The first of these involves reversible complex formation between the substrate and the oxidant in a fast-step followed by slow irreversible decomposition of complex into the products[19]. In the second mechanism, the complex formation is a slow-step and its consequent decomposition into the products is fast reaction.[21] In the present investigation, the observed negative entropy of activation Table III supports the latter mechanism. Various mechanistic steps are given in Scheme I. This scheme envisages oxygen atom transfer from the oxidant which is in accord with our earlier obser-



Scheme I

vations on pyridinium chlorochromate[8] oxidation of the substrates **1** and **2**.

With Eq. (ii) in Scheme I as the rate-determining step, the rate law can be written as,

$$\text{rate} = -\frac{d[PFC]}{dt} = k_r\,[\text{substrate}]\,[PFCH^+] \quad ...(1)$$

Taking advantage of the preliminary protonation equilibrium of PFC, the final rate expression becomes.

$$\textbf{rate} = k_r K_p[PFC]\,[\textbf{substrate}][H_3O^+] \quad ...(2)$$

Analysis of the rate data presented in Table III shows that *trans*-2,6-diphenyltetrahydrothiopyran-4-one **2** reacts at a faster rate than the *cis*-isomer **1**. In the latter case the approach of the oxidant towards sulphur of the ring sulphide to form the intermediate complex becomes difficult due to the non-bonding interactions with equatorially oriented phenyl groups[12]. It is a well-known fact that the two phenyl groups in the *cis*-isomer are qauasiperpendicular to the plane of the molecule and hinder the approach of the reactant[22], Whereas in the *trans*-isomer, one of the phenyl groups is axially oriented, the steric hindrance encountered by the approaching oxidant is less severe and hence the rate enhancement. If the decomposition of the complex is the slow-step, the reverse trend would have been observed. Hence, the observed rates support the proposed mechanism.

When alkyl groups such as $-CH_3$ or $-C_2H_5$ are introduced in the *trans*-isomer, the resulting compounds, *r*-2-*trans*-6-diphenyl-*cis*-3-methyltetrahydrothiopyran-4-one **3** and *r*-2-*trans*-6-diphenyl-*cis*-3-ethyltetrahydrothiopyran-4-one **4** respectively, undergo oxidation at a slower rate. The rate retardation is more for ethyl than for methyl. It is obviously due to steric factor. In each case, the phenyl group at C-2 is axially disposed while the methyl or ethyl at C-3 is in equatorial position[23]. The results of the X-ray studies on these compounds reported[13] earlier indicate that there is non-bonding interaction between alkyl and axial phenyl group. Moreover, ethyl group experiences a greater steric interaction with the axial phenyl group than is true for a methyl group. This fact explains the observed order of reactivity.

**Sulphone ketones**

In the sulphone ketone since the $-SO_2-$ group is inert to oxidative attack by PFC, the reaction site is changed to ketonic region. With the result the ring opening takes place leading to dicarboxylic acid. Therefore, a comparison between oxidation of sulphide ketone and sulphone ketone is meaningless.

In the light of the kinetic and non-kinetic data the mechanism as shown in Scheme II has been proposed. PFC, being an efficient two-electron oxidant[24], prefers to attack the enol form of the ketone. The intermediacy of enol in Cr(VI) oxidation of ketones has been reported in earlier studies[25]. In the present work also the oxidation of sulphone ketone is primarily the oxidation of enol similar to that of cyclohexanone[26]. Formation of enol cannot be the rate-determining step since the rate depends on the concentration of PFC.

With step IV in Schme II as the rate-determining step the rate of the reaction can be given by Eqn (3).

$$\text{rate} = -\frac{d\,[PFC]}{dt} = k_3\,[\text{enol}]\,[PFCH^+] \quad ...(3)$$

Applying steady state treatment to $(SH^+]$ and assuming $k_1 > k_2$ it can be shown that,

$$[\text{enol}] = \frac{k_1\,k_2\,[S]\,[H_3O^+]}{(k_{-1} + k_2)(k_{-2}\,[H_3O^+] + [PFCH^+])} \quad ...(4)$$

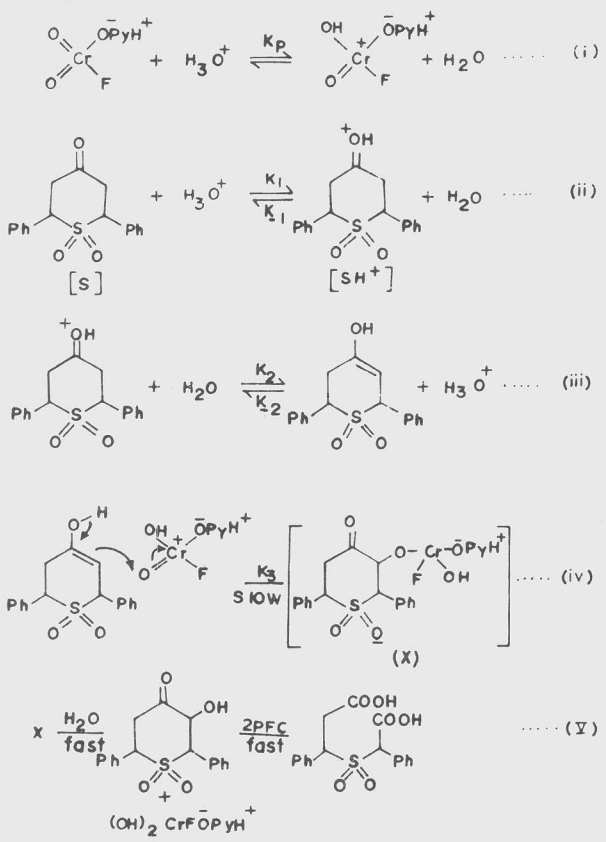
$$\text{rate} = \frac{k_1\,k_2\,k_3\,[S]\,[PFCH^+]\,[H_3O^+]}{(k_{-1} + k_2)(k_{-2}\,[H_3O^+]\,k_3 + [PFCH^+])} \quad ...(5)$$

Under the present experimental conditions namely, $[H_3O^+] > [PFCH^+]$, Eqn 5 reduces to Eqn 6.

$$\text{rate} = k_r\,[S][PFC][H_3O^+] \quad ...(6)$$

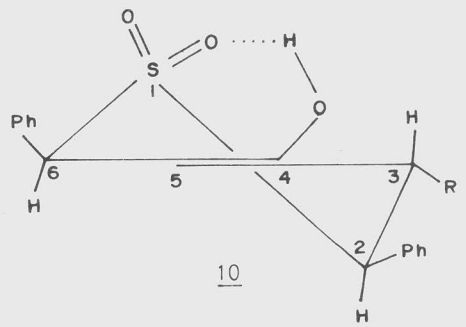
where $k_r = \dfrac{k_1 k_2 k_3 k_p}{(k_{-1} + k_2)k_{-2}}$

A perusal of rate data presented in Table IV shows the the *trans*- isomers are oxidised at a faster rate than



**Scheme II**

the *cis*-isomers. The *cis*-isomer, *cis*-2,6-diphenyltetrahydrothipyran-4-one-1,1-dioxide **5** is shown to exist in the anchored chair conformation [12,23] with both the phenyl groups in the most stable equatorial position. On the contrary, in the *trans*- isomer **7** one of the phenyl groups will have to occupy an axial position and severe non-bonded 1,3-diaxial repulsive interaction between phenyl and hydrogen would destabilise the chair form. Hence, the *trans*-isomer prefers to exist in a flexible non-chair conformation. Since the enolisation is proposed to be the necessary step prior to the oxidation of the sulphone ketone, analysis of conformation and stability of enol becomes significant. The enol form of **5** in its half-chair conformation **10** is stabilised through intramolecular hydrogen bonding between -OH and -$SO_2$ groups. Possibility of such interaction of the heteroatom effect (gamma effect) on the carbonyl carbon has been indicated earlier[28]. Such stabilisation is less probable in the case of *trans*-enol as one of the phenyl groups have to occupy the less stable axial position. It is expected, therefore, that the more stable *cis*-enol is reluctant to undergo oxidation as compared to *trans*-enol which is less stable.



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The fact that the *trans*-isomer undergoes bromination[7] at a slower rate compared to *cis*-isomer is in support of enol oxidation in the present study.

The subtle difference in the rate between **5** and **6** may be due to the electron-repelling inductive effect of the pseudoequatorial -$CH_3$ group in 6, rendering the release of enolic proton difficult in the rate-determining step. It is interesting to note that the alkyl groups in the α-position with respect to carbonyl group enhance the rate of oxidation. The rate enhancement is less pronounced in the case of ethyl **(9)** as compared to methyl **(8)**. This is obviously due to steric interactions[23] between carbonyl and equatorial alkyl groups at C-3. This interaction may increase as the alkyl group changes from methyl to ethyl.

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