CONVERSION OF o-ALLYLPHENOL TO COUMARIN USING SINGLET OXYGEN

S. PANDITA AND S. S. CHIBBER
Department of Chemistry, University of Delhi
Delhi 110007, India

The sensitized photooxygenations of variously substituted 2'-hydroxychalcones give ring closed products due to the participation of 2'-hydroxyl function. In the light of the above effect of ortho-hydroxy in assisting ring closure, it was thought worthwhile to investigate the sensitized photooxygenation of o-allyl phenols.

In a typical photooxygenation procedure, a solution of the substrate in MeOH or CCl₄ containing a catalytic amount of methylene blue or Rose Bengal as sensitizer was irradiated with a 100 W tungsten filament lamp while air was slowly and continuously passed through the solution. The progress of photooxygenation was monitored by TLC and the reaction worked up by removing excess solvent under reduced pressure, extracting the crude photolysate with ether, chloroform and ethyl acetate respectively, and finally subjecting the combined extracts to column chromatography over silica gel. Participation of singlet oxygen was proved by running the reactions in presence of DABCO (O₂ quencher). Blank runs were also carried out in the presence of sensitizer and in absence of air.

Of the five substrates studied, only 2-allylphenol reacted within 30 hr giving two products, one of which has been identified as coumarin (yield 20%) on the basis of spectral data and comparison with an authentic sample. A plausible mechanism (scheme I) for the formation of coumarin involves the initial formation of an allylic hydroperoxide (I) which dehydrates to the α, β-unsaturated aldehyde (II). Molecular oxygen brings about the oxidation of (II) to o-hydroxycinnamic acid (III), which undergoes spontaneous cyclization to afford the observed product.

Of the other substrates, 6-allyl-2-methylphenol and 2-allyl-4-methylphenol failed to react even after 60 hr of irradiation, 1-allyl-2-naphthol showed some reactivity but the reaction was very sluggish with 8-
allyl-7-hydroxy-4-methylocoumarin. The last two substrates gave photoproducts in very low yields which were found to be insufficient for spectral studies.

Further work in this regard is in progress.

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STERIC ENHANCEMENT OF RESONANCE: KINETICS OF OXIDATION OF SUBSTITUTED ACETOPHENONES WITH PHENYL IODOSOACETATE

M. Uma and C. S. Kalavathi
Department of Chemistry, Annamalai University, Annamalainagar 608 002, India

Following the first report on steric enhancement of resonance from the study of dipole moments of substituted anisoles, several investigators have claimed evidence for this phenomenon by kinetic methods. In additions to kinetic studies, the studies on diamagnetic susceptibilities and dissociation constants of some benzene derivatives give additional evidence. Recent studies in our laboratory on the kinetics of bromination of substituted acetophenones both in acidic and basic media, oxidation of corresponding acetophenones by chloramine-T and the pyridine-catalysed iodination of acetophenones are also in favour of the above concept. In the present investigation we report the kinetic data of the oxidation of substituted acetophenones with phenyl iodosooacetate as further evidence for steric enhancement of resonance.

All the ketones employed for this study were prepared and purified following the procedure in the literature. Phenyl iodosooacetate was prepared and purified according to the modified method of Boesken and Schneider. The kinetics of the reaction was performed under pseudo unimolecular conditions and the progress of the reaction was followed by estimating the unreacted phenyl iodosooacetate iodometrically to a starch end point.

It has been established that in the reaction of ketones with phenyl iodosooacetate in acidic media, the order with respect to phenyl iodosooacetate is zero and unity with respect to ketone, pointing to the rate law. This establishes that

\[-d [\text{PIA}] / dt = k_0 [\text{ketone}],\]

following mechanism involving the rate determining enolisation of ketones followed by the oxidation of the enol by phenyl iodosooacetate in a fast step giving the products,

\[\text{O} \quad \text{OH} \quad \phi \rightarrow \text{C} - \text{CH}_3 + \text{H}^+ \quad \text{fast} \quad \phi \rightarrow \text{C} - \text{CH}_3 \quad \text{slow} \quad \text{OH} \quad \phi \rightarrow \text{C} = \text{CH}_2 + \text{H}^+ \quad \text{fast} \quad \text{Products} \quad \text{PIA}\]

The zero order rate constants \(k_0\) and the first order rate constants \(k_1\), \([k_0 \text{ (ketone)}]\) obtained for the oxidation of some mono, di- and tri-substituted acetophenones with phenyl iodosooacetate at 35°C in 50% (v/v) aqueous acetic acid containing 1M sulphuric acid are given in table 1. This data reveal the following order of reactivity for monosubstituted acetophenones.

\[p\text{-OCH}_3 > H > m\text{-Br} > m\text{-CH}_3 > m\text{-Cl}\]

4-Methoxyacetophenone reacts faster than acetophenone and 4-methoxy-3-methylacetophenone reacts still faster. A comparison of the rate constants calculated on the basis of additivity principle for 4-methoxy-3-methylacetophenone \((3.98 \times 10^{-4} \text{ min}^{-1})\) with the observed rate constant \((6.06 \times 10^{-4} \text{ min}^{-1})\) indicates that the 3-methyl group sterically enhances the electron-releasing mesomeric interaction of the methoxy group with the aromatic ring. Due to restricted rotation the chances of the methoxy group attaining coplanarity with the benzene ring increases and hence the resonance interaction of the methoxy group with the aromatic ring increases resulting in a greater electron release to the carbonyl group. The same trend has been observed in the case of 3-chloro-4-methoxy 3-bromo-4-methoxyacetophenones.

The observed rate constants for these compounds are higher than the calculated values due to steric enhancement of resonance.

Among the 3-haloeno-4-methoxyacetophenones, the extent of steric enhancement of resonance seems to be more in the case of 3-bromo-4-methoxyacetophenone compared with 3-chloro-4-methoxyacetophenone as is seen from the \(k_{obs}/k_{cal}\) values. This is due to the bulk effect (i.e., the size of the halogen increases, the enhancement of resonance also increases. The lower rates of 3,5-dimethyl-4-methoxyacetophenone and 3,5-dibromo-4-methoxyacetophenone compared to that of 4-methoxy-acetophenone are due to steric inhibition of resonance.