

Acetone will be more strongly held on an oxidised catalyst. Separate experiments on poisoning studies show that acetone strongly inhibits the reaction. Hence the desorption of acetone can be considered to be the rate-determining step. The competitive adsorption of acetone and 2-propanol shows that the active sites for the adsorption of acetone and the adsorption of 2-propanol are the same.

When Fe^{+2} is surrounded by Fe^{+3} ions there would be delocalisation of electron charge from Fe^{+2} to Fe^{+3} resulting in acetone, which is adsorbed by a donor mechanism, being held strongly to the surface. This results in a reduction in the adsorption of 2-propanol. When the number of Fe^{+2} ions present in the vicinity of the point of adsorption is large, the desorption of acetone becomes easier. Therefore, the reduction of the catalyst increases the activity of the catalyst for dehydrogenation and oxidation reduces it. A used catalyst shows more activity than a fresh one.

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PHOTOCYCLIZATION OF 2'-HYDROXY-3'-BROMO-5'-METHYLCHALCONE

G. C. DUBEY, P. B. GANDHI,
SUBHA JAIN and M. M. BOKADIA

*School of Studies in Chemistry,
Vikram University, Ujjain 456 010, India.*

THE photocyclization of stilbene and *N*-benzylidene-aniline¹⁻³, *N*-(2-propylidene)-2-aminobiphenyls⁴, pyridiniumylide⁵, transnitrones⁶, azobenzene⁷, 4-phenylvinyl-2-pyridones⁸, *N*-2-alkenyl and *N*-3-alkenyl phthalimide⁹ and flavone^{10,11} has been studied and reviewed by various workers.

In the present study the photocyclization of 2'-hydroxy-3'-bromo-5'-methylchalcone has been reported.

2'-hydroxy-3'-bromo-5'-methylchalcone, benzophenone and ethanol used were chemically pure. The chalcone (200 mg) was dissolved in ethanol (50 ml) and benzophenone (0.5 mg) was added to this solution. It was made alkaline by adding five drops of NaOH solution (0.1 M) and irradiated with a medium arc lamp (Phillips, 80 watt) kept at 8 cm. After 10 hr, a solid started separating out from the reaction mixture and the separation was nearly complete after 15 hr.

The solid was filtered, washed with ethanol and recrystallized from benzene [yield 90 mg, m.p. 228°C and mole formula $\text{C}_{16}\text{H}_{11}\text{O}_2\text{Br}$]. It gave a positive test for bromine.

$$\text{UV } (\lambda_{\text{max}}^{\text{benzene}}) = 276, 255 \text{ and } 244 \text{ nm.}$$

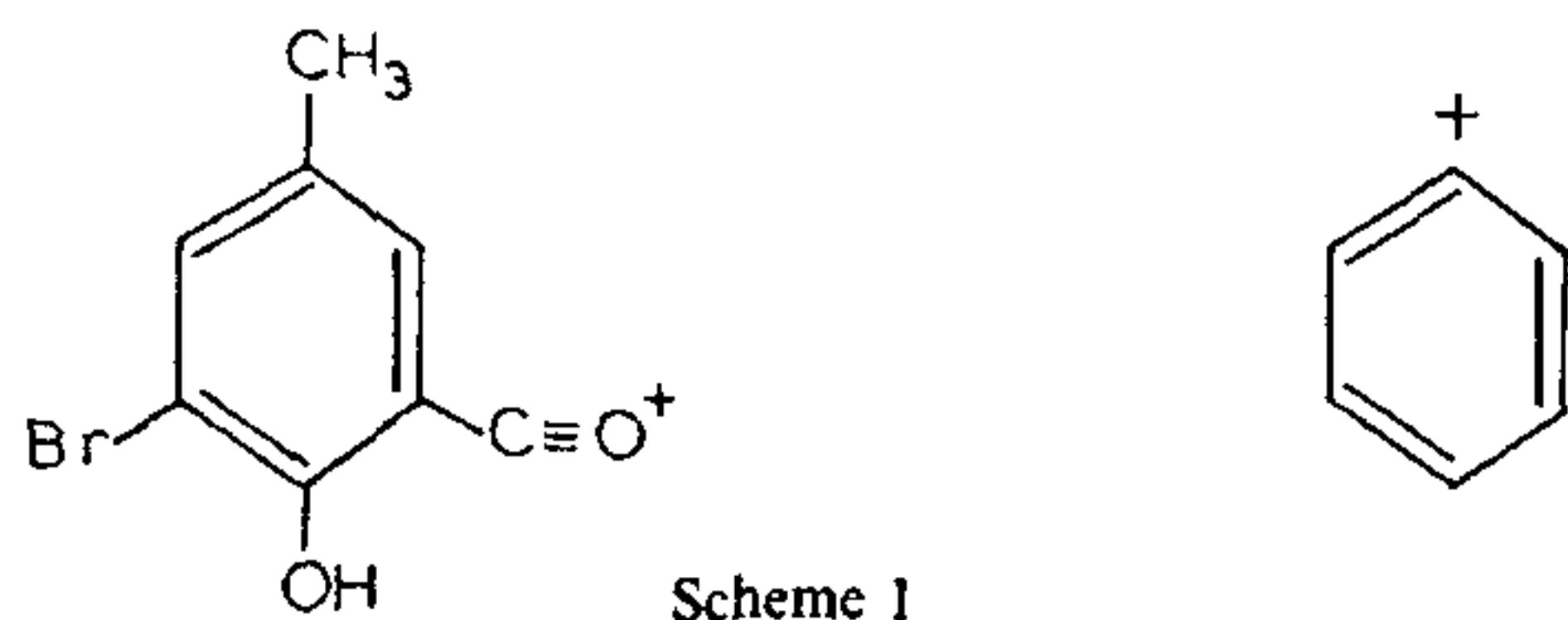
The UV spectrum of the parent compound showed a peak at 322 nm indicating the presence of a conjugated system which had shifted towards shorter wavelength (276 nm) in the product, showing the disappearance of conjugation.

$$\text{IR}-(\text{KBr})^{\text{cm}^{-1}}-3420, 2920, 1700, 1640, 1600, \\ 1470, 1385, 1265 \text{ and } 1150.$$

The IR spectrum of the product resembles that of the parent compound except for a slight shift towards larger wave numbers and the strong absorption at 1700 cm^{-1} which may be attributed to a cyclopentanone ring.

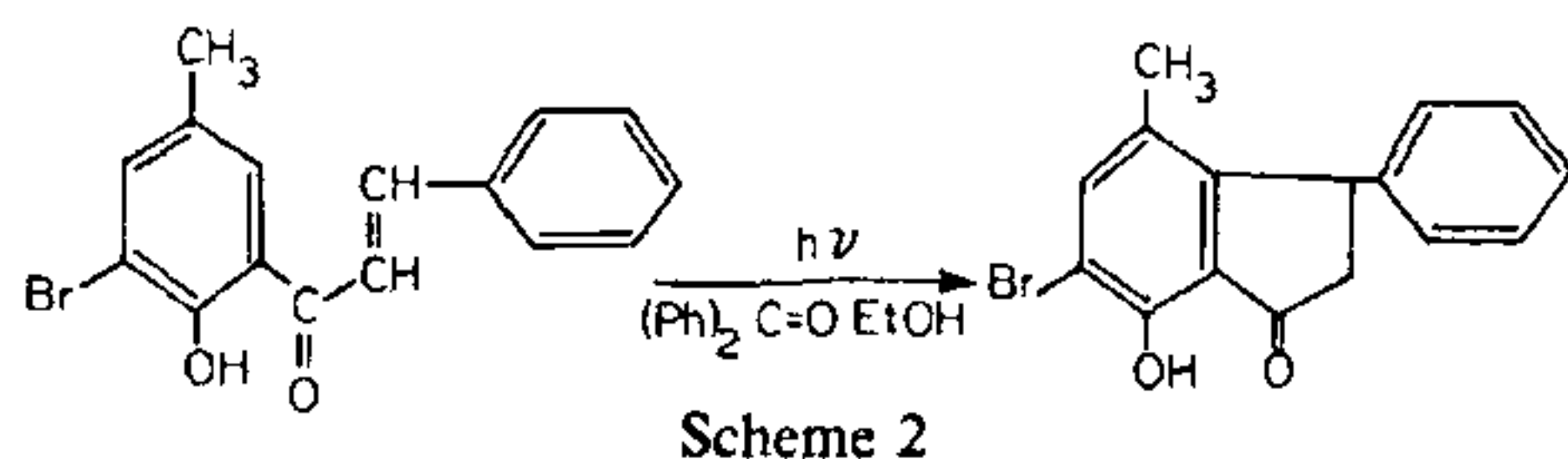
The mass spectrum (m/e 316) indicated the formation of a compound with the same molecular weight. Other intense peaks obtained were at m/e 217 and 77 (Scheme 1).

The effect of photon in the photocyclization was confirmed by carrying out the reaction in the absence of UV radiation when no product was formed. In the



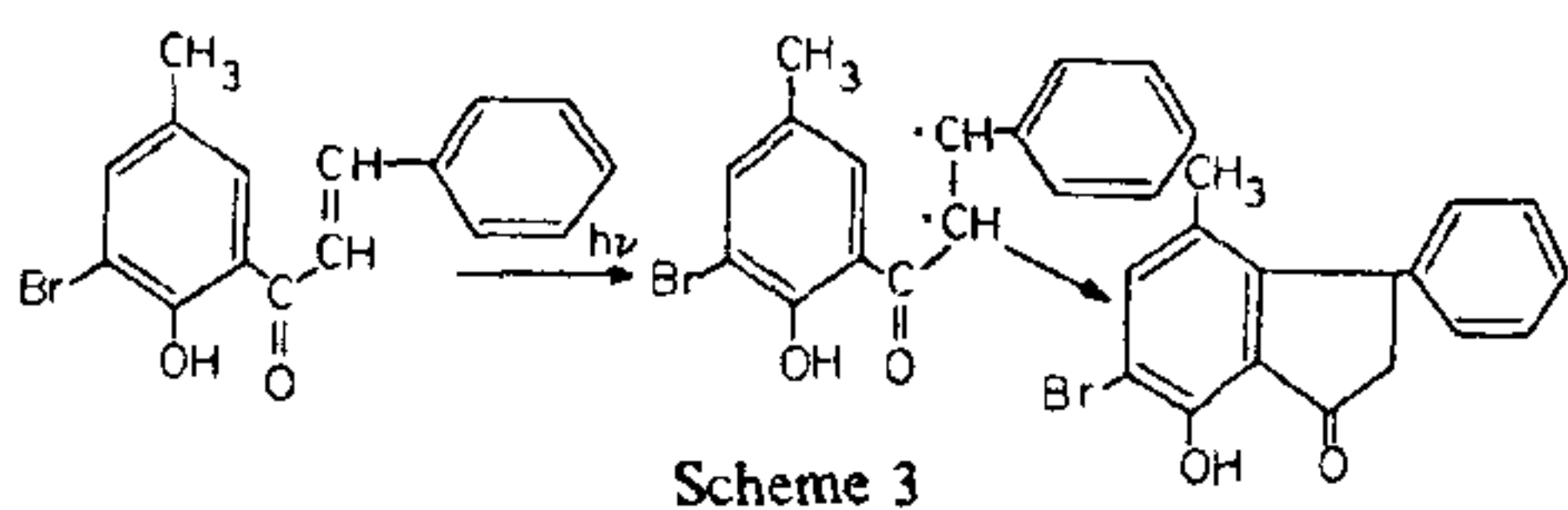
absence of benzophenone the yield was extremely poor. This clearly shows that benzophenone acts as sensitizer. On addition of alkali, the yellow colour changes to reddish orange. However, in the absence of alkali, the substrate did not dissolve and there was no reaction.

The spectral data of the product suggest that the reaction involves synchronous hydrogen migration from C₆' to α-carbon following by bond formation between C₆' and β-carbon atom (Scheme 2).



Mechanism

This intramolecular photocyclization of 2'-hydroxy-3'-bromo-5'-methylchalcone may be explained by a free radical mechanism. The primary photoprocess may proceed by hydrogen radical at α-carbon atom, followed by cyclization between C₆' and β-carbon atom (Scheme 3). The scope, the limitation and the detailed mechanism of this reaction are under investigation.



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KINETICS AND MECHANISM OF THE CHLORINATION OF 2-METHYL PHENOL BY SODIUM N-CHLOROBENZENE-SULPHONAMIDE IN HYDROCHLORIC ACID MEDIUM

B. N. USHA, H. S. YATHIRAJAN and RANGASWAMY

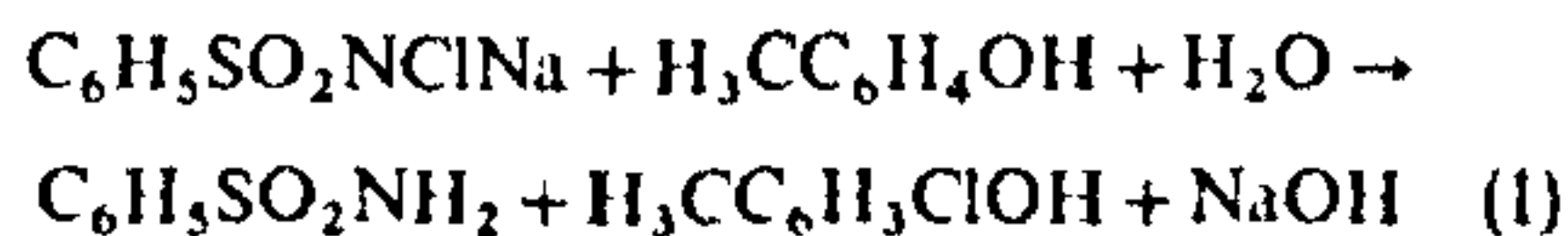
Department of Chemistry, University of Mysore, Manasagangothri, Mysore 570 006, India.

THE kinetics of oxidation of substituted benzyl alcohols¹, unsaturated alcohols^{2,3} and dimethylsulphoxide⁴ by chloramine-B (CAB) have been reported.

2-Methyl phenol (Naarden, b.p. 191°C) was distilled under reduced pressure. The requisite amount of phenol was accurately weighed and dissolved in ethanol. Aqueous solution of chloramine-B was standardized by iodometry. All the other chemicals used were of analytical grade.

The kinetic studies were carried out at an ionic strength of 0.5 M (using NaClO₄) at 35°C under pseudo first order conditions. The reaction rate was determined by estimating the unreacted CAB iodometrically. The stoichiometry of the reaction was 1:1 and the product was 2-chloro-6-methyl phenol as shown by TLC.

The reaction can be represented as:



At constant [H⁺] (0.05 M) and [phenol] (0.1 M), a first order dependence of the rate on [CAB] (0.003-0.007 M) is noted. The pseudo first order rate