THE REACTION OF 3-HYDROXYCOUMARINS WITH CHALCONE

V.K. Ahluwalia, K. Bhat and Chandra Prakesh
Department of Chemistry, University of Delhi, Delhi-110007 (India)

Abstract: The reaction of 3-hydroxycoumarins with chalcone in presence of pyridine-piperidine afforded 2-hydroxy-2,4-diphenyl-10-oxo-3,4-dihydropyrano(2,3-c) (1) benzopyrans. The structures have been established spectroscopically.

3-Hydroxycoumarin (I) has an inhibiting effect on growth of avena roots and 3-aminocoumarins which are intermediates for the synthesis of 3-hydroxycoumarins are found to have antibacterial properties. These are also known to react with different reagents to give 4-substituted derivatives. It was observed that 3-hydroxycoumarin gives 4-isonitroso-, 4-iodo- and 4-ary derivatives with nitrous acid, iodine-iodic acid and p-benzoquinone respectively. The formation of these derivatives can be explained due to ketonic character of 3-hydroxycoumarins, which has also been confirmed by the formation of quinoxalin derivatives with o-phenylene diamine. In view of above interesting reactions, we were prompted to study the reactions of 3-hydroxycoumarin with \( \alpha, \beta \)-unsaturated ketone.

A typical experiment involves the condensation of 3-hydroxycoumarin (1a) (1.62 g) with chalcone (11) (2.08 g) by refluxing in pyridine-piperidine at 120\(^{\circ}\) for 40 h to give a crystalline compound (2.30 g), \( \text{C}_{24}\text{H}_{18}\text{O}_{4}, \text{m.p. 181-182}^{\circ}\). In the IR (KBr) spectrum of the compound, a band at 1700 cm\(^{-1}\) confirmed the retention of the coumarin ring, while bands at 1220 cm\(^{-1}\) and 3300 cm\(^{-1}\) were indicative of an ether linkage and \( \text{-OH} \) group respectively. Its UV spectrum (MeOH) showed a maximum at 240 nm (\( \varepsilon \) 12000) and no shift was observed with NaOH and \( \text{AlCl}_3 \). NMR(CDCl\(_3\)) showed two double doublets at \( \delta \) 3.82 (\( J \) 6 Hz, 17.5 Hz) and 4.60 (\( J \) 9 Hz, 17.5 Hz) each integrating for one proton assigned to two protons at C\(_3\); one double doublet at \( \delta \) 5.40 (\( J \) 6 Hz, 9Hz) equivalent to one proton for C\(_4\) in addition to two multiplets at \( \delta \) 7.50 and 8.10 corresponding to 14 protons in all. The above spectral data led us to assign the structure 2-hydroxy-2,4-diphenyl-10-oxo-3,4-dihydropyrano(2,3-c) (1) benzopyran (IIla) to the product. The alternative...

* Author to whom all correspondence be made.

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tive structure, viz. 4-hydroxy-2,4-diphenyl-10-oxo-3,4-dihydropyran-2,3-c(1)
benzopyran (IV) was excluded on the basis of NMR spectrum, which is expected to
show down field shift for C2 proton (δ 5.9-6.2) due to deshielding effect of
neighbouring oxygen atom. The presence of hydroxyl group in (IIIa) was further
confirmed by its methylation to methyl ether, m.p. 119-120°, viz., 2-methoxy-2,4-
diphenyl-10-oxo-3,4-dihydropyran-2,3-c(1) benzopyran (Va). Its IR spectrum
showed the absence of hydroxy group and NMR(CDCl3) showed in addition to usual
signals, a singlet at δ 3.64 equivalent to 3 protons assigned to methoxyl group.
Acetylation of (IIIa) with acetic anhydride – pyridine (room temperature) gave
its O-acetyl derivative, m.p. 167-168°, viz., 2-acetoxy-2,4-diphenyl-10-oxo-3,4-
dihydropyran-2,3-c(1) benzopyran (Via); its structure was also in agreement
with the NMR spectral data.

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\begin{align*}
(\text{I}) & \\
(\text{II}) & \\
(\text{IIIa}) & R = H; R_1 = H \\
(\text{IIIb}) & R = H; R_1 = OCH_3 \\
(Va) & R = CH_3; R_1 = H \\
(Vb) & R = CH_3; R_1 = OCH_3 \\
(Via) & R = COCH_3; R_1 = H \\
(VIb) & R = COCH_3; R_1 = OCH_3
\end{align*}
\]

Similarly, condensation of chalcone (II) (2.08 g) with 3-hydroxy-7-methoxy-
coumarin (Ib) (1.92 g) gave (IIIb) (2.20 g), m.p. 175-176°, which on methylation
with dimethyl sulphate yielded methyl ether (Vb), m.p. 180-181°. Acetylation of (IIIb) (acetic anhydride/pyridine) gave (VIb), m.p. 160-161°. The spectral data were in agreement with the proposed structures.

A plausible mechanism for the formation of (III) would involve the facile attack of the ambident 3-hydroxycoumarin anion (VII) at the β-position of the carbon-carbon double bond of chalcone (II) to yield a stable anion, which abstracts a proton from the solvent to produce enol form of the product. It is rapidly equilibrated to the more stable keto form, which gets cyclized. The various steps are shown below:

All compounds analysed well for C and H.

Acknowledgement

Our thanks are due to University Grants Commission, New Delhi for research grant.
References


Received, 15th June, 1979