Synthesis and Characterization of Nitro Aurones

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ABSTRACT

2 -Hydroxy- 5- nitro acetophenone & 2-hydroxy- 3-bromo-5- nitro acetophenone in glacial acetic acid at its boiling point treated with ICloffords ω-iodo-2-hydroxy-5-nitro acetophenone (Ia) and ω- iodo-2-hydroxy- 3-bromo-5- nitro acetophenone (Ib) condensed with substituted benzaldehyde in 40% NaOH gives aurones (IIa-l).The structure of aurones where confirmed by chemical and spectral data.

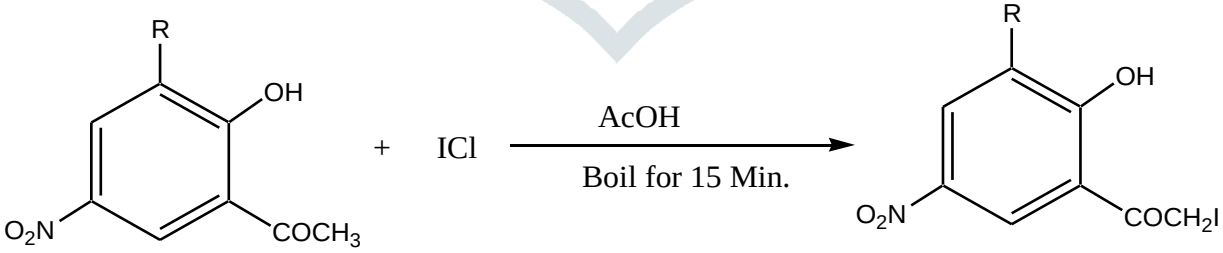
Key words : 2-hydroxy chalcones, 2-benzylidene coumaran- 3- one

INTRODUCTION:

2-Hydroxy chalcones in acetic acid reacts with $Mn(OAC)_2$ affords 2-benzylidene coumaran- 3- one (aurones)[1].Chalcone reacts with mercuric acetate in DMSO solvent gives 2-benzylidene coumaran- 3- one[2,3,4].Chalcone bromide is kept in cold ethanol for 24 hours then treated with alkali gives aurones[5,6] . Some chalcones are directly oxidized by air to give auromes[7]. ω- bromo-2-hydroxy acetophenone condenses with substituted benzaldehyde in 40 % NaOH affords 2-substituted benzylidenecoumaran-3-one[8,9] ω-bromo-2-hydroxy acetophenone and substituted benzaldehyde dissolved in ethanol and the solution treated with triethanolamine[10] gives to2-substituted benzylidenecoumaran-3-one. ω- bromoacetophenone used for preparation aurones. Hence it was thought interesting to prepare ω- iodoacetophenone and is used to prepare 2- benzylidenecoumaran- 3-one.

Preparation of ω-iodo-2-hydroxy-5-nitroacetophenone :

2 -Hydroxy-5-nitroacetophenone (0.01mole) was dissolved in 10 ml glacial acetic acid. To this mixture ICl in acetic acid (0.001mole) was added drop by drop, with constant stirring boiled for 15 minutes, allowed to stand for 1 hour diluted with water. The mixture was extracted from benzene/ether. The benzene/ether was evaporated to get solid mass. Finally crystalizedfrom ethanol to get ω-iodo-2-hydroxy-5-nitro acetophenone (Ia) M.P. 59^0C yield 78%. Similarly other compounds were prepared by above method. They are reported in Table-1.



I (a-b)

Properties of the compounds(Ia)

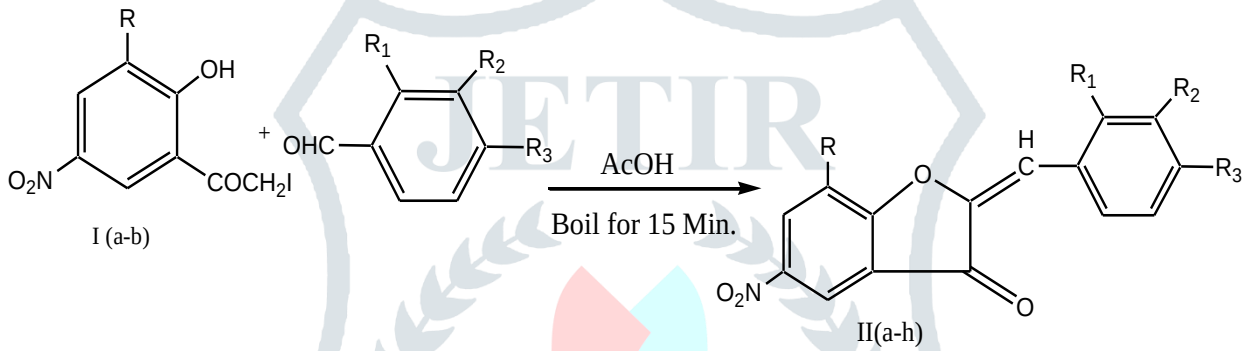
1. It is brown coloured compound M.P. 59^0C
2. Alcoholic solution of Ia gives red colouration with neutral ferric chloride solution indicates that it contains phenolic –OH group.
3. From the analytical data the molecular formula was found to be $C_8H_6O_4NI$. The molecular weight being found to be 306 g.

Table-1: ω- iodo-3 -substituted -5-nitroacetophenone

Sr.No.	R	M.P. ^{0}C	Yield %
Ia	H	55	78
Ib	Br	92	62

Properties of 2-benzylidene- 5-nitrocoumaran- 3- one :

ω- iodo-2-hydroxy-5-nitroacetophenone (Ia) (0.01mole) and benzaldehyde (0.01mole) was dissolved in 20 ml ethanol. The solution warmed and 40% NaOH(6-8ml) was added with constant stirring till red colourpersist.The mixture was allowed to stand for 6 hours, and diluted the mass with 1:1 HCl solid separated get crystalized from ethanol to get (IIa). M.P.88^{0}C. Similarly, other compounds were prepared by above method and they are reported in the Table -2.



Properties of the compounds(IIa-h)

1. It is golden yellow coloured crystalline compound with M.P. 96^{0}C .
2. It gives negative ferric chloride test indicating involvement of phenolic – OH group in cyclization.
3. From the analytical data the molecular formula was found to be $C_{15}H_9O_4N$. The molecular weight being found to be 207g.
4. The IR spectrum was recorded in nujol

   3025 (Ar C-H str.)

   1724 (C=O stretching in 5 membered ring)

   1576.7, 1463.8 (C=C in aromatic ring)

   1180 (C-O stretching) and

   640 (C-N stretching)

5. The PMR was recorded in $CDCl_3$ with TMS as internal standard

   4.5δ (S, H, = CH-)

   6.9 – 8.1 δ (m, 8H, Ar-H)

From chemical and spectral data compound (IIa) is 2-benzylidene- 5-nitrocoumaran-3-one

Table-2 : Synthesized aurone M.P.(s), yield %

Sr.No	R	R_1	R_2	R_3	M.P. ^{0}C	Yield %

IIa	H	H	H	H	92	70
IIb	H	H	H	OCH_3	158	65
IIc	H	OH	H	H	144	60
IId	H	H	NO_2	H	172	72
IIe	Br	H	H	H	115	82
IIf	Br	H	H	OCH_3	202	70
IIg	Br	OH	H	H	218	72
IIh	Br	H	NO_2	H	175	73

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REFERENCES :

1. Kurosawa Kerze, *Bull. Chem. Soc .Japn***42**,5
2. S. K. Doifode and A. G. Doshi*Orient. J.Chem.***11** (2),189-190 (1995)
3. V. B. Kaduand A. G. Doshi*Orient.J.Chem.***13** (3),281-284 (1997)
4. A. S. Sahathrabuddhe,*Ph.D.Thsis*, Nagpur University. (1992)
5. T. S. Wheelar,et.al.,*Pruc.Ind.Acad.Sci*.,**2**,439(1935).
6. M. G. Marathe, *J.Uni. Poona*, **2**,7(1952)
7. M. J. Simokoriyand, *Am. Chem.Soc*.**79,** 399 (1957).
8. K. B. DoifodeandM. G. Marathe M.G. *J.Org.Chem*., **29**, 2025 (1964)
9. M. V. Parajape and K. N. Wadokar,*Indian. J. Chem*.**20B**, 808- 809 (1981)
10. P. A. Soni. Study of Bromination and Debromination on flavanoids, chalcones and Aurones*Ph.D.Thesis* Nagpur University (1977)