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Note

A new process for the synthesis of aurones by using mercury (II) acetate in pyridine and cupric bromide in dimethyl sulfoxide

Nitin N Agrawal* & P A Soni

Department of Chemistry, Government Vidarbha Institute of Science and Humanities, Amravati 444 604, India

E-mail: nitinnagrawal@rediffmail.com

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Syntheses of aurones **2a-i** have been achieved by the oxidation of 2'-hydroxychalcones **1a-i** with molar amount of mercury (II) acetate in pyridine and in catalytic amount of $CuBr_2$ in DMSO in good yields. The structures of the compounds **2a-i** have been established on the basis of IR and NMR and m.m.p. with an authentic sample.

Keywords: Mercury (II) acetate, cupric bromide, aurones, 2'-hydroxychalcones

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Aurones are useful in alleviating allergic manifestations such as allergic asthma, allergic rhinitis and a topic dermatitis[1-5]. Antifungal, antibacterial, antiplasmodial, antileishmanicidal and antiviral activities of aurones have also been reported[6-9]. Therefore, the syntheses of these compounds are largely on account of their biological activities.

DMSO and pyridine showed very good oxidizing properties[10-12]. In view of this, it was interesting to study different reaction conditions for this reaction.

Both mentioned methods are superior to that of conventional one as the products obtained are in good yield and also they appear to be of general applicability. Thus, this constituted a new synthetic route for the synthesis of aurones.

Experimental Section

2'-Hydroxychalcones **1a-i** have been prepared by the literature procedure[13,14]. The melting points were taken in an open capillary tube and are uncorrected. IR spectra in KBr were recorded on a Perkin-Elmer 1800 spectrometer; and ^{1}HNMR in $CDCl_3$ at 300 MHz on a Brucker AC 300 F spectrometer (chemical shifts in δ, ppm). All the compounds prepared were checked by TLC.

Synthesis of aurones 2a-i

Method A — Using pyridine-Hg $(OAc)_2$. 2'-Hydroxychalcones **1a-i** (0.005 mole) were dissolved in catalytic as well as in molar amount of Hg $(OAc)_2$ in pyridine and kept overnight. In neither case was cyclization affected and the chalcones remained unchanged.

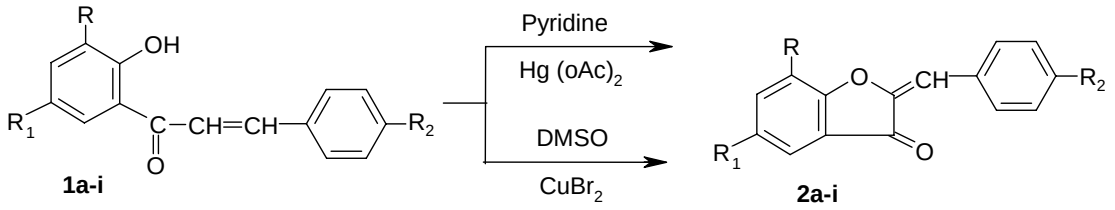
In the next series of experiments the reaction conditions were changed. Molar amount of Hg $(OAc)_2$ (0.001 mole) was dissolved in pyridine in cold (10 mL) and to this solution 2'-hydroxychalcones **1a-i** (0.001 mole) were added and solution was refluxed for 10-15 min. The reaction mixture was cooled, treated with dil. HCl, then diluted with ice-cold water and crystallized from rectified spirit to get pure aurones **2a-i (Scheme I)**, which were identified by m.p. and super imposable m.m.p. with those of an authentic sample[13-15] and their IR and ^{1}HNMR data. The results are shown in **Table I**.

2a: IR: 1699 (-C=O), 1649 (-C=CH), 1025 (-OCH_3), 751 cm^{-1} (-C-O-C); ^{1}HNMR: δ3.90 (s, 3H, -OCH_3), 6.89 (s, 1H, =CHPh), 7.89-7.91 (d, 2H, *J* = 6 Hz, Ar-H), 6.98-7.00 (d, 2H, *J* = 6 Hz, Ar-H), 7.31-7.82 (m, 4H, Ar-H); Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.19; H, 4.76. Found: C, 76.06; H, 4.69%.

2d: IR: 1701 (-C=O), 1649 (-C=CH), 1022 (-OCH_3), 786 cm^{-1} (-C-O-C); ^{1}HNMR: δ2.38 (s, 3H, -CH_3), 3.85(s, 3H, -OCH_3), 6.83(s, 1H, =CHPh), 6.92-6.98 (d, 2H, *J*=18 Hz, Ar-H), 7.82-7.88 (d, 2H, *J* = 18 Hz, Ar-H), 7.56 (s, 1H, Ar-H), 7.41-7.44 (d, 1H,

Table I — Physical data of compounds **2a-i**

Compd	Using pyridine-Hg $(OAc)_2$		Using DMSO-$CuBr_2$	
	m.p. °C	Yield (%)	m.p. °C	Yield (%)
2a	137-38	84	134-35	76
2b	100-101	78	100	76
2c	170	80	174	78
2d	154-55	83	150	74
2e	118-19	80	115	77
2f	182-83	82	185	80
2g	173-74	87	169-70	70
2h	170	77	167	72
2i	190	85	185	73



Compd	R	R_1	R_2
2a	H	H	OCH_3
2b	H	H	H
2c	H	H	Cl
2d	H	CH_3	OCH_3
2e	H	CH_3	H
2f	H	CH_3	Cl
2g	Br	CH_3	OCH_3
2h	Br	CH_3	H
2i	Br	CH_3	Cl

Scheme I

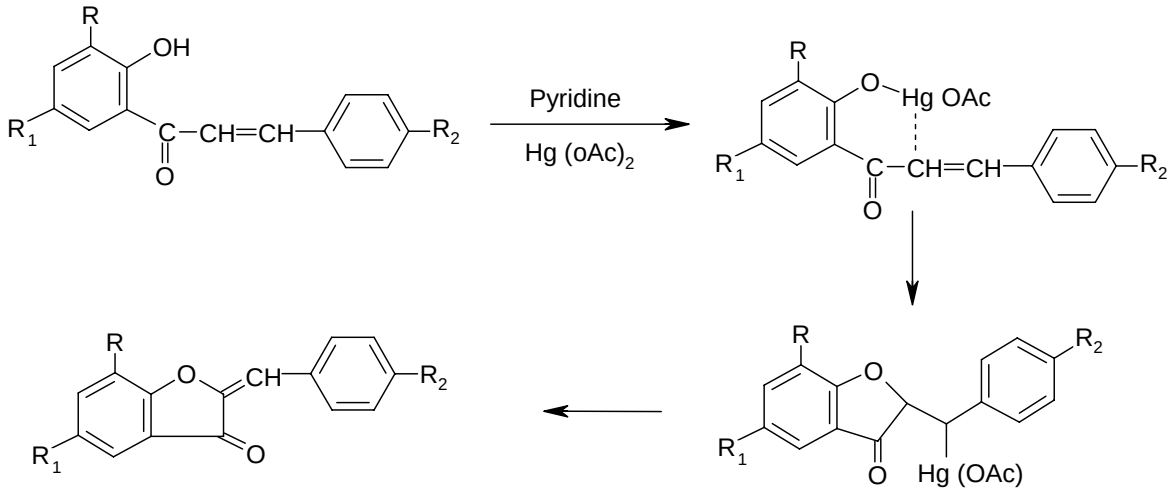


Chart I

J = 9 Hz, Ar-H), 7.17-7.20 (d, 1H, *J* = 9 Hz, Ar-H); Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.69; H, 5.26. Found: C, 76.60; H, 4.11%.

2i: IR: 1707 (-C=O), 1648(-C=CH), 778 cm^{-1} (-C-O-C); ^{1}HNMR: δ 2.39(s, 3H, $-CH_3$), 6.83(s, 1H, =CHPh), 7.42-7.44(d, 2H, *J* = 6 Hz, Ar-H), 7.85-7.87 (d, 2H, *J* = 6 Hz, Ar-H), 7.50 (s, 1H, Ar-H), 7.62 (s, 1H, Ar-H); Anal. Calcd for $C_{16}H_{10}O_2BrCl$: C, 54.93; H, 2.86; Br, 22.88; Cl, 10.15. Found: C, 54.85; H, 2.79; Br, 22.80; Cl, 10.08%.

Method B — Using DMSO - $CuBr_2$. $CuBr_2$ (10-15 mg) was added to DMSO (10 mL) and 2'-hydroxychalcones **1a-i** (0.002 mole) were dissolved in this solution and the solution was refluxed for 1 to 1½ hr. The reaction mixture was cooled, poured on ice-cold water and kept at room temperature for 10-15 min. The product was filtered and crystallized from EtOH to give pure aurones **2a-i**

An attempt to carry out the reaction at lower temperature was unsuccessful. Also higher or molar amount of $CuBr_2$ gave no results.

2g: IR: 1701 (-C=O), 789(-C-O-C), 1647 (-C=CH), 1009 cm^{-1} ($-OCH_3$); ^{1}HNMR: δ2.40 (s, 3H, CH_3), 3.89(s, 3H, $-OCH_3$), 6.99-7.02(d, 2H, *J* = 9Hz, ArH), 7.92-7.95(d, 2H, *J* = 9Hz, ArH), 6.92(s, 1H, =CHPh), 7.52 (s, 1H, ArH), 7.62 (s, 1H, ArH); Anal. Calcd for $C_{17}H_{13}O_3Br$: C, 59.13; H, 3.76; Br, 23.18. Found: C, 59.05; H, 3.65; Br, 23.09%.

Mechanism

Method A — The first step in the reaction is the formation of Ar-O-Hg $(OAc)_2$ group. This group attacks C-H bonds in a suitable spatial position, which is α-hydrogen in this case to give aurones (**Chart I**). The formation of 5 membered rings is due to the bulkiness of Hg $(OAc)_2$.

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