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Iodination of some hydroxylated aromatic aldehydes and ketones with iodine and iodic acid by microwave assisted and conventionally stirring method

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ABSTRACT

A simple and convenient method for iodination of some hydroxylated aldehyde and ketones by iodine and iodic acid combination as iodinating reagent under microwave irradiation and by conventional stirring method is reported. A combination of iodine and iodic acid has been found to be an efficient reagent for iodination of aromatic aldehydes and ketones. For microwave assisted reactions, the reaction time were shortened, but the yields were nearly same as those afforded by conventional method.

Key words: Iodination, aldehydes, ketones, iodine and iodic acid, microwave, conventional stirring.

INTRODCTION

The iodination of aromatic carbonyl compounds has been the subject of numerous studies due to the potential of the product to serve as intermediates in organic synthesis and act as bacterial and fungicidal agents[1].Iodohydroxy aromatic ketones can be prepared by Fries rearrangment[2] of iodinated phenyl aromatic esters; however, after Fries rearrangement stem distillation is required to separate the isomer which is a time consuming and iodophenols required for preparation of phenyl aromatic esters are not easily available.

Recently the iodination of various organic compounds such as aryl hydroxyl ketones[3], hydroxylated aromatic ketones[4,5]and anilines[6] were studied by us with iodine and iodic acid combination as an iodination reagent. In course of our study to extend the scope of iodine and iodic acid combination as iodinating reagent we are first time here reporting the synthesis of iodohydroxy aldehydes and ketons by microwave irradiation as well as by and compaired with conventional stirring method. The attractive feature of microwave irradiation method is simple procedure, cleaner reaction and short reaction time.

EXPERIMENTAL SECTION

Melting points (uncorrected) were determined in open capillary tubes. The purity of compounds was checked by TLC using silica gel G. The I.R. spectra (Nujol) were recorded on a Perkin-Elmer Spectrophotometer and ^{1}HNMR Spectra were recorded on Gemini 300-MHz instrument in $CDCl_3$ as solvent and TMS as an internal standard. The mass spectra were recorded on an automated Finningan MAT1020c mass spectrometer using ionization energy of 70 eV. LG make (450W) microwave oven was used.

(A) General procedure for iodination by conventional method.

Substrate (0.05 mol.), iodine (0.02 mol) were dissolved in ethyl alcohol (15 ml) and solution was heated to 35 ^{o}C. To this hot solution, iodic acid (0.01 mol.) in minimum amount of water was added and reaction mixture stirred for one to one and half hour or till solid separate out. Separated solid was treated with saturated sodium thiosulphate to decompose traces of unreacted iodine.Solid obtained was washed with water and crystallized from ethanol.

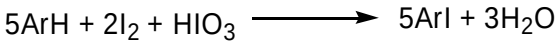
(B) General Procedure for iodination under microwave irradiation:

Substrate of (0.05 mol.) and iodine (0.02mol.) was dissolved in ethanol (20 ml), iodic acid (0.01mol) dissolved in water (1.0 ml) was added. The flask was placed in a microwave oven (450 W) and irradiated for seven second six times (total 42 sec.) with short interval of time to avoid evaporation of solvent. The reaction mixture on cooling solid separated was filtered and washed with sodium thiosulphate solution followed by water and crystallized from ethyl alcohol.

RESULTS AND DISCSSION

Due to poor electrophilic strength of iodine, direct iodination of aromatic compound with iodine is difficult and requires the presence of an activated agents in order to produce a strongly electrophilic I^+ species .In combination of iodine and iodic acid reagent, the iodic acid was dissolved in to the water to prodce H_3O^+ and IO^-_3 to facilitate the oxidation of diiodine by HIO_3 and to produce the I^+species,the oxidation capable to effectively iodinate a number of hydroxylated aldehyde and ketones. (Table 1). The iodination of hydroxylated aldehyde and ketones by iodine and iodic acid combination as iodinating reagent under microwave irradiation is found to be simple,convenient and efficient methodas compaired to conventional method. For microwave assisted reactions, the reaction time were shortened, but the yields were nearly same as those afforded by conventional method. A combination of iodine and iodic acid has been found to be an efficient reagent for iodination of aromatic aldehydes and ketones.The scheme and overall reaction for iodination is as follows:

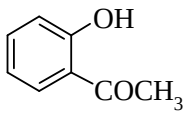
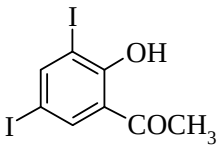
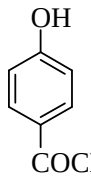
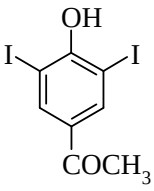
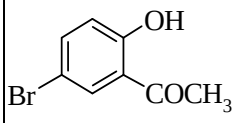
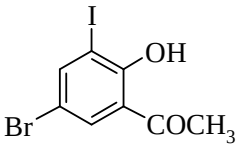
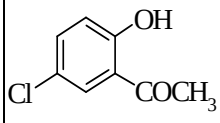
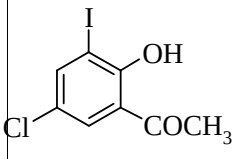
R = H or CH_3
R1= H, OH, Cl, Br, OCH_3

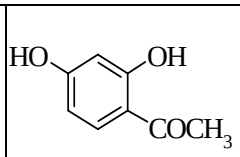
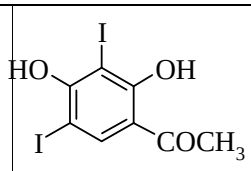
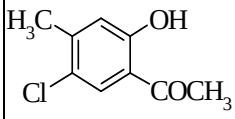
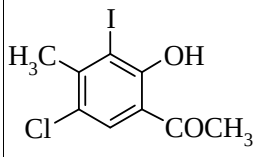
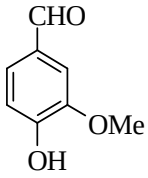
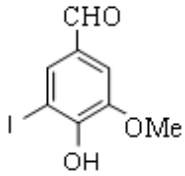
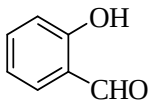
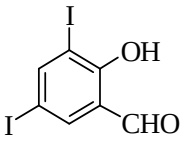
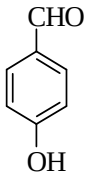
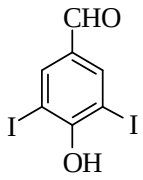
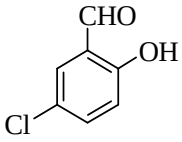
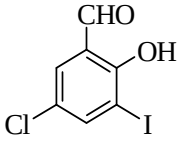
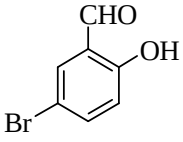
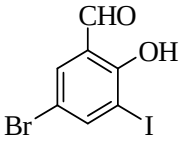


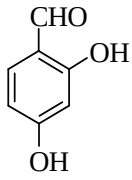
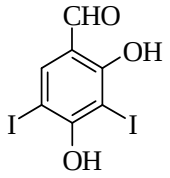
Spectral and Analytical Data of Some Selected Compounds

5-Chloro-2-hydroxy-3-iodoacetophenone : IR (cm^{-1}):1630 (C=O), 1570 (C=C). ^1H NMR ($CDCl_3$) δ: 2.75 (s, 3H, $COCH_3$), 7.60 (s, 1H, 4Ar-H), 7.83 (s,1H, 6Ar-H), 12.85 (s, 1H, OH). Anal. calcd for $C_8H_6ClIO_2$: C, 32.37; H,2.02; I, 42.83. Found C, 32.31; H, 2.11; I, 42.71.

Table 1: **Iodination of Reactive aromatics by Iodine and Iodic acid**

Entry	Starting material	Product	Conventional Method Yield (%)	Microwave method Yield (%)	M.P. (^0C) Found (reported)
1			84	81	132 (132)[5]
2			80	79	160 (162)[7]
3			85	84	104 (105)[5]
4			89	86	90 (89)[5]

5			82	79	177 (178)[8]
6			81	79	79 (76)[5]
7			85	82	184 (185)[9]
8			82	80	111 (110)[10]
9			86	83	194 (193)[11]
10			79	78	77 (78)[9]
11			87	86	80 (81)[9]

12			83	81	172 (172)[9]

2-4-Dihydroxy-3,5-diiodoacetophenone : IR (cm^{-1}): 1640 (C=O),1610(C=C). ^1H NMR ($CDCl_3$) δ: 2.68 (s, 3H, $COCH_3$), 8.68 (s 1H, 6Ar-H), 8.35 (s, 1H, OH), 11.82 (s, 1H, OH). Anal. calcd for $C_8H_6I_2O_3$: C, 23.76; H,1.48; I, 62.87. Found C, 23.69; H,1.71; I, 62.89.

2-Hydroxy-3,5-diiodobenzaldehyde: IR (cm^{-1}): 2845 (C-H of CHO), 2719 (C-H of CHO), 1658 (-C=O), 1587 (C=C). ^1H NMR ($CDCl_3$) δ: 8.01 (s, 1H, 6 Ar-H), 8.13 (s, 1H, 4 Ar-H), 9.97 (s, 1H, CHO), 11.82 (s, 1H, OH). Anal. calcd for $C_7H_4I_2O_2$: C, 22.45; H, 1.06; I, 67.91. Found C, 22.34; H, 1.72; I, 67.83.

2,4-Dihydroxy-3,5-diiodobenzaldehyde: IR (cm^{-1}):2811 (C-H of CHO), 2716 (C-H of CHO), 1648 (-C=O), 1575 (C=C).^1H NMR ($CDCl_3$)δ: 7.86 (s, 1H, 6 Ar-H), 8.38 (s, 1H, OH), 10.08 (s, 1H, CHO), 11.85 (s, 1H, OH). Anal. calcd for $C_7H_4I_2O_3$, C, 21.53; H, 1.02; I, 65.12. Found C, 21.49; H, 1.12; I, 65.19.

CONCLUSION

A comparative study was carried out for iodination of some aromatic aldehydes and ketones with iodine and iodic acid by microwave and conventional stirring method. A combination of iodine and iodic acid has been found to be an efficient reagent for iodination of aromatic aldehydes and ketones. For microwave assisted reactions, the reaction time were shortened, but the yields were nearly same as those afforded by conventional method.

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