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A Mild and Efficient System for A-Monohaloganation of Carbonyl Compounds Using NBS & $SICL_4$

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Abstract*: *A simple and efficient method for alphahalogenation of hydroxilated aromatic ketone using NXS & SiCl4 in acetonitrile at room temperature is investigated. Using inexpensive and readily available reagents and mild reaction conditions are the major benefits of present method.
Keywords*: Tetrachlorosilane, N-halosuccinimide, α-monohaloganation, Hydroxilated aromatic ketone.

I. INTRODUCTION

The Halo carbonyl compounds have wide utility in organic synthesis [1-3]. These are the building blocks for the synthesis of various heterocycles, [4] natural products[5], and many functionalized compounds[6]. A number of α Halocarbonyl compounds possess biological activity[7]. It is well known that the molecular halogen (Br_2/Cl_2/I_2) in presence of some protic acids or Levis acids is the common reagents for the synthesis of α haloketones from ketones. This method has several drawbacks like toxic and corrosive nature of reagents, difficulty in handling, over halogenations and incompatibility with acid sensitive or easily oxidisable groups[8]. Alternating reagents were reported in the literature for example, Cupric Bromide[9], NH_4Br-oxane[10]. In addition to this a superior haloganating agent such as N-halosuccinimide[11] was utilized for α haloganation of carbonyl compounds using a radical initiator such as AIBN[12], in ionicliquid[13], photochemical energy [14], sonochemical energy [15] some other catalyst like sulfonic acid functionalized silica[18], montmorilonite K10[19]. It is well recognized that solids play a significant role in the development of cleaner technologies through their abilities to act as catalyst support reagents, entrain byproducts, and influence product selectivity and several books on application of solids in organic synthesis have appeared. The development of novel synthetic strategies for haloganation which have advantages with respect to using less expensive and readily available reagents, mild reaction conditions, cleaner and simple isolation of the product are of interest. In exploring the utility of in situ reagents based on tetrachlorosilane (TCS)[20] in organic synthesis. Here we have reported a general method for the α halogenations of hydroxilated aromatic carbonyl compounds. The process involves sequential reaction of the carbonyl compounds with a combination of inexpensive and readily available tetrachlorosilane and N-halosuccinimide (NXS) under mild conditions in acetonitrile.

II. EXPERMENTAL

All the chemicals were obtained from E-Merck, India (AR grade) and were used without further purification. Melting points were taken in an open capillary tube. IR spectra were recorded on a Shimadzu Dr-8031 instrument. 1H NMR spectra of the synthesized compounds were recorded on a Bruker-Avance (300MHz) and Varian-Gemini (200MHz) spectrophotometer using CDCl3 solvent and TMS as an the internal standard.

A. General Procedure

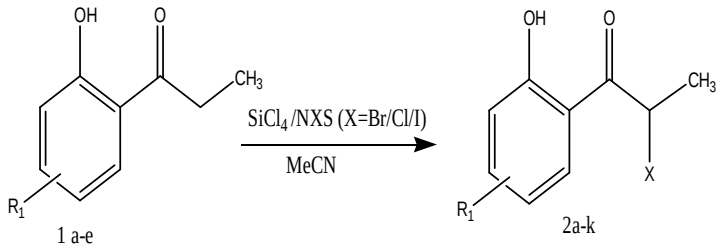
To a mixture of 2-hydroxy aryl ketone (100 mmole) and NXS (200mmole) in acetonitrile at room temperature was added SiCl4 (200 mmole) and the reaction mixture left to stir until the TLC shows disappearance of starting material. Then the reaction mixture was poured in water and extracted with CH_2Cl_2. The extracts were combined, dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by recrystallization using pet. Ether and diethyl ether (3:1).

III. RESULT AND DISCUSSION

Melting points were determined in an open capillary tube and are uncorrected. IR spectra were recorded in KBr on a FT-IR Perkin-Elmer spectrometer. 1HNMR spectra were recorded in $CDCCl_3$ as solvent ant TMS as internal standard. The purity of compounds was checked by TLC on silica gel.

Scheme

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	a	B	C	D	E	f	G	h	I	j	k
R_1	4-CH_3	3-CH_3	5-CH_3	5-Cl	4-Cl	4-CH_3	3-CH_3	5-CH_3	5-Cl	4-Cl	3-CH_3
X	Br	Br	Br	Br	Br	Cl	Cl	Cl	I	I	I

2-Bromo-1-(2-Hydroxy-4-methyl-phenyl)-propan-1-one (2a):Yield 68 %, m.p.144^{0}C; IR (KBr): 1645 (>C=O), 1590 (>C=C<), 1167 (>C-O) cm-1; ^{1}HNMR (CDCl3): δ1.21 (d, 3H,-CHX- CH3), 2.29(s, 3H, 4Ar-CH3), δ3.05 (q, 1H,-CHX-CH3), δ8.12 (m,1H, 3Ar-H)ppm; Anal. Calcd. For C10H11BrO2, C, 49.41; H, 4.56; Br, 32.87;, 13.16 %.

2-Bromo-1-(2-Hydroxy-3--methyl-phenyl)-propan-1-one (2b):Yield 68 %, m.p.144^{0}C; IR (KBr): 1647 (>C=O), 1595 (>C=C<), 1167 (>C-O) cm-1; ^{1}HNMR (CDCl3): δ1.21 (d, 3H,-CHX- CH3), 2.37(s, 3H, 4Ar-CH3), δ3.02 (q, 1H,-CHX-CH3), δ8.12 (m,1H, 3Ar-H)ppm; Anal. Calcd. For C10H11BrO2, C, 49.41; H, 4.56; Br, 32.87;, 13.16 %.

2-Bromo-1-(2-Hydroxy-5-methyl-phenyl)-propan-1-one (2c):Yield 68 %, m.p.148^{0}C; IR (KBr): 1645 (>C=O), 1591 (>C=C<), 1167 (>C-O) cm-1; ^{1}HNMR (CDCl3): δ1.21 (d, 3H,-CHX- CH3), 2.37(s, 3H, 4Ar-CH3), δ3.02 (q, 1H,-CHX-CH3), δ8.17 (m,1H, 3Ar-H)ppm; Anal. Calcd. For C10H11BrO2, C, 49.41; H, 4.56; Br, 32.87;, 13.16 %.

2-Bromo-1-(2-Hydroxy-5-chloro-phenyl)-propan-1-one (2d):Yield 81 %, m.p.168^{0}C; IR (KBr): 1647 (>C=O), 1593 (>C=C<), 1169 (>C-O) cm-1; ^{1}HNMR (CDCl3): δ1.20 (d, 3H,-CHX- CH3), 2.38(s, 3H, Ar-CH3), δ3.02 (q, 1H,-CHX-CH3), δ8.15 (m,1H, 3Ar-H)ppm; Anal. Calcd. For $C_9H_8BrClO2$, C, 41.02; H, 3.06; Br, 30.62; Cl , 13.45; O, 12.14 %.

2-Bromo-1-(2-Hydroxy-5-chloro-phenyl)-propan-1-one (2e):Yield 62 %, m.p.158^{0}C; IR (KBr): 1645 (>C=O), 1590 (>C=C<), 1167 (>C-O) cm-1; ^{1}HNMR (CDCl3): δ1.21 (d, 3H,-CHX- CH3), 2.37(s, 3H, 4Ar-CH3), δ3.02 (q, 1H,-CHX-CH3), δ8.12 (m,1H, 3Ar-H)ppm; Anal. Calcd. For $C_9H_8BrClO2$, C, 41.02; H, 3.06; Br, 30.62; Cl , 13.45; O, 12.14 %.

2-Chloro-1-(2-Hydroxy-4-methyl-phenyl)-propan-1-one (2f):Yield 69 %, m.p.128^{0}C; IR (KBr): 1645 (>C=O), 1590 (>C=C<), 1167 (>C-O) cm-1; ^{1}HNMR (CDCl3): δ1.21 (d, 3H,-CHX- CH3), 2.37(s, 3H, 4Ar-CH3), δ3.02 (q, 1H,-CHX-CH3), δ8.12 (m,1H, 3Ar-H)ppm; Anal. Calcd. For $C_9H_8BrClO2$, C, 60.46; H, 5.58; Cl , 17.85; O, 16.11 %.

2-Chloro-1-(2-Hydroxy-3-methyl-phenyl)-propan-1-one (2g):Yield 72 %, m.p.138^{0}C; IR (KBr): 1649 (>C=O), 1595 (>C=C<), 1169 (>C-O) cm-1; ^{1}HNMR (CDCl3): δ1.21 (d, 3H,-CHX- CH3), 2.38(s, 3H, 4Ar-CH3), δ3.03 (q, 1H,-CHX-CH3), δ8.10 (m,1H, 3Ar-H)ppm; Anal. Calcd. For $C_9H_8BrClO2$, C, 60.46; H, 5.58; Cl , 17.85; O, 16.11 %.

2-Chloro-1-(2-Hydroxy-5-methyl-phenyl)-propan-1-one (2h):Yield 62 %, m.p.132^{0}C; IR (KBr): 1644 (>C=O), 1595 (>C=C<), 1167 (>C-O) cm-1; ^{1}HNMR (CDCl3): δ1.21 (d, 3H,-CHX- CH3), 2.39(s, 3H, 4Ar-CH3), δ3.05 (q, 1H,-CHX-CH3), δ8.17 (m,1H, 3Ar-H)ppm; Anal. Calcd. For $C_9H_8BrClO2$, C, 60.46; H, 5.58; Cl , 17085; O, 16.11 %.

2-Iodo-1-(2-Hydroxy-5-chloro-phenyl)-propan-1-one (2i):Yield 80 %, m.p.155^{0}C; IR (KBr): 1647 (>C=O), 1594 (>C=C<), 1162 (>C-O) cm-1; ^{1}HNMR (CDCl3): δ1.21 (d, 3H,-CHX- CH3), 2.37(s, 3H, 4Ar-CH3), δ3.02 (q, 1H,-CHX-CH3), δ8.12 (m,1H, 3Ar-H)ppm; Anal. Calcd. For $C_9H_8BrClO2$, C, 60.46; H, 5.58; Cl , 17085; O, 16.11 %.

2-Iodo-1-(2-Hydroxy-4-methyl-phenyl)-propan-1-one (2j):Yield 62 %, m.p.148^{0}C; IR (KBr): 1645 (>C=O), 1590 (>C=C<), 1167 (>C-O) cm-1; ^{1}HNMR (CDCl3): δ1.21 (d, 3H,-CHX- CH3), 2.37(s, 3H, 4Ar-CH3), δ3.02 (q, 1H,-CHX-CH3), δ8.12 (m,1H, 3Ar-H)ppm; Anal. Calcd. For $C_9H_8BrClO2$, C, 34.81; H, 2.60; Cl , 11.42; I, 40.87; O, 10.31 %.

2-Iodo-1-(2-Hydroxy-4-methyl-phenyl)-propan-1-one (2k):Yield 62 %, m.p.148^{0}C; IR (KBr): 1645 (>C=O), 1590 (>C=C<), 1167 (>C-O) cm-1; ^{1}HNMR (CDCl3): δ1.21 (d, 3H,-CHX- CH3), 2.37(s, 3H, 4Ar-CH3), δ3.02 (q, 1H,-CHX-CH3), δ8.12 (m,1H, 3Ar-H)ppm; Anal. Calcd. For $C_9H_8BrClO2$, C, 34.81; H, 2.60; Cl , 11.42; I, 40.87; O, 10.31 %.

IV. CONCLUSIONS

The we have developed a practical and efficient method for the α monohaloganation of carbonyl compounds using cheap and readily available tetrachlorosilane and N-halosuccinimide. This method can be applied to a wide range of carbonyl compounds. The

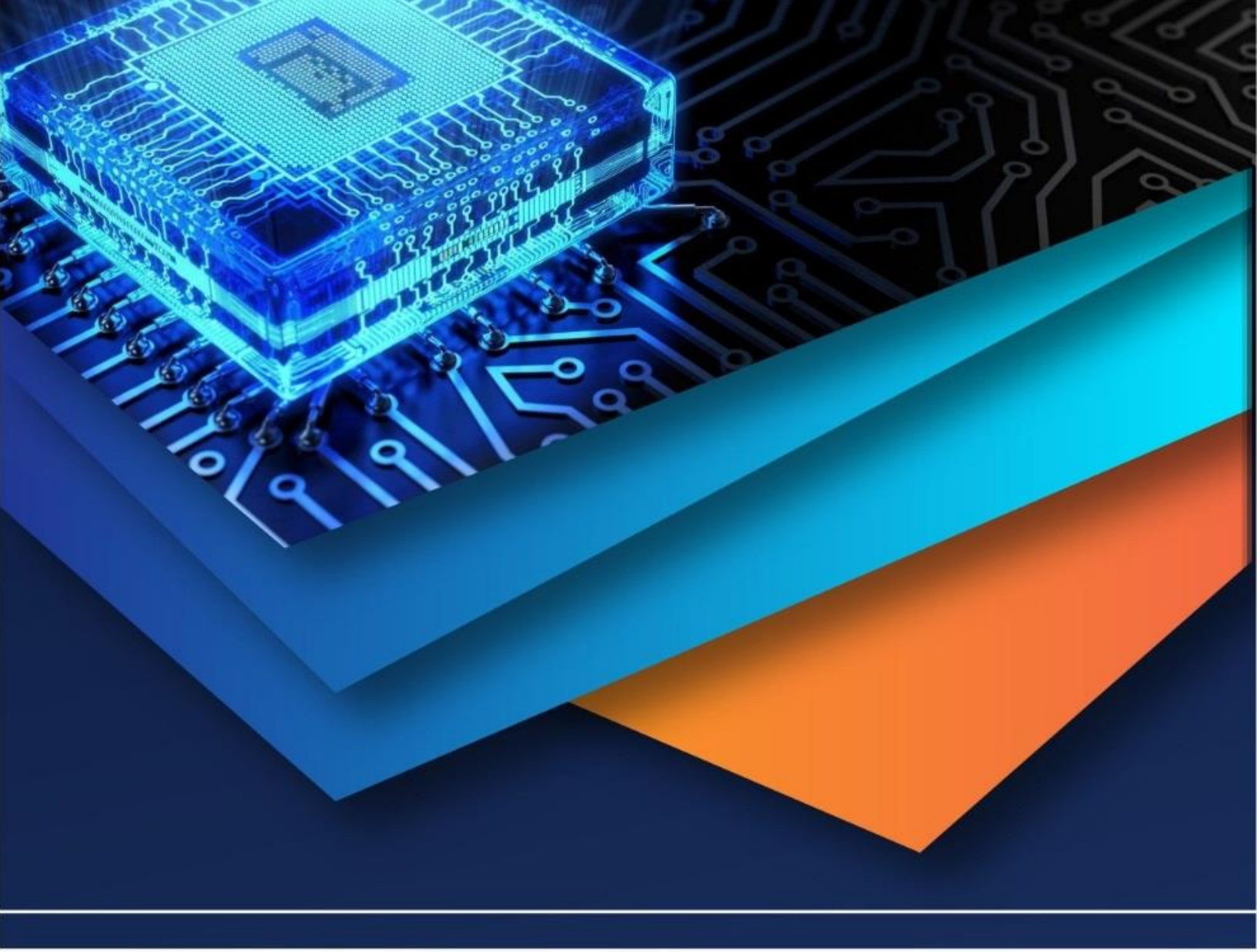
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halogen atom can be introduced to the substrate with high rigeoselectivity. The mild reaction conditions, easy work up procedure and simple operation are advantages of this procedure.

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