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# Mortar-Pestle Assisted Electrophilic Nitration of Aromatic Compounds by Quinolinium bound Hypervalent Chromium Reagents using Sodium Nitrite and Thiocyanation using Ammonium Thiocyanate

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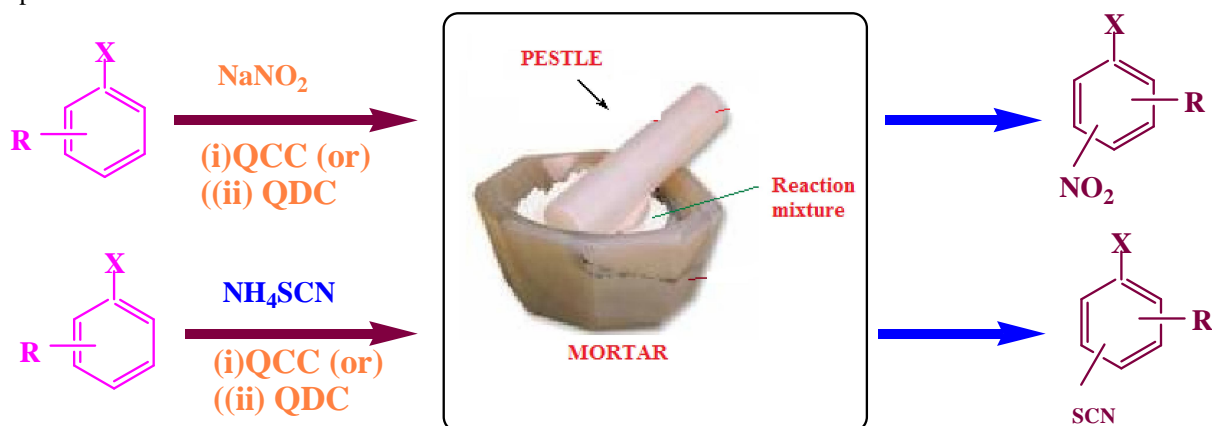
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(\*Present work forms a part of the thesis of to be submitted to the Department of Chemistry Rayalaseema University, Kurnool (A.P), by Kodali Satish Babu (PP.CHE-028)\*)

## Graphical Abstract



Where  $X = OH, CHO, NH_2$ ;  $R = EWG$  or  $EDG$

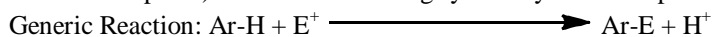
## Scheme-1: QCC/QDC mediated Mortar-Pestle EAS Reactions

**Abstract:** In the present study we have accomplished Grind-Stone assisted (GSA) Electrophilic nitration of aromatic compounds by quinolinium bound hypervalent Chromium reagents using sodium nitrite and thiocyanation using ammonium thiocyanate. Quinolinium dichromate (QDC) and quinolinium chlorochromate (QCC) have been explored as Quinolinium bound hypervalent Chromium reagents for this purpose. The reactions underwent smoothly under solvent free (solid state) conditions. Both the developed protocols revealed significant rate accelerations and offered very good product yields. However, the nitration reactions were relatively faster than the corresponding thiocyanation reactions with more product yields. Observed rate enhancements in GSA reactions could be attributed to faster activation of a larger fraction of reactant molecules by absorbing the heat arising from frictional (mechanical) energy due to grinding the reactants with a mortar in a pestle under solvent free conditions. Thus, the developed protocols are more greenery than the conventional solvent/ liquid phase reactions.

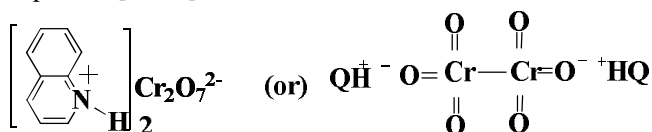
**Keywords:** Mortar-Pestle technique; Quinolinium chlorochromate; Quinolinium dichromate; nitration using  $\text{NaNO}_2/\text{KHSO}_4$ ; Thiocyanation using  $\text{NH}_4\text{SCN}/\text{KHSO}_4$ ; Aromatic compounds; Rate enhancements

## I. INTRODUCTION

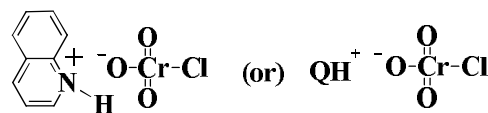
Electrophilic aromatic substitution (EAS) reactions are important tools in synthetic organic chemist's toolbox, which allow the introduction of many different functional groups onto an aromatic ring system [1]. The overall reaction involves the substitution of hydrogen (or sometimes multiple H) on the aromatic ring system by an electrophile, designated  $\text{E}^+$ .



The electrophilic nitration and thiocyanation of aromatic and heteroaromatic compounds afforded carbon-heteroatom bond (C-N, and C-S) formation reactions in organic synthesis, which opened a gateway for the synthesis of several important intermediates that are useful as precursors for the production of pharmaceutical, agrochemical and industrial products [2,3]. Over the years several commercial processes were developed to produce such materials [3-8]. But many classical protocols pertaining to nitration and thiocyanation procedures commonly lead to mixtures of regioisomers. Unspent acids sent through industrial laboratory drains often cause environmental pollution. In recent years several new approaches have been developed to gain control over the regiochemistry of the reactions [9, 10]. Quinolinium dichromate [11, 12] and quinolinium chlorochromate [13, 14] are the few most effective "Onium halo chromates" and "Onium dichromates", which were earlier explored for oxidation as well as oxyhalogenation of organic compounds [11-18].

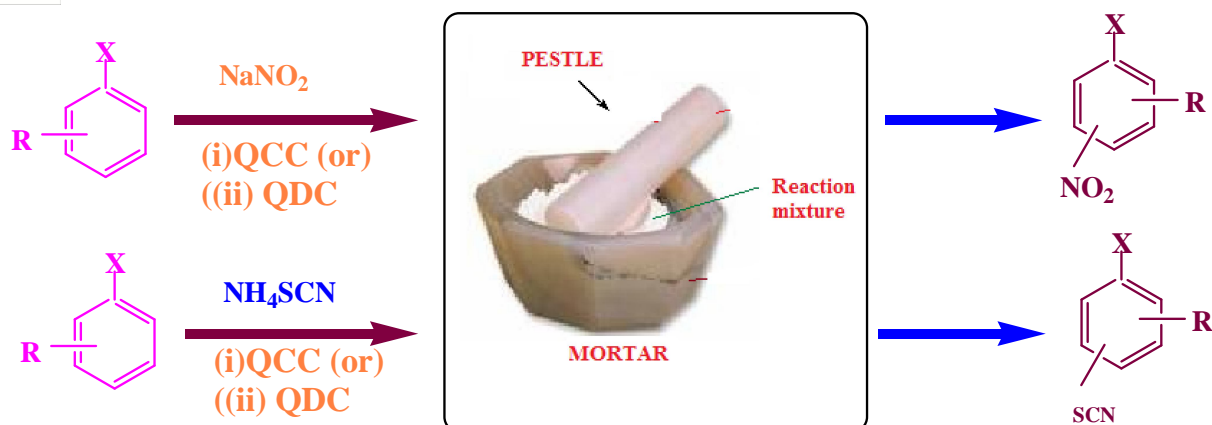


**(I) Quinolinium dichromate (QDC)**



**(II) Quinolinium chlorochromate (QCC)**

Recently, our research has accomplished the use of isoquinolinium dichromate (IQDC) and isoquinolinium chlorochromate (IQCC) as efficient catalysts to trigger oxidative halogenation of aromatic hydrocarbons with  $\text{KBr}/\text{KI}$  and  $\text{KHSO}_4$  under acid-free conditions. Reactions were assisted by sonication, microwave irradiation techniques. On the other hand reactions were also taken up in micellar media. In all these protocols reaction times reduced highly significantly followed by corresponding mono halo derivatives in very good yield with high regioselectivity [19-21]. Recently the authors have also explored the use of quinolinium bound chromium (VI) reagents (QDC (I) and QCC (II)) for efficient electrophilic aromatic nitration and thiocyanation reactions using sodium nitrate and ammonium thiocyanate in micellar media, and ultrasonic and microwave assisted conditions [22]. Solvent-free Mortar-Pestle Grind-Stone) assisted reactions are also other important protocols according to the Green-Chemistry principles as suggested by Paul Anastas and John Walter in the green chemistry formulations [23]. Literature survey revealed several reports published pioneering workers in chemical sciences [24, 25]. In the present study, the authors embarked on exploring Mortar-Pestle technique as a green synthetic method for quinolinium dichromate and quinolinium chlorochromate triggered *in situ* electrophilic nitration of aromatic compounds using sodium nitrite and thiocyanation of aromatic compounds by using thiocyanate using under solvent free conditions. Nevertheless, we have studied the reactions under conventional solution phase conditions as reported in our recent publication [22], for comparison the data are referred in tables 1-4.



Where X= OH,CHO,NH<sub>2</sub> ;R= EWG or EDG

### Scheme-1: QCC/QDC mediated Mortar-Pestle EAS Reactions

#### II. EXPERIMENTAL DETAILS

All the reagents and substrates used were of laboratory reagent grade, which were obtained from E-Merck, SD –fine chemicals or Alfa-Aesar. Acetonitrile (MeCN) was purified according to standard literature procedure. Agate Mortar and Pestle Set (200 mm x 165mm x 50 mm) used in this study, was procured from SPI- Supplies. Quinolinium dichromate [(C<sub>9</sub>H<sub>7</sub>NH<sup>+</sup>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>] or QDC) was prepared according to the method of Balasubramanian et al. [8, 9], while Quinolinium chlorochromate (QCC) was prepared according to the method of Singh et al [10].

##### A. General procedure for aromatic nitration and thiocyanation under conventional conditions using (QDC/QCC) reagent:

Round-Bottomed reaction containing centimolar (0.01 mol) organic substrate, 0.02 moles of NaNO<sub>2</sub> and about 0.015 moles of Cr(VI) reagent (QDC/QCC), about 50 mg of KHSO<sub>4</sub>, and solvent (MeCN) was immersed in oil bath placed on a hot-plate/magnetic stirrer and allowed to react with constant stirring at room temperature. After completion of the reaction (as confirmed by TLC), the reaction mixture was treated with 5% sodium thiosulphate solution, followed by the addition of ethyl acetate. The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum, purified with column chromatography using pet-ether and ethyl acetate to get pure product. In case of aromatic compounds nitro aromatic derivatives were obtained, which were analyzed from spectroscopic studies. Procedure for thiocyanation reactions is almost similar, and the reactions are carried out with 0.02 moles of NH<sub>4</sub>SCN.

##### B. General procedure for Mortar-Pestle Assisted aromatic nitration and thiocyanation reactions:

A mixture of the aromatic compound (0.01 mol), NaNO<sub>2</sub> (0.02 moles), about 0.015 moles of Cr(VI) reagent (QDC/QCC), about 50 mg of KHSO<sub>4</sub> was taken in a Agate Mortar and ground with a pestle at room temperature, till a slurry was observed. Progress of the reaction was monitored with TLC. Upon completion of the reaction, the reaction mixture was treated with sodium thiosulfate; the organic layer was diluted with dichloromethane (DCM), and separated from aqueous layer. Crude product mixture was purified with ethyl acetate DCM mixture. The purity was checked with TLC. The products were identified by comparison of their NMR, IR spectra, TLC and physical data with those of authentic samples. For thiocyanation reactions 0.02 moles of NH<sub>4</sub>SCN is used under otherwise similar conditions.

#### III. RESULTS AND DISCUSSION

##### A. Quinolinium Chlorochromate/ Nano<sub>2</sub> And Quinolinium Dichromate/Nano<sub>2</sub> Triggered Nitration Of Aromatic Compounds

The nitration reactions of aromatic compounds were conducted using quinolinium dichromate (QDC)/NaNO<sub>2</sub>, and quinolinium chlorochromate (QCC)/NaNO<sub>2</sub> combinations in aqueous KHSO<sub>4</sub> under mineral acid free conditions (Scheme -1). Described methods worked out well for an array of functionalities such as phenols, anilines or aldehydes etc. The yields of major products are compiled in tables 1 to 3. The nitration of aromatic compounds required four to five hours under conventional conditions at reflux temperatures, which were reduced to few (30 to 40) minutes in Mortar-Pestle assisted reactions followed by considerable yield

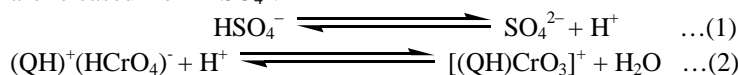
enhancements. The products of these reactions were characterized by spectroscopic and physical data with authentic samples and found to be satisfactory with literature reports [3-7,22].

**B. Quinolinium Chlorochromate/ $\text{NH}_4\text{SCN}$  And Quinolinium Dichromate/  $\text{NH}_4\text{SCN}$  Triggred Thiocyanation Of Aromatic Compounds**  
Quinolinium dichromate (QDC)/  $\text{NH}_4\text{SCN}$ , and quinolinium chlorochromate (QCC)/  $\text{NH}_4\text{SCN}$  triggered thiocyanation of aromatic compounds in aqueous  $\text{KHSO}_4$  under mineral acid free conditions with different functional groups such as phenols, anilines including certain heteroaromatic compounds (Scheme -1). The thiocyanation reactions were generally more sluggish than corresponding nitration reactions, which required more than ten hours under conventional conditions at reflux temperatures (Tables-1 and 2). However, the reaction times are drastically reduced to about 25 to 40 minutes followed by considerable yield enhancements in Mortar-Pestle assisted reactions. Comparison of reaction times and product yields presented in tables 1 and 2 revealed that QDC mediated reactions are generally faster than corresponding QCC mediated reactions. The products of these reactions were characterized by spectroscopic and physical data with authentic samples and found to be satisfactory with literature reports [3-7].

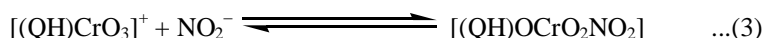
In present work Mortar-pestle assisted solid state grinding reactions appeared to be superior to the corresponding solution phase reactions, because grinding technique is eco-friendly, high yielding, non-hazardous, simple and convenient which requires a mortar and pestle. In solid state molecules are generally arranged tightly and regularly in the crystal. In solution phase molecules are randomly distributed and the molecules are generally solvated. In solution phase reaction occurs due to the random molecular collisions among the reactive species leading to form activated reactive species (activated molecules). It is well known that reaction occurs when activated reactive species decompose or rearrange themselves products are formed. Reactions occurring at high temperatures (sometimes reflux/elevated temperatures) facilitate rate accelerations and there by enhanced yields. Thus reactions taking place is a step-wise process and require lot of time and energy in organic synthesis. But mortar-pestle reactions occurring under solvent free conditions avoid the use of toxic solvents and cumbersome reaction set-up; and reactions take place easily. Rate accelerations in this method could be explained due to the conversion of mechanical energy (kinetic energy exerted due to grinding) into heat energy, which drives the reactant species for a faster/better activation. The kinetic energy supplied during grinding can have several effects on a crystalline solid [24,25] including: heating, reduction of particle size (with concomitant increase in surface area and the generation of fresh surfaces), formation of defects and dislocations in crystal lattices, local melting and even phase changes to alternative polymorphs. Collisions between crystals during grinding can also lead to local deformations and potentially melting. Importantly, grinding also provides mass transfer, i.e. it is a sort of 'stirring'.

### C. Mechanism of the substitution reactions

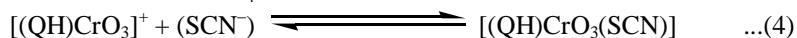
We have also tried to explain the mechanism of the QDC and QCC mediated nitration reaction by considering the nature of Cr(VI) reactive species in the lines of dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) species. On the basis of literature reports and our publications [12,19-22], we feel that protons are released from  $\text{HSO}_4^-$ :



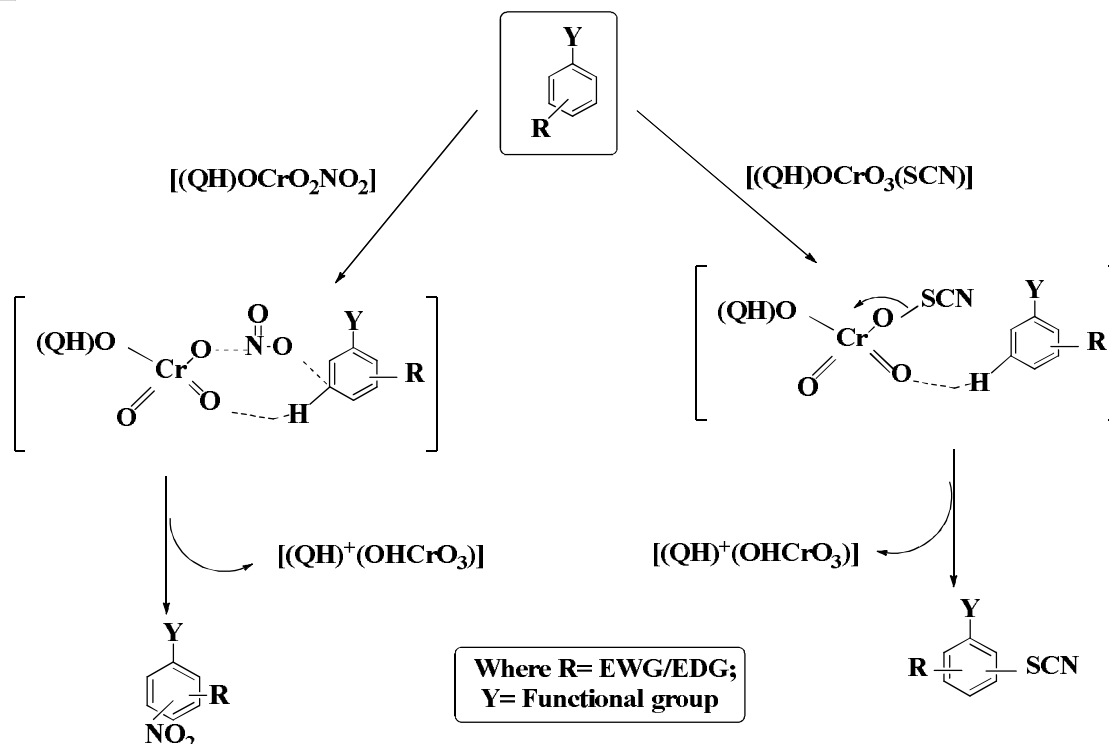
Active species thus formed may further react with nitrite ion to afford  $[(\text{QH})\text{CrO}_3\text{NO}_2]$  species, since the reactions are conducted in excess  $\text{NaNO}_2$ .



Similar type of reactive species could be formed with thiocyanide ( $\text{SCN}^-$ ) ion to afford  $[(\text{QH})\text{CrO}_3(\text{SCN})]$  species, since the reactions are conducted in excess of  $\text{NH}_4\text{SCN}$ .

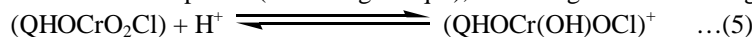


Finally, aromatic substrates undergo electrophilic substitution when the *in situ* formed electrophile ( $\text{NO}_2^+$  or  $\text{SCN}^+$ ) attacks on aromatic ring as shown in the following schematic steps.

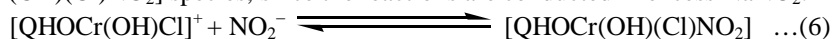


**Scheme-2: QDC Electrophilic aromatic substitution of aromatic compounds**

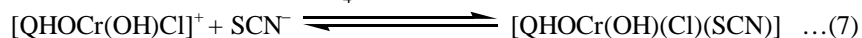
On the other hand, the most plausible mechanism in QCC (Quinolinium chlorochromate) triggered reactions could be proposed by formulating quinolinium chlorochromate (QCC) in the lines of other “onium halo chromate” species [19-22]. Since the reactions are studied in aqueous  $\text{KHSO}_4$  medium, QCC could exist as  $(\text{QHOCrO}_2\text{Cl})$  and its protonated form  $(\text{QHOCr}(\text{OH})\text{Cl})^+$ , by capturing proton ( $\text{H}^+$ ) from the dissociated bisulfate species (according to eq-2), according to the following equilibria.



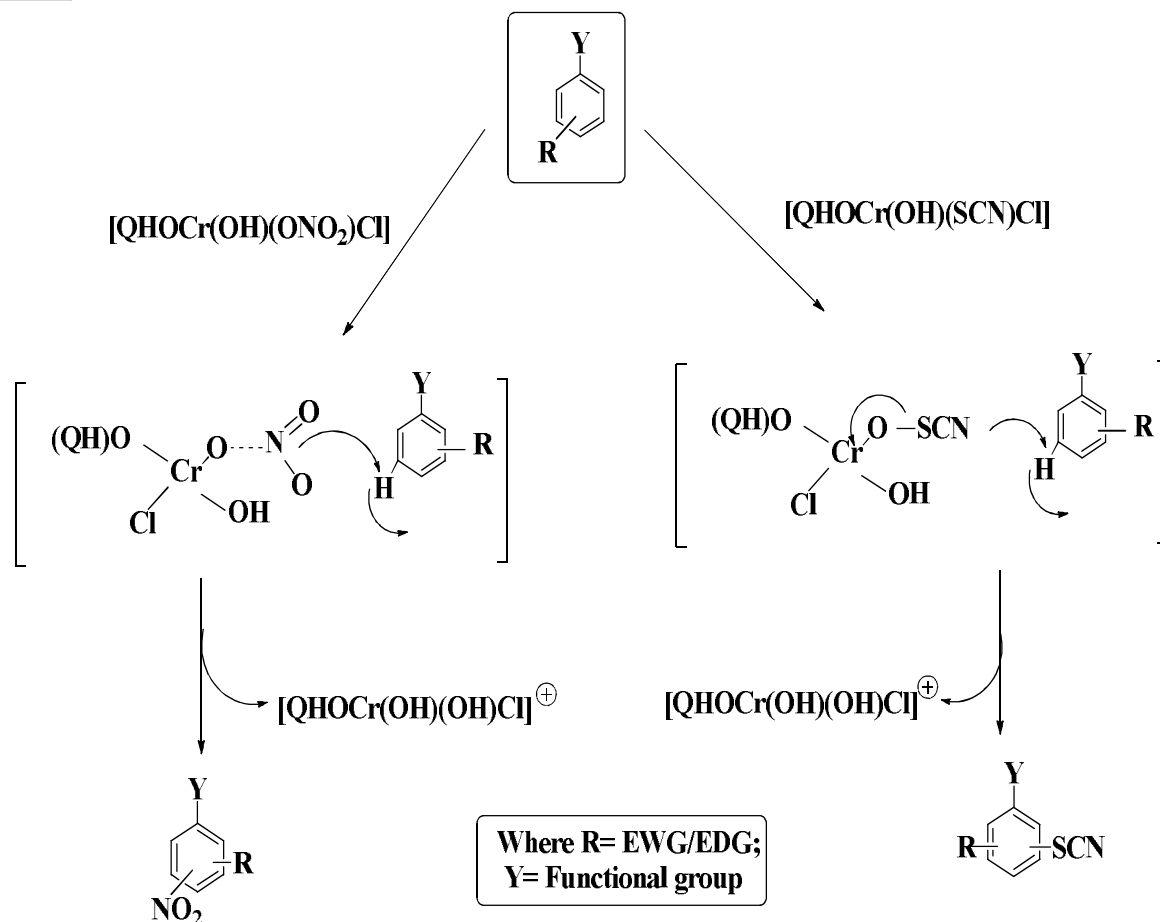
The protonated Cr(VI) species thus formed  $(\text{QHOCr}(\text{OH})\text{Cl})^+$  being a stronger electrophile, may further react with nitrite ion to afford  $[\text{QHOCr}(\text{OH})(\text{Cl})\text{NO}_2]$  species, since the reactions are conducted in excess  $\text{NaNO}_2$ .



Similar type of reactive species could be formed with thiocyanate ( $\text{SCN}^-$ ) ion to afford  $[\text{QHOCr}(\text{OH})(\text{Cl})(\text{SCN})]$  species, since the reactions are conducted in excess of  $\text{NH}_4\text{SCN}$



On the basis of foregoing discussions, mechanism of electrophilic substitution in aromatic substrates could be explained through the attack of electrophile on the aromatic ring ( $\text{NO}_2^+$  released *in situ* from  $[\text{QHOCr}(\text{OH})(\text{Cl})\text{NO}_2]$  for nitration; and  $\text{SCN}^+$  released *in situ* from  $[\text{QHOCr}(\text{OH})(\text{SCN})\text{Cl}]$  for thiocyanation) to afford the products, as shown in the sequence of steps of Scheme-3.



#### IV. CONCLUSIONS

In conclusion, the authors have established Mortar-Pestle assisted quinolinium dichromate (QDC) and quinolinium chlorochromate (QCC) triggered for electrophilic aromatic nitration using sodium nitrite and thiocyanation by using ammonium thiocyanate under solvent free assisted conditions. Mortar-Pestle assisted reactions underwent more efficiently than conventional reactions with very short reaction times and good product yields. However, the reactions were faster with comparatively shorter reaction times, and better yields in nitration reactions than in thiocyanation protocols.

1) *Acknowledgments:* The authors sincerely thank the authorities of Osmania University, Hyderabad; Rayalaseema University, Kurnool; RGUKT, Basar for constant encouragement at all stages of the work.

Table -1. QCC/ $\text{NaNO}_2$  triggered Nitration of aromatic compounds

Entry	Substrate	Product	Conventional (Reference-22)		Mortar-Pestle (Present work)	
			RT (min)	% Yield	RT (min)	% Yield
1	$\text{C}_6\text{H}_5\text{OH}$	$2\text{-NO}_2\text{C}_6\text{H}_4\text{OH}$	60	70	30	75
2	$2\text{-CH}_3\text{C}_6\text{H}_4\text{OH}$	$2\text{-CH}_3\text{-4-NO}_2\text{C}_6\text{H}_3\text{OH}$	60	68	30	70
3	$4\text{-CH}_3\text{C}_6\text{H}_4\text{OH}$	$4\text{-CH}_3\text{-2-NO}_2\text{C}_6\text{H}_3\text{OH}$	60	65	30	75
4	$3\text{-CH}_3\text{C}_6\text{H}_4\text{OH}$	$3\text{-CH}_3\text{-4-NO}_2\text{C}_6\text{H}_3\text{OH}$	60	70	30	70
5	$2\text{-ClC}_6\text{H}_4\text{OH}$	$4\text{-NO}_2\text{-2-ClC}_6\text{H}_3\text{OH}$	65	62	30	70
6	$4\text{-ClC}_6\text{H}_4\text{OH}$	$2\text{-NO}_2\text{-4-ClC}_6\text{H}_3\text{OH}$	70	60	30	75

7	4-Br C <sub>6</sub> H <sub>4</sub> OH	2-NO <sub>2</sub> 4-Br C <sub>6</sub> H <sub>3</sub> OH	60	65	35	73
8	4-OH C <sub>6</sub> H <sub>4</sub> OH	2- NO <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -1,4-OH	50	72	30	75
9	α-Naphthol	2- NO <sub>2</sub> -1-Naphthol	55	70	30	72
10	β-Naphthol	1-NO <sub>2</sub> -2-Naphthol	60	70	30	70
11	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	185	74	40	75
12	C <sub>6</sub> H <sub>5</sub> CHO	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	190	73	50	75
13	4- NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OH	2,-4- NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OH	190	73	50	75
14	4-Cl- C <sub>6</sub> H <sub>4</sub> CHO	4-Cl-3-NO <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> CHO	80	60	45	65
15	2-OH C <sub>6</sub> H <sub>4</sub> CHO	2-OH-5-NO <sub>2</sub> - C <sub>6</sub> H <sub>3</sub> CHO	80	65	45	62
16	4-OH C <sub>6</sub> H <sub>4</sub> CHO	4-OH-3-NO <sub>2</sub> - C <sub>6</sub> H <sub>3</sub> CHO	80	60	40	65
17	C <sub>6</sub> H <sub>5</sub> COOH	3-NO <sub>2</sub> - C <sub>6</sub> H <sub>4</sub> COOH	190	76	50	75
18	Furan	2-NO <sub>2</sub> furan	170	69	50	73
19	Thiophene	2-NO <sub>2</sub> thiophene	190	73	50	75
30	Naphthalene	1-NO <sub>2</sub> Naphthalene	300	74	55	76
21	Cl C <sub>6</sub> H <sub>5</sub>	1-Cl, 2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	180	76	40	75
22	Br- C <sub>6</sub> H <sub>5</sub>	1-Br, 2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	190	75	50	76
23	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	1- CH <sub>3</sub> , 2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	180	75	55	74
24	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	2- NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	190	76	60	77
30	2-OH C <sub>6</sub> H <sub>4</sub> COOH	2-OH 4-NO <sub>2</sub> C <sub>6</sub> H <sub>3</sub> COOH	300	74	60	78
26	C <sub>6</sub> H <sub>5</sub> CN	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CN	230	76	60	76
27	C <sub>6</sub> H <sub>5</sub> CONH <sub>2</sub>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CONH <sub>2</sub>	240	72	64	76

Table -2. QDC/NaNO<sub>2</sub> triggered Nitration of aromatic compounds

Entry	Substrate	Product	Conventional (Reference-22)		Mortar-Pestle (Present work)	
			RT (min)	% Yield	RT (min)	% Yield
1	$C_6H_5OH$	$2-NO_2C_6H_4OH$	45	70	30	73
2	$2-CH_3 C_6H_4OH$	$2-CH_3- 4-NO_2 C_6H_3OH$	45	68	30	69
3	$4-CH_3 C_6H_4OH$	$4-CH_3- 2-NO_2 C_6H_3OH$	45	65	30	72
4	$3-CH_3 C_6H_4OH$	$3-CH_3- 4-NO_2 C_6H_3OH$	45	70	23	70
5	$2-Cl C_6H_4OH$	$4-NO_2 2-Cl C_6H_3OH$	50	62	26	70
6	$4-Cl C_6H_4OH$	$2-NO_2 4-Cl C_6H_3OH$	50	60	30	65
7	$4-Br C_6H_4OH$	$2-NO_2 4-Br C_6H_3OH$	55	65	30	68
8	$4-OH C_6H_4OH$	$2- NO_2 C_6H_3-1,4-OH$	40	72	30	70
9	$\alpha$ -Naphthol	$2- NO_2-1$ -Naphthol	45	70	23	72
10	$\beta$ -Naphthol	$1-NO_2-2$ -Naphthol	45	70	22	68
11	$C_6H_5NH_2$	$3-NO_2 C_6H_4NH_2$	60	74	35	77
12	$C_6H_5CHO$	$3-NO_2 C_6H_4NH_2$	80	73	55	79
13	$4- NO_2C_6H_4OH$	$2,4- NO_2C_6H_4OH$	70	73	45	75
14	$4-Cl- C_6H_4CHO$	$4-Cl-3-NO_2C_6H_3CHO$	65	60	40	62
15	$2-OH C_6H_4CHO$	$2-OH-5-NO_2- C_6H_3CHO$	65	65	40	62
16	$4-OH C_6H_4CHO$	$4-OH-3-NO_2- C_6H_3CHO$	60	60	35	65
17	$C_6H_5COOH$	$3-NO_2- C_6H_4COOH$	160	76	50	75
18	Furan	$2-NO_2$ furan	140	69	45	73
19	Thiophene	$2-NO_2$ thiophene	150	73	50	75
30	Naphthalene	$1-NO_2$ Naphthalene	175	74	50	76
21	$Cl C_6H_5$	$1-Cl, 2-NO_2 C_6H_4$	160	76	35	75
22	$Br- C_6H_5$	$1-Br, 2-NO_2 C_6H_4$	150	75	40	76
23	$CH_3 C_6H_5$	$1- CH_3, 2-NO_2 C_6H_4$	140	75	45	74
24	$C_6H_5 CH_2OH$	$2- NO_2 C_6H_4CH_2OH$	130	76	50	77
30	$2-OH C_6H_4COOH$	$2-OH 4-NO_2 C_6H_3COOH$	180	74	50	78
26	$C_6H_5CN$	$3-NO_2 C_6H_4CN$	185	76	65	76
27	$C_6H_5CONH_2$	$3-NO_2 C_6H_5CONH_2$	190	72	74	76

Table-3: Thiocyanation of aromatic compounds in presence of QCC/NH<sub>4</sub>SCN

Entry	Substrate	Product	Conventional (Reference-22)		Mortar-Pestle (Present work)	
			R. T (hrs)	Yield (%)	R. T (min)	Yield (%)
1	$C_6H_5NH_2$	4- $SCNC_6H_4NH_2$	11	77	30	85
2	2- $ClC_6H_4NH_2$	2-Cl 4- $SCNC_6H_4NH_2$	10	84	35	83
3	3- $CH_3O C_6H_4NH_2$	3- $CH_3O$ 4- $SCNC_6H_4NH_2$	10	78	45	81
4	N- $CH_3C_6H_5NH_2$	4- $SCN$ N- $CH_3C_6H_5NH_2$	11	81	50	78
5	Diphenyl amine	4-Thiocyanato diphenylamine	13	86	45	84
6	$C_6H_5OH$	2- $SCNC_6H_4OH$	11	85	35	81
7	4- $CH_3C_6H_4OH$	4- $CH_3$ 2- $SCNC_6H_3OH$	10	79	45	85
8	4- $NO_2C_6H_4OH$	4- $NO_2$ 2- $SCNC_6H_3OH$	13	83	50	79
9	4- $ClC_6H_4OH$	4- $Cl$ 2- $SCNC_6H_3OH$	13	77	35	82
10	2- $NO_2C_6H_4OH$	2- $NO_2$ 4- $SCNC_6H_3OH$	11	82	45	89
11	Pyrrole	2-Thiocyanato 1H-pyrrole	12	88	50	90
12	Furan	2-Thiocyanato furan	11	82	40	81
13	Thiophene	2-Thiocyanato thiophene	13	84	45	87
14	Indole	3-Thiocyanato 1H-indole	12	82	50	84
15	5-Br indole	5-Bromo 3-thiocyanato indole	13	72	35	85
16	N-Methyl indole	3-thiocyanato N-Methyl- indole	12	76	45	90

Table-4: Thiocyanation of aromatic compounds in presence of QDC/ $NH_4SCN$ 

Entry	Substrate	Product	Conventional (Reference-22)		Mortar-Pestle (Present work)	
			R. T (hrs)	Yield (%)	R. T (min)	Yield (%)
1	$C_6H_5NH_2$	4- $SCNC_6H_4NH_2$	10	82	30	78
2	2- $ClC_6H_4NH_2$	2-Cl 4- $SCNC_6H_4NH_2$	12	74	30	74
3	3- $CH_3O C_6H_4NH_2$	3- $CH_3O$ 4- $SCNC_6H_4NH_2$	11	77	30	77
4	N- $CH_3C_6H_5NH_2$	4- $SCN$ N- $CH_3C_6H_5NH_2$	12	72	30	72
5	Diphenyl amine	4-Thiocyanato diphenylamine	14	74	35	81
6	$C_6H_5OH$	2- $SCNC_6H_4OH$	13	69	30	81
7	4- $CH_3C_6H_4OH$	4- $CH_3$ 2- $SCNC_6H_3OH$	12	76	40	77
8	4- $NO_2C_6H_4OH$	4- $NO_2$ 2- $SCNC_6H_3OH$	14	80	40	72
9	4- $ClC_6H_4OH$	4- $Cl$ 2- $SCNC_6H_3OH$	14	77	30	87
10	2- $NO_2C_6H_4OH$	2- $NO_2$ 4- $SCNC_6H_3OH$	12	80	35	79
11	Pyrrole	2-Thiocyanato 1H-pyrrole	11	81	30	91
12	Furan	2-Thiocyanato furan	13	62	40	72
13	Thiophene	2-Thiocyanato thiophene	14	79	40	82
14	Indole	3-Thiocyanato 1H-indole	13	77	30	77
15	5-Br indole	5-Bromo 3-thiocyanato indole	14	69	40	69
16	N-Methyl indole	3-thiocyanato N-Methyl- indole	12	76	35	88

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