Asian Journal of Green Chemistry 2 (2018) 70-84

Contents lists available at Avicenna Publishing Corporation (APC)

Asian Journal of Green Chemistry

Journal homepage: www.ajgreenchem.com

Orginal Research Article

Quinolinium bound chromium(VI) reagents for efficient electrophilic aromatic nitration and thiocyanation reactions using sodium nitrate and ammonium thiocyanate

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ARTICLE INFORMATION

Received: 19 October 2017
Received in revised: 16 Novamber 2017
Accepted: 17 Novamber 2017
Available online: 11 December 2017

DOI: 10.22631/ajgc.2017.101557.1031

KEYWORDS

Quinolinium chlorochromate
Quinolinium dichromate
$NaNO_2/KHSO_4$
Nitration
$NH_4SCN/KHSO_4$

ABSTRACT

Quinolinium dichromate (QDC) and quinolinium chlorochromate (QCC) were studied as efficient reagents for electrophilic aromatic nitration using sodium nitrite and thiocyanation by using ammonium thiocyanate under conventional, ultrasonic and solvent-free microwave assisted conditions. The microwave-assisted protocols exhibited remarkable rate acceleration and offered selective thiocyanation of the aromatic and heteroaromatic compounds with good yields. Addition of anionic (SDS) micelle to the reaction medium afforded considerable rate enhancements, while cationic (CTAB) and nonionic (Tx-100) micelles did not affect the rate noticeably. These protocols have were extended to regioselective thiocyanation of various aromatic compounds. Results were are completely similar to the nitration protocols. However, the reactions revealed comparatively shorter reaction times, and better yields in nitration reactions than in thiocyanation protocols. Catalytic effect of the SDS was attributed to the electrostatic stabilization of the cationic electrophile (NO_2^+ in nitration, and SCN^+ in thiocyanation).

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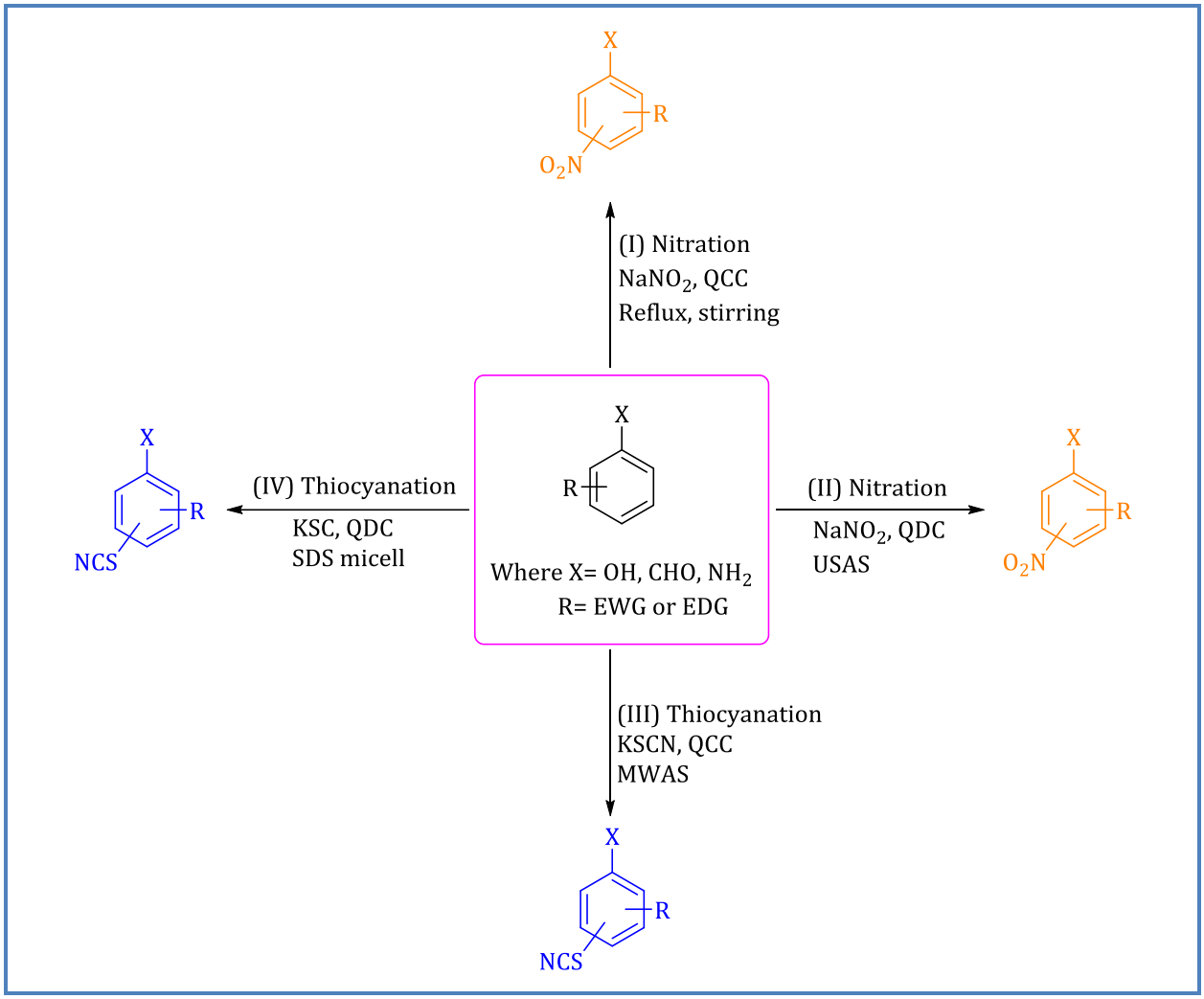
Graphical Abstract



Introduction

Electrophilic aromatic substitution (EAS) reactions occupy a prime place in synthetic organic chemistry, which introduce different functional groups on an aromatic ring system [1, 2]. Overall electrophilic aromatic substitution reaction involves the substitution of hydrogen (or sometimes multiple H) on the aromatic ring system by an electrophile, designated E^+.

Nitration and thiocyanation of the aromatic and heteroaromatic compounds are typical electrophilic substitution reactions which affect the formation of carbon-heteroatom (C–N, and C–S) bond formation reactions in the organic synthesis. Compounds obtained by these reactions are useful as precursors for the production of pharmaceutical, agrochemical and industrial products. Over the years, several commercial processes were developed to produce such materials. However, many of the classical protocols pertaining to the nitration and thiocyanation procedures commonly lead to

mixtures of regioisomers. The unspent acids left out in these protocols often cause environmental pollution. In recent years, several new approaches have been developed to control the regiochemistry of the reactions [3–20].

Recently, we have accomplished the use of quinolinium dichromate and quinolinium chlorochromate as efficient catalysts to trigger oxidative bromination and iodination of aromatic hydrocarbons with KBr/KI and $KHSO_4$ under acid-free conditions. Reaction times reduced significantly under the sonication, followed by corresponding mono bromo derivatives with a good yield and high regioselectivity [21]. In the present study, the authors embarked on exploring quinolinium dichromate and quinolinium chlorochromate as efficient reagents to trigger in situ electrophilic nitration and thiocyanation of aromatic compounds using sodium nitrite and thiocyanate respectively. Neverthless, sevral "Onium halochromates and dichromates" were earlier explored for oxidation as well as oxyhalogenation of the organic compounds [22–24].

In this study, the authors also explored the use of micelle forming surfactants, ultrasound and microwave to assist the QCC and QDC mediated reactions with a view to accelerate reaction rates for achieving better yields as well as improving the greenery of the reaction protocols (Scheme 1) [25].

Experimental

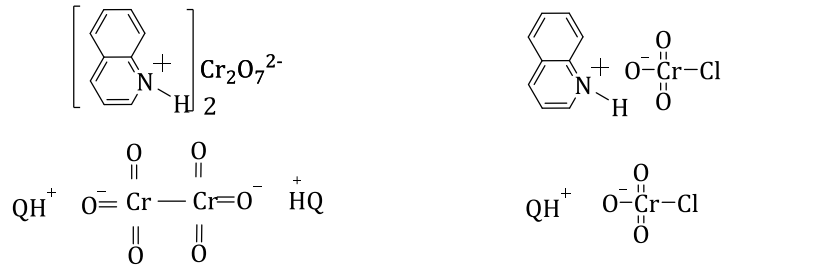
Matreials and methods

Acetonitrile (MeCN) was purified according to the standard literature procedures [26]. Binary compositions of the acetonitrile and water were used as solvent in the present investigation. Laboratory distilled water was further purified over alkaline $KMnO_4$ and acidified $K_2Cr_2O_7$ in a sequence. Quinolinium dichromate ($[(C_9H_7NH^+)_2\ Cr_2O_7]$ or QDC) was prepared according to the method of *Bala Subramanian* et al. [22, 23]. Quinolinium chlorochromate (QCC) was prepared according to the reported method of *Singh* et al. [24]. The purity of the QCC was checked by iodometric method, according to standard procedures. The other chemicals used were of either Analar BDH or Merck samples.

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

A centimolar (0.01 mol) organic substrate, 0.02 mol of $NaNO_2$ and about 0.015 moles of Cr(VI) reagent (QDC/QCC), about 50 mg of $KHSO_4$, and solvent (MeCN) were taken in a previously cleaned in a round bottom flask and stirred for about 1 to 2 h at room temperature. After completion of the reaction, as confirmed by TLC, the reaction mixture is treated with 5% sodium thiosulfate solution,

Scheme 1. Structure of QDC and QCC



Quinolinium dichromate (QDC) Quinoliniumchlorochromate (QCC)

followed by the addition of ethyl acetate. The organic layer was separated, dried over Na_2SO_4 and evaporated under vacuum. Then, it was purified by column chromatography using pet-ether and ethyl acetate to get pure product. In case of nitration of aromatic compounds, nitroaromatic derivatives were obtained, and characterized by the spectroscopic analysis. Procedure for thiocyanation reactions is almost similar, and the reactions are carried out with 0.02 mol of NH_4SCN.

General procedure for aromatic nitration and thiocyanation under sonication

Methodology for the ultrasonically assisted reactions are similar to the conventional methods. Organic substrate, $NaNO_2$, oniumCr(VI) reagent (QDC/QCC), about 50 mg of $KHSO_4$, and solvent (MeCN) were taken in a clean conical flask at room temperature and immersed in a sonicator. Progress of the reaction was checked by TLC. After completion, the reaction mixture is further processed for the isolation of product as detailed in earlier sections. For thiocyanation reactions 0.02 mol of NH_4SCN is used under otherwise similar conditions.

General procedure for microwave assisted aromatic nitration and thiocyanation under solvent-free MW conditions

Organic substrate (0.01 mol), $NaNO_2$ (0.02 mol), about 0.015 mol of Cr(VI) reagent (QDC/QCC), about 50 mg of $KHSO_4$, and silicagel were mixed thoroughly in a beaker. The resulting reaction mixture was placed in a controlled microwave synthesizer (Biotage Initiator + SP Wave model- 0.200 W at 2.45 GHz, capped at 60 W during steady state) for a few minutes (attains temperature 100 °C and 2 bar pressure) till the reaction is completed. Progress of the reaction was monitored by TLC. After completion, the reaction mixture is further processed for the isolation of product as detailed in earlier sections. For thiocyanation reactions 0.02 mol of NH_4SCN is used under otherwise similar conditions.

General procedure for aromatic nitration and thiocyanation under micellar conditions using (QDC/QCC) reagent

A centimolar (0.01 mol) organic substrates 0.01 mol of $NaNO_2$ and about 0.015 moles of Onium

Cr(VI) reagent (QDC/QCC), micelle forming surfactant (5×5 ML) of 0.05 M cetyltrimethyl ammonium bromide (CTAB), sodium dodecylsulfate (SDS) or Triton-X-100), about 50 mg of $KHSO_4$, and solvent (MeCN) were taken in a previously cleaned round bottom flask and stirred for about 1 to 2 hours at room temperature. After completion of the reaction, as confirmed by TLC, the reaction mixture was treated with 5% sodium thiosulfate solution, followed by the addition of ethyl acetate. The organic layer was separated, dried over Na_2SO_4 and evaporated under vacuum, purified by column chromatography using pet-ether and ethyl acetate to get the pure product. In case of nitration of aromatic compounds, nitroaromatic derivatives were produced and analyzed from spectroscopic studies. However, for thiocyanation reactions 0.02 mol of NH_4SCN are used under otherwise similar conditions.

Results and discussion

Earlier reviews and publications on micelle mediated [27–31], ultrasonic [32, 33] and microwave [34–36] assisted organic synthesis revealed that these protocols satisfy both economic and environmental demands, as recommended by *Paul Anestas* and *John Walter* in the green chemistry formulations [25].

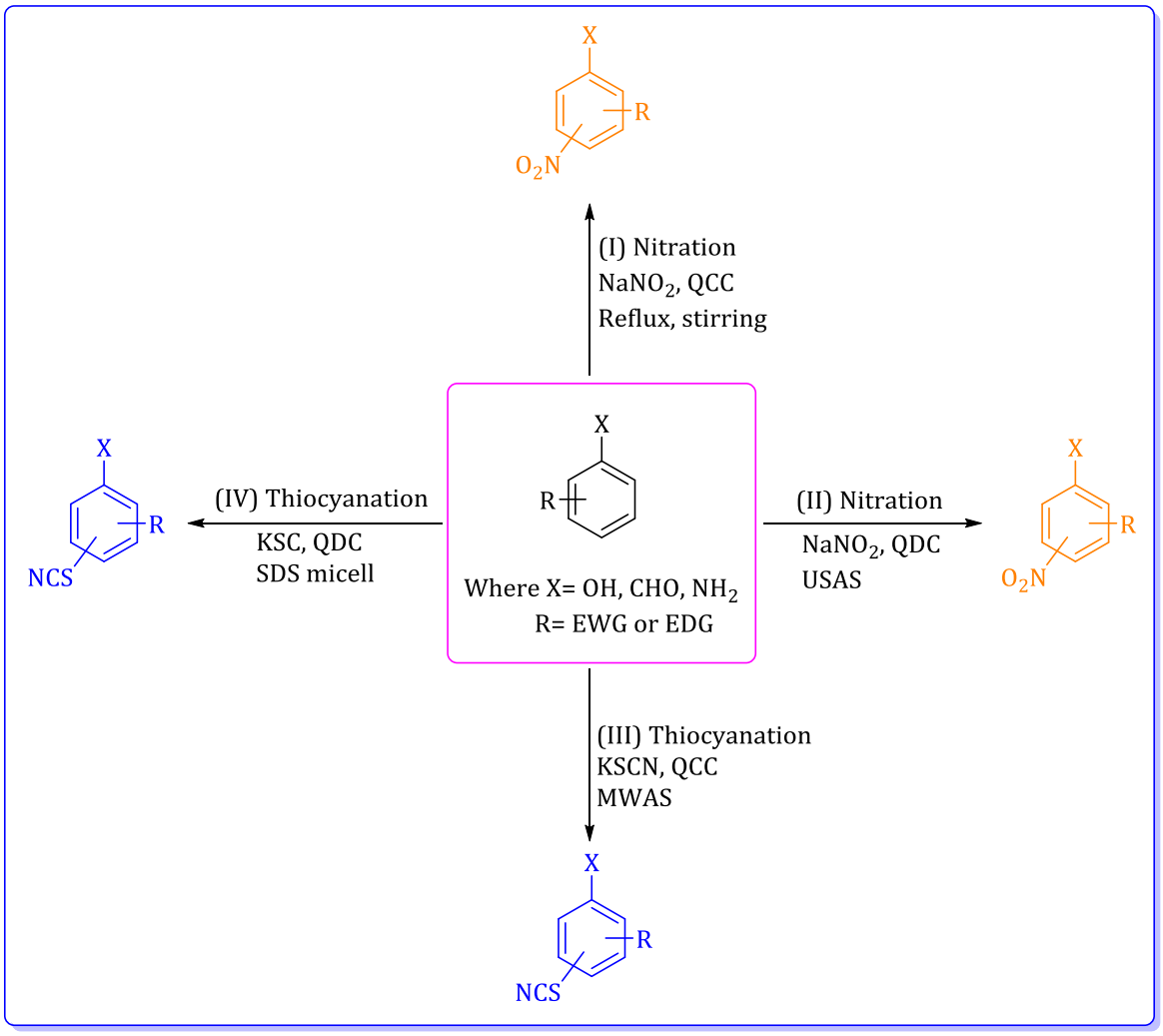
Quinolinium chlorochromate/ $NaNO_2$ and quinolinium dichromate/$NaNO_2$ triggered nitration of aromatic compounds

The nitration reactions of aromatic compounds were conducted using (QDC)/$NaNO_2$, and (QCC)/$NaNO_2$ combinations in the aqueous $KHSO_4$ under the mineral acid free conditions (Scheme 2). The described methods worked out well for an array of functionalities including phenols, and anilines. The yields of the major products are compiled in Table 1, 2, and 3. The nitration of aromatic compounds required 4–5 h under the conventional conditions at reflux temperatures. However, under the sonication, the reaction times were drastically reduced to about 30–40 min followed by considerable yield enhancements.

Quinolinium chlorochromate/ NH_4SCN and quinolinium dichromate/ NH_4SCN triggred thiocyanation of aromatic compounds

Quinolinium dichromate (QDC)/ NH_4SCN, and quinolinium chlorochromate (QCC)/ NH_4SCN reagents rtriggered thiocyanation of the aromatic compounds in aqueous $KHSO_4$ under mineral acid-free conditions. Aromatic compounds such as phenols, anilines and certain heteroaromatic compounds were used for thiocyanation as shown in Scheme 2. The thiocyanation reactions were generally more sluggish than the nitration reactions, which required more than 10 h under the conventional conditions at reflux temperatures (Table 4 and 5). But, under the sonication, the reaction times were considerably reduced to about 25–40 min followed by a significant yield enhancements. Comparing the reaction times and product yields

presented in Table 4 and 5 revealed that QDC mediated reactions are generally faster than the corresponding QCC mediated reactions.



Scheme 2. QCC/QDC mediated electrophilic aromatic substitution reactions under different conditions

Table 1. Nitration of aromatic compounds in presence of $QCC/NaNO_2$

Entry	Product	Conventional		USAR		MWA R	
		Time (min)	Yield (%)	Time (min)	Yield (%)	Time (sec)	Yield (%)
1	$2\text{-}NO_2C_6H_4OH$	60	70	25	73	150	75
2	$2\text{-}CH_3\text{-}4\text{-}NO_2\ C_6H_3OH$	60	68	25	69	150	75
3	$4\text{-}CH_3\text{-}2\text{-}NO_2\ C_6H_3OH$	60	65	25	72	150	73
4	$3\text{-}CH_3\text{-}4\text{-}NO_2\ C_6H_3OH$	60	70	25	70	150	72
5	$4\text{-}NO_2\ 2\text{-}Cl\ C_6H_3OH$	65	62	30	70	180	68
6	$2\text{-}NO_2\ 4\text{-}Cl\ C_6H_3OH$	70	60	30	65	120	68
7	$2\text{-}NO_2\ 4\text{-}Br\ C_6H_3OH$	60	65	35	68	120	70

8	2- NO_2 C_6H_3-1,4-OH	50	72	20	70	120	70
9	2- NO_2-1-Naphthol	55	70	25	72	120	75
10	1-NO_2-2-Naphthol	60	70	25	68	120	72
11	3-NO_2 $C_6H_4NH_2$	185	74	40	77	180	82
12	3-NO_2 $C_6H_4NH_2$	190	73	60	79	180	82
13	3-OH-4-NO_2 acetophenone	65	60	40	65	120	65
14	2,-4- $NO_2C_6H_4OH$	190	73	50	75	180	80
15	4-Cl-3-$NO_2C_6H_3CHO$	80	60	45	62	120	65
16	2-OH-5-NO_2- C_6H_3CHO	80	65	45	62	120	60
17	4-OH-3-NO_2- C_6H_3CHO	80	60	40	65	120	65
18	3-NO2- C_6H_4COOH	190	76	60	75	180	75
19	2-NO_2 furan	170	69	50	73	180	77
20	2-NO_2 thiophene	190	73	60	75	180	79
21	1-NO_2 Naphthalene	200	74	55	76	220	80
22	1-Cl, 2-NO_2 C_6H_4	180	76	40	75	180	80
23	1-Br, 2-NO_2 C_6H_4	190	75	50	76	220	78
24	1- CH_3, 2-NO_2 C_6H_4	180	75	55	74	180	78
25	2- NO_2 $C_6H_4CH_2OH$	190	76	60	77	230	78
26	2-OH 4-NO_2 C_6H_3COOH	200	74	60	78	230	78
27	3-NO_2 C_6H_4CN	220	76	80	76	300	80
28	3-NO_2 $C_6H_5CONH_2$	240	72	84	76	300	78

Table 2. Nitration of aromatic compounds in presence of QDC/$NaNO_2$

Entry	Product	Conventional		USAR		MWA R	
		Time (min)	Yield (%)	Time (min)	Yield (%)	Time (sec)	Yield (%)
1	2-$NO_2C_6H_4OH$	45	70	20	73	130	75
2	2-CH_3-4-NO_2 C_6H_3OH	45	68	20	69	130	75
3	4-CH_3-2-NO_2 C_6H_3OH	45	65	20	72	135	73
4	3-CH_3-4-NO_2 C_6H_3OH	45	70	23	70	140	72
5	4-NO_2-2-Cl C_6H_3OH	50	62	26	70	160	68
6	2-NO_2 4-Cl C_6H_3OH	50	60	25	65	110	68
7	2-NO_2-4-Br C_6H_3OH	55	65	30	68	105	70
8	2- NO_2 -C_6H_3-1,4-OH	40	72	20	70	110	70
9	2- NO_2-1-Naphthol	45	70	23	72	110	75
10	1-NO_2-2-Naphthol	45	70	22	68	110	72
11	3-NO_2 $C_6H_4NH_2$	60	74	35	77	160	82
12	3-NO_2 $C_6H_4NH_2$	80	73	55	79	165	82
13	3-OH-4-NO_2- acetophenone	60	60	35	65	115	65
14	2,-4- $NO_2C_6H_4OH$	70	73	45	75	165	80
15	4-Cl-3-$NO_2C_6H_3CHO$	65	60	40	62	110	65
16	2-OH-5-NO_2- C_6H_3CHO	65	65	40	62	114	60
17	4-OH-3-NO_2- C_6H_3CHO	60	60	35	65	115	65

18	3-NO2-C_6H_4COOH	160	76	50	75	160	75
19	2-NO_2 furan	140	69	45	73	155	77
20	2-NO_2 thiophene	150	73	50	75	160	79
21	1-NO_2 Naphthalene	175	74	50	76	200	80
22	1-Cl, 2-NO_2 C_6H_4	160	76	35	75	160	80
23	1-Br, 2-NO_2 C_6H_4	150	75	40	76	213	78
24	1- CH_3, 2-NO_2 C_6H_4	140	75	45	74	158	78
25	2- NO_2 $C_6H_4CH_2OH$	130	76	50	77	200	78
26	2-OH 4-NO_2 C_6H_3COOH	180	74	50	78	200	78
27	3-NO_2 C_6H_4CN	185	76	65	76	260	80
28	3-NO_2 $C_6H_5CONH_2$	190	72	74	76	260	78

Table 3. QDC/$NaNO_2$ and QCC/$NaNO_2$ mediated nitration of aromatic compounds in SDS medium

Entry	Product	QCC/ $NaNO_2$		QDC/ $NaNO_2$	
		Time (min)	Yield (%)	RT (min)	Yield (%)
1	2-$NO_2C_6H_4OH$	45	73	35	83
2	2-CH_3- 4-NO_2 C_6H_3OH	45	69	33	79
3	4-CH_3- 2-NO_2 C_6H_3OH	45	72	35	80
4	3-CH_3- 4-NO_2 C_6H_3OH	45	70	35	75
5	4-NO_2 2-Cl C_6H_3OH	50	70	40	75
6	2-NO_2 4-Cl C_6H_3OH	50	65	40	70
7	2-NO_2 4-Br C_6H_3OH	55	68	45	78
8	2- NO_2 C_6H_3-1,4-OH	40	70	30	76
9	2- NO_2-1-Naphthol	45	72	35	79
10	1-NO_2-2-Naphthol	45	68	35	73
11	3-NO_2 $C_6H_4NH_2$	60	77	55	82
12	3-NO_2 $C_6H_4NH_2$	80	79	70	85
13	3-OH-4-NO_2-acetophenone	60	65	50	75
14	2,-4- $NO_2C_6H_4OH$	70	75	60	78
15	4-Cl-3-$NO_2C_6H_3CHO$	65	62	55	72
16	2-OH-5-NO_2- C_6H_3CHO	65	62	55	76
17	4-OH-3-NO_2- C_6H_3CHO	60	65	50	74
18	3-NO2- C_6H_4COOH	80	75	65	81
19	2-NO_2 furan	70	73	58	78
20	2-NO_2 thiophene	80	75	68	78
21	1-NO_2 Naphthalene	75	76	65	82
22	1-Cl, 2-NO_2 C_6H_4	60	75	50	84
23	1-Br, 2-NO_2 C_6H_4	70	76	60	82
24	1- CH_3, 2-NO_2 C_6H_4	75	74	55	79
25	2- NO_2 $C_6H_4CH_2OH$	80	77	65	83
26	2-OH 4-NO_2 C_6H_3COOH	80	78	75	84
27	3-NO_2 C_6H_4CN	80	76	65	82
28	3-NO_2 $C_6H_5CONH_2$	84	76	75	82

Mechanism of the substitution reactions

It is well established in earlier reports that in aqueous acid media potassium dichromate ($K_2Cr_2O_7$) or chromium(VI) exists in several reactive forms such as $HCrO_4^-$, H_2CrO_4, $[HCrO_3]^+$, and $HCrO_3B$ (where B = HSO_4^-, ClO_4^- or NO_2^-). Since the quinolinium dichromate (QDC) is related to $K_2Cr_2O_7$, we have formulated similar types of reactive species with quinolinium ion background [26] according to the following equilibria.

$$(QH)_2Cr_2O_7 + H_2O \rightleftharpoons 2[(QH)^+(HCrO_4)^-] \quad (2)$$

The QDC may further protonated to from active $[(QH)^+(HCrO_4)^-]$ (Quinolinium bound chromic acid) species, using the (H^+) thus released from the dissociation of HSO_4^- , as shown below

$$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+ \quad (3)$$

$$(QH)^+(HCrO_4)^- + H^+ \rightleftharpoons [(QH)CrO_3]^+ + H_2O \quad (4)$$

Active species, thus formed may further react with nitrite ion to afford $[(QH)CrO_3NO_2]$ species, since the reactions are conducted in excess $NaNO_2$.

$$[(QH)CrO_3]^+ + NO_2^- \rightleftharpoons [(QH)OCrO_2NO_2] \quad (5)$$

Similar type of reactive species could be formed with thiocyanide (SCN^-) ion to afford $[(QH)CrO_3(SCN)]$ species, since the reactions are conducted in excess of NH_4SCN. Finally, aromatic substrates undergo electrophilic substitution when the in situ formed electrophile (NO_2^+ or SCN^+) attacks on aromatic ring as shown in the following schematic steps**.**

$$[(QH)CrO_3]^+ + (SCN^-) \rightleftharpoons [(QH)CrO_3(SCN)] \quad (6)$$

On the otherhand, the most plausible mechanism in QCC (Quinolinium chlorochromate) triggered reactions could be proposed by considering $(QHOCr(OH)Cl)^+$ (the protonated form of QCC), which is formed according to the following equilibrium:

$$(QHOCrO_2Cl) + H^+ \rightleftharpoons (QHOCr(OH)OCl)^+ \quad (7)$$

The protonated QCC species thus formed $(QHOCr(OH)OCl)^+$ being a stronger electrophile, may further react with nitrite ion to afford $[QHOCr(OH)(Cl)NO_2]$ species, since the reactions were conducted in excess $NaNO_2$.

$$[QHOCr(OH)Cl]^{+} + NO_2^{-} \rightleftharpoons [QHOCr(OH)(Cl)NO_2] \quad (8)$$

Similar type of reactive species could be formed with thiocyanate (SCN^{-}) ion to afford the [QHOCr(OH)(Cl)(SCN)] species, since the reactions are conducted in excess of NH_4SCN.

$$[QHOCr(OH)Cl]^{+} + SCN^{-} \rightleftharpoons [QHOCr(OH)(Cl)(SCN)] \quad (9)$$

On the basis of foregoing discussions, mechanism of electrophilic substution in aromatic substrates could be explained through the attack of electrophile on the aromatic ring (NO_2^{+} released *in situ* from $[QHOCr(OH)(Cl)NO_2]$ for nitration; and SCN^{+} released *in situ* from [QHOCr(OH)(SCN)Cl] for thiocyanation) to afford the products, as shown in the sequence of steps of Scheme 3.

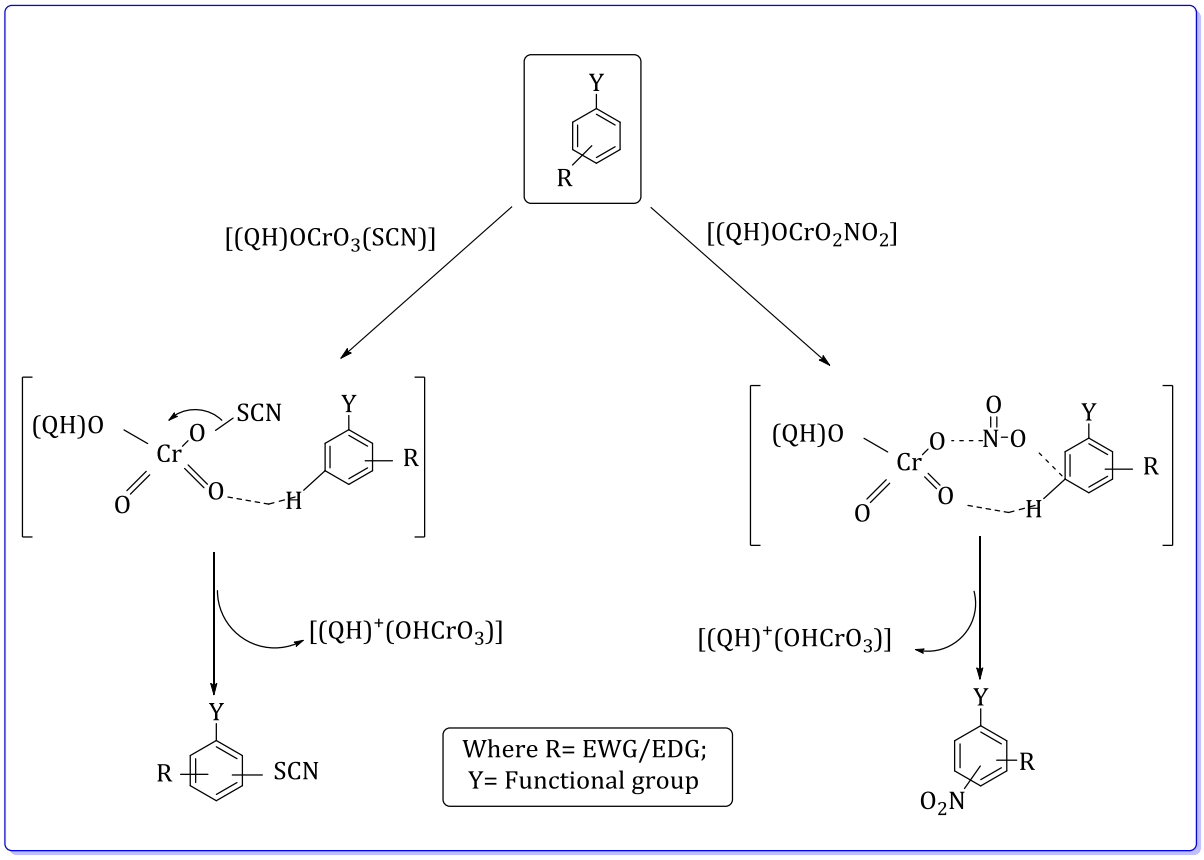
Table 4. Thiocyanation of aromatic compounds in presence of QDC/NH_4SCN

Entry	Product	Conventional		Sonication	
		Time (h)	Yield (%)	Time (min)	Yield (%)
1	4- $SCNC_6H_4NH_2$	10	82	25	78
2	2-Cl 4- $SCNC_6H_4NH_2$	12	74	25	74
3	3-CH_3O 4- $SCNC_6H_4NH_2$	11	77	20	77
4	4- SCN N- $CH_3C_6H_5NH_2$	12	72	30	72
5	4-Thiocyanato N, N-dimethyl aniline	11	70	35	83
6	4-Thiocyanato diphenylamine	14	74	35	81
7	2-$SCNC_6H_4OH$	13	69	25	81
8	4-$CH_3$2-$SCNC_6H_3OH$	12	76	40	77
9	4-$NO_2$2-$SCNC_6H_3OH$	14	80	40	72
10	4-Cl2-$SCNC_6H_3OH$	14	77	30	87
11	2-$NO_2$4-$SCNC_6H_3OH$	12	80	35	79
12	2-Thiocyanato 1H-pyrrole	11	81	30	91
13	2-Thiocyanato furan	13	62	40	72
14	2-Thiocyanato thiophene	14	79	40	82
15	3-Thiocyanato 1H-indole	13	77	30	77
16	5-Bromo 3-thiocyanato indole	14	69	40	69
17	3-thiocyanato N-Methyl- indole	12	76	35	88

Table 5. Thiocyanation of aromatic compounds in presence of QCC/NH_4SCN

Entry	Product	Conventional		Sonication	
		Time (h)	Yield (%)	Time (min)	Yield (%)
1	4- $SCNC_6H_4NH_2$	11	77	30	85
2	2-Cl 4- $SCNC_6H_4NH_2$	10	84	35	83
3	3-CH_3O 4- $SCNC_6H_4NH_2$	10	78	45	81
4	4- SCN N- $CH_3C_6H_5NH_2$	11	81	50	78
5	4-Thiocyanato N, N-dimethyl aniline	12	71	50	86
6	4-Thiocyanato diphenylamine	13	86	45	84

7	2-$SCNC_6H_4OH$	11	85	35	81
8	4-$CH_3$2-$SCNC_6H_3OH$	10	79	45	85
9	4-$NO_2$2-$SCNC_6H_3OH$	13	83	50	79
10	4-Cl2-$SCNC_6H_3OH$	13	77	35	82
11	2-$NO_2$4-$SCNC_6H_3OH$	11	82	45	89
12	2-Thiocyanato 1H-pyrrole	12	88	50	90
13	2-Thiocyanato furan	11	82	40	81
14	2-Thiocyanato thiophene	13	84	45	87
15	3-Thiocyanato 1H-indole	12	82	50	84
16	5-Bromo 3-thiocyanato indole	13	72	35	85
17	3-thiocyanato N-Methyl-indole	12	76	45	90



Scheme 3. QDC Electrophic aromatic substitution of aromatic compounds

Salient features of ultrasonic and microwave assisted reactions

The observed reaction times and product yields presented in Table 1, 2, 3, 4, and 5 revealed a magnificent rate enhancement in the both ultrasonically assisted nitration and thiocyanation protocols. This is basically attributed to the ultrasonic cavitation effects. The chemical effects of the ultrasound do not come from a direct interaction with the molecular species. It arises from the

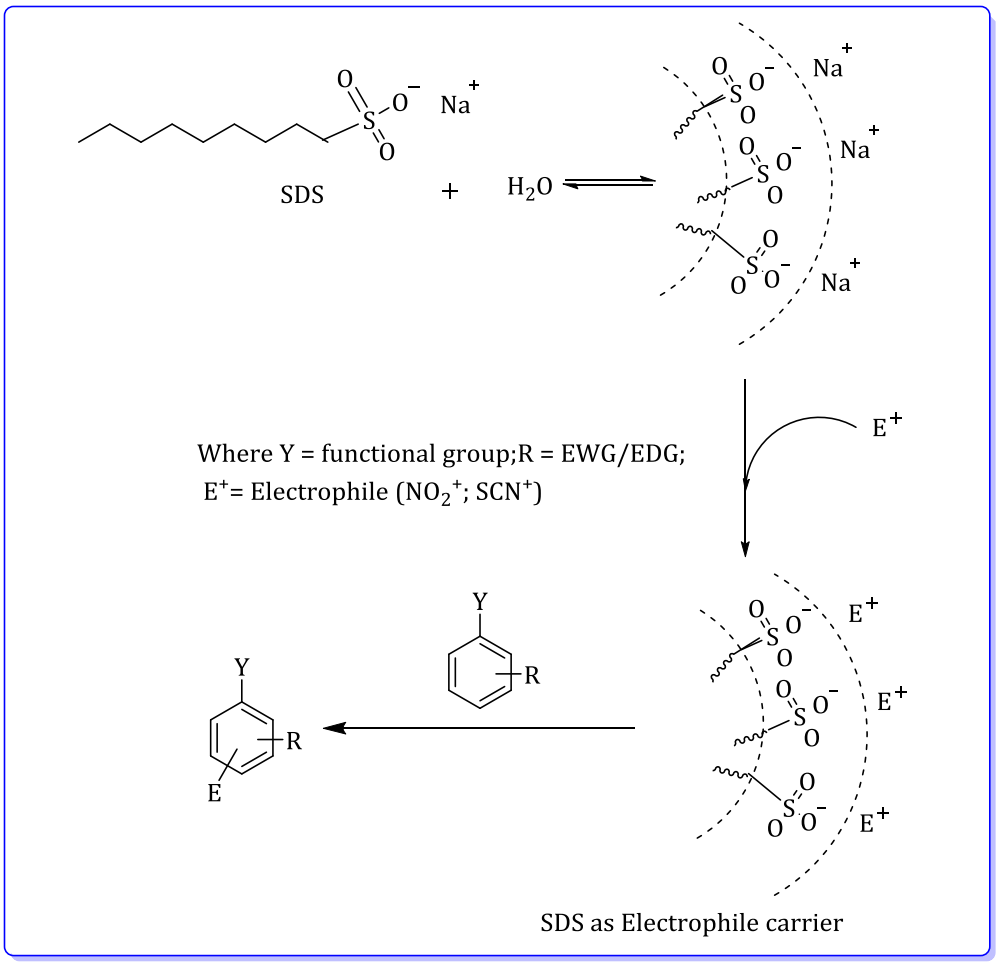
acoustic cavitation the formation, growth, and implosive collapse of bubbles in a liquid [31, 32]. Cavitation is a physical process that creates, enlarges, and implodes gaseous and vaporous cavities in an ultrasonically assisted (Irradiated) liquid. It induces very high local temperatures in the reaction mixture and enhances mass transfer [33–36]. Thus, ultrasonic assisted organic synthesis (USAOS) is a powerful green approach, which is being used to accelerate synthesis of organic compounds. It is an environmentally benign synthesis, which minimized the use of the precious metal catalysts and led to the development of new eco-friendly protocols [25]. After obtaining successful results in USA methods we were enthusiastic to see whether these reaction times could be further affected under microwave irradiation. Observed results under microwave assisted synthesis (MWAS) are compiled in Table 1 and 2 for nitration reactions. Interestingly, the reaction times further decreased enormously from several (≥ 25) min minutes to 2-3 min), followed by high yields. Microwaves have no effect on molecular bonds or electron clouds such as infrared (IR) or the visible region of electromagnetic radiation has. This dramatic rate enhancement could be attributed to the bulk activation of the molecules, which is due to the rapid superheating of the polar solvents and pressure effects [33–36].

Quinolinium chlorochromate and quinolinium dichromate triggred nitration and thiocyanation of aromatic compounds in micellar media

Encouraged by the promising catalytic activities of micelle forming surfactants, cetyltrimethyl ammoniumbromide (CTAB), sodium dodecylsulphate (SDS), and Triton-X-100 were selected as the most promising candidates to optimize the reaction conditions for the proposed nitration and thiocyanation. The nitration of aromatic compounds in the presence of SDS underwent a rapid substitution with nitronium and thiocyanate electrophiles affording high yields of corresponding mono substituted compounds with good regioselectivity (Table 3 and 5). The observed rapid substitution with nitronium and thiocyanate electrophiles in aqueous SDS media could be due to the role of SDS micelles, which act as electrophile (Nitronium and thiocyanate ions) carriers in the nitration and thiocyanation reactions, as shown in Scheme 4. However, the reactions with CTAB and Tx-100 did not bring out any changes either in the nitration or thiocyanation reactions.

Conclusion

We have accomplished the quinolinium dichromate (QDC) and quinolinium chlorochromate (QCC) as effecient reagents for the electrophilic aromatic nitration using the sodium nitrite and thiocyanation by using ammonium thiocyanate under conventional, ultrasonic and solvent free microwave assisted conditions. The microwave assisted reactions underwent most effeciently with



Scheme 4. SDS as electrophile carrier in electrophilic substitution of aromatic compounds

very short reaction times and good product yields. Addition of anionic (SDS) micelle to the reaction medium afforded a considerable rate, while cationic (CTAB) micelle did not show much catalytic effect. These protocols have been extended to the regioselective thiocyanation of various aromatic compounds. Results were similar to the nitration protocols. However, the reactions exhibited comparatively shorter reaction times, and better yields in nitration reactions than in thiocyanation protocols.

Acknowledgments

The authors would like to appreciate the Osmania University, Hyderabad; Rayalaseema University, Kurnool, and Govt. City College, Hyderabad for their invaluable support.

Disclosure statement

No potential conflict of interest was reported by the authors.

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How to cite this manuscript: Satish Babu Kodali, Narendar Reddy Jakku, CHinna Rajanna Kamatala*, Rajeshwar Rao Yerraguntla, Ivon Chakravarthi Elisha. Quinolinium bound chromium(VI) reagents for efficient electrophilic aromatic nitration and thiocyanation reactions using sodium nitrate and ammonium thiocyanate. *Asian Journal of Green Chemistry*, 2018, 2, 70-84. DOI: 10.22631/ajgc.2017.101557.1031