



- (51) **International Patent Classification:**
C07C 17/12 (2006.01) *C07C 25/02* (2006.01)
- (21) **International Application Number:**
PCT/IN2017/050097
- (22) **International Filing Date:**
17 March 2017 (17.03.2017)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
201611009675 21 March 2016 (21.03.2016) IN
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- (81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM,

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) **Title:** AN IMPROVED ONE POT, ONE STEP PROCESS FOR THE HALOGENATION OF AROMATICS USING SOLID ACID CATALYSTS

(57) **Abstract:** The present invention disclosed an improved one pot, one step process for halogenation of compound of formula (II) to afford corresponding halogenated compound of formula (I) having improved yield and increased selectivity under very mild conditions.



AN IMPROVED ONE POT, ONE STEP PROCESS FOR THE HALOGENATION OF AROMATICS USING SOLID ACID CATALYSTS

FIELD OF THE INVENTION:

5 The present invention relates to halogenation of aromatics using solid acid catalysts. More particularly, the present invention relates to an improved one pot, one step process for the halogenation of compound of formula (II) to afford corresponding halogenated compound of formula (I) having improved yield and increased selectivity.

10 BACKGROUND AND PRIOR ART OF THE INVENTION:

Halogenated hydrocarbons have many important industrial and technical uses which make these compounds extremely valuable, and which therefore make the possibility of producing such compounds in quantity and in an easily controllable, inexpensive manner extremely desirable. Halogenated aromatic hydrocarbons are particularly valuable as starting materials
15 for many purposes, such as for the production of dyes, synthetic resins and insecticides. The functional halogen group of such compounds may be varied in many respects in order to give the obtained products a higher degree of color, a higher degree of flame-proofing, or even toxicity. The production of such halogenated aromatic compound is particularly difficult. The halogenation with elementary halogen usually results in a large loss of solvents, requires
20 carefully controlled conditions, and thorough purification of the final product, one half of the utilized halogen is converted to the corresponding hydrogen halide compound and is thus lost for the halogenation.

Further, aryl iodides are important intermediates in organic synthesis, medicine and
25 biochemistry. They are also valuable and reactive intermediates for various cross-coupling reactions, for example, Heck, Stille and Negishi cross-coupling. Direct iodination using I_2 is a simple method, but is not straight forward and requires the oxidation of iodine to the more reactive species with a pronounced I^+ nature. Iodination of aromatic compounds has been carried out using molecular iodine together with strong oxidizing agents such as nitric acid,
30 sulphuric acid, iodic acid, sulphur trioxide and hydrogen peroxide, ceric ammonium nitrate, bismuth (III) nitrate pentahydrate, sodium hypochlorite and urea-hydrogen peroxide. Several reagents reported for iodination of aromatic compounds include iodine and 1,4-bis(triphenylphosphonium)-2-butene peroxodisulfate, iodine and pyridine/dioxane, $AgNO_3/I_2$, $I_2/NaBO_3 \cdot 4H_2O$ in ionic liquid, I_2/HIO_3 , heat, I_2/CrO_3 , $NaClO_2/NaI/HCl$, KI/K_2FeO_4 in water,

N-iodosuccinimide and catalytic trifluoroacetic acid, pyCl/CH₃OH, I₂/Pb(OAc)₄, KI/H₂O₂, KI/KIO₃/H⁺, KClO₃/KI/HCl, NCS/NaI and iodine with H₂O₂ and O₂. Strong Lewis acids or Bronsted acids, such as trifluoroacetic acid, trifluoromethanesulfonic acid and BF₃.OEt₂-H₂O have been utilized for electron-withdrawing groups on the aromatic ring, which is not suitable for acid sensitive functional groups.

Hence, there is an increasing demand for new greener methods for iodination without catalyst and solvent. Iodination using ICl is usually carried out in polar solvents, such as methanol, water and acids such as acetic acid, trifluoroacetic acid, aq. hydrochloric acid, sulphuric acid, etc., in which the heterolytic dissociation facilitates electrophilic attack of iodine. Iodination using ICl is carried out in Lewis acids such as Hg(OTf)₂ and AgOTf. Very few ammonium ICl₂ - salts have been reported for the iodination of aromatic compounds. Hexamethylene bis(Nmethylimidazolium) bis(dichloroiodate) an ionic liquid iodinating reagent has been used for iodination of aromatic amines. The drawback was that the reaction requires CaCO₃ as base and the recycle yields are less (82%). Benzyltrimethylammonium dichloroiodate was used for iodination. The drawback was the use of MeOH as solvent and the requirement of CaCO₃ as a base. A variety of 1,3- dialkylimidazolium trihalide-based ionic liquids were used for iodochlorination for alkenes and alkynes and not for iodination.

US 6,22,5514 disclosed a method of halogenating the ring of an aromatic compound. The aromatic compound is contacted with a halogenating agent in the presence of a heterogeneous catalyst. The catalysts of this invention, commonly known as "solid acid catalysts," can be made by reacting a dopant with a support. Examples of suitable dopants include H₂SO₄, (NH₄)₂SO₄, (NH₄)HSO₄, SO₃, WO₃, H₂WO₄, H₂MoO₄, (NH₄)₂WO₄, (NH₄)₂MoO₄, Mo(NO₃)₆, W(NO₃)₆, MoO₃, H₃PO₄, (NH₄)₃PO₄, (NH₄)₂HPO₄, (NH₄)H₂PO₄, Cr₂O₃, and mixtures thereof. Supports that can be used include TiO₂, ZrO₂, HfO₂, MnO₂, Fe₂O₃, Fe₃O₄, GeO₂, SnO₂, TiO₃, Nb₂O₅, Ta₂O₅, SC₂O₃, La₂O₃, SiO₂, and mixtures thereof.

Article titled "Regiospecific Oxyhalogenation of Aromatics Over SBA-15-Supported Nanoparticle Group IV–VI Metal Oxides" by L Saikia et al. published in *Catalysis Letters*; 2010, Volume 137, Issue 3, pp 190–201 reports Nanoparticulate WO_x, MoO_x, TiO_x and VO_x supported on SBA-15 for efficient catalytic activity for oxyhalogenation of aromatic compounds. The reaction occurs at 298 K and moderate acidic pH (3–5). The catalytic

activity of these catalysts is higher than most of the hitherto known solid catalysts and unsupported metal oxides.

US 6,16,6272 disclosed a method of fluorinating a substrate comprising reacting said
5 substrate with a fluorinating agent in the presence of about 0.01 to about 2 wt % molybdenum trioxide at a temperature between about 40 and about 100° C.

Article titled “Iodination of activated aromatic compounds using nanostructure solid acid catalyst” by A Hosseini et al. published in *Synthetic Communications*, 2012; 42; pp 2407–
10 2414 reports iodination of aromatic compounds catalyzed by Nanoporous silica anchored with sulfonic acid groups. The reaction was performed in water using hydrogen peroxide as oxidant. The recyclability of catalyst in green media significantly contributes to the environmental friendliness of the procedure.

Article titled “Studies on heteropoly acid supported zirconia: III: Oxidative bromination of phenol using phosphotungstic acid supported on zirconia” by S Mallick et al. published in *Journal of Molecular Catalysis A: Chemical*; 2007, 261(2), pp 172–179 reports a series of ecofriendly solid acid catalyst synthesized by supporting phosphotungstic acid onto hydrous zirconia by an incipient wetness impregnation method in order to contribute towards clean
20 technology. Further, Phosphotungstic acid supported on hydrous zirconia acts as an efficient and stable solid acid catalyst for oxybromination of phenol.

Article titled “A new, environment friendly protocol for iodination of electron-rich aromatic compounds” by S Adimurthy et al. published in *Tetrahedron Letters*, 2003, 44 (27), pp
25 5099–5101 reports a new environment friendly procedure for effective aromatic iodination. A mixture of potassium iodide and potassium iodate is used in the presence of an acid for in situ iodination of aromatic compounds.

Therefore, there is need to overcome prior art problems such as use of strong mineral acids,
30 carried out at high temperature and high oxygen pressure, solvents are not environmental friendly and excess use of reagents and more importantly prior art fails to disclose the process for selectively obtaining ortho-halogenated compound. Accordingly, the present invention provides an environment friendly single pot process for halogenation of aromatic compounds

under milder conditions with improved conversion and increased selectivity towards ortho substituted compounds using heterogeneous solid acid catalysts.

OBJECTIVE OF THE INVENTION:

- 5 The main objective of the present invention is to provide an improved one pot, one step process for the halogenation of compound of formula (II) to afford corresponding halogenated compound of formula (I) having improved yield and increased selectivity.

- 10 Another objective of the present invention is to provide an improved one pot, one step process for iodination of aromatics of compound of formula (II) to corresponding iodo compound of formula (I) in presence of suitable catalyst using I_2 having improved yield and increased selectivity.

- 15 Yet another objective of the present invention is to provide an improved one pot, one step process for the halogenation of aminoaromatic or hydroxy aromatic or aromatic aldehyde compound using suitable halogenating agent and solid acid catalyst to afford corresponding halogenated compound having improved yield and increased selectivity.

SUMMARY OF THE INVENTION:

- 20 Accordingly, the present invention provides an improved one pot, one step process for the halogenation of substituted aromatic compound comprises addition of halogenating agent and solid acid catalyst to the mixture of substituted aromatic compound in solvent followed by stirring the reaction mixture at temperature in the range of 25 to 150°C for the period in the range of 2 to 6 hrs to afford corresponding halogenated compound.

- 25 In preferred embodiment, said substituted aromatic compound is selected from aminoaromatic compound, hydroxy aromatic compound, aromatic aldehyde compound, halo substituted aromatics, amide substituted aromatic compound.

- 30 In another preferred embodiment, said aminoaromatic compound is selected from aniline, 4-Chloroaniline, 4- Bromoaniline, 2,6 dimethyl aniline, anthranilamide, 2,6 diethyl aniline.

In yet another preferred embodiment, wherein said hydroxy aromatic compound is selected from phenol.

In still another preferred embodiment, said aromatic aldehyde compound is benzaldehyde.

5 In yet still another preferred embodiment, said corresponding *ortho*-halogenated compound is selected from 4-chloro-2-iodoaniline, 2-iodoaniline, 4-bromo-2-iodoaniline, 4-iodo-2,6-dimethylaniline, 3-iodobenzaldehyde, 2-iodophenol, 2-amino-3-iodobenzamide, 2,6-diethyl-4-iodoaniline, 4-chloro-2,6-dimethylaniline and 4-bromo-2,6-dimethylaniline.

10 In yet still another preferred embodiment, said solid acid catalyst is selected from SiO₂, MoO₃/TiO₂, MoO₃/TiO₂, WO₃/TiO₂, WO₃/TiO₂ and 5% Mo Si/Al (7.5) Impr.

15 In yet still another preferred embodiment, said solvent is selected from ethylene dichloride, methanol, hexane, toluene, dichloromethane, ethanol, higher alcohols, dimethylsulfoxide, dioxane, dimethylformamide, acetone, diethyl ether, butanol and benzylalcohol.

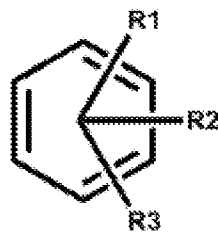
In yet still another preferred embodiment, selectivity towards said corresponding *ortho*-halogenated aromatic compound is in the range of 50 to 100%.

20 In yet still another preferred embodiment, said process is carried out in batch mode or continuous mode.

DETAILED DESCRIPTION OF THE INVENTION:

25 The invention will now be described in detail in connection with certain preferred and optional embodiments, so that various aspects thereof may be more fully understood and appreciated.

In the view of above, the present invention provides an improved one pot, one step process for the halogenation of compound of formula (II) ;



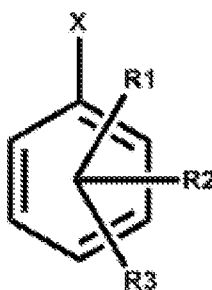
Formula (II)

Wherein;

R1 is selected from alkyl, amines, carbonyl containing compounds, halides, amides and acids;

R2 and R3 is selected from the hydrogen, halogen, alkyl, aryl and amine;

5 to afford corresponding halo compound of formula (I)



Formula (I)

Wherein;

X is selected from chlorine, bromine, iodine;

R1 is selected from alkyl, amines, carbonyl containing compounds, halides, amides and acids;

10 R2 and R3 is selected from the hydrogen, halogen, alkyl, aryl and

having improved yield and increased selectivity.

In an embodiment, the present invention provides an improved one pot, one step process for iodination of aromatics of compound of formula (II) to corresponding iodo compound of formula (I) in presence of suitable catalyst and solvent using I₂ as iodinating agent having improved yield and increased selectivity.

In another embodiment, the present invention provides an improved one pot, one step process for the halogenation of substituted aromatic compound comprises addition of halogenating agent and solid acid catalyst to the mixture of substituted aromatic compound in solvent followed by stirring the reaction mixture at temperature in the range of 25 to 150°C for the period in the range of 2 to 6 hrs to afford corresponding halogenated compound.

In preferred embodiment, said substituted aromatic compound is selected from aminoaromatic compound, hydroxy aromatic compound, aromatic aldehyde compound, halo substituted aromatics, amide substituted aromatic compound.

5

In another preferred embodiment, said aminoaromatic compound is selected from aniline, 4-Chloroaniline, 4- Bromoaniline, 2,6 dimethyl aniline, anthranilamide, 2,6 diethyl aniline.

10

In yet another preferred embodiment, wherein said hydroxy aromatic compound is selected from phenol.

In still another preferred embodiment, said aromatic aldehyde compound is benzaldehyde.

15

In yet still another preferred embodiment, said corresponding *ortho*-halogenated compound is selected from 4-chloro-2-iodoaniline, 2-iodoaniline, 4-bromo-2-iodoaniline, 4-iodo-2,6-dimethylaniline, 3-iodobenzaldehyde, 2-iodophenol, 2-amino-3-iodobenzamide, 2,6-diethyl-4-iodoaniline, 4-chloro-2,6-dimethylaniline and 4-bromo-2,6-dimethylaniline.

20

In yet still another preferred embodiment, said solid acid catalyst is selected from SiO₂, MoO₃/TiO₂, MoO₃/TiO₂, WO₃/TiO₂, WO₃/TiO₂ and 5% Mo Si/Al (7.5) Impr.

25

In yet still another preferred embodiment, said solvent is selected from ethylene dichloride, methanol, hexane, toluene, dichloromethane, ethanol, higher alcohols, dimethylsulfoxide, dioxane, dimethylformamide, acetone, diethyl ether, butanol and benzylalcohol.

In yet still another preferred embodiment, selectivity towards said corresponding *ortho*-halogenated aromatic compound is in the range of 50 to 100%.

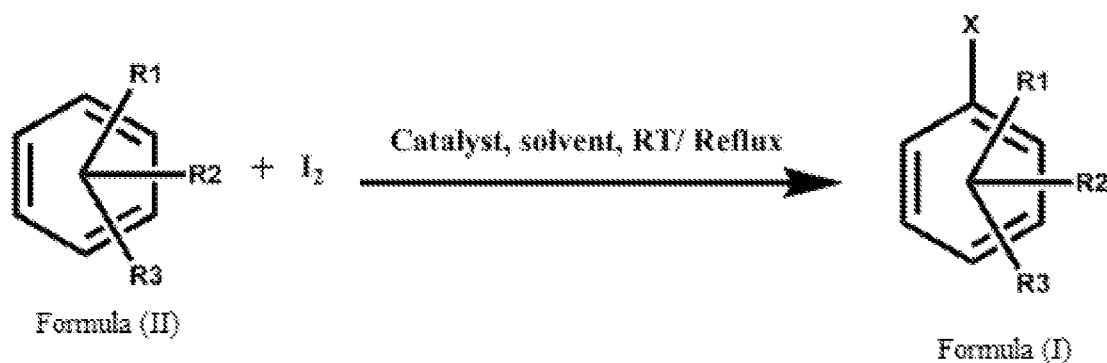
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In yet still another preferred embodiment, said process is carried out in batch mode or continuous mode.

The halogenation is carried out in batch mode.

The halogenation is carried out in continuous mode in down-flow reactor.

The improved one pot, one step process for the halogenation of compound of formula (II) is to afford corresponding halo compound of formula (I) is depicted in scheme 1 below:



5

Scheme: 1

A range of heterogeneous solid acid catalysts are used for iodination of aromatics to corresponding iodo compounds with upto 97% conversion and 100% selectivity using I₂ as iodinating agent and ethylene dichloride as solvent at only 80 °C.

10

The following examples, which include preferred embodiments, will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purpose of illustrative discussion of preferred embodiments of the invention.

15 EXAMPLES:

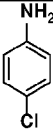
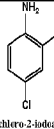
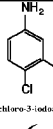
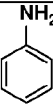
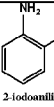
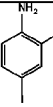
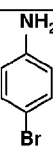
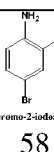
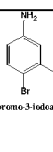
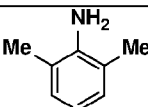
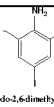
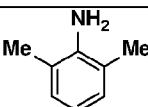
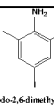
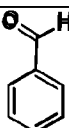
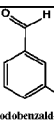
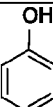
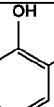
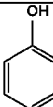
Following examples are given by way of illustration and therefore should not be construed to limit the scope of the invention.

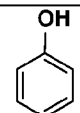
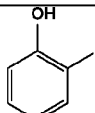
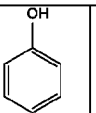
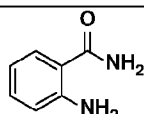
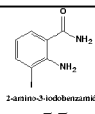
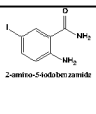
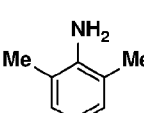
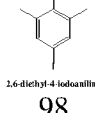
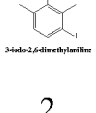
Example: 1 General procedure for the synthesis of halo compound of formula (I):

20 A 25 mL two-necked round bottom flask was fitted with condenser. Initially 0.1 g substrate (0.001 mol) was added to the flask followed by 10 mL solvent. After this 0.28 g iodine (0.001 mol) was added to the same flask followed by addition of 0.02 g catalyst. The reaction was carried out at different temperatures (Table 1) for 2-6 hrs. After completion of the reaction, 5 mL water was added to the reaction flask to stop the reaction. The reaction was monitored by
 25 GC analysis.

The compounds which are used for the iodination of aromatics are listed in table 1 below:

Table 1: Liquid phase iodination of aromatics

Ex no.	Substrate	Catalyst	Temp, °C	Molar ratio of Sub : I ₂	Solvent	% Catalyst loading wrt substrate	% Conv.	% Selectivity		
1	 4-Chloroaniline	SiO ₂	28 °C	1:0.5	Hexane	10	45	 4-chloro-2-iodoaniline 94	 4-chloro-3-iodoaniline 6	
2	 Aniline	20% MoO ₃ /TiO ₂	65 °C	1:1	MeOH	5	91	 2-iodoaniline 92	 2,4-diiodoaniline 8	
3	 4- Bromoaniline	2% WO ₃ /TiO ₂	68 °C	1:0.5	Hexane	20	48	 4-bromo-2-iodoaniline 58	 4-bromo-3-iodoaniline 20	#OP 22
4	 2,6 dimethyl aniline	20 wt% WO ₃ /SiO ₂	28 °C	1:1.2	EDC	10	85	 4-iodo-2,6-dimethylaniline 100		
5	 2,6 dimethyl aniline	20 mol% MoO ₃ /SiO ₂	28 °C	1:1.2	EDC	10	65	 4-iodo-2,6-dimethylaniline 100		
7	 Benzaldehyde	5% Mo Si/Al (7.5) Impr	40 °C	1:1.2	EDC	5	3	 3-iodobenzaldehyde 100		
8	 Phenol	20 wt% WO ₃ /SiO ₂	28 °C	1:1.2	MeOH	20	11	 2-iodophenol 90	 4-iodophenol 10	

9	 Phenol	20 wt% WO ₃ /SiO ₂	65 °C	1:1.2	MeOH	20	22	 2-iodophenol 90	 4-iodophenol 10	
10	 Anthranilamide	20 wt% MO ₃ /SiO ₂	84 °C	1:1.2	EDC	20	88	 2-amino-3-iodobenzamide 55	 2-amino-5-iodobenzamide 30	#OP 15
11	 2,6 dimethyl aniline	20 wt% MO ₃ /SiO ₂	84 °C	1:1.2	EDC	20	88	 2,6-diethyl-4-iodoaniline 98	 3-iodo-2,6-diethylaniline 2	

#OP = Other products

Example 2: Catalyst preparation:**a) SiO₂:**

5 In a typical procedure, SiO₂ catalyst was synthesized by dissolving ES-40 (50.0 g) in IPA (35 mL) with constant stirring. To this solution 3 mL dil. NH₄OH (2.5%) solution was added. The solution was stirred until white gel was obtained. The resultant gel was air dried and further calcined at 500 °C in air in a muffle furnace for 5 h.

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b) 20% WO₃/SiO₂:

In a typical procedure, 20 WS catalyst was synthesized by dissolving 5.31 g AMT in 10 mL distilled water. This solution was added drop wise to the dry IPA solution (35 mL) of ES-40 (50.0 g) with constant stirring. To this solution 3 mL dil. NH₄OH (2.5%) solution was added. The solution was stirred until white gel was obtained. The resultant gel was air dried and further calcined at 500 °C in air in a muffle furnace for 5 h. Similarly catalysts with 1, 5, 10, 15, 25 and 30 wt% tungsten oxide loadings were prepared.

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c) 20 mol % MoO₃/SiO₂:

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In a typical procedure, 20 mol% MoO₃/SiO₂ catalyst was synthesized by dissolving 14.11 g of AHM in 40 ml of water at 80 °C. This hot solution was added dropwise to

a dry isopropyl alcohol solution of ethyl silicate-40 (48.0 g) with constant stirring. The resultant transparent greenish gel was air-dried and calcined at 500 °C in air in a muffle furnace for 12 h. Similarly, catalysts with 1, 10 and 30 mol% molybdenum oxide loading were prepared.

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d) 20% MoO₃/TiO₂:

In typical procedure Titanium(IV) tetrabutoxide hydrolysed with deionized water (500 mL) and stirred vigorously for 10 min. The resulting titanium hydroxide precipitate separated by decantation and thoroughly washed with water until the alcohol generated during the hydrolysis of titanium alkoxide completely removes. Then precipitate dissolved in aqueous hydrogen peroxide (50%), which resulted in a very exothermic reaction. Additional water (200 mL) added to reduce the reaction rate and avoid the development of a highly viscous polymeric gel phase. A clear yellow solution formed within 30 min, the colour of which is characteristic of a titanium peroxo complex. To it added the aqueous solution of precursor MoO₃ dropwise with stirring. Then the solution was kept overnight to form the uniform gel. After gelation air dried the gel, crushed it. The resulting powder dried in oven @ 100 °C then calcined @ 500 °C for 5 hr. (heating rate 2 °C/min.).

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e) 2% WO₃/TiO₂:

In typical procedure Titanium(IV) tetrabutoxide hydrolysed with deionized water (500 mL) and stirred vigorously for 10 min. The resulting titanium hydroxide precipitate separated by decantation and thoroughly washed with water until the alcohol generated during the hydrolysis of titanium alkoxide completely removes. Then precipitate dissolved in aqueous hydrogen peroxide (50%), which resulted in a very exothermic reaction. Additional water (200 mL) added to reduce the reaction rate and avoid the development of a highly viscous polymeric gel phase. A clear yellow solution formed within 30 min, the colour of which is characteristic of a titanium peroxo complex. To it added the aqueous solution (in 50% H₂O₂) of precursor AMT dropwise with stirring. Then the solution was kept overnight to form the uniform gel. After gelation air dried the gel, crushed it. The resulting powder dried in oven @ 100 °C then calcined @ 500 °C for 5 hr. (heating rate 2 °C/min.).

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f) 5% Mo Si/Al (7.5) Impr:

In typical procedure aluminium isopropoxide was taken in a beaker to this IPA was added, kept for stirring. To dissolve aluminium isopropoxide HNO_3 was added ml by ml till it dissolves. In a separate beaker TEOS + IPA was taken, kept for stirring. To the clear solution of aluminium isopropoxide, TEOS + IPA mixture was added drop wise with stirring. The homogeneous mixture was stirred for 2hrs then NH_3 (1% NH_3 in IPA) was added drop wise for gelation. The viscous liquid kept for gelation. Formed gel was oven dried at 60°C . The dried, grinded gel kept for calcination for 5hr at 500°C . Then aqueous solution of ammonium heptamolybdate added to silica alumina support in an impregnation method. This mixture was stirred on hot plate to dry with stirring. The dried catalyst was calcined at 500°C for 5hr.

Example 3: Recycle study for liquid phase iodination of aromatics:

A 250 mL two-necked round bottom flask fitted with condenser was charged 1 g 2,6 Dimethyl aniline (0.01 mol), 2.5 g iodine (0.01 mol), 100 mL 1,2-dichloroethane, and 0.2 g catalyst. The flask was flushed with argon. The reaction was carried out at room temperature (Table 2) for 1 hr. The reaction was monitored by GC analysis. The reaction mixture decanted leaving catalyst in the RB. The RB was charged with fresh reactants and it was stirred for 1 hr. The cycle was repeated 3 times.

Table 2: Recycle study

Sr. No.	Recycle no.	% conversion
1	0	77
2	1	74
3	2	78
4	3	76

Example 4: Continuous flow iodination:

In 10 cm fixed bed reactor 2 g 20% WO_3/SiO_2 was loaded. Reaction mixture containing 1 g aniline (0.01 mol), 2.8 g Iodine (0.01 mol) dissolved in 50 mL ethylene dichloride passed through the reactor at the flow rate of 3.5 ml/hr. Samples were collected at regular intervals and analyzed with GC. (Table 3)

Table 3: Continuous flow iodination

Sr. No.	Sample (hrs)	% conversion
1	0.25	69
2	0.5	68
3	0.75	68
4	1	70
5	3.5	69
6	7	68
7	18	70

Example 5: Bromination of aniline:

A 25 mL two-necked round bottom flask was fitted with condenser. Initially 0.1 g aniline (0.001 mol) was added to the flask followed by 10 mL solvent. After this 0.1 g bromine (0.0012 mol) was added to the same flask followed by addition of 0.02 g 20% WO_3/SiO_2 catalyst. The reaction was carried out at room temperature (25 °C) for 10 mins. The reaction was monitored by GC analysis. There was 100% aniline conversion observed with 40, 50 and 10% selectivity for 2-bromo aniline, 4-bromo aniline and 2,4-dibromo aniline respectively.

Example 6: Chlorination of aniline:

A 25 mL two-necked round bottom flask was fitted with condenser. Initially 0.1 g aniline (0.001 mol) was added to the flask followed by 10 mL solvent. After this 0.02 g of catalyst 20% WO_3/SiO_2 added. Later 0.027 g of chlorine (0.001 mol) gas was passed through the reaction flask. The reaction was carried out at room temperature (25 °C) for 10 mins. The reaction was monitored by GC analysis. There was 40% aniline conversion observed with 40 and 60% selectivity for 2-chloro aniline and 4-chloro aniline respectively.

Example 7: Chlorination of aniline :

A 25 mL two-necked round bottom flask was fitted with condenser. Initially 0.1 g aniline (0.001 mol) was added to the flask followed by 10 mL solvent. After this 0.02 g of catalyst 20% WO_3/SiO_2 added. Later 0.04 g of chlorine (0.0015 mol) gas was passed through the reaction flask. The reaction was carried out at room temperature (25 °C) for 60 mins. The reaction was monitored by GC analysis. There was 100% aniline conversion observed with 40 and 60% selectivity for 4-chloro aniline and 2,4-dichloro aniline respectively.

ADVANTAGES OF THE INVENTION:

1. Halogenation of anilines can be carried out with >90% conversion in only 30 mins.
2. Very mild reaction conditions, No harmful or hazardous reagents needed for the reaction.
- 5 3. Ease of catalyst handling due to heterogeneous catalyst working at mild reaction conditions, Catalysts could be recycled very easily by just filtration or decantation.
4. No decrease in the conversion as well as selectivity in recycle runs.
5. No need to regenerate the catalyst or activate the catalyst for next cycles.
6. The iodination carried out in continuous mode in down-flow reactor at room temperature
10 (at 25-28 °C).

CLAIMS:

1. An improved one pot, one step process for the halogenation of substituted aromatic compound comprises addition of halogenating agent and solid acid catalyst to the mixture of substituted aromatic compound in solvent followed by stirring the reaction mixture at temperature in the range of 25 to 150°C for the period in the range of 2 to 6 hrs to afford corresponding halogenated compound.
2. The process as claimed in claim 1, wherein said substituted aromatic compound is selected from aminoaromatic compound, hydroxy aromatic compound, aromatic aldehyde compound, halo substituted aromatics, amide substituted aromatic compound.
3. The process as claimed in claim 2, wherein said aminoaromatic compound is selected from aniline, 4-Chloroaniline, 4- Bromoaniline, 2,6 dimethyl aniline, anthranilamide, 2,6 diethyl aniline.
4. The process as claimed in claim 2, wherein said hydroxy aromatic compound is selected from phenol.
5. The process as claimed in claim 2, wherein said aromatic aldehyde compound is benzaldehyde.
6. The process as claimed in claim 1, wherein said corresponding *ortho*-halogenated compound is selected from 4-chloro-2-iodoaniline, 2-iodoaniline, 4-bromo-2-iodoaniline, 4-iodo-2,6-dimethylaniline, 3-iodobenzaldehyde, 2-iodophenol, 2-amino-3-iodobenzamide, 2,6-diethyl-4-iodoaniline, 4-chloro-2,6-dimethylaniline and 4-bromo-2,6-dimethylaniline.
7. The process as claimed in claim 1, wherein said solid acid catalyst is selected from SiO₂, MoO₃/TiO₂, MoO₃/TiO₂, WO₃/TiO₂, WO₃/TiO₂ and Mo Si/Al (7.5) Impr.
8. The process as claimed in claim 1, wherein said solvent is selected from ethylene dichloride, methanol, hexane, toluene, dichloromethane, ethanol, higher alcohols, dimethylsulfoxide, dioxane, dimethylformamide, acetone, diethyl ether, butanol and benzylalcohol.

9. The process as claimed in claim 1, wherein selectivity towards said corresponding *ortho*-halogenated compound is in the range of 50 to 100%.

5 10. The process as claimed in claim 1, wherein said process is carried out in batch mode or continuous mode.

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INTERNATIONAL SEARCH REPORT

International application No

PCT/IN2017/050097

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C17/12 C07C25/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PAOLO CARNITI ET AL: "Direct Green Iodination of Phenol over Solid Acids", CATALYSIS LETTERS, KLUWER ACADEMIC PUBLISHERS-PLENUM PUBLISHERS, NE, vol. 137, no. 1-2, 16 April 2010 (2010-04-16), pages 55-62, XP019815163, ISSN: 1572-879X the whole document	1-10
X	----- US 5 473 084 A (WANG SHIAN-JY [TW] ET AL) 5 December 1995 (1995-12-05) the whole document	1-10
X	----- GB 2 155 009 A (BRITISH PETROLEUM CO PLC; UNIV SWANSEA) 18 September 1985 (1985-09-18) the whole document	1-10
	----- -/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

4 July 2017

Date of mailing of the international search report

17/07/2017

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2017/050097

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IN2017/050097

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