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(54) Title: PROCESS FOR THE PREPARATION OF 3-BROMO - 4 - FLUOROBENZALDEHYDE

(57) Abstract: The invention relates to a process of manufacturing 3-bromo-4- fluorobenzaldehyde using zinc bromide as a catalyst.

PROCESS FOR THE PREPARATION OF 3-BROMO - 4 - FLUOROBENZALDEHYDE

Field of the Invention

This invention relates to bromination reactions.
Particularly, the present invention relates to a catalyst for bromination reactions.
Still particularly, the present invention relates to a process for manufacturing 3-bromo-4- fluorobenzaldehyde using zinc bromide as a catalyst.
Still particularly, the present invention relates to a process for manufacturing of zinc bromide.

Background of the invention

Bromination is a chemical reaction that incorporates a bromine atom into a molecule.

In this specification, the term bromination will mean electrophilic aromatic bromination which is a type of electrophilic aromatic substitution. This organic reaction is typical of aromatic compounds and a very useful method for adding substituents to an aromatic system. Some aromatic compounds, such as phenol react without a catalyst, but for typical benzene derivatives with less reactive substrates, a Lewis acid catalyst is required. Typical Lewis acid catalysts include AlCl3, FeCl3, FeBr3, and ZnCl2. The bromination reaction works by forming a highly electrophilic complex which attacks the benzene ring.

Generally, bromo aromatics are widely used as intermediates in the manufacture of pharmaceuticals, agrochemicals and other specialty chemical products. 3-bromo-4- fluorobenzaldehyde (BFBA) which is used as an intermediate in the production of 4-Fluoro-3-phenoxybenzaldehyde (FPBA) which is used in the production of pyrethroid insecticides.

In the conventional methods of bromination, large amount of $AlCl_3$ is used as a catalyst. The amount of catalyst $AlCl_3$ used, is in excess (twice or thrice the mole ratio) of the 4-fluoro benzaldehyde. This leads to a large amount of waste generation which in turn causes serious effluent problems. Furthermore, the process also needs expensive and difficult treatment for the purification.

Prior Art

US 6036937 discloses a method for making zinc bromide from metallic zinc and bromine which comprises contacting zinc with bromine dissolved in a reaction solvent containing a metal halide salt. The reaction temperature is maintained at less than 60° C. The reaction solvent preferably comprises an alkali, alkaline earth or transition metal halide and the halide salt preferably comprises a chloride or a bromide. One method includes the step of recirculating the zinc bromide product stream, back to the reaction vessel. The reaction vessel can comprise either a one stage or a multiple stage reactor. The resulting product stream comprises zinc bromide solution.

US 4446075 discloses a process for the manufacture of 3-bromo-4-fluorobenzaldehyde comprising the steps of preparing 4-

fluorobenzalbromide by reacting 4-fluorotoluene with bromine, forming 4-fluorobenzaldehyde by hydrolyzing the 4-fluorobenzalbromide and preparing 3-bromo-4-fluorobenzaldehyde by subjecting the 4-fluorobenzaldehyde to direct bromination at a temperature of 20^0C to 200^0C with bromine in an amount of 0.9 to 1.3 moles per mol of 4-fluorobenzaldehyde in the presence of 0.02 to 0.3 moles of iodine or of 0.02 to 0.3 moles of a trivalent metal or of 1 to 1.2 moles of a halide of a trivalent metal, in each case per mol of 4-fluorobenzaldehyde.

WO1999038833 discloses a method for the preparation of 3-bromo-4-fluorobenzaldehyde (BFBA), which is used as an intermediate in the production of FPBA. The reaction is carried out by the catalytic bromination of 4-fluorobenzaldehyde, using $AlCl_3$ as a catalyst.

The aforesaid processes do not provide a comparatively pure product. Also, these processes lead to large amount of waste generation when $AlCl_3$ is utilized for catalytic bromination which in turn causes serious effluent problems. Furthermore, the process also needs expensive and difficult treatment for the purification of the final product.

Therefore, there is felt a need for preparation of a catalyst which accelerates the bromination reaction and which controls the formation of a large amount of sludge. Also, there is a need for the process for manufacture of 3-bromo-4-fluorobenzaldehyde in high yield and purity in a cost-effective manner.

Objects of the Invention

It is an object of the present invention to provide an improved process for the manufacture of 3-bromo-4-fluorobenzaldehyde.

Another object of the present invention is to provide a process for the manufacture of 3-bromo-4-fluorobenzaldehyde in high yield and purity.

Yet another object of the present invention is to provide a process for the manufacture of 3-bromo-4-fluorobenzaldehyde which has higher selectivity towards the product.

Still another object of the present invention is to provide a cost-effective and economically feasible process for the preparation of 3-bromo-4-fluorobenzaldehyde.

According to one aspect of the present invention there is also provided a process for manufacturing of a catalyst for bromination reactions.

According to yet another aspect of the present invention there is provided a process for preparation of zinc bromide which accelerates the bromination reaction.

According to yet another aspect of the present invention there is provided a process for preparation of zinc bromide which shows higher selectivity towards the product.

Summary of the Invention

In accordance with the present invention there is provided a process for manufacturing of 3-bromo-4-fluorobenzaldehyde comprising the following steps:

a. adding dropwise 4-fluorobenzaldehyde to a mixture containing predetermined quantities of oleum, iodine and zinc bromide under continuous stirring at a temperature in the range of about 5^0C to about 35^0C for about 2 hrs to obtain a resultant mass;

b. adding bromine dropwise to the resultant mass at a temperature in the range of about 25^0C to about 45^0C for a period of about 3 hrs to obtain a reaction mixture;

c. stirring the reaction mixture at a temperature in the range of about 25^0C to about 65^0C for about 2 hrs to obtain a reaction product containing crude 3-bromo-4-flurobenzaldehyde ;

d. quenching the reaction product containing crude 3-bromo-4-fluorobenzaldehyde in water at a temperature below 25^0C to separate the organic layer and the aqueous layer;

e. iterative washings of the organic layer with water to obtain crude 3-bromo-4-flurobenzaldehyde; and

f. distilling crude 3-bromo-4-benzaldehyde to obtain 3-bromo-4-benzaldehyde having purity greater than 95%.

In accordance with another aspect of the present invention, the separation in process step (d) includes extracting 3-bromo-4-fluorobenzaldehyde with a solvent selected from a group of solvents consisting of ethylacetate, ethylene

dichloride and aromatic hydrocarbon solvents like toluene, xylene, benzene, etc.

Typically, the weight ratio of 4-fluorobenzaldehyde to oleum is in the range of about 1:5 to about 1:15.

Typically, the iodine is introduced in an amount of about 1% to about 20% by weight, relative to 4-fluorobenzaldehyde.

Typically, the molar ratio of bromine to 4-fluorobenzaldehyde is in the range of about 0.5 to about 1.

Preferably, the molar ratio of bromine to 4-fluorobenzaldehyde is 0.6.

Typically, the SO_3 content in oleum is in the range of about 5% to about 65%.

Preferably, the SO_3 content in oleum is 20%.

Typically, the yield of 3-bromo-4-fluorobenzaldehyde having purity greater than 95% is greater than 90%.

In accordance with another aspect of the present invention, there is provided a process for manufacturing of zinc bromide which comprises the following steps:

a. slowly adding hydrogen bromide to zinc oxide in deionized water at a temperature of about 0^0C to about 35^0C and further stirring the mixture for

about 2 to about 4 hrs at a temperature of about 35^0C to about 80^0C to obtain a reaction mass;

b. azeotropically removing water by adding toluene to the reaction mass;

c. evaporating toluene from the reaction mass to obtain a wet cake containing zinc bromide; and

d. drying wet cake containing zinc bromide at a temperature of about 120^0C under vacuum to obtain white solid powder of zinc bromide having purity greater than 98%.

Typically, the molar ratio of zinc oxide to hydrogen bromide is in the range of about 1:1 to about 1:5.

Typically, the molar ratio of zinc oxide to hydrogen bromide is 1:2.

Typically, the yield of zinc bromide having purity greater than 98% is greater than 97%.

Detailed description of the Invention

A variety of methods for the bromination of aromatics have been reported in the literature. The methods for bromination of aromatic compounds involve the use of non-selective hazardous acidic reagents such as mineral acids and Lewis acid like $AlCl_3$, which can lead to separation difficulties and unacceptable levels of toxic and corrosive wastes.

Accordingly, the present invention provides a cost-effective process for manufacturing of 3-bromo-4-fluorobenzaldehyde in high yield and purity using zinc bromide as a catalyst.

In accordance with the present invention, there is provided a process for manufacturing of zinc bromide which accelerates the rate of the bromination reaction thereby increasing the final yield and purity of the product.
Zinc bromide is a white crystalline powder which is soluble in water and alcohol. It is used in the manufacture of medicines. It is also used in the manufacture of rayon and photography and in a radiation viewing screen. It is also used as a completion in oil field drilling applications.

The invention envisages the process for the preparation of 3-bromo-4-fluorobenzaldehyde by bromination of 4-fluorobenzaldehyde in the presence of zinc bromide as a catalyst. The overall yield of 3-bromo-4-fluorobenzaldehyde is above 90% with about 95% purity.

In accordance with one aspect of the present invention, there is provided a process for manufacturing of 3-bromo-4-fluorobenzaldehyde which is as follows:

4-fluorobenzaldehyde is added dropwise to a mixture containing predetermined quantities of oleum, iodine and zinc bromide under continuous stirring at a temperature in the range of about 5^0C to about 35^0C for about 2 hrs to obtain a resultant mass. Bromine is added dropwise to the resultant mass at a temperature in the range of about 25^0C to about 45^0C for a period of about 3 hrs to obtain a reaction mixture. The reaction mixture is

stirred at a temperature in the range of about 25^0C to about 65^0C for about 2 hrs to obtain a reaction product containing crude 3-bromo-4-flurobenzaldehyde. The reaction product containing crude 3-bromo-4-fluorobenzaldehyde is quenched in water at a temperature below 25^0C to separate the organic layer and the aqueous layer. The organic layer containing 3-bromo-4-fluorobenzaldehyde is extracted in toluene, the toluene is then evaporated and pale yellow 3-bromo-4-fluorobenzaldehyde having purity greater than 95% is isolated by distillation.

In another embodiment of the present invention, there is provided a process for manufacturing 3-bromo-4-fluorobenzaldehyde wherein the aqueous layer and the water washings together constitute an effluent which contains acid and metal impurities especially zinc. The effluent is passed over cation exchange resin activated with acid to remove zinc metal to less than 200ppm. The number of times the effluent is passed over the cation exchange resin ensures the maximum removal of metal impurities to less than 5ppm.

In accordance with another aspect of the invention there is provided a process for manufacturing of Zinc Bromide ($ZnBr_2$) which is as follows:
Hydrogen bromide is added slowly to zinc oxide in deionized water at a temperature of about 0^0C to about 35^0C and further stirring the mixture for about 2 to about 4 hrs at a temperature of about 35^0C to about 80^0C to obtain a reaction mass. The water is removed azeotropically by adding toluene to the reaction mass. The toluene is evaporated from the reaction mass to obtain a wet cake containing zinc bromide. The wet cake containing zinc

bromide is dried at a temperature of about 120^0C under vacuum to obtain white solid powder of zinc bromide having purity greater than 98%.

The uniqueness of the present invention lies in the process for the preparation of zinc bromide ($ZnBr_2$) which results in better selectivity towards the product obtained in the bromination reaction and improves the yield and purity of the product. Furthermore, the catalyst employed in the present invention eliminates the effluent problems thereby making the process environmental friendly.

The invention will now be described with respect to the following examples which do not limit the invention in any way and only exemplify the invention.

EXAMPLES:

Preparation of 3-bromo-4-fluorobenzaldehyde

Example 1: Using Zinc Bromide as a catalyst and Oleum (20%)

Into a 500 mL four necked flask fitted with an overhead stirrer, a condenser and a thermometer pocket, 20% Oleum 204g (7.5 times w.r.t 4-Fluorobenzaldehyde) was added to the flask slowly followed by Iodine 1.36g (5 wt% w.r.t 4-Fluorobenzaldehyde) addition. The mixture was stirred under N_2 atm for 5 min. Then zinc bromide 0.68g (2.5 wt% w.r.t 4-Fluorobenzaldehyde) was added to the reaction mass and the stirring was continued for another 5.0min. Then 4-Fluorobenzaldehyde 27.2g

(0.219mole) was added dropwise over a period of 1.0 h at 27-29°C. The resulting mixture was stirred for 15 min and then bromine (6.8mL, 0.6 Mol) was added drop wise over a period of 3h at 30°C. The reaction mass was then heated to 40°C and maintained at same temp for 90 min. and the reaction was monitored by G.C every 30 min.

G.C area% showed 97% product formation. The reaction mass was cooled to 10°C and was quenched in ice (128.0g) for a period of 2h at a temperature below 25°C. The organic portion was extracted with 2x 100 mL of toluene followed by washing with 3x100mL water. The organic layer was treated with thiosulfate to remove unreacted bromine present in the crude. The final mass was washed with water and then the organic layer was separated and dried over Na_2SO_4 and the liquid was evaporated to give crude pale yellow product 42.72 gm (96% isolated yield with GC purity 96%).

The aqueous layer and the water washings together constitute an effluent which contains acid and metal impurities especially zinc. The effluent is passed over cation exchange resin activated with acid at a temperature of 60^0C to 80^0C to remove zinc metal to less than 200ppm. The number of times the effluent is passed over the cation exchange resin ensures the maximum removal of metal impurities to less than 5ppm.

Example 2: Using Zinc Bromide as a catalyst and Oleum (65% SO_3)

Into a 500 mL four necked flask fitted with an overhead stirrer, a condenser and a thermometer pocket, 65% Oleum 204g (7.5 times w.r.t. 4-

Fluorobenzaldehyde) was added to the flask slowly followed by iodine 0.27g (1 wt% w.r.t 4-Fluorobenzaldehyde) addition. The mixture was stirred under N_2 atm. for 5 min. Then zinc bromide 0.68g (2.5wt% w.r.t 4-Fluorobenzaldehyde) was added to the reaction mass and the stirring was continued for another 5.0min. Then 4-Fluorobenzaldehyde (27.2g, 0.219mole) was added dropwise over a period of 1.0 h at temperature below 30°C. The resulting mixture was stirred for 15 min and then bromine (6.8mL, 0.131mol) was added drop wise over a period of 3h at a temperature below 30°C. Then the reaction mass was heated to 40°C and maintained at same temperature for 90 min. and the reaction was monitored by G.C every 30 min. G.C area% showed 98% product formation. The reaction mass was cooled to 10 °C and was quenched in ice (128.0g) over a period of 2h at a temperature below 25 °C. The organic portion was extracted with 2x 100 mL of toluene followed by washing with 3x100mL water. The organic layer was treated with thiosulfate to remove unreacted bromine present in the crude. The final mass was washed with water and then the organic layer was separated and dried over Na_2SO_4 and the liquid was evaporated to give crude pale yellow product 43.19 gm (97% yield). GC purity was 96%.

Example 3: Using Zinc Sulphate as a catalyst

Into a flask as mentioned above, 20% Oleum (204g) was added to the flask slowly followed by iodine (1.36g, 5.0% with BFB) addition and the mixture was stirred under N_2 atm for 5.0min. Then zinc sulfate (0.68g, 2.5wt% w.r.t 4-Fluorobenzaldehyde) was added to the reaction mass and the stirring was continued for 5.0 min. Into the mixture, 4-Fluorobenzaldehyde (27.2g,

0.219mole) was added dropwise over a period of 1.0h below 28°C. The reaction mass was stirred for 15 min and then bromine (6.8mL, 0.131mol) was added dropwise over a period of 3h at 30°C. Reaction mass was heated to 40°C and maintained at same temp for 90 min. The progress of the reaction was monitored by G.C with time intervals of 30 min. G.C result showed 95% product formation. The reaction mass was then cooled to 10 °C and followed by quenching in ice (128.0g) over a period of 2h below 25 °C. The reaction mass was extracted with 2 x 100 mL of toluene followed by 3x100mL water washing to the combined organic layer. Organic layer was dried with Na_2SO_4 and evaporated to give crude pale yellow product 40.94 gm (92% yield with GC purity 94 %.)

Example 4: Using Zinc Sulphate as catalyst

Into the flask mentioned in example 1, 20% Oleum (204g) was added slowly followed by iodine (0.55 g, 2 wt% w.r.t 4-Fluorobenzaldehyde) addition and the mixture was stirred under N_2 for 5.0 min. Zinc sulfate (0.68g, 2.5%) was added to the reaction mass and the stirring was continued for 5.0 min. It was then followed by 4-Fluorobenzaldehyde addition (27.2g, 0.219mole, 1.0mol eq.) dropwise over a period of 1.0 h below 30°C. The reaction mass was stirred for 15 min and then bromine (6.8mL, 0.6 Mol Eq, 0.131mol) was added drop wise over a period of 3h at 30°C. Reaction mass was heated to 40°C and maintained at same temperature for 2.5 h. The progress of the reaction was monitored by G.C with time interval of 30 min. G.C results showed 96% product formation. The reaction mass was cooled to 10 °C and was quenched in ice (128.0g) in a period of 2h below 25 °C. The organic mass was extracted with 2 x100 mL of toluene followed by

washing with 3x100mL water. Organic layer was dried with Na_2SO_4 and evaporated to give resulted pale yellow product, 39.16 gm (88% yield, GC purity 95%).

Example 5: Using Aluminium Sulphate as a catalyst

Into a flask as mentioned in example 1, 20% Oleum (204g) was added slowly followed by iodine (1.36g, 5wt% w.r.t 4-Fluorobenzaldehyde) addition and the mixture was stirred under N_2 atm for 5.0 min. Aluminum sulfate (0.68g, 2.5%) was added to the reaction mass and continued stirring for 5.0min. It was then followed by 4-Fluorobenzaldehyde addition (27.2g, 0.219mole, 1.0mol eq.) dropwise over a period of 1.0h below 29°C. The reaction mass was stirred for 15 min and then was added bromine (6.8mL, 0.6 Mol Eq, 0.131mol) drop wise in a period of 3h at 30°C. The resulting reaction mass was heated to 40°C and maintained at same temp for 2h. The reaction was monitored by G.C with time interval of 30 min.
G.C result showed 95% product formation. The reaction mass was cooled to 10 °C and was quenched in ice (128.0g) over a period of 2.0h below 25 °C. The organic layer was extracted with 2x 100 mL of toluene followed by washing with 3x100mL water. The organic layer was then dried with Na_2SO_4 and evaporated to give pale yellow product, 40.94 gm (92% yield, GC purity 94%).

Example 6: Using TriCalcium Phosphate as a catalyst

Into a flask as mention in example 1, 20% Oleum (204g) was added to the flask slowly followed by iodine (1.36g, 5 wt% w.r.t 4-Fluorobenzaldehyde)

addition and the mixture was stirred under N_2 atm for 5.0min. Tri calcium phosphate (0.68g, 2.5%) was added to the reaction mass and continued stirring for 5.0min. It was then followed by 4-Fluorobenzaldehyde addition (27.2g, 0.219mole, 1.0mol eq.) dropwise over a period of 1.0h below 27~29°C. Then the reaction mass was stirred for 15 min and then added bromine (6.8mL, 0.6 Mol Eq, 0.131mol) drop wise in a period of 3h at 30°C. The resulting reaction mass was heated to 40°C and maintained at same temp for 2.0h. Reaction was monitored by G.C with time interval of 30 min. G.C result showed 97% product formation. The reaction mass was cooled to 10 °C and was quenched in ice (128.0g) over a period of 2h below 25 °C. The reaction mass was extracted with 2x100 mL of toluene followed by washing with 3 x100mL water. The organic layer was dried with Na_2SO_4 and evaporated to give pale yellow product with a yield of 42.27 gm (95% yield with GC purity of 95%).

Preparation of Zinc bromide ($ZnBr_2$) catalyst

Example

16.2 gm (0.2 moles) zinc oxide was stirred with 100 ml deionized water in 250 ml round bottom flask of three necks. To this 74.8 gm (0.44 mol) of HBr 47% solution was added slowly. The solution obtained was stirred for 4 hrs at 50°C. The water was removed azeotropically by toluene. The toluene was then evaporated to give zinc bromide which was further dried under vaccum at 120^0C to give white solid powder with the purity greater than 98% and with 97% yield.

Table-I

Comparison of yield and purity of 3-bromo-4-fluorobenzaldehyde using different catalyst:

Examples	Catalyst	Crude Yield	Purity
1	$ZnBr_2$/Oleum (20% SO_3)	96% **	96%
2	$ZnBr_2$/Oleum (65% SO_3)	97%	96%
3	$ZnSO_4$	92%	95%
5	$Al_2(SO_4)_3$	92%	94%
6	$Ca_3(PO4)_2$	95%	95%

** refers to isolated yield after distillation

While considerable emphasis has been placed herein on the specific steps of the preferred process, it will be appreciated that additional steps can be made and that many changes can be made in the preferred steps without departing from the principles of the invention. These and other changes in the preferred steps of the invention will be apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the invention and not as a limitation.

Claims:

1. A process for the preparation of 3-bromo-4-fluorobenzaldehyde which comprises:

a. adding dropwise 4-fluorobenzaldehyde to a mixture containing predetermined quantities of oleum, iodine and zinc bromide under continuous stirring at a temperature in the range of about 5^0C to about 35^0C for about 2 hrs to obtain a resultant mass;

b. adding bromine dropwise to the resultant mass at a temperature in the range of about 25^0C to about 45^0C for a period of about 3 hrs to obtain a reaction mixture;

c. stirring the reaction mixture at a temperature in the range of about 25^0C to about 65^0C for about 2 hrs to obtain a reaction product containing crude 3-bromo-4-flurobenzaldehyde ;

d. quenching the reaction product containing crude 3-bromo-4-fluorobenzaldehyde in water at a temperature below 25^0C to separate the organic layer and the aqueous layer;

e. iterative washings of the organic layer with water to obtain crude 3-bromo-4-flurobenzaldehyde; and

f. distilling crude 3-bromo-4-benzaldehyde to obtain 3-bromo-4-benzaldehyde having purity greater than 95%.

2. The process as claimed in claim 1, wherein the separation step(d) includes extracting 3-bromo-4-fluorobenzaldehyde with a solvent selected from a group of solvents consisting of ethylacetate, ethylene dichloride and aromatic hydrocarbon solvents like toluene, xylene, and benzene.

3. The process as claimed in claim 1, wherein the weight ratio of 4-fluorobenzaldehyde to oleum is in the range of about 1:5 to about 1:15.

4. The process as claimed in claim 1, wherein the iodine is present in an amount of about 1% to about 20% by weight, relative to 4-fluorobenzaldehyde.

5. The process as claimed in claim 1, wherein the molar ratio of bromine to 4-fluorobenzaldehyde is in the range of about 0.5 to about 1.

6. The process as claimed in claim 1, wherein the molar ratio of bromine to 4-fluorobenzaldehyde is 0.6.

7. The process as claimed in claim 1, wherein the SO_3 content in oleum is in the range of about 5% to about 65%.

8. The process as claimed in claim 1, wherein the SO_3 content in oleum is 20%.

9. The process as claimed in any one of the preceding claims, wherein the yield of 3-bromo-4-fluorobenzaldehyde having purity greater than 95% is greater than 90%.

10. The process as claimed in claim 1, wherein the zinc bromide is obtained by the process comprising following steps:

a. slowly adding hydrogen bromide to zinc oxide in deionized water at a temperature of about 0^0C to about 35^0C and further stirring the mixture for about 2 to about 4 hrs at a temperature of about 35^0C to about 80^0C to obtain a reaction mass;

b. azeotropically removing water by adding toluene to the reaction mass;

c. evaporating toluene from the reaction mass to obtain a wet cake containing zinc bromide; and

d. drying wet cake containing zinc bromide at a temperature of about 120^0C under vacuum to obtain white solid powder of zinc bromide having purity greater than 98%.

11. The process as claimed in claim 10, wherein the molar ratio of zinc oxide to hydrogen bromide is in the range of about 1:1 to about 1:5.

12. The process as claimed in claim 10, wherein the ratio of zinc oxide to hydrogen bromide is 1:2.

13. The process as claimed in any one of the preceding claims, wherein the yield of zinc bromide having purity greater than 98% is greater than 97%.

14. The process as claimed in claim 1, wherein the aqueous layer is passed through the cation exchange resin activated with acid to obtain treated aqueous layer.

15. The process as claimed in claim 14, wherein the concentration of zinc metal in the treated aqueous layer is less than 200 ppm.

16. The process as claimed in claim 15, wherein the concentration of zinc metal in the treated aqueous layer is less than 5 ppm.

17. A process for manufacturing of 3-bromo-4-fluorobenzaldehyde as described in the description and examples of the accompanying specification.