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(54) Titre : PROCÉDE DE PRÉPARATION D'ALCANES HALOGENES
(54) Title: PROCESS FOR THE PREPARATION OF HALOGENATED ALKANES

(57) Abrégé/Abstract:

A process for the preparation of halogenated alkanes is provided . In particular, a process is provided for the highly selective preparation of haloalkanes, including 1,1,1,3,3-pentachloropropane, pentachlorobutane, and heptachlorohexane, in good yield.



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(54) Title: PROCESS FOR THE PREPARATION OF HALOGENATED ALKANES (57) Abstract A process for the preparation of halogenated alkanes is provided . In particular, a process is provided for the highly selective preparation of haloalkanes, including 1,1,1,3,3-pentachloropropane, pentachlorobutane, and heptachlorohexane, in good yield.		

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PROCESS FOR THE PREPARATION OF HALOGENATED ALKANES

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Field of the Invention

The present invention relates to a process for the preparation of halogenated alkanes. In particular, the present invention provides a process for the highly selective preparation of haloalkanes in good yield.

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Background of the Invention

The production of haloalkanes by the addition of olefins to starting material haloalkanes is well known in the art. Further, it is known that the product's carbon chain length increases by at least one carbon atom compared to the starting material, which drastically increases the product's boiling point making recovery of the product difficult and diminishing product yield.

Several addition reactions for producing synthetically useful haloalkanes, such as 1,1,1,3,3-pentachloropropane ("HCC-240"), are described in the prior art. For example, Kotori et al. "Addition of Tetrachloromethane to Halogenated Ethenes Catalyzed by Transition Metal Complexes", 77 J. Molec. Catal. 51 - 60 (1992) disclose the preparation of HCC-240 from carbon tetrachloride and vinyl chloride using both cuprous chloride and $\text{Cu}[(\text{CH}_3\text{-CN})_4]\text{ClO}_4$ complexes with an n-butylamine cocatalyst. Catalyst and cocatalyst removal is achieved by water wash which destroys the catalyst. Additionally, the use of perchlorates in the process poses handling problems because perchlorates are extremely explosive.

Kotori et al., "Selective Addition of Polyhalogenated Compounds to Chlorosubstituted Ethenes Catalyzed by a Copper Complex", 44 React. Kinet. Catal. Lett. 415 - 19 (1991) disclose the preparation of HCC-240 from carbon tetrachloride and vinyl chloride using a cuprous chloride complex catalyst with 2-

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propylamine as a cocatalyst. The reported HCC-240 yield, however, is only 71%. Zhiryukina et al. "Synthesis of Polychloroalkanes With Several Different Chlorine-Containing Groups", 1 Izv. Akad. Nauk SSR, Ser. Khim. 152 - 57 (1983) disclose a process for preparing HCC-240 from carbon tetrachloride and vinyl chloride
5 using an $\text{Fe}(\text{CO})_5$ - ethanol catalyst, which process reportedly yields 25% HFC-240. Both of these disclosed processes are disadvantageous in that they have a low selectivity for HFC-240. The Zhiryukina et al. process is further disadvantageous because it uses a highly toxic catalyst.

None of the prior art processes provides for haloalkane production in high
10 yield and for the recycle of unreacted materials. Thus, a need exists for an efficient and economical process for the preparation of haloalkanes in high yield.

Description of the Invention and Preferred Embodiments

The present invention provides a highly selective process for the production
15 of halogenated alkanes in good yield in which process unreacted materials may be recycled. More specifically, the invention provides a process for producing halogenated alkanes which halogenated alkanes include, without limitation, prior art haloalkanes such as HCC-240 as well as haloalkanes not seen in the prior art such as pentachlorobutane ("HCC-360") and heptachlorohexane ("HCC-580").
20 HCC-240, 360, and 580 may be used as intermediates for the production of 1,1,1,3,3-pentafluoropropane ("HFC-245fa"), pentafluorobutane ("HFC-365"), and heptafluorohexane ("HFC-587"), respectively, which end-products are refrigerants, insulating gases, aerosol carriers, and solvents.

In general, the process of this invention uses a catalyst with an organic
25 ligand cocatalyst, flash distillation of organic feeds, catalyst filtration and recycle, and vacuum distillation, optionally in the presence of a metal chelating compound,

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to produce and recover product in high yield. The process may be carried out in either a batchwise or a continuous system. The production system may be closed to provide complete recycle of the unreacted feed material haloalkane and haloalkene.

5 In the first step (A) of the process of the present invention, the feed material, a haloalkane and a haloalkene, are reacted in the presence of a catalyst and cocatalyst. The specific haloalkane and haloalkene used as feed material, as well as the catalyst, cocatalyst, and reaction conditions used will depend on the desired product. Suitable feed material is commercially available. Haloalkanes
10 useful in the process of the present invention are of the formula $C_nH_mX_p$ wherein n is an integer from 1 to 200, preferably from 1 to 20, most preferably from 1 to 4, X is a halogen such as fluorine, chlorine, bromine, iodine, or mixtures thereof, and m and p are each independently 0 to $2n + 2$ provided that $m + p = 2n + 2$. Exemplary haloalkanes include, without limitation, carbon tetrachloride, 1,1,1-
15 trichloroethane, dichlorofluoromethane, 1,1,1-trichlorotrifluoroethane, 1,1,2-trichlorotrifluoroethane, tetrachloroethane, pentachloroethane, and hexachloroethane. Useful haloalkene feed material is of the formula $C_nH_yX_z$ wherein n is an integer from 2 to 200, preferably from 2 to 20 and most preferably from 2 to 4, X is a halogen such as fluorine, chlorine, bromine, iodine, or mixtures
20 thereof, and y and z are each independently 0 to $2n$ provided that $y + z = 2n$. Exemplary haloalkenes include, without limitation, vinyl chloride, 1,1-dichloroethene, trichloroethene, tetrachloroethene, chlorofluoroethene, 1,2-dichloroethene, 1,1-dichloro-difluoroethene, 1-chloro-1-propene, and 1-chloro-1-butene. For the production of HCC-240, the preferred feed materials are carbon
25 tetrachloride, available from Vulcan Chemicals, Birmingham, Alabama and vinyl chloride, available from PPG Industries, Pittsburgh, Pennsylvania. For HCC-360 production, 1,1,1-trichloroethane and 1,1-dichloroethene, both available from PPG

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Industries, are preferred. For HCC-580 production, pentachlorobutane and 1,1-dichloroethene are preferred.

Generally, the mole ratio of haloalkane to haloalkene is from about 0.02 : 1 to about 50 : 1. Preferably, the ratio is from about 1.2 : 1 to about 4.0 : 1 and
5 more preferably from about 1.5 : 1 to about 2.5 : 1 haloalkane to haloalkene.

The catalysts useful in the present invention include metal ions. Suitable catalysts include cuprous salts, organometallic cuprous compounds, iron powder, and iron chloride. Exemplary cuprous salts and organometallic cuprous compounds include, without limitation, cuprous chloride, cuprous bromide,
10 cuprous cyanide, cuprous sulfate, and cuprous phenyl. The iron powder used in this invention is a fine powder of pure metallic iron, preferably with a particle size smaller than 325 mesh. Preferably, cuprous chloride or iron powder is used.

The cocatalyst of the present invention is an organic ligand capable of forming a complex with the catalyst used and bringing the catalyst into solution..
15 Suitable ligands include organic amines, such as, without limitation, tert-butylamine, n-butylamine, sec-butylamine, 2-propylamine, benzylamine, tri-n-butylamine, and pyridine. The preferred organic amine is tert-butylamine. Alternatively, the cocatalyst may be a nitrile including, without limitation, acetonitrile, propionitrile, n-butyronitrile, benzonitrile, and phenylacetonitrile. The
20 preferred nitrile is acetonitrile. As yet another alternative, the cocatalyst may be an amide including, without limitation, hexamethylphosphoramide and dimethylformamide. Hexamethylphosphoramide is the preferred amide.

The catalysts and cocatalysts useful in the present invention are commercially available. Preferably, the catalyst-cocatalyst system is cuprous
25 chloride - tert-butylamine or iron powder-hexamethylphosphoramide. Most preferably, iron powder-hexamethylphosphoramide is used.

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The catalyst and cocatalyst are used in amounts sufficient to catalyze the reaction of the feed material. Generally, the amount used is a mole ratio of catalyst to cocatalyst from about 0.01 : 1 to about 50 : 1, preferably from about 0.1 : 1 to about 3 : 1. The mole ratio of copper to t-butylamine is about 0.05 : 1 to about 2.0 : 1, preferably about 0.02 : 1 to 1.0 : 1, and more preferably about 0.1 : 1 to about 0.7 : 1. The mole ratio of iron powder to hexamethylphosphoramide may be about 0.05 : 1 to about 10.0 : 1, preferably about 1.0 : 1 to about 3.0 : 1, and more preferably about 1.5 : 1 to about 2.5 : 1. The preferred concentration of the catalyst in the reaction mixture is from about 0.01 to about 10 weight percent, preferably from about 1 to about 5 weight percent, and more preferably from about 1.5 to about 2.5 weight percent.

The catalyst may be added to the reactor containing the haloalkane, haloalkene, and cocatalyst. Alternatively, the haloalkane and haloalkene may be added to a reactor containing the catalyst and cocatalyst. As yet another alternative, and preferably, the catalyst, cocatalyst and haloalkane are mixed first, the mixture degassed by quick partial evacuation of the vapors, with or without cooling of the mixture, and the haloalkene is added to the mixture.

The reactor is heated to a temperature of from about 40° C to about 180° C, preferably from about 85° C to about 110° C, with agitation and under the vapor pressure of the reagents. The reaction is carried out until a conversion higher than 95% is achieved, generally for a period of from about 6 hours to about 24 hours, preferably from about 6 hours to about 12 hours.

After an initial period of high reaction rates, the reactor pressure may fall. At this point, optionally, the temperature may be increased an additional 10° to 60° to improve conversion.

In the second-step (B) of the process, the product stream from step (A) is flash-distilled to remove unreacted haloalkane and haloalkene feed materials and

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cocatalyst. The distillation may be performed in one or more distillation columns which are well known in the art. Preferably, the flash distillation is conducted in two steps: first, flash distillation is conducted under atmospheric pressure at about 85° C followed by vacuum flash distillation to remove unreacted haloalkane,
5 haloalkene, and cocatalyst. The vacuum flash distillation should be carried out until the pressure falls to 50 mm Hg at 80° C. The distilled, unreacted haloalkane, haloalkene, and cocatalyst may be recycled back to the reactor.

In the third step (C), the "bottoms" stream, containing crude product and catalyst, from the flash distillation step (B) are filtered by any commonly known
10 filter, preferably using vacuum or an inert gas pressure, such as nitrogen, to push the liquid through the filter. The catalyst may be recycled back to the reactor.

The fourth step (D) of the process of the present invention, provides for the purification of the crude product by distillation. Fractional vacuum distillation is carried out at about 5 to about 50 mm Hg and a temperature of about 89° C to
15 about 110° C to recover the product. It has been discovered that, when step (D) is carried out in the presence of a trialkyl phosphate such as tributyl phosphate or other metal chelating compound, the distillation yield of purified product is significantly improved. Although not seeking to be bound by any particular theory, it is believed that the tributyl phosphate acts to prevent the decomposition of the
20 product haloalkane. Thus, in a preferred embodiment, step (D) includes the addition of an amount of a metal chelating compound sufficient to improve the haloalkane product yield. Preferably, 5 weight percent of tributyl phosphate is used.

The process of the present invention and its use will be clarified further by a
25 consideration of the following examples.

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Examples

Example 1

1.56 g vinyl chloride and 64.25 g CCl_4 were added to an evacuated 100 ml
5 pressure bottle containing 0.59 g iron powder and 1.0 g
hexamethyphosphoramide. The bottle was immersed in an ultrathermostatic bath
and equipped with a magnetic stirring bar and pressure gauge. The agitation was
turned on and the bath warmed quickly to 100° C. The reaction was interrupted
after six hours by quickly cooling the bath. The crude product, 63.63 g, was
10 analyzed by GC and indicated formation of 1.12 g HCC-240. Selectivity was
100% based on vinyl chloride.

Example 2

0.52 g CuCl was added gradually to a mixture of 9.94 g vinylidene
chloride, 50.20 g 1,1,1-trichloroethane, and 1.0 g t-butylamine in a 100 ml pressure
15 bottle. The pressure bottle was immersed in an ultrathermostatic bath and
equipped with a magnetic stirring bar and pressure gauge. The agitation was
turned on and the bath quickly warmed to 95° C. The reaction was interrupted
after 6 hours by quick cooling of the bath. The crude product, 56.16 g, was
analyzed using gas chromatography and an FID detector. Analysis of the crude
20 product indicated formation of 0.82 g HCC-360. Selectivities were 82% based on
vinylidene chloride and 90% based on 1,1,1-trichloroethane. Selectivity toward
HCC-580 was 18.05% based on vinylidene chloride.

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Example 2a

56.1 g of the crude reaction mixture is prepared as in Example 2 and is fractionally distilled at about 71° C, initially at atmospheric pressure and subsequently under reduced pressure, down to 20 mm Hg to recover the starting materials. Solid catalyst is precipitated from the distillation flask and is filtered off. The filtrate, 9.48 g is fractionally distilled using a fractional distillation high vacuum column. 8.2 g pentachlorobutane is separated at 10 mm Hg and 71° C. Two isomers, 1,2,2,3,3-pentachlorobutane and 1,1,1,3,3-pentachlorobutane are seen.

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Example 2b

Vacuum distillation as in Example 2a is continued with a two-stage oil vacuum pump. The material remaining in the distillation flask is distilled at 0.2 mm Hg and 84° C. 1.28 g pure heptachlorohexane is distilled. Four isomers, 1,2,2,4,4,5,5-heptachlorohexane, 1,1,1,3,3,5,5-heptachlorohexane, 1,2,2,3,3,5,5-heptachlorohexane and 1,1,1,4,4,5,5-heptachlorohexane are seen.

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Example 3

0.20 g CuCl was added gradually to a mixture of 1.81 g vinyl chloride and 65.47 g CCl₄ containing 0.50 g t-butylamine in a 100 ml pressure bottle. The bottle was immersed in an ultrathermostatic bath and equipped with a magnetic stirring bar and pressure gauge. The agitation was turned on and the bath quickly warmed to 100° C. The reaction was interrupted after six hours by quickly cooling the bath. The crude product, 63.68 g, was analyzed by GC and indicated formation of 0.86 g HCC-240. Selectivity was 97.7% based on vinyl chloride.

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Comparative Example 3

0.20 g CuCl was added gradually to a mixture of 4.52 g vinyl chloride and 61.55 g CCl₄ containing 1.08 g n-butylamine in a 100 ml pressure bottle. The
5 bottle was immersed, equipped, agitated, warmed, reacted, and cooled as for Example 3. The crude product, 57.20 g, was analyzed using GC Analysis and indicated formation of 14.79 g HCC-240. Selectivity was 91.6% based on vinyl chloride.

The foregoing examples demonstrate that the use of t-butyl amine
10 cocatalyst resulted in a higher selectivity than n-butylamine cocatalyst. Further, t-butyl amine boils at a lower temperature than n-butyl amine making it easier to recover by flash distillation so that it may be recycled.

Example 4

Flash distillation to recover unreacted material and cocatalyst was
15 demonstrated using a synthetic mixture. Crude HCC-240 reaction product was simulated by mixing 1524 g crude HCC-240, 1481 g CCl₄, 28.05 g t-butylamine, and 14.24 g CuCl. CCl₄ and t-butylamine were recovered using flash distillation carried out in a 2 in. diameter, 2 ft long, column, initially under atmospheric pressure. When output of the distillation stopped, the pressure was gradually
20 reduced to 55 mm Hg to ensure a continuous and steady distillation output. Almost all of the t-butylamine and CCl₄ was recovered from flash distillation. Solid catalyst, CuCl/CuCl₂, was precipitated out of the solution in the distillation flask.

Example 5

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The solid -containing solution remaining in the distillation flask of Example 4 was removed to a Buchner funnel and filtered with No. 1 Whatman filter paper. The filtration was conducted using 60 mm Hg vacuum in an open system. The mother liquor consisted mainly of HCC-240. ICAP analysis indicated that it
5 contained only 168 ppm copper catalyst.

Example 6

684.0 g of the filtered crude HCC-240 of Example 5 was charged to a 1000
10 ml round bottom flask in a vacuum distillation apparatus. 10.2 g tri(n-butylphosphate) was added. The charged material was flash distilled under 50 mm Hg vacuum at 89 - 90° C. The distillation was interrupted when the reboiler flask was almost empty and no more droplets of distillate were observed. The residual material contained 2.7 g HCC-240, a loss of 0.4% of the starting material and was
15 brown in color without the presence of tars. The distillate weighed 668.6 g, 97.74% of the starting weight. Weight accountability of the distillation was 98.14%.

Comparative Example 6

721.1 g of the filtered crude HCC-240 of Example 5 was charged to a 1000
20 ml round bottom flask in a vacuum distillation apparatus. No tri(n-butylphosphate) was added. The material was distilled under 50 mm Hg vacuum at 89 - 90° C. The distillation was interrupted when beginning decomposition of the reboiler material was observed. The residual material in the reboiler flask became tarry and the distilled material dropping from the condenser turned brown. The reboiler was
25 quickly cooled and the residual material weighed. The residue was tarry and difficult to remove from the flask. The weight of HCC-240 lost as reboiler residue

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was 55.5 g, 7.7% of the starting weight. The distillate weighed 642.1 g, 89.04% of the starting weight. Weight accountability of the distillation was 96.74%.

Examples 6 and Comparative Example 6 illustrate that the use of a metal chelating compound provides improved distillation yields and prevents the decomposition of product and tar formation.

Other embodiments of this invention will be apparent from a consideration of this specification or the practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only with the true scope and spirit of the invention being indicated in the following claims.

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What is claimed is:

1. A process for producing a haloalkane, comprising the steps of:
 - (A) reacting a feed material comprising a haloalkane and a haloalkene in the
5 presence of a catalyst and a cocatalyst under conditions suitable to produce a
haloalkane product stream;
 - (B) flash-distilling the haloalkane product stream of step (A) to produce a
first stream comprising unreacted feed material and the cocatalyst and a second
stream comprising a haloalkane product and the catalyst;
 - 10 (C) filtering the second stream of step (B) to remove the catalyst from the
haloalkane product; and
 - (D) distilling the haloalkane product.
2. The process of claim 1 wherein step (D) is carried out in the presence of a
15 metal chelating compound present in an amount sufficient to improve the
haloalkane product yield.
3. The process of claims 1 or 2 wherein the haloalkane is carbon tetrachloride and
20 the haloalkene is vinyl chloride.
4. The process of claims 1 or 2 wherein the haloalkane is 1,1,1-trichloroethane and
the haloalkene is 1,1-dichloroethene.
- 25 5. The process of claims 1 or 2 wherein the haloalkane is pentachlorobutane and
the haloalkene is 1,1,-dichloroethene.
6. A process for producing a haloalkane, comprising the steps of:

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(A) reacting a feed material comprising a haloalkane and a haloalkene in the presence of a catalyst and a cocatalyst under conditions suitable to produce a haloalkane product stream;

(B) flash-distilling the haloalkane product stream of step (A) to produce a first stream comprising unreacted feed material and the cocatalyst and a second stream comprising a haloalkane product and the catalyst;

(C) recycling the first stream of step (B) to step (A);

(D) filtering the second stream of step (B) to remove the catalyst from the haloalkane product;

(E) recycling the catalyst removed in step (D) to step (A); and

(F) distilling the haloalkane product.

7. A process for producing a haloalkane, comprising the steps of:

(A) reacting a feed material comprising a haloalkane and a haloalkene in the presence of a catalyst and a cocatalyst under conditions suitable to produce a haloalkane product stream;

(B) flash-distilling the product stream of step (A) to produce a first stream comprising unreacted feed material and the cocatalyst and a second stream comprising a haloalkane product and the catalyst;

(C) recycling the first stream of step (B) to step (A);

(D) filtering the second stream of step (B) to remove the catalyst from the haloalkane product;

(E) recycling the catalyst removed in step (D) to step (A); and

(F) purifying the haloalkane product in the presence of a metal chelating compound present in an amount sufficient to improve the haloalkane product yield.

8. A process of any one of claims 1, 6 or 7 wherein the haloalkane product is pentachlorobutane.

9. A process of any one of claims 1, 6 or 7 wherein the haloalkane product is heptachlorohexane.
10. The process of claim 6, wherein step (F) comprises distilling the haloalkane product in the presence of a metal chelating compound, present in
5 an amount sufficient to improve the haloalkane product yield.