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(54) Process for the dehalogenation of organic compounds

Verfahren zur Dehalogenierung von Organoverbindungen

Procédé pour la déshalogénation de composés organiques

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Description

Field of The Invention

The present invention relates to a process for the dehalogenation of organic compounds. More particularly, the invention relates to the degradation and detoxification of organic compounds containing halogen atoms.

Background of The Invention

Organic halogenated compounds are obtained in relatively large amounts as by-products of various industrial processes. Representative - but not limitative - examples of such compounds are chloro- or bromo-aromatic compounds, such as polychlorinated and polybrominated biphenyls (PCBs and PBBs), polychloro heterocyclic compounds, such as p-hexachlorocyclohexane, and organic solvents such as chlorobenzene. These products are toxic and hazardous, and must be disposed of in an effective manner.

Disposal of PCBs by incineration is expensive, due to the thermal stability of these compounds and it is complicated because highly toxic substances, such as 2,3,7,8-tetrachlorodibenzo-p-dioxin may be emitted during the process. Only a few specialized incinerators are licensed to handle such dangerous materials, and the facilities in which these processes are carried out are accused of causing environmental pollution [New Scientist, 14.10.89]. Because of these problems, many efforts have been made in the art to develop effective and safe processes for the chemical degradation of halogenated organic compounds, especially PCBs.

The Prior Art

Many processes have been provided in the art, including processes for the chemical treatment and reclamation of oils and liquids containing various quantities of halogenated hydrocarbons. Processes of this type can be divided into two main categories. The first type of process includes the reductive dehalogenation, wherein the organic substances are treated with hydrogen gas (e.g., US-A-4,840,721, US-A-4,818,368, EP-A-306,164 and EP-A-299,149), or with other hydrogen donating compounds such as alkali hydride (GB-A-2,189,804), hypophosphite (US-A-4,618,686), sodium borohydride (US-A-4 804 779. These processes present several severe drawbacks, because they usually involve either complicated hydrogenation processes using explosive gases at high temperatures and pressures, which must be performed in specially designated reactors, or they involve the use of special reagents which are unfavored in industry for economical and safety reasons. Furthermore, HCl is produced in the process, which, as will be apparent to a skilled chemist, represents an added complication.

The second type of dehalogenation processes involves the reactions of metals, alkali earth metals, alkali metals, or compounds of these metals which are chemically capable of causing the degradation of a carbon-halogen bond, and which lead to the transformation of the organic halogen into an inorganic halogen bonded to the metal. Some examples of such processes are the use of metal or metals compounds such as tin, lead, aluminum, chloroaluminates, titanium, aluminum oxide, etc. (EP-A-277,858, EP-A-184,342 and US-A-4,435,379). The most used compounds are alkali metals and alkali metal compounds such as sodium/sodium hydroxide (US-A-4,755,628, CA-A-1,185,265 and EP-A-99,951), sodium naphthalene, sodium polyethylene glycol (EP-A-140,999 and EP-A-60,089), sodium carbonate, bicarbonate, alcoholates, etc. (US-A-4,631,183 and EP-A-306,398).

Processes of this type also present considerable drawbacks. For the less reactive metals, dehalogenation usually involves high temperatures, in the order of 500-1000°C, which are needed for the cleavage of the stable carbon-chlorine bond, and for the purpose of bringing the metal into contact with the organic compound in the form of molten salt, fine dispersion, etc.

Active metallic compounds, on the other hand, may react at lower temperatures, in the order of 300-600°C. However, a large excess of expensive reagents are needed, and the process involves separation and purification steps which render it both complicated and expensive.

Metallic compounds capable of inducing the dehalogenation at low temperatures are very reactive, and therefore their handling and use are limited by the need for rigorous anhydrous conditions and inert atmosphere, which are required to avoid the danger of uncontrolled exothermic decomposition of these compounds. These processes, therefore, are highly hazardous and expensive.

It is therefore clear that it would be highly desirable to provide a process for the dehalogenation of waste organic compounds which is both simple and inexpensive.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide such a process, which overcomes the drawbacks of the prior art, which does not require specially designed equipment, which is simple, inexpensive and non-hazardous.

The process for the dehalogenation of organohalides according to the invention comprises reacting an organohalide or a mixture of two or more organohalides with an alkali hydroxide in an alcoholic solution and in the presence of a heterogeneous transfer hydrogenolysis catalyst and in the abscence of added hydrogen.

Detailed Description of The Invention

Preferably, the alcohol found in the alcoholic solution is a lower alcohol. The preferred alkali hydroxide is sodium or potassium hydroxide, although of course other hydroxides may be employed.

As to the catalyst, any transfer hydrogenolysis catalyst may be employed, as long as a catalytically effective amount is provided. A preferred catalyst would be, e.g., palladium-on-carbon. This catalyst is usually provided as 5% or 10% palladium-on-carbon.

The process of the invention is very convenient as far as temperatures are concerned. Preferred reaction temperatures are comprised between 50° and 150°C. Although higher temperatures could be employed, this is generally not required. Likewise, the reaction can proceed at low pressures, e.g., atmospheric pressure in an open vessel. Normally it will be preferred to carry out the reaction in a closed reactor at pressures lower than 3-4 atmospheres. This, as will be apparent to a skilled person, is a considerable advantage over the prior art, which requires considerably higher temperatures and pressures.

Furthermore, the process of the invention does not require anhydrous conditions and may be conveniently carried out in the presence of high water concentrations (e.g., 25%). This is an additional advantage of the invention, since anhydrous conditions require efforts and expenses.

Preferably, the concentration of the organohalides in the reaction mixture is comprised between 0.1-10% of the reaction mixture, and the alkali hydroxide is present in a stoichiometric excess over the organohalides. Usually, the concentration of organohalides remaining in the reaction mixture under normal conditions is lower than the detection limits.

The catalyst used in the reaction can be quantitively recovered after completion of the reaction, washed with water, and reused in a subsequent reaction. Therefore, this process is highly efficient also from the point of view of catalyst usage.

The invention also encompasses a process for the purification and the reclamation of fluids which are contaminated with organohalides, which process comprises contacting the fluid to be purified with a stoichiometric excess of an alkali hydroxide, with respect to the organohalide, in an alcoholic solution and in the presence of a catalytically effective amount of a heterogeneous transfer hydrogenolysis catalyst. Examples of such contaminated fluids are, e.g., mineral oils, silicon oils, lube oils, gas oils, transformation oils, which may be contaminated, e.g., with chlorinated organic compounds in a concentration range of about 0.1-60%.

The above and other characteristics and advantages of the invention will now be better understood through the following illustrative and non-limitative examples of preferred embodiments thereof. In the following examples a commercial dielectric liquid "Pyralene" was used to determine the effectiveness of the process. "Pyralene" is a trade name for a dielectric fluid produced by "Progil Fabrique-France". Pyralene contains about 40% by weight trichlorobenzene and 60% PCBs mixture. Total chlorine contents in Pyralene is approximately 60%. Quantification of total PCB contents in Pyralene was performed according to the method of A. Kuchen, O. Blaster and B. Marek [Fresenius Z. Anal. Chem., 326, 747 (1987)], using sodium aluminum hydride for analytical reductive dehalogenation. A value of 22% by weight of dehalogenated biphenyl was obtained.

Example 1

0.2 ml, 286 mg Pyralene, 780 mg sodium hydroxide (19.5 mmol) and 30 mg palladium on carbon 10% (0.03 mA palladium) were placed in a glass reactor and 2.5 ml methanol were added. The reactor was purged twice with nitrogen, sealed and heated to 100°C for 16 hours. At the conclusion of the reaction, the catalyst was separated by filtration or centrifugation, washed with tetrahydrofuran (THF) and methanol, and the combined filtrates were subjected to GC and HPLC analysis.

No observable remainder of Pyralene were detected. Organic products were mainly benzene and biphenyl (68 mg, 24.5% weight of starting Pyralene) indicating total dehalogenation of PCBs, based on dechlorination quantification. The dehalogenated reaction mixture was subjected to GC analysis using EC detector. The chromatogram (Fig. 1) reveals that none of the components of the starting Pyralene remained in any detectable amount after the dehalogenation. The chromatogram of 12 ppm solution of Pyralene (Fig. 2) consists of 8-10 components with retention times of 43-206 min. Taking into account that 10% of these components would still be observable, one can conclude that the concentration of Pyralene components dropped from 120,000 ppm to less than 1.0 ppm, which means over 99.999% decomposition.

Example 2

Example 1 was repeated but without introduction of catalyst. No change in the starting Pyralene was observed in GC-EC analysis and no biphenyl was detected, as observed in GC-FID and HPLC analysis.

Example 3

Example 1 was repeated but without nitrogen purging. No residual Pyralene was observed, indicating less than 1.0 ppm PCBs contents. Biphenyl (24.5% weight) was determined by GC and HPLC, indicating total hydrogenolysis of PCBs.

Example 4

Example 1 was repeated but 0.25 ml water was introduced in addition to the methanol. Biphenyl (25% weight) was determined after the reaction was concluded. GC analysis revealed that no residual Pyralene components were left. A sole product with low retention time (20 min.) was detected in a concentration scale 1/10,000 lower than the starting Pyralene.

Example 5

1 ml (1.475 gr) of Pyralene, 3.6 gr sodium hydroxide (90 mmol) and 50 mg palladium on carbon 10% were placed in a 100 ml flask provided with a magnetic stirrer and a reflux condenser. 8 ml methanol and 2 ml water were added and the mixture was heated with stirring to 80°C for 18 hours. At the conclusion of the reaction the catalyst was separated and the filtrate was analyzed by GC.

No observable remainders of Pyralene were detected by GC-EC detector. Traces of products with lower retention times were detected. After completion of the reaction, 385 mg of biphenyl (26%) were found in the mixture by GC analysis.

Example 6

Catalyst from example 5 was washed with water and with THF and then dried under vacuum at 100°C to constant weight (57 mg). This catalyst was added together with 1.54 gr Pyralene, 3.6 gr sodium hydroxide, 10 ml methanol and 2 ml water into the reaction flask. The mixture was heated to 80°C for 18 hours.

At the conclusion of the reaction 308 mg biphenyl (20% weight) were determined in the mixture, indicating that the recycled catalyst is effective.

Example 7

Reclamation of Mineral Oil

Example 1 was repeated but 0.5 ml mineral oil contaminated with 0.2 ml (280 mg) Pyralene were added to the dehalogenation mixture. After completion of the reaction, the oil was separated from the methanol by means of phase separation. The solid was washed with methanol and the combined methanol fractions were subjected to GC and HPLC analysis. The oil phase was dissolved in THF and was subjected to GC and HPLC analysis.

No observable remainders of Pyralene were detected in the solutions. Organic products contain mainly benzene and biphenyl (68.6 mg), 24.5% weight of starting Pyralene.

Examples 8-20

Various halogenated compounds were dehalogenated according to the following procedure.

Halogenated compound (1 mmol), 0.72 gr sodium hydroxide (18 mmol), and 10 mg 10% palladium on carbon (0.01 mAtom Pd) were placed in a glass reactor, and 2.5 ml of methanol were added to this mixture. The reactor was purged twice with nitrogen, sealed and heated to 100°C for 16 hours.

The results of these reactions are summarized in Table I below.

Example 21

Example 1 was repeated, but with 1 gr (18 mmol) of potassium hydroxide as a base. After the conclusion of the reaction, no residual Pyralene was detected by GC (EC detector) analysis. Biphenyl (70.5 mg, 24.5% weight) was determined by GC and HPLC, indicating a highly efficient dehalogenation reaction.

Example 22

Example 1 was repeated but with 2.5 ml of ethanol as a hydrogen donor and solvent. After the conclusion of the reaction no observable remainders of Pyralene were detected in the solution, using GC (EC detector) analysis. Biphenyl (70.0 mg, 24.8 weight %) and benzene were the main organic products in the GC and HPLC analysis. An additional, unidentified minor organic product was eluted at lower retention time (24 min.) in GC analysis.

Example 23

Defluorination of fluoroaromatic compounds also takes place using similar reaction conditions. For example, 190 mg (1 mmol) 4,4'-difluorobiphenyl was subjected to the reaction conditions described for Examples 8 - 20. However, a longer reaction time was needed. When the reaction was continued for 70 hr., no starting difluorobiphenyl was detected in the solution. 4-Fluorobiphenyl (17 mg, 0.1 mmol, 10%) and biphenyl (123 mg, 0.8 mmol) were determined by GC as sole products in the reaction.

In the described process the environmental considerations are satisfied with regard to high efficiency of PCBs destruction and also to the recycling or disposal of all other reagents involved in the process.

Dehalogenated organic products may be used as a source of heat and contribute to an additional energy credit of the process. Inorganic products are harmless salts such as sodium chloride and sodium formate. The latter is a useful and saleable product, and the resulting revenue may reduce operating costs.

A schematic flow diagram for a dechlorination unit, according to one process of the invention, is shown in Fig. 3. The work-up process after the conclusion of the reaction starts with the evaporation of the solvents through condenser (1) and recycling the methanol using a solvent still and condenser (2). The non-volatile residue is washed with water into a liquid-liquid extraction unit, useful for the recovery of purified oils. The basic aqueous solution may be reused in the following dehalogenation process or may be neutralized with hydrochloric acid, followed by evaporation of water to dryness. Methanol is then added, allowing separation of soluble sodium formate from sodium chloride, which is disposed to waste.

The above description and examples have been provided for the purpose of illustration and are not meant to limit the invention.

Table I

Example	compound	untreated sample/ppm	treated sample ppm			detection limits/ppm
			starting comp.	dihalo deriv.	monohalo deriv.	
8	C_6H_5Cl	45,000	n.d.	--	n.d.	10
9	1,2-$C_6H_4Cl_2$	60,000	n.d.	n.d.	100	10
10	1,3-$C_6H_4Cl_2$	60,000	n.d.	n.d.	n.d.	10
11	1,4-$C_6H_4Cl_2$	60,000	n.d.	n.d.	n.d.	10
12	1,2,3-$C_6H_3Cl_3$	180,000	n.d.	n.d.	n.d.	10
13	1,2,4-$C_6H_3Cl_3$	180,000	n.d.	n.d.	n.d.	10
14	1,3,5-$C_6H_3Cl_3$	180,000	n.d.	n.d.	n.d.	10
15	hexachloro cyclohexane	116,000	n.d.	--	--	10
16	1,2,3-$C_6H_3Cl_3$ in mineral oil (0.5 ml)	180,000	n.d.	n.d.	n.d.	10
17	1-chloronaphthalene	66,000	n.d.	--	n.d.	1.0
18	4,4'-dichlorobiphenyl	86,000	n.d.	n.d.	n.d.	1.0
19	1,4-$C_6H_4Br_2$	95,000	n.d.	n.d.	n.d.	10
20	4,4'-dibromobiphenyl	125,000	n.d.	n.d.	n.d.	1.0
n.d. = not detectable						

Claims

1. A. process for the dehalogenation of organohalides wherein an organohalide or a mixture of two or more organohalides is brought into contact with an alkali hydroxide in an alcoholic solution in the presence of a heterogeneous transfer hydrogenolysis catalyst and in the absence of added hydrogen.

2. A process according to claim 1, wherein the alcoholic solution comprises a lower alcohol.

3. A process according to claim 1 or 2, wherein the alkali hydroxide is selected from the group consisting of sodium and potassium hydroxide.

4. A process according to any one of claims 1 to 3, wherein the transfer hydrogenolysis catalyst is a palladium-on-carbon catalyst.

5. A process according to any one of claims 1 to 4, wherein the dehalogenation reaction is carried out at a temperature comprised between about 50° and about 150°C.

6. A process according to claim 5, wherein the dehalogenation reaction is carried out at a pressure below about 4 atmospheres (405.2 kPa).

7. A process according to claim 5 or 6, wherein the reaction is carried out in an atmosphere containing air.

8. A process according to any one of claims 1 to 7, wherein the concentration of the organohalides in the reaction mixture is comprised between 0.1-10% of the reaction mixture.

9. A process according to any one of claims 1 to 8, wherein the reaction is continued until less than 10 ppm of organohalide remains in the reaction mixture.

10. A process according to any one of claims 1 to 9, wherein the catalyst is recovered after completion of the reaction, washed and reused in a subsequent reaction.

11. A process for the purification and reclamation of fluids contaminated with organohalides, comprising contacting the fluid to be purified with a stoichiometric excess of an alkali hydroxide, with respect to the organohalide, in an alcoholic solution and in the presence of a heterogeneous transfer hydrogenolysis catalyst.

12. A process according to claim 11, wherein the fluid to be purified comprises mineral oils, silicon oils, lube oils, gas oils, transformator oils and the like.

Patentansprüche

1. Verfahren zur Dehalogenierung von Organohalogeniden, bei dem ein Organohalogenid oder ein Gemisch von zwei oder mehr Organohalogeniden mit einem Alkalihydroxid in einer alkoholischen Lösung in Gegenwart eines heterogenen Übertragungs-Hydrogenolyse-Katalysators und in Abwesenheit von zugesetztem Wasserstoff in Kontakt gebracht wird.

2. Verfahren nach Anspruch 1, bei dem die alkoholische Lösung einen niederen Alkohol enthält.

3. Verfahren nach Anspruch 1 oder 2, bei dem das Alkalihydroxid ausgewählt wird aus der Gruppe, die besteht aus Natriumhydroxid und Kaliumhydroxid.

4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem der Übertragungs-Hydrierungs-Katalysator ein Palladium-auf-Kohlenstoff-Katalysator ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, bei dem die Dehalogenierungsreaktion bei einer Temperatur zwischen etwa 50 und etwa 150°C durchgeführt wird.

6. Verfahren nach Anspruch 5, bei dem die Dehalogenierungsreaktion bei einem Druck unterhalb etwa 4 Atmosphären (405,2 kPa) durchgeführt wird.

7. Verfahren nach Anspruch 5 oder 6, bei dem die Reaktion in einer Luft enthaltenden Atmosphäre durchgeführt wird.

8. Verfahren nach einem der Ansprüche 1 bis 7, bei dem die Konzentration der Organohalogenide in der Reaktionsmischung zwischen 0,1 und 10 %, bezogen auf die Reaktionsmischung, liegt.

9. Verfahren nach einem der Ansprüche 1 bis 8, bei dem die Reaktion fortgesetzt wird, bis weniger als 10 ppm Organohalogenid in der Reaktionsmischung verbleiben.

10. Verfahren nach einem der Ansprüche 1 bis 9, bei dem der Katalysator nach Beendigung der Reaktion zurückgewonnen (abgetrennt), gewaschen und in einer nachfolgenden Reaktion wiederverwendet wird.

11. Verfahren zur Reinigung und Regenerierung von Flüssigkeiten (Fluids), die mit Organohalogeniden verunreinigt sind, bei dem die zu reinigende Flüssigkeit (Fluid) mit einem stöchiometrischen Überschuß eines Alkalihydroxids, bezogen auf das Organohalogenid, in einer alkoholischen Lösung und in Gegenwart eines heterogenen Übertragungs-Hydrogenolyse-Katalysators in Kontakt gebracht wird.

12. Verfahren nach Anspruch 11, bei dem die zu reinigende Flüssigkeit (Fluid) Mineralöle, Silicionöle, Schmieröle, Gasöle, Transformatoröle und dgl. umfaßt.

Revendications

1. Procédé pour la déshalogénation d'halogénures organiques, dans lequel un halogénure organique ou un mélange de deux ou plus de deux halogénures organiques est mis en contact avec un hydroxyde de métal alcalin dans une solution alcoolique en présence d'un catalyseur d'hydrogénolyse par transfert hétérogène et en l'absence d'hydrogène ajouté.

2. Procédé suivant la revendication 1, dans lequel la solution alcoolique comprend un alcool inférieur.

3. Procédé suivant la revendication 1 ou 2, dans lequel l'hydroxyde de métal alcalin est choisi dans le groupe consistant en hydroxyde de sodium et hydroxyde de potassium.

4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le catalyseur d'hydrogénolyse par transfert consiste en un catalyseur au palladium sur du carbone.

5. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel la réaction de déshalogénation est conduite à une température comprise dans l'intervalle d'environ 50° à environ 150°C.

6. Procédé suivant la revendication 5, dans lequel la réaction de déshalogénation est conduite à une pression inférieure à environ 4 atmosphères (405,2 kPa).

7. Procédé suivant la revendication 5 ou 6, dans lequel la réaction est conduite dans une atmosphère contenant de l'air.

8. Procédé suivant l'une quelconque des revendications 1 à 7, dans lequel la concentration des halogénures organiques dans le mélange réactionnel est comprise dans l'intervalle de 0,1 à 10 % du mélange réactionnel.

9. Procédé suivant l'une quelconque des revendications 1 à 8, dans lequel la réaction est maintenue jusqu'à ce que moins de 10 ppm d'halogénure organique persistent dans le mélange réactionnel.

10. Procédé suivant l'une quelconque des revendications 1 à 9, dans lequel le catalyseur est récupéré après achèvement de la réaction, lavé et réutilisé dans une réaction ultérieure.

11. Procédé pour la purification et la régénération de fluides contaminés avec des halogénures organiques, comprenant la mise en contact du fluide à purifier avec un excès stoechiométrique d'un hydroxyde de métal alcalin, par rapport à l'halogénure organique, dans une solution alcoolique et en présence d'un catalyseur d'hydrogénolyse par transfert hétérogène.

12. Procédé suivant la revendication 11, dans lequel le fluide à purifier comprend des huiles minérales, des huiles dérivées du silicium, des huiles lubrifiantes, des gas-oils, des huiles pour transformateurs, etc.

Fig. 2

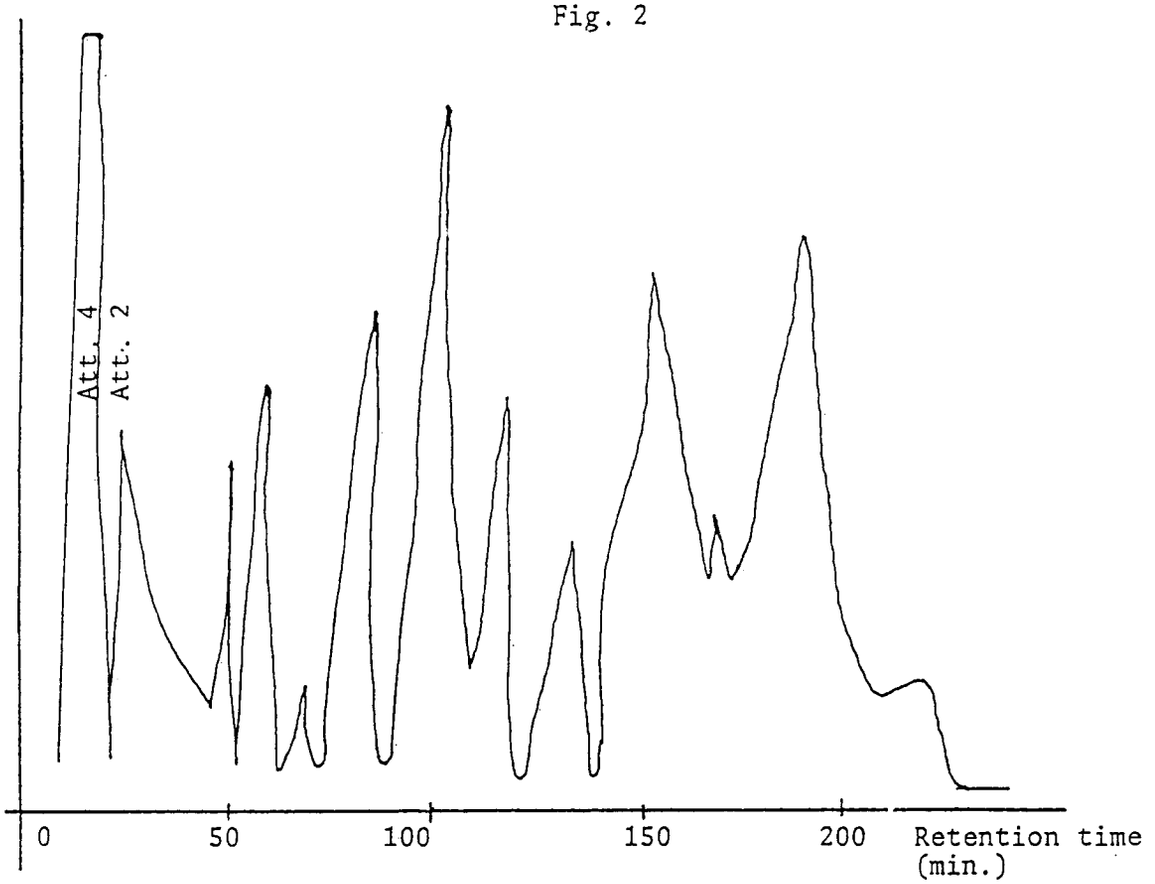
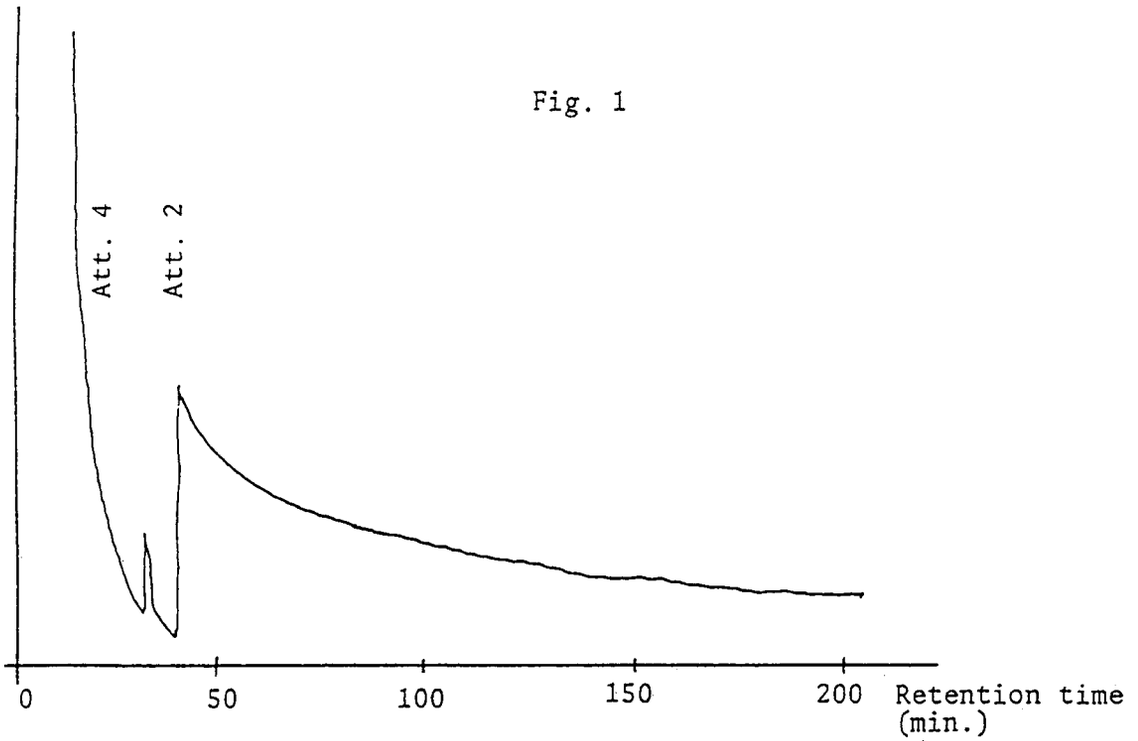

Att. 4
Att. 2
0
50
100
150
200
Retention time
(min.)

Fig. 1


Att. 4
Att. 2
0
50
100
150
200
Retention time
(min.)

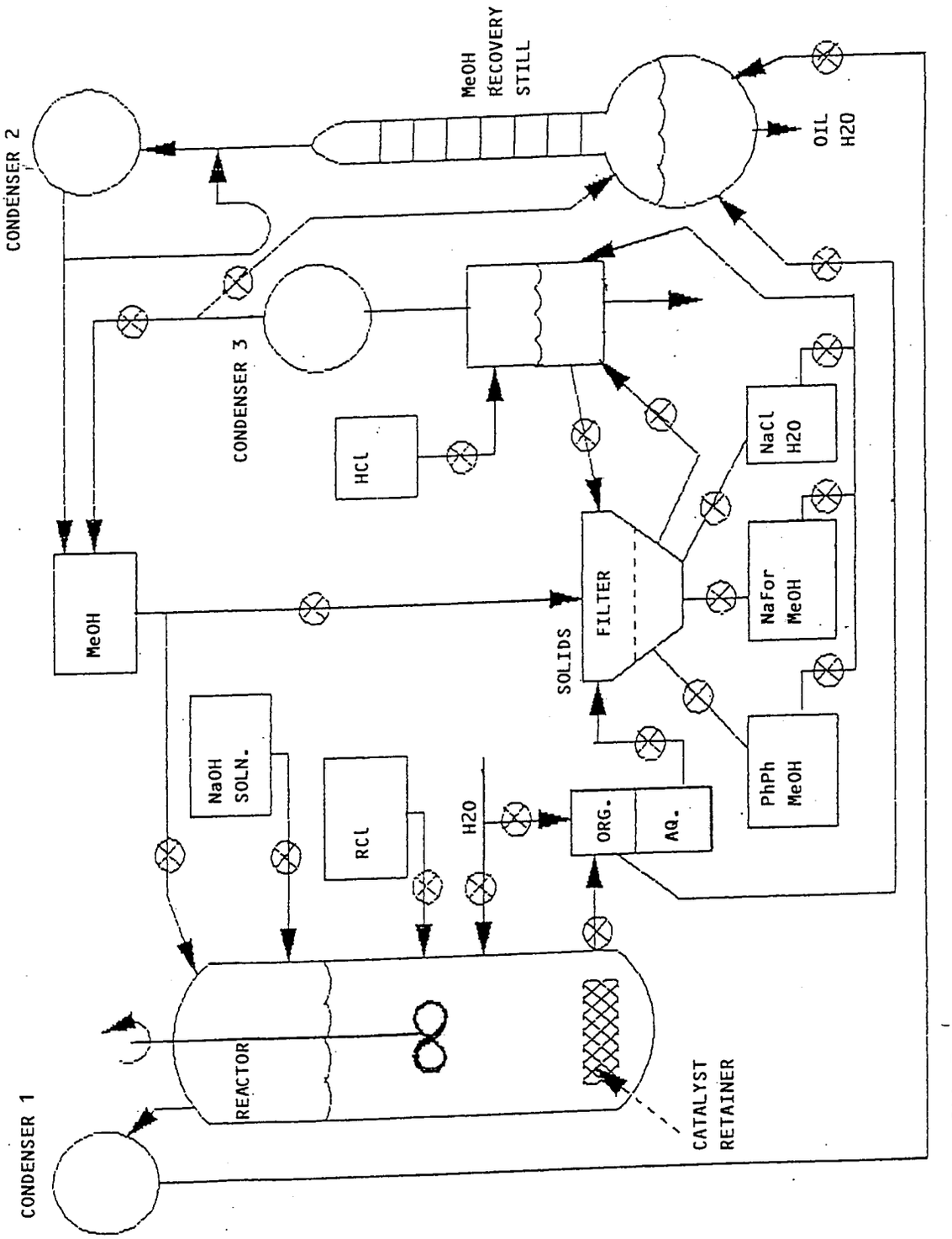

CONDENSER 2
MeOH RECOVERY STILL
OIL
H2O
CONDENSER 3
HCl
NaCl H2O
MeOH
FILTER
SOLIDS
NaFor MeOH
PhPh MeOH
NaOH SOLN.
RCl
H2O
ORG.
AQ.
REACTOR
CATALYST RETAINER
CONDENSER 1

FIG. 3