DEHYDROHALOGENATION PROCESS
Van C. Vives, Bartlettville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware
No Drawing. Filed Feb. 29, 1968, Ser. No. 709,183
Int. Cl. C07c 11/00, 11/04
U.S. Cl. 260—677

ABSTRACT OF THE DISCLOSURE

Dehydrohalogenation of halogenated hydrocarbons by contacting with an acidic dehydrohalogenation catalyst and a basic compound containing trivalent nitrogen to promote the production of linear unbranched unsaturated hydrocarbons.

BACKGROUND OF THE INVENTION

This invention relates to a process for the dehydrohalogenation of organic halides. In accordance with one aspect, this invention relates to a process for the dehydrohalogenation of halogenated hydrocarbon compounds in the presence of a basic compound containing trivalent nitrogen to produce olefins wherein the formation of branched-chain olefins through isomerization is minimized. In accordance with a further aspect, this invention relates to the addition of a minor amount of ammonia or an amine to an alkyl chloride feed subjected to dehydrochlorination to improve the yield of linear olefins.

Currently, considerable interest and much research effort have been devoted to the production of bio-degradable detergents. A proposed method comprises halogenating normal paraffins, dehydrohalogenating the resulting alkyl halides to produce olefins, alkylating benzene or other aromatics with these olefins in the presence of HF, and subsequently sulfonating the product alkylate to produce a bio-degradable detergent. These produced alkyl-benzene sulfonates are rapidly degraded by bacteria because of the lack of branching of the substituent alkyl groups.

It has been observed that in the production of olefins by the dehydrohalogenation of alkyl halides employing conventional dehydrohalogenation process conditions and catalysts, isomerization of the carbon skeleton of the produced olefins is the result. While, for some uses, this is not damaging, branched olefins are of little value when it is desired to form bio-degradable detergents via alkylation for reasons previously stated.

Accordingly, an object of this invention is to provide an improved process for the dehydrohalogenation of halogenated hydrocarbons whereby the prior art problems of isomerization and/or cracking are obviated.

Another object of this invention is to provide a process for the dehydrohalogenation of straight chain alkyl halides to produce with a high degree of selectivity straight chain olefins.

A further object of this invention is to provide a process for the dehydrohalogenation of alkyl halides to produce olefins wherein the formation of branched-chain olefins through isomerization is minimized.

Other aspects, objects and several advantages of this invention will be readily apparent to those skilled in the art from a reading of this disclosure and the appended claims.

SUMMARY OF THE INVENTION

In accordance with the invention, unsaturated hydrocarbons are produced by the dehydrohalogenation of halogenated hydrocarbons over a catalyst in the presence of a basic compound containing trivalent nitrogen in an amount sufficient to promote the production of linear unbranched unsaturated hydrocarbons.

In accordance with the invention, it has been found that basic compounds containing trivalent nitrogen such as amines, ammonia, amides, and the like, promote production of linear unbranched olefins by dehydrohalogenation of halogenated hydrocarbons. It has been found that the addition of a minor amount of one of these basic compounds to an alkyl chloride feed, for example, improves the yield of linear olefins upon dehydrochlorination.

In accordance with one embodiment of the invention, the addition of 0.001 to 100 atomic weights of trivalent nitrogen per each 100 molecular weights of halogenated hydrocarbon to be dehydrohalogenated, as demonstrated by the specific examples hereinbelow, the yield of linear olefins is increased when compared to a similar run carried out in the absence of a basic compound containing trivalent nitrogen.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The basic compounds containing trivalent nitrogen that can be employed according to the invention include ammonia, amides and amines, including polyamines, polymides, and primary, secondary and tertiary amines, as well as aromatic amines, or mixtures thereof.

More specifically, the basic compounds that contain trivalent nitrogen which can be employed according to the process of this invention can have in the range of 1 to 12 nitrogen atoms, in the range of 0 to 12 oxygen atoms, and in the range of 0 to 40 carbon atoms, nitrogen being bonded only to hydrogen or carbon, and the oxygen, if any, being present only in amide moieties.

Examples of basic compounds containing trivalent nitrogen that can be employed include: ammonia, methylamine, trimethylamine, pyridine, pipidine, piperazine, ethylenediamine, tetramethylurea, methylenediamine, urea, triethylentetraamine, aniline, quinoline, dimethyl formamide, N,N,N,N'-tetramethyl -1,6 - hexanedicarboxamide, 2,3,4,6,7,9,10,11,12,14,15,16 - eicosanodecane-carboxamide, isouquinoline, dibenzylamine N-methylpyrrolidone tripropylamine, mixtures thereof, and the like. Preferably, at least one nitrogen atom is bonded to at least one hydrogen atom. Preferably, an excess of amine over the amount required to produce the desired inhibition of branching is avoided, otherwise hydrogen halides that are preferably recycled may be difficult to separate from the reaction effluent.

The present invention is broadly suitable for the dehydrohalogenation of halogenated hydrocarbons, and is particularly suitable for dehydrohalogenation of halogenated alkanes, including mono- and polyhalo-substituted alkanes of the straight-chain, branched-chain and cyclic type. The invention is particularly suitable to the dehydrohalogenation of straight-chain alkyl halides to produce straight-chain olefins.

The halogenated hydrocarbons employed in the dehydrohalogenation process are compounds generally containing from 4 to 20 carbon atoms per molecule. The halogen atom(s) can be chlorine, iodine, bromine, fluoride, or mixtures thereof. However, the invention is particularly applicable to the dehydrohalogenation of alkyl chlorides.

Representative examples of applicable alkyl halides are:

1-chlorobutane
2-bromopentane
1-iodohexane
3-iodooctane
2-fluorononane
3-fluorooctane
3,523,982

1-chlorononane
1-chlorododecane
1-bromononane
1-chloropentadecane
1-chloroocotadecane
1,4-dichlorobutane
1-chloro-3-methylbutane
1-bromo-4-methylcyclohexane
2-chloro-3-hexylcyclohexane
1,3,5-trichlorobenzene
1,3,5,7-tetrachlorotetradecane
1-chloreicosane

and the like.

Examples of some olefins which can be produced by the process of this invention include:

1-butene
2-pentene
1-hexene
3-octene
1-decene
2-dodecene
1-pentadecene
1-octadecene
3-methyl-1-butenone
4-methyl-1-octene
5-ethyl-2-dodecene
2-eicosene

and the like.

The dehydrohalogenation catalyst to be employed according to the process of this invention can be any conventional dehydrohalogenation catalyst having substantial acid sites situated thereon. Illustrative of such catalysts are alumina, chromium-alumina, silica-alumina, etc. Preferably, the dehydrohalogenation catalyst to be employed is a catalyst comprised of a diatomaceous earth and an alkali metal salt of a boric acid, as disclosed in U.S. Pat. 3,341,616.

The dehydrohalogenation process of this invention is conducted at temperatures in the range of about 150°C to 600°C, preferably within the range of about 250°C to 450°C. The flow rate of the halogenated compound to be dehydrohalogenated over the catalyst, based on the halogenated compound in its liquid state, generally ranges from about 0.1 to 5, preferably about 0.3 to 3, volumes per volume of catalyst per hour. Although the reaction can be carried out in the liquid phase, it is preferably carried out in the gaseous phase. The reaction pressure is ordinarily atmospheric or lower; however, higher pressures, for example, to about and including 100 psi, can be employed. If desired, a non-reactive diluent such as nitrogen, another inert gas, or a paraffinic hydrocarbon can be present. Such a non-reactive diluent can comprise as much as 95 percent or more by weight of the material charged to the reactor.

The dehydrohalogenation process of this invention can be conducted as a batch or continuous process, utilizing either liquid phase or vapor phase operation. A preferred method of operation is to pass a volatilized organohalide containing feed through a bed of borate-diatomaceous earth catalyst at a rate so chosen as to provide the desired degree of conversion. Unconverted material can be separated from the reaction zone effluent by conventional separation methods and recycled to the reaction zone. Furthermore, as activity of the catalyst decreases, operation at successively higher temperatures can be employed until regeneration of the catalyst is required. In an exemplary operation, wherein the dehydrohalogenation process is conducted substantially completely in the liquid phase, the dehydrohalogenation zone liquid effluent can be passed through a first distillation zone wherein dissolved hydrogen halide is separated from the liquid effluent. The liquid fraction comprising the product olefins and unconverted alkyl halides can be passed from the first distillation zone to a second distillation zone wherein the product olefins are separated from the unconverted alkyl halides. The separated alkyl halides can be recycled to the dehydrohalogenation zone.

Other methods such as removal of hydrogen halide with an aqueous or caustic wash and the like can also be employed to purify the product.

In carrying out the invention when the dehydrohalogenation process is exemplarily conducted in the vapor phase, the dehydrohalogenation zone vapor effluent can be partially condensed to separate the hydrogen halide therefrom, and the condensed liquid fraction passed to a distillation zone wherein the product olefins are separated from the unconverted alkyl halides.

The value and operability of this invention are clearly demonstrated by the following example.

**EXAMPLE**

The vapor phase dehydrochlorination of a mixture of isomeric linear monochlorododecane was carried out in the presence of nitrogen-containing compounds. The following table presents results of comparative runs. Results of two control runs, wherein no nitrogen-containing compound was employed in the feed, are presented for comparison. All runs were effected in a tubular reactor at atmospheric pressure. Temperature ranged from 375°F to 390°F. The liquid hourly space velocity (LHSV) of the alkyl halides containing feed ranged from 1.23 to 1.58 volumes of liquid feed per volume of catalyst per hour. The catalyst containing an alkali metal tetraborate was prepared by treating crushed Celite 408 (3/8-inch pellets of diatomaceous earth from Johns-Manville Corporation) with the required amount of alkali metal tetraborate (sodium tetraborate) in sufficient water to thoroughly wet the Celite 408, after which the water was removed by volatilization. The finished catalyst contained 10 weight percent sodium tetraborate. The effluent from the dehydrochlorination reactor was passed into water. After the effluent and water were thoroughly shaken to remove hydrogen chloride from the organic phase, the organic phase was separated and analyzed by gas chromatography.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Amin Additive</th>
<th>Temp. °C.</th>
<th>LHSV, vol./vol./hr.</th>
<th>Conv. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole percent selectivity</td>
<td>Linear Branched</td>
<td>Other</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>0.37% ammonia</td>
<td>96.3</td>
<td>1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>2.</td>
<td>0.3% ammonia</td>
<td>98.1</td>
<td>1.9</td>
<td>130</td>
</tr>
<tr>
<td>3.</td>
<td>0.3% dimethylamine</td>
<td>96.0</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>4.</td>
<td>0.3% ethylamine</td>
<td>96.0</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>5.</td>
<td>0.3% dimethylamine</td>
<td>96.1</td>
<td>1.4</td>
<td>130</td>
</tr>
<tr>
<td>6.</td>
<td>None</td>
<td>96.1</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>7.</td>
<td>None</td>
<td>96.1</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>8.</td>
<td>None</td>
<td>96.2</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>9.</td>
<td>None</td>
<td>96.2</td>
<td>0.8</td>
<td>0.9</td>
</tr>
</tbody>
</table>

* Based on the weight of nitrogen compound per weight of alkyl halide feed (including hydrocarbon and alkyl halide).
* Based on the volume of a feed comprised of 66.4 weight percent dodecan, 35.8 percent weight percent secondary dodecyl chloride, and 4.8 weight percent of primary dodecyl chloride per volume of catalyst (25ml.) per hour.
* Based on the alkyl halides charged.

The foregoing runs clearly demonstrate that employment of a basic compound that contains trivalent nitrogen reduces branching of olefins that are produced by dehydrohalogenation of organic halides. Control run 7 further demonstrates that treatment of the catalytic composition with the basic compound that contains trivalent nitrogen prior to the conversion reaction does not achieve the desired effect.
I claim:

1. A process for preparing aliphatically unsaturated hydrocarbons by dehydrohalogenation which comprises contacting a halogenated hydrocarbon with an acidic dehydrohalogenation catalyst in the presence of a basic compound containing trivalent nitrogen in an amount sufficient to promote the production of linear unoriented unsaturated hydrocarbons wherein said basic compound containing trivalent nitrogen is selected from ammonia, and amines containing from 1 to 12 nitrogen atoms, and 0 to 40 carbon atoms, wherein the nitrogen is bonded only to hydrogen or carbon.

2. A process according to claim 1 wherein the amount of basic compound present during said contacting is in the range of 0.001 to 100 atomic weights of trivalent nitrogen per each 100 molecular weights of halogenated hydrocarbon.

3. A process according to claim 1 wherein said catalyst comprises diatomaceous earth and an alkali metal borate and said halogenated hydrocarbon is a chlorinated hydrocarbon whereby dehydrochlorination is effected during said contacting.

4. A process according to claim 1 wherein the temperature of said contacting is conducted in the range of about 150° C. to 600° C.

5. A process according to claim 1 for producing linear olefins with high selectivity and conversion wherein said halogenated hydrocarbon compound is an alkyl halide having from 4 to 20 carbon atoms per molecule.

6. A process according to claim 5 wherein said alkyl halide is a mixture of monochlorododecanes and wherein said catalyst is diatomaceous earth and sodium tetraborate and wherein said basic compound is selected from ammonia, monomethylamine and ethylenediamine.

References Cited

UNITED STATES PATENTS

3,277,205 10/1966 Hughes 260—677
3,349,120 10/1967 Wiseman et al. 260—505
3,352,935 11/1967 Maham et al. 260—677

FOREIGN PATENTS


DELBERT E. GANTZ, Primary Examiner
J. M. NELSON, Assistant Examiner

U.S. Cl. X.R. 260—653.5