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TREATMENT OF VINYL TYPE HALIDES

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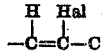
10 Claims. (Cl. 260—593)

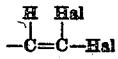
This invention relates to the treatment of unsaturated halides and more particularly pertains to the production of carbonyl compounds, i. e., compounds comprising an aldehyde and/or a ketone group, from non-tertiary vinyl-type halides containing at least four carbon atoms.

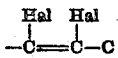
The process of the invention is preferably executed by reacting a non-tertiary vinyl-type halide containing at least four carbon atoms with an aqueous solution comprising a strong mono- or polybasic mineral acid-acting oxyacid, and separating the carbonyl compound thus produced from the reaction mixture. The process may also be executed by first contacting a non-tertiary vinyl-type halide containing at least four carbon atoms with a strong mono- or polybasic mineral acid-acting oxyacid in the substantial absence of water, the carbonyl compound being thereafter formed upon subsequent treatment of the reaction mixture with water.

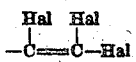
The nature of the carbonyl compound obtained by reacting a non-tertiary vinyl-type halide with a mineral acid-acting oxyacid according to the process of the invention is dependent upon the structure of the particular halide or halides treated.

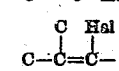
Vinyl-type halides are distinguished from non-vinyl-type unsaturated halides in that they contain at least one halogen atom which is attached to an unsaturated carbon atom. Thus, any organic compound embracing any one or more of the structures or groupings,

(I) 

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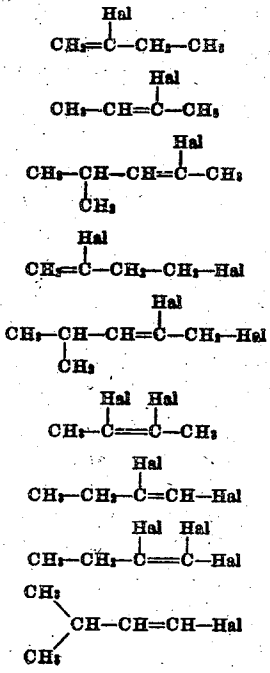
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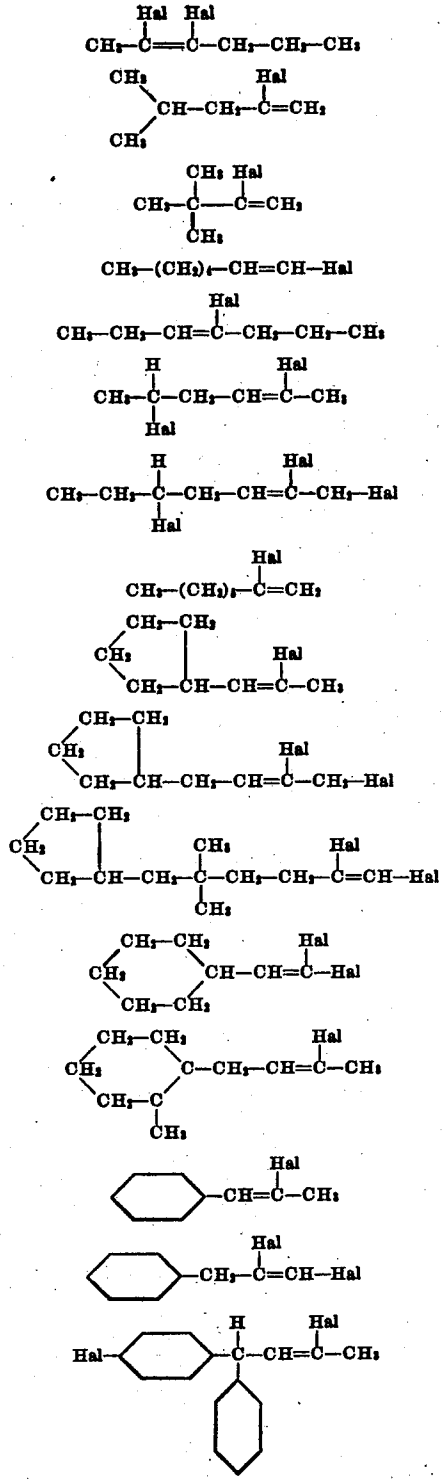
(IV) 

(V) 

may be properly designated a vinyl-type halide, while the term "vinylic carbon atom" may be applied to either of the unsaturated carbon atoms in each grouping. The grouping may comprise part of an iso or normal alkyl chain which may or may not be attached to a cyclic radical as of the aromatic, alicyclic, and heterocyclic series or may comprise part of an alicyclic structure. The organic compound may or may not contain one or more halogen atoms in addition to the halogen atom or atoms contained in one or more of the above groupings comprised therein.

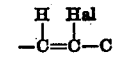
The vinyl-type halides to which the present process is applicable are non-tertiary, that is, they contain a vinylic grouping wherein neither of the vinylic carbon atoms is tertiary, i. e., attached to three other carbon atoms. Hence a compound comprising grouping V, supra, alone is unsuited for the purpose of the invention. The term "non-tertiary" as used herein and in the appended claims is intended to exclude such compounds. It is to be understood, however, that the treated compound may comprise a vinylic grouping wherein one of the vinylic carbon atoms is tertiary if it also contains a vinylic grouping wherein the vinylic carbon atoms are either primary or secondary, i. e., connected to only one or two other carbon atoms, but in general it is preferred to execute the process with vinyl-type halides devoid of tertiary vinylic carbon atoms. The treated compound may, of course, contain one or more non-vinylic tertiary carbon atoms. A suitable group of vinyl-type halides includes, among others, compounds such as the following together with their homologues, analogues and suitable substitution products.





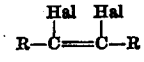
It should be understood that in the vinyl-type halides treated the hydrogen atoms other than those included in the vinylic groupings may be substituted by alkyl, alkoxy, aralkyl, aralkoxy, carbocyclic, heterocyclic and/or aryloxy groups which may or may not be further substituted as well as by any suitable organic radical or monovalent substituent. Most preferably the halogen atom or atoms of the compound treated are either bromine, chlorine, or iodine.

As stated, the nature of the carbonyl compound obtained upon execution of the present process depends upon the structure of the vinyl type halide treated. For example, if the treated halide comprises grouping I, that is, the group

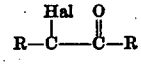


wherein the halogenated vinylic carbon atom is a secondary carbon atom, the overall reaction results in the formation of a ketonic compound. On the other hand, should the treated compound contain a primary halogenated vinylic carbon atom, i. e., a halogenated vinylic carbon atom which is attached to only one other carbon atom, namely the vicinal vinylic carbon atom, the reaction according to the invention results in the formation of an aldehydic compound.

When the compound subjected to treatment contains a plurality of halogenated vinylic carbon atoms including a primary halogenated vinylic carbon atom, a product may be obtained which is both aldehydic and ketonic, while the presence in the treated compound of a plurality of secondary halogenated vinylic carbon atoms may result either in the production of a compound containing a like number of ketone groups, or of a halogenated ketone, depending upon whether the halogenated vinylic carbon atoms are vicinal. In the case of a compound such as



only one of the halogens will, in general, be split off, so that the product will ordinarily be a halogenated ketone,



Halogenated carbonyl compounds are also obtainable by the process of the invention, by the treatment of compounds comprising one or more halogen atoms attached to carbon atoms other than the vinylic carbon atoms contained therein. Compounds containing a vinylic carbon atom of tertiary character, which compounds do not also contain a vinylic grouping wherein the carbon atoms are either primary or secondary, when treated according to the invention do not give carbonyl compounds but rather halohydrins, and hence are without the scope thereof as previously herein stated.

The invention may be executed employing a wide variety of strong mineral acid-acting oxyacids. Among the many suitable acids may be mentioned the strong mineral oxyacids, H_2SO_4, HPO_3, $H_2S_2O_7$, $H_4P_2O_6$, H_3PO_3, H_3PO_4, $H_4P_2O_7$; the aromatic sulfonic acids such as benzene sulfonic acid, and the halo-sulfonic acids, particularly chlorosulfonic and bromo-sulfonic acids. When operating with the halo-sulfonic acids the treated halide is first contacted with the acid in the substantial absence of water according to the second stated mode of executing the process. The term "mineral acid-acting oxyacids" as used hereinafter in the specification and appended claims is intended as encompassing the strong mineral oxyacids such as those specifically named as well as other strong oxyacids which act as mineral acids. In the majority of cases, for reasons of economy, availability and general convenience of operation, it is preferred to employ sulfuric acid (H_2SO_4). The sulfuric acid is usually employed as an aqueous solution having a sulfuric acid concentration in the range of about 60% to about 96%, according to the preferred mode of executing the invention. The best results are usually obtained with those aqueous

solutions containing from 80% to 90% H_2SO_4. When lower acid concentrations are used, the reaction may proceed too slowly and incompletely for general practical purposes. The use of sulfuric acid in concentrations in excess of about 90% is disadvantageous in some cases due to the occurrence of undesirable polymerization and condensation reactions, but it is often possible to offset this effect by operating at lower temperatures and/or by shortening the contact time. When acids other than sulfuric are used, such acids may be applied in corresponding concentrations depending on their strength and activity as compared to sulfuric acid. The use of weaker acids may require the employment of higher operating temperatures.

It is preferred to effect the reaction of a suitable unsaturated halide and a suitable aqueous mineral acid-acting oxyacid at a temperature at which the reaction proceeds rapidly with a minimum of polymerization. The reaction is preferably effected in a temperature range of from about 20° C. to about 40° C., although in some cases temperatures substantially above this range (up to 60° C.) may be advantageously applied. The optimum reaction temperature will usually be dependent on the specific reactants, the concentration and strength of the acid applied and/or the contact time of the reactants. To avoid polymerization losses due to local overheating, it is preferred to slowly add the aqueous acid to the unsaturated halide. The reaction is usually exothermic, the heat liberated usually necessitating cooling of the reaction mixture. Agitation of the reaction mixture is advantageous since it may afford more efficient contact of the reactants and aid in maintaining a more uniform temperature throughout the reaction mixture. While it may be desirable in some instances to effect the reaction in the presence of a suitable inert organic compound such as an ester, hydrocarbon, halogenated hydrocarbon, and the like, in general such practice is not followed since it is necessary to use excess acid to achieve satisfactory conversions and since recovery of the diluent entails special procedures and equipment best avoided. In the absence of an inert diluent, it is usually preferable when employing sulfuric acid to add the acid in the proportion of about 1 mol thereof for each vinylic grouping present in the treated halide. This practice results in the most complete utilization of acid, although higher conversions may be attained with little loss of yield by using an excess of acid. Under the preferred conditions of operation, that is, by operating with 80% to 90% aqueous sulfuric at a temperature within the range of from about 20° C. to about 40° C., a contact time of one hour is normally sufficient for a high conversion and yield of the desired product.

When the process of the invention is executed by first contacting the unsaturated halide with the selected oxyacid in the substantial absence of water, that is, with an essentially anhydrous acid, or with an anhydrous solution of the acid in an inert solvent, formation of the desired carbonyl product may be subsequently effected by diluting the reaction mixture with water. The temperature of the reaction mixture before and during the dilution is preferably maintained at or below about 20° C. but permissibly at any temperature below about 40° C. Usually, where sulfuric acid has been employed, enough water is added to the reaction mixture to reduce its acid concentration to less than about 25%, preferably 10% to 15% H_2SO_4. A convenient method of effecting the dilution comprises the slow addition of the reaction mixture to a mixture of ice and/or water, the ice and/or water being present in an amount sufficient to reduce the acid concentration to the desired value. The resulting carbonyl compound may be recovered from the relatively dilute acidic mixture in a wide variety of suitable manners, depending upon the specific carbonyl compound to be recovered and on the particular taste of the operator.

While the present process has been referred to herein as executable by either one of two modes, it will be understood that the invention is not limited to such modes of execution. For example, a modified method of operation may be employed wherein the treated halide is subjected to the action of the mineral acid-acting oxyacid in the presence of only enough water to effect partial conversion thereof to the desired carbonyl product, the reaction mixture being thereafter treated with sufficient additional water to convert the remainder of the halide to product.

When the process has been executed according to the preferred method with 80% to 90% aqueous sulfuric acid, recovery of the carbonyl product is best preceded by dilution of the reaction mixture, preferably with water, to an acid concentration of between about 25% to 75%. In many cases it is preferred to recover the carbonyl compound by subjecting the diluted acidic reaction mixture to a distillation or fractionation treatment under a subatmospheric or atmospheric pressure whereby the product is usually recovered per se or as a constant boiling mixture with water and/or the unreacted halide, if any is present. Not infrequently it is desirable to effect the distillation under a subatmospheric pressure to prevent the carbonyl compound from arranging to a less desirable product or products as might occur at the kettle temperature necessary to effect the distillation at atmospheric pressure. If desired, the dilute acidic reaction mixture may be neutralized by the addition of an equivalent amount of a suitable basic substance. In general, the reaction product may be recovered from the aqueous acidic or neutral reaction mixture by any suitable means such as fractionation, stratification, dehydration, extraction, and the like. Similar means may be employed to recover the carbonyl compound from the condensate if the condensate comprises besides the carbonyl product other constituents, for example, water and/or unreacted halide.

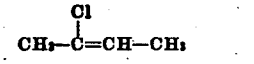
In the recovery of methyl ethyl ketone from the reaction mixture resulting from reacting 2-chlorobutene-2 with sulfuric acid and water according to the preferred method of executing the invention, it has been found desirable to strip the reaction mixture subsequent to dilution with steam. By such practice sulfuric acid of a concentration of from 40% to 50%, suitable for reconcentration and re-use, can be recovered without difficulty from the bottom of the stripping column. The steam distillation is best conducted under a reduced pressure where the acid concentration of the reaction mixture is greater than 60%. The top product from the stripper consists of a mixture of methyl ethyl ketone, water, unreacted 2-chlorobutene-2 and a minor amount of polymer. These may be separated, for example, by extracting the ketone with a suitable solvent, such as hot water, or by fractionation.

The present process is of particular value as applied to effect the conversion of 2-chlorobutene-2, which is a cheap by-product material for which few uses are known and which is available in large quantities, to methyl ethyl ketone, an excellent low boiling solvent which may be substituted in many instances for relatively more expensive solvents. The anhydrous hydrogen chloride produced as a result of the reaction between 2-chlorobutene-2 and sulfuric acid is easily recoverable and finds ready application, for example, in the manufacture of molecular chlorine according to the Deacon process and modifications thereof.

The following examples, introduced in illustration of the process of the invention as applied to the production of methyl ethyl ketone from 2-chlorobutene-2, are not to be construed as limiting the invention to the treatment of this specific vinyl-type halide or to the conditions of operation disclosed.

Example I

Approximately 4 mols of 2-chlorobutene-2,



were charged to a glass flask fitted with a stirrer. About 5 mols of aqueous sulfuric acid of a concentration of about 84% was then added to the flask as quickly as possible. The reactants were permitted to remain in contact for about one hour, the HCl evolved being caught in a water scrubber. The very small amounts of other gases produced were discarded. Upon expiration of the contact period during which the average temperature within the reactor was 28° C., the mixture in the flask was diluted with water to an acid concentration of about 60% on an organic-free basis and stripped with steam without reflux in a continuously operated column, the reaction mixture being fed to the top of the column, the steam being introduced at the bottom thereof. Analysis of the product from the stripper revealed that about 64% of the 2-chlorobutene-2 had been converted to methyl ethyl ketone. The yield of methyl ethyl ketone on the basis of the reacted chloride was between 84% and 85%.

Example II

The experiment of Example I was repeated, the mol ratio of the acid and chloride being approximately 1:1 as compared to 5:4 as in the first experiment. The average temperature within the reactor was 31° C. while the contact time was halved to 30 minutes. The reaction mixture was diluted to 25% acid prior to the steam stripping step which was accomplished batchwise. Between 59% and 60% of the 2-chlorobutene-2 reacted, the yield of methyl ethyl ketone being 85%.

Example III

The experiment of Example I was again repeated, the treated chloride being diluted to fifty weight per cent with a synthetic octane solvent. An excess of acid was used (5 mols 84% acid to 3.18 mols of 2-chlorobutene-2). Other conditions were substantially the same. 0.69 mol of the chloride did not react. The yield of methyl ethyl ketone on the basis of the reacted chloride was about 87%.

Example IV

A continuous reactor consisting of a packed column 85 cm. long by 4.5 cm. in diameter was employed. About 7⅓ mols of undiluted 2-chlorobutene-2 was continuously passed into the bottom of the column while about 8½ mols of 84% aqueous sulfuric acid was continuously introduced at the top. The average column temperature was about 30° C., while the rate of material feed was so regulated as to give a contact time of the reactants of roughly 60 minutes. After the reaction was started all of the unreacted 2-chlorobutene-2 was carried out as vapor with the hydrogen chloride. 3.86 mols of anhydrous HCl were recovered. The reaction mixture withdrawn from the bottom of the column was collected and subsequently steam stripped. The run resulted in a 70% conversion of the 2-chlorobutene-2 and an 80% yield of methyl ethyl ketone.

We claim as our invention:

1. A process for the production of methyl ethyl ketone which comprises reacting 2-chlorobutene-2 with aqueous sulfuric acid of a concentration between about 80 and about 90 per cent at a temperature in the range of from about 20° C. to 40° C., diluting the reacted mixture with water to a sulfuric acid concentration between about 25 and about 75 per cent, and steam distilling the diluted reacted mixture to separate the methyl ethyl ketone therefrom.

2. A process for the production of methyl ethyl ketone which comprises reacting 2-chlorobutene-2 with sulfuric acid in the substantial absence of water at a temperature between about 20° C. and about 40° C., treating the resulting mixture with sufficient water to reduce the acid concentration to below about 25 per cent, and steam distilling the diluted reacted mixture to separate methyl ethyl ketone therefrom.

3. A process for preparing methyl ethyl ketone which comprises reacting 2-chlorobutene-2 with a concentrated aqueous solution of a strong mineral oxyacid at a temperature not substantially above 60° C. for a sufficient period of time to convert a substantial portion of the 2-chlorobutene-2 to methyl ethyl ketone, and recovering the methyl ethyl ketone.

4. A process for the production of methyl ethyl ketone which comprises reacting 2-chlorobutene-2 with sulfuric acid.

5. A process for the production of methyl ethyl ketone which comprises reacting 2-chlorobutene-2 with a strong mineral oxyacid and water.

6. A process for the production of methyl ethyl ketone which comprises reacting 2-chlorobutene-2 with a mineral oxyacid.

7. A process for the production of a carbonylic compound which comprises reacting a mono-olefinic halide which contains at least four carbon atoms, wherein the olefinic carbon atoms are of the group consisting of primary and secondary olefinic carbon atoms, and wherein at least one of the olefinic carbon atoms is directly linked to a halogen atom, with aqueous sulfuric acid of a concentration between about 60% and 90% at a temperature not substantially above 60° C. for a sufficient period of time to convert a substantial portion of the olefinic halide to a carbonylic compound, diluting the reacted mixture with water to an acid concentration below about 25%, and steam distilling the diluted mixture to separate the carbonylic product.

8. A process for the production of a carbonylic compound which comprises reacting a mono-olefinic halide which contains at least four carbon atoms, wherein the olefinic carbon atoms are of the group consisting of primary and secondary olefinic carbon atoms, and wherein at least one

of the olefinic carbon atoms is directly linked to a halogen atom, with a concentrated aqueous solution of a strong mineral oxy acid.

9. A process for the production of a carbonylic compound which comprises reacting a mono-olefinic halide which contains at least four carbon atoms, wherein the olefinic carbon atoms are of the group consisting of primary and secondary olefinic carbon atoms, and wherein at least one of the olefinic carbon atoms is directly linked to a halogen atom, with a concentrated aqueous solution of sulfuric acid.

10. A process for the production of a carbonylic compound which comprises reacting a mono-olefinic chloride which contains at least four carbon atoms, wherein the olefinic carbon atoms are of the group consisting of primary and secondary olefinic carbon atoms, and wherein at least one of the olefinic carbon atoms is directly linked to a chlorine atom with a concentrated aqueous solution of surfuric acid.

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