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MIXED UNSYMMETRICAL KETONES AND A PROCESS FOR PRODUCING THEM

Reginald L. Wakeman, Pittsburgh, Pa., assignor to Allied Chemical & Dye Corporation, a corporation of New York

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This invention relates to compositions of matter which are adapted to be employed as ingredients of perfumes and for other purposes, and to a process for preparing such compositions.

It is an object of the invention to provide mixtures of organic compounds which are valuable as ingredients of perfumes and which can be prepared efficiently from readily available and inexpensive raw materials. Another object of the invention is to provide an economical process for the preparation of such valuable mixtures of organic compounds. Another object of the invention is to provide a process wherein higher petroleum fractions and similar hydrocarbon mixtures are utilized for the production of valuable compositions of matter.

Other objects of the invention in part will be obvious and in part will appear hereinafter.

It has been discovered in accordance with the present invention that by condensing a hydrocarbon mixture of the type of a petroleum distillate of which the major portion is composed of saturated hydrocarbons (i. e., saturated aliphatic and/or saturated alicyclic hydrocarbons) containing 9 to 14 carbon atoms with a lower aliphatic acid chloride in the presence of a volatile, substantially anhydrous aluminum halide, that is to say, a member of the group consisting of anhydrous aluminum chloride, aluminum bromide, and aluminum iodide, and preferably aluminum chloride, valuable mixed products can be obtained. The condensation products which are formed are composed largely of a mixture of unsymmetrical ketones which contain, on one side of the carbonyl group, the alkyl residue which is present in the lower aliphatic acid chloride, and on the other side, the hydrocarbon residues of constituents of the hydrocarbon mixture of the type of a petroleum distillate. These ketonic condensation products possess a pleasant odor and hence are adapted for use as ingredients of perfumes. They also are valuable raw materials for use in the production of other organic compounds; for example, they may be sulfonated and thereby converted into mixed products having surface active properties and available for use as detergents, wetting, and emulsifying agents and the like.

The hydrocarbon mixtures used in the preparation of the ketonic condensation products are preferably petroleum distillates which boil within the range 140° to 250° C. at atmospheric pressure, for example, kerosenes. As is well known, petroleum distillates such as kerosenes are mainly mixtures of saturated, straight and branched chain hydrocarbons of the aliphatic series and hydrocarbons of the cycloaliphatic series. Such mixtures may contain various proportions of unsaturated and/or aromatic constituents depending upon the source of the petroleum, but such constituents are generally present in relatively small amounts, and are usually removed to a considerable extent in the refining process. The petroleum distillates preferably used in the present process which boil within the range 140° to 250° C. are composed principally of saturated aliphatic and cycloaliphatic hydrocarbons containing from about 9 to about 14 carbon atoms.

The lower aliphatic acid chloride used in the preparation of the products of the invention contains at least two carbon atoms and preferably not more than 4 carbon atoms. It has been found that the more valuable products are obtained when acetyl chloride or propionyl chloride is used in the reaction. These products are composed to a large extent of mixtures of unsymmetrical ketones having one lower alkyl radical containing one or two carbon atoms. While the condensation can be carried out with the use of other anhydrous, volatile aluminum halides, it has been found that the process proceeds in a satisfactory manner if anhydrous aluminum chloride is used as the catalyst.

In carrying out the present process in accordance with a preferred manner of proceeding, a mixture of the lower aliphatic acid chloride and a fraction of a Pennsylvania or Mount Pleasant, Michigan, petroleum boiling within the range 140° to 250° C. and containing anhydrous aluminum chloride is heated under reflux at a temperature sufficiently high to cause condensation but preferably as low as possible in order to avoid the occurrence of undesirable side reactions. The temperatures preferably employed will vary depending upon a number of factors, such as the particular materials making up the reaction mixture, the apparatus employed, and the like, but it has been found in general that temperatures from 50° to 100° C. and especially 60° to 70° C. are suitable. The reaction can be carried out at pressures other than atmospheric but since atmospheric pressures have been found to be satisfactory, they are preferred for the sake of simplicity of operation. In the usual case the reaction is completed in a period of about 10 to about 20 hours.

The proportions of the materials entering into the reaction can be varied. For example, about one mol equivalent of the hydrocarbon mixture on the basis of its average molecular weight can

be used for each mol of the lower aliphatic acid chloride; but in order to afford maximum utilization of the lower aliphatic acid chloride, resulting in greater economy, an excess of the hydrocarbon mixture is preferably employed. Thus, in general it has been found to be preferable to use about three mols of the hydrocarbon mixture for each mol of the lower aliphatic acid chloride. Also, it has been found that the reaction proceeds efficiently with the use of about one mol of aluminum chloride for each mol of the lower aliphatic acid chloride.

When the reaction is completed as indicated when evolution of hydrogen chloride has substantially ceased, the reaction mixture is washed with dilute aqueous sodium carbonate in order to remove the aluminum and hydrogen halides. The washed oily material is then dried; for example, by means of anhydrous calcium chloride, anhydrous sodium sulfate, or the like, and is then fractionally distilled. The lower boiling fraction consists chiefly of unreacted hydrocarbons and may be distilled at atmospheric pressure. The higher boiling fractions are distilled at reduced pressures, preferably between 10 and 80 mm. of mercury. The several fractions are collected and may be used separately or combined. The higher fractions are the products of the invention and consist of mixtures of compounds chiefly of ketonic nature. They are characterized by pleasant odors and consequently are valuable as ingredients of perfume compositions.

In the following example there is described the preparation of preferred products by the process of the invention. The parts are by weight:

Example.—282 parts of a kerosene fraction of a Pennsylvania petroleum distillate which boils between 170° and 200° C. at a pressure of 760 mm. of mercury are mixed with about 50 parts of acetyl chloride, and about 85 parts of anhydrous aluminum chloride are added. The mixture is heated in a reaction vessel equipped with a reflux condenser, maintaining a temperature of 60° C. to 70° C. for a period of about 16 to about 20 hours. The reaction mixture is then drowned in dilute aqueous hydrochloric acid at a temperature between 0° C. and 5° C. The oily layer which forms is separated from the aqueous layer, which contains aluminum chloride, and the aqueous portion is discarded. The oily material is washed with a dilute aqueous solution of sodium carbonate, once more separated from the aqueous solution, and dried by means of anhydrous sodium sulfate. The dried oil is distilled at atmospheric pressure until the vapor temperature reaches 206° C. The collected distillate consists principally of unreacted kerosene. About 116 parts of kerosene are recovered in this way. The distillation is then continued under reduced pressure; 53 parts of a fraction boiling between 130° C. and 150° C. at 85 mm. of mercury are first obtained, then 48 parts of a fraction boiling between 135° C. and 175° C. at 45 mm. of mercury and finally 20 parts of a fraction boiling between 175° C. and 275° C. at 25 mm. of mercury. The three fractions are characterized by pleasant odors, and are valuable products for the preparation of perfumes. This result is surprising in view of the unpleasant, characteristic odor of the kerosene employed as starting material.

In a similar manner by the use of other hydrocarbon mixtures of the type of petroleum distillates; for example, other fractions of petroleum boiling within the range 140° to 250° C., and another lower aliphatic acid chloride, other products of the invention can be prepared. It will be understood that if desired a mixture of lower aliphatic acid chlorides can be used in the process, whereby products are obtained containing mixtures of compounds in which the lower alkyl radicals present therein are different.

Since certain changes may be made in the above-described products and process without departing from the scope of the invention it is intended that the description shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. A ketonic condensation product comprising essentially a mixture of unsymmetrical ketones in which one radical is a lower alkyl radical and the other radical is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals containing 9 to 14 carbon atoms, said unsymmetrical ketones differing from one another with respect to said hydrocarbon radicals, said hydrocarbon radicals being identical with the residues of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons present in a hydrocarbon mixture of the type of a petroleum distillate, said ketonic condensation product being obtainable by condensing a lower aliphatic acid chloride with a hydrocarbon mixture of the type of a petroleum distillate of which the major portion is composed of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons containing 9 to 14 carbon atoms.

2. A mixture of unsymmetrical ketones in which one radical is a lower alkyl radical and the other radical is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals containing 9 to 14 carbon atoms, said unsymmetrical ketones differing from one another with respect to said hydrocarbon radicals, said hydrocarbon radicals being identical with the residues of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons present in a petroleum distillate, said mixture being obtained by condensing a petroleum distillate of which the major portion is composed of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons containing 9 to 14 carbon atoms with a lower aliphatic acid chloride in the presence of aluminum chloride.

3. A mixture of unsymmetrical ketones in which one radical is a lower alkyl radical and the other radical is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals containing 9 to 14 carbon atoms, said unsymmetrical ketones differing from one another with respect to said hydrocarbon radicals, said hydrocarbon radicals being identical with the residues of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons present in a kerosene fraction of petroleum boiling within the range 140 to 250° C. at atmospheric pressure, said mixture being obtainable by condensing a lower aliphatic acid chloride with a kerosene fraction of petroleum boiling within the range 140 to 250° C. at atmospheric pressure of which the major portion is composed of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons.

4. A ketonic condensation product comprising essentially a mixture of unsymmetrical ketones in which one radical is a methyl radical

and the other radical is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals containing 9 to 14 carbon atoms, said unsymmetrical ketones differing from one another with respect to said hydrocarbon radicals, said hydrocarbon radicals being identical with the residues of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons present in a kerosene fraction of petroleum boiling within the range 140 to 250° C. at atmospheric pressure, said ketonic condensation product being obtained by condensing a kerosene fraction of petroleum boiling within the range 140 to 250° C. at atmospheric pressure, of which the major portion is composed of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons, with acetyl chloride in the presence of aluminum chloride.

5. A ketonic condensation product comprising essentially a mixture of unsymmetrical ketones in which one radical is an ethyl radical and the other radical is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals containing 9 to 14 carbon atoms, said unsymmetrical ketones differing from one another with respect to said hydrocarbon radicals, said hydrocarbon radicals being identical with the residues of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons present in a kerosene fraction of petroleum boiling within the range 140 to 250° C. at atmospheric pressure, said ketonic condensation product being obtained by condensing a kerosene fraction of petroleum boiling within the range 140 to 250° C. at atmospheric pressure, of which the major portion is composed of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons, with propionyl chloride in the presence of aluminum chloride.

6. The process for the production of a ketonic condensation product containing a mixture of unsymmetrical ketones in which one radical is a lower alkyl radical and the other radical is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals containing 9 to 14 carbon atoms, which comprises condensing a hydrocarbon mixture of the type of a petroleum distillate, of which the major portion is composed of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons containing 9 to 14 carbon atoms, with a lower aliphatic acid chloride in the presence of a volatile, substantially anhydrous aluminum halide selected from the group consisting of aluminum chloride, aluminum bromide and aluminum iodide.

7. The process for the production of a ketonic condensation product containing a mixture of unsymmetrical ketones in which one radical is a lower alkyl radical and the other radical is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals containing 9 to 14 carbon atoms, which comprises heating a mixture containing a hydrocarbon mixture of the type of a petroleum distillate, of which the major portion is composed of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons containing 9 to 14 carbon atoms, a lower aliphatic acid chloride and an anhydrous, volatile aluminum halide to cause hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons in said hydrocarbon mixture to condense with the lower aliphatic acid chloride and thereby form said ketonic condensation product.

8. The process for the production of a ketonic condensation product containing a mixture of unsymmetrical ketones in which one radical is a lower alkyl radical and the other radical is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals containing 9 to 14 carbon atoms, which comprises heating under reflux at a temperature of 50 to 100° C. a mixture containing a kerosene fraction of petroleum boiling within the range 140 to 250° C. at atmospheric pressure a lower aliphatic acid chloride and an anhydrous volatile aluminum halide to cause hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons present in the kerosene fraction to condense with the lower aliphatic acid chloride and form a mixture containing unsymmetrical ketones.

9. The process for the production of a ketonic condensation product containing a mixture of unsymmetrical ketones in which one radical is a lower alkyl radical and the other radical is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals containing 9 to 14 carbon atoms, which comprises heating under reflux at a temperature of 50° to 100° C. a mixture containing a kerosene fraction of petroleum boiling within the range 140° to 250° C. at atmospheric pressure, of which the major portion is composed of aliphatic and cycloaliphatic hydrocarbons containing 9 to 14 carbon atoms, a lower aliphatic acid chloride, and an anhydrous aluminum halide to cause hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons present in the kerosene fraction to condense with the lower aliphatic acid chloride and form a resulting mixture containing the unsymmetrical ketones, separating said resulting mixture into fractions, and collecting a fraction having a pleasant odor.

10. The process for the production of a ketonic condensation product containing a mixture of unsymmetrical ketones in which one radical is a methyl radical and the other radical is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals containing 9 to 14 carbon atoms, which comprises heating under reflux at a temperature of 50 to 100° C. a mixture containing a kerosene fraction of petroleum boiling within the range 140 to 250° C. at atmospheric pressure, of which the major portion is composed of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons, acetyl chloride, and anhydrous aluminum chloride to cause hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons present in the kerosene fraction to condense with the acetyl chloride and form a mixture containing unsymmetrical ketones.

11. The process for the production of a ketonic condensation product containing a mixture of unsymmetrical ketones in which one radical is an ethyl radical and the other radical is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals containing 9 to 14 carbon atoms, which comprises heating under reflux at a temperature of 50 to 100° C. a mixture containing a kerosene fraction of petroleum boiling within the range 140 to 250°

C. at atmospheric pressure, of which the major portion is composed of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons, propionyl chloride, and anhydrous aluminum chloride to cause hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons present in the kerosene fraction to condense with the propionyl chloride and form a mixture containing unsymmetrical ketones.

12. The process for the production of a ketonic condensation product containing a mixture of unsymmetrical ketones in which one radical is a methyl radical and the other radical is a hydrocarbon radical selected from the group consisting of aliphatic and cycloaliphatic radicals containing 9 to 14 carbon atoms, which comprises heating under reflux at a temperature of 50 to 100° C. a mixture containing about three mols of a kerosene fraction of petroleum boiling within the range 140 to 250° C. at atmospheric pressure, of which the major portion is composed of hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons, one mol of acetyl chloride, and about one mol anhydrous aluminum chloride to cause hydrocarbons selected from the group consisting of aliphatic and cycloaliphatic hydrocarbons present in the kerosene fraction to condense with the acetyl chloride and form a mixture containing unsymmetrical ketones.

REGINALD L. WAKEMAN.