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METHOD OF STABILIZING HALOGENATED KETONES

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My invention relates to a method for inhibiting the deterioration of alpha-monohalogenated ketones which tend to decompose on standing. More particularly, it relates to a method for preserving alpha-monohalogenated aliphatic ketones containing a methyl group in which a halogen has been substituted.

It is well known that alpha-monohalogenated ketones are relatively unstable compounds, particularly the lower members of the aliphatic series. On standing, these compounds tend to liberate the corresponding hydrogen halide, simultaneously forming an unsaturated molecule which polymerizes very readily, especially in the presence of metals, acids or light. The liberation of the hydrogen halide during the course of decomposition also gives rise to increased pressures which may become extremely hazardous when attempting to store compounds of this type in sealed containers for any length of time. In numerous instances, alpha-monohalogenated ketones have spontaneously decomposed and built up sufficient pressure to cause the rupture of the vessels containing them when stored in the above manner. Because of these characteristics, it has been very impractical to prepare and store compounds of this nature in sizable quantities in view of the fact that no satisfactory method was known for inhibiting the deterioration thereof.

In view of this undesirable decomposition, the alpha-monohalogenated ketones of lower molecular weight, on standing for any length of time, tend to become contaminated with impurities. It is therefore necessary to distill the impure halogenated ketone immediately before use in case a pure product is desired, such as for example, in syntheses. It is thus seen that because of the lack of an efficient stabilizer there is considerable, but unavoidable waste of these alpha-halogenated ketones unless they are used immediately after preparation.

I have now discovered that decomposition and resinification of alpha-monohalogenated ketones, and particularly the alpha-monohalogenated methyl ketones in which the halogen has substituted in the methyl group, can be satisfactorily inhibited by the addition of small amounts of water thereto, thus giving products which are stable over extended periods of time.

The present invention is particularly advantageous in that it provides a satisfactory method whereby the unstable alpha-monohalogenated ketones may be prepared and stored on a large scale with a high degree of safety and without the formation of substantial quantities of undesirable contaminating products. It has been found that the alpha-monohalogenated ketones can not only be safely stored over extended periods, in accordance with my invention, but also that they will remain in a water-white condition without any indications of decomposition or polymerization occurring. It is possible in this manner to prevent the extensive waste of the alpha-monohalogenated ketones previously encountered, thus correspondingly reducing the actual cost of these heretofore unstable alpha-monohalogenated ketones.

My invention consists essentially of adding water to the freshly prepared alpha-monohalogenated ketone in concentrations from 0.1% by weight up to the saturation point thereof. In this manner I have found that both alpha-monochloro- and alpha-monobromoketones may be satisfactorily preserved, showing no signs of coloration or polymerization after having been exposed to light for several months.

Although water may be present in the alpha-monohalogenated ketone in concentrations varying from 0.1% up to the saturation point of the halogenated ketone, I prefer to employ a concentration thereof which is not substantially below 0.5% by weight. Monohalogenated ketones in general, having the halogen atom in the alpha position which tend to decompose with the liberating of hydrogen halide on standing, may be stabilized in accordance with the present invention; however, I have found that my invention is most useful when applied to the stabilization of the alpha-monohalogenated ketones of low molecular weight, and in particular to the alpha-monohalogenated methyl ketones in which the halogen has substituted in the methyl group, since the latter type compounds exhibit an especially strong tendency to liberate the corresponding hydrogen halide and subsequently polymerize.

My invention may be further illustrated by the following specific examples:

Example I

The reaction mixture obtained from the chlorination of acetone was fractionated and the portion boiling between 118° and 119°/760 mm. (monochloroacetone) was collected. This fraction was then divided into two equal volumes and placed in colorless glass bottles. Water was added to one of the bottles in 0.5% by weight concentration and tightly stoppered. The second bottle was stoppered without the addition of water and both samples were then exposed to diffused light. In less than two days' time the

monochloracetone, in which no water was present, began to darken and show signs of polymerization, whereas the sample containing 0.5% water remained colorless for a period of 5 months with no indication of deterioration at the end of that time.

Example II

The reaction mixture obtained from the bromination of acetone was fractionated and the portion boiling between 136° and 137°/725 mm. (monobromoacetone) was collected. This fraction was then divided into two equal volumes and placed in colorless glass bottles. Water was added to one of the bottles in 0.5% by weight concentration and tightly stoppered. The second bottle was stoppered without the addition of water and both samples were exposed to diffused light. In less than two days the monobromoacetone, in which no water was present, began to darken and show signs of polymerization, whereas the sample containing 0.5% water remained colorless for a period of 5 months with no indication of deterioration at the end of that time.

Although I have only mentioned, by way of examples, the monochloro- and monobromo derivatives of acetone, it is to be understood that my invention is similarly applicable to the higher alpha-monohalogenated homologs of acetone which tend to deteriorate on standing, as for example, 1-chloro-2-butanone, and 1-bromo-2-butanone.

My invention now having been described, what I claim is:

1. The method of preserving alpha-monohalogenated aliphatic ketones which tend to decompose on standing, comprising incorporating water in freshly-prepared alpha-monohalogenated aliphatic ketone in an amount sufficient to inhibit substantially the decomposition of said ketone, and maintaining the ketone-water mixture in a closed vessel.

2. In a process in which an alkyl halomethyl ketone is distilled, and the freshly-distilled ketone is placed in a closed storage vessel, the step which comprises incorporating in said freshly-distilled ketone sufficient water to inhibit subsequent discoloration of said ketone on storage.

3. In a process in which monochloroacetone is distilled and the freshly-distilled monochloroacetone is placed in a closed storage vessel, the step which comprises incorporating water in said freshly-distilled chloroacetone in a concentration from 0.1% by weight to the amount required to saturate said monochloroacetone.

4. In a process in which monobromoacetone is distilled and the freshly-distilled monobromoacetone is placed in a closed storage vessel, the step which comprises incorporating water in said freshly-distilled monobromoacetone in a concentration from 0.1% by weight to the amount required to saturate said monobromoacetone.

5. Packaged alpha-monohalogenated aliphatic ketone, comprising a closed container having therein substantially colorless alpha-monohalogenated aliphatic ketone, together with sufficient water to inhibit subsequent discoloration of said alpha-halogenated aliphatic ketone on storage.

6. Packaged alkyl halomethyl ketone, comprising a closed container having therein substantially colorless alkyl halomethyl ketone, together with sufficient water to inhibit subsequent discoloration of said alkyl halomethyl ketone on storage.

7. Packaged monochloroacetone comprising a closed container having therein substantially colorless monochloroacetone together with water in a concentration from 0.1% by weight to the amount required to saturate said monochloroacetone.

8. Packaged monobromoacetone comprising a closed container having therein substantially colorless monobromoacetone together with water in a concentration from 0.1% by weight to the amount required to saturate said monobromoacetone.

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