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PREPARATION OF POLYCYCLIC AROMATIC COMPOUNDS

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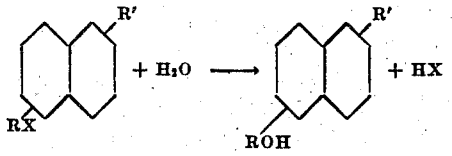
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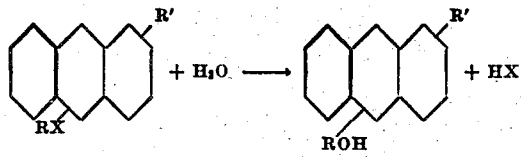
The present invention relates to polycyclic aromatic compounds and derivatives thereof and more particularly to the preparation of polycyclic aromatic alcohols from mono- and poly-haloalkyl substituted polycyclic aromatic hydrocarbons.

In accordance with the present invention a mono- or poly-haloalkyl substituted polycyclic aromatic compound is hydrolyzed at an elevated temperature in an aqueous medium or in an aqueous medium containing a small quantity of a material having an alkaline reaction, to produce the corresponding monohydric or polyhydric polycyclic aromatic alcohol. In addition to mono- or poly-haloalkyl substituents the polycyclic aromatic hydrocarbon may contain other aliphatic substituents. The probable reaction mechanism is illustrated by the following equations in which naphthalene and anthracene are used for the purpose of illustration, although other polycyclic or condensed ring aromatic hydrocarbons such as, for example, phenanthrene, can be used.

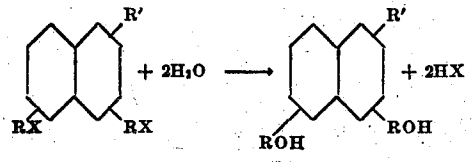
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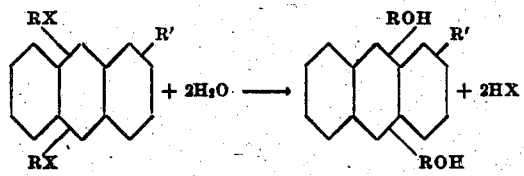
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(4)



in which R is a bivalent aliphatic radical such as those derived from methane, ethane, butane, pentane, hexane, and the like, X is a halogen such as chlorine, bromine, etc. and R' represents hydrogen or one or more aliphatic radicals such as methyl, ethyl, amyl, etc. When R' is an aliphatic substituent it may be the same as or different from R.

The haloalkyl substituted polycyclic aromatic compound from which the alcohol is obtained may be prepared by reacting a polycyclic aromatic hydrocarbon with an aliphatic aldehyde in the presence of hydrochloric acid at an elevated temperature of from about 100° F. to about 200° F. The aromatic compound may be naphthalene, alkyl substituted naphthalenes, anthracene, alkyl substituted anthracene, phenanthrene, alkyl substituted phenanthrenes, catalytic reformate polymers, polycyclic hydrocarbons from the catalytic cracking of hydrocarbons, and other aromatic compounds. Aliphatic aldehydes such as formaldehyde, paraformaldehyde, acetaldehyde and the like can be employed. The reaction if desired can be carried out in a suitable solvent such as a petroleum naphtha.

While the monohydric polycyclic aromatic alcohols are obtained from the mono-haloalkyl polycyclic aromatic hydrocarbons, the polyhydric polycyclic aromatic alcohols are obtained from the poly-haloalkyl polycyclic aromatic hydrocarbons or from the poly-haloalkyl substituted alkyl substituted polycyclic aromatic hydrocarbons. The following example is illustrative of a method of obtaining poly-haloalkyl substituted alkyl substituted polycyclic aromatic hydrocarbons.

Dichloromethyl beta methyl naphthalene was prepared by heating a mixture of 50 grams of beta methyl naphthalene, 31 grams of paraformaldehyde, 10 grams of $ZnCl_2$ and 100 c. c. of 37% aqueous HCl at 140° F.–145° F. for two hours while agitating and passing in a slow stream of HCl gas. The temperature was then raised to 170° F.–175° F. and held at this temperature for four hours while passing in a stream of HCl and vigorously stirring the mixture. The mixture was then cooled, extracted with benzene and the benzene layer washed with water until free of acid. The benzene solution was then vacuum distilled until 33 grams of monochloromethyl beta methyl naphthalene distilled over. The residue remaining in the flask was a brown solid which was recrystallized in naphtha to a white crystalline solid having a melting point of 205° F.–210° F. and a softening point of about 190° F. The material was dichloromethyl beta methyl naphthalene which had a molecular weight of 238 as determined by the Menzies method.

Likewise other poly-haloalkyl substituted alkyl substituted polycyclic aromatic hydrocarbons can be prepared by employing the suitable alkyl polycyclic aromatic for example the dichloromethyl

methyl anthracene may be obtained by starting with a methyl anthracene.

The mono- or polyhydric polycyclic aromatic alcohols are obtained by hydrolyzing the monohaloalkyl or the poly-haloalkyl aromatic compounds of the type above described. The hydrolysis of these compounds is conducted at a temperature from 100° F. to about 350° F. in the presence of water or higly diluted aqueous solutions of a substance having an alkaline reaction such as sodium hydroxide, potassium hydroxide, sodium carbonate and the like. When the solution used is not sufficiently diluted to dissolve all of the alcohols formed the product obtained may be a mixture of the alcohol and the corresponding ether. Mixtures of alcohol and ether are also obtained when the hydrolysis takes place in alcoholic solutions.

The following examples are illustrative:

Example 1

A mixture of 1 gram of 1-chloromethyl-2-methyl naphthalene, 1 gram of $NaHCO_3$ and 800 c. c. of water were refluxed for one hour and filtered hot to remove an undissolved material. The filtrate was then cooled to +40° F. and the white needle shaped crystals of 1-methylol 2-methyl naphthalene separated by filtration. A yield of 0.65 gram (72% of the theoretical) of the product was obtained.

Example 2

One gram of 1-chloromethyl 2-methyl naphthalene in 800 c. c. water were refluxed for one hour, filtered while hot and the filtrate cooled to +40° F. A yield of 0.63 gram (70% of the theoretical) of 1-methylol 2-methyl naphthalene was obtained.

Example 3

Two 5 gram portions of 1-chloromethyl 2-methyl naphthalene were added in a boiling solution of 10 grams of $NaHCO_3$ in 150 c. c. ethyl alcohol, 150 c. c. water at 15 minute intervals and refluxed for one hour. The mixture was then cooled, diluted with 1000 c. c. water and precipitated 1-methylol 2-methyl naphthalene filtered off. A yield of 7 grams (78% of the theoretical) was obtained.

Example 4

A mixture of 2.5 grams of 1-chloromethyl 2-methyl naphthalene, 1 gram NaOH, 50 c. c. acetone and 50 c. c. water was refluxed for three hours, cooled and diluted with water to a volume of 500 c. c. The diluted solution was then extracted with ether and the ether layer evaporated. A yield of 1.9 grams (73% of the theoretical) of 1-methylol 2-methyl naphthalene was obtained.

Example 5

A mixture of 10 grams of 1-chloromethyl 5-chloromethyl naphthalene, 1 gram Na_2CO_3 and 350 c. c. water was refluxed one-half hour and filtered while hot to remove undissolved solids. The solid was then added to a fresh portion of 350 c. c. water containing 1 gram $NaHCO_3$, the mixture refluxed for another one-half hour and filtered while hot to remove undissolved solids. This procedure was repeated five times. The combined filtrates were reduced to a volume of 200 c. c., cooled, and 1.5-dimethylol naphthalene separated, as a white crystalline solid having a melting point of 310° F.–315° F., a softening point of 280° F. and a found molecular weight of 184 (calc. 188). A yield of 5.9 grams was obtained.

Example 6

A mixture of 2 grams of dichloromethyl beta methyl naphthalene, 2 grams $NaHCO_3$ and 300 c. c. water were heated at refluxing temperature for four hours. The hot solution was then filtered to remove undissolved material and the filtrate evaporated substantially to dryness. The residue was then dissolved in 200 c. c. benzene and refluxed for one hour, the hot solution filtered and the filtrate cooled to room temperature. A white crystalline solid was obtained having a melting point of 290° F.–295° F. and a softening point of about 280° F. The product was dimethylol beta methyl naphthalene and had a molecular weight of 210 as determined by the Menzies method, as compared to a calculated molecular weight of 202 for this compound.

The mono and polyhydric aromatic alcohols of the present invention may be employed for many uses. For example, monohydric aromatic alcohols when heated with phthalic and phosphorus acids yield products useful as plasticizers for plastics. The polyhydric aromatic alcohols when heated with dibasic acids such as maleic and phthalic acids or their anhydrides yield valuable plastics for coating compounds.

Although the present invention has been described in connection with a specific embodiment thereof, it is to be understood that it is not intended that the same shall be limitative of the scope of the invention except insofar as included in the accompanying claims.

I claim:

1. The method of preparing a polycyclic aromatic alcohol comprising mixing an haloalkyl substituted polycyclic aromatic compound with a hydrolyzing agent selected from the group consisting of water and a sufficiently dilute alkaline aqueous solution to dissolve substantially all of the alcohol formed, heating the mixture and subsequently recovering the resulting polycyclic aromatic alcohol.

2. The method of claim 1 in which the haloalkyl substituted polycyclic aromatic compound is an haloalkyl substituted naphthalene.

3. The method of claim 1 in which the haloalkyl substituted polycyclic aromatic compound is a chloroalkyl naphthalene.

4. The method of claim 1 in which the haloalkyl substituted polycyclic aromatic compound is a bromoalkyl naphthalene.

5. The method of claim 1 in which the haloalkyl substituted polycyclic aromatic compound is a chloromethyl naphthalene.

6. The method of preparing an alkyl-substituted polycyclic aromatic alcohol comprising mixing a haloalkyl substituted alkyl-substituted polycyclic aromatic compound with a hydrolyzing agent selected from the group consisting of water and a sufficiently dilute alkaline aqueous solution to dissolve substantially all of the alcohol formed, heating the mixture and subsequently recovering the resulting alkyl-substituted polycyclic aromatic alcohol.

7. The method of preparing an alkyl-substituted monohydric aromatic alcohol comprising mixing a monohaloalkyl-substituted alkyl-substituted polycyclic aromatic compound with a hydrolyzing agent selected from the group consisting of water and a sufficiently dilute alkaline aqueous solution to dissolve substantially all of the alcohol formed, heating the mixture and subsequently re-

covering the alkyl-substituted monohydric polycyclic aromatic alcohol.

8. The method of preparing a monomethylol alkyl-substituted polycyclic aromatic compound comprising heating a chloromethyl-alkyl-substituted polycyclic aromatic compound in a sufficiently dilute alkaline aqueous solution to dissolve substantially all of the mono-methylol-alkyl-substituted polycyclic aromatic compound formed, cooling the mixture to precipitate the methylol alkyl-substituted polycyclic aromatic compound, and subsequently removing the same from the supernatant liquid.

9. The method of preparing methylol methyl naphthalene comprising heating a chloromethyl methyl naphthalene with a sufficiently dilute alkaline aqueous solution to dissolve substantially all of the methylol methyl naphthalene formed, filtering the hot mixture to remove undissolved material therefrom, cooling the filtrate, to precipitate the methylol methyl naphthalene, and recovering the precipitated methylol methyl naphthalene.

10. The method of preparing methylol methyl naphthalene comprising heating chloromethyl methyl naphthalene with water, filtering the hot mixture to remove undissolved material therefrom, cooling the filtrate to precipitate the methylol methyl naphthalene and recovering the precipitated methylol methyl naphthalene.

11. The method of preparing a polycyclic aromatic polyhydric alcohol comprising mixing a poly haloalkyl substituted polycyclic aromatic compound with a hydrolyzing agent selected from the group consisting of water and a sufficiently dilute alkaline aqueous solution to dissolve substantially all of the polycyclic aromatic polyhydric alcohol formed, heating the mixture and subsequently recovering the polycyclic aromatic polyhydric alcohol formed.

12. The method described in claim 11 in which the mixture is heated at a temperature within the range of about 100° F. to about 350° F.

13. The method of preparing an alkyl-substituted polycyclic aromatic dihydric alcohol comprising mixing a dihaloalkyl substituted alkyl-substituted polycyclic aromatic compound with an aqueous solution of an alkaline reagent sufficiently diluted to dissolve substantially all of the alkyl-substituted polycyclic aromatic dihydric alcohol formed, heating the mixture and subsequently recovering the alkyl-substituted polycyclic aromatic dihydric alcohol formed.

14. The method of preparing a polycyclic aromatic dihydric alcohol comprising mixing a dihaloalkyl substituted polycyclic aromatic compound with a sufficiently dilute aqueous solution of an alkaline reagent to dissolve substantially all of the polycyclic aromatic dihydric alcohol formed, heating the mixture and subsequently recovering the alkyl-substituted polycyclic aromatic dihydric alcohol.

15. The method of preparing a dimethylol alkyl-substituted polycyclic aromatic compound comprising heating a dichloromethyl alkyl-substituted polycyclic aromatic compound in a sufficiently dilute aqueous solution of an alkaline reagent to dissolve substantially all of the dimethylol alkyl-substituted polycyclic aromatic compound formed, cooling the mixture to precipitate the dimethylol alkyl-substituted polycyclic aromatic compound and subsequently removing the same from the supernatant liquid.

16. The preparation of dimethylol methyl naphthalene comprising heating dichloromethyl methyl naphthalene with water, filtering the hot mixture to remove undissolved material therefrom, cooling the filtrate to precipitate dimethylol methyl naphthalene and recovering the precipitated dimethylol naphthalene.

17. As a new composition of matter dimethylol methyl naphthalene.

CHESTER E. ADAMS.