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METHOD OF BROMINATING THE SIDE CHAIN OF AN ALKYL BENZENE

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ABSTRACT OF THE DISCLOSURE

Side chain bromination of an alkyl benzene is carried out by subjecting a reaction mixture which consists essentially of an alkyl benzene and free bromine to ionizing radiation having an energy of between 0.001 and 20 mev. at a dose rate of between 0.5–100,000 rad./sec.

The present invention relates to a method of brominating the side chain of an alkyl benzene and, more particularly the present invention is directed to brominating the side chain of a lower alkyl benzene such as toluene or xylene.

Some organic compounds of high bromine content find use as additives to various synthetic plastics and the like due to the reduction in flammability, or fire extinguishing effects of certain plastics containing such additive. Aromatic hydrocarbons which are brominated in their side chain or side chains, such as side chain-brominated alkyl benzenes are suitable for this purpose.

Particularly, w,w,w',w'-tetrabromoxylene, pentabromoxylene, hexabromoxylene and mixtures thereof possess properties which can be advantageously utilized in producing non-inflammable synthetic materials.

Up to now, the bromine derivatives of benzene homologs which were substituted with bromine in the side chain are mainly produced by a bromination process which is activated by exposure to light, heat and organic peroxides. However, these processes are primarily suitable only for laboratory work and not suitable for large scale industrial production of the side chain brominated products.

In the conventional bromination processes which are activated with ultraviolet light, the relatively short distance for which such light penetrates the reaction mixture is found to impair the desired reaction. During bromination to a higher degree of bromine content, the speed of the reaction is reduced. In the reaction mixture an excess of molecular bromine will accumulate and substitutions will also take place in the aromatic nucleus of the organic compound. This prolongs the cycle of operation and results in obtaining a mixture of bromine derivatives in which the bromine is bound to the aromatic nucleus as well as to the side chain. Consequently, only a low yield of the desired product is obtained and the working-up of the reaction mixture becomes more difficult.

It is therefore an object of the present invention to overcome the above discussed difficulties and disadvantages in the side chain bromination of alkyl benzenes.

It is a further object of the present invention to provide a method which permits side chain bromination of alkyl benzene to be carried out to the desired degree and in a simple and economical manner.

Other objects and advantages of the present invention will become apparent from a further reading of the description and of the appended claims.

With the above and other objects in view, the present invention contemplates a method of brominating the side chain of an alkyl benzene, comprising the steps of forming a reaction mixture consisting essentially of an alkyl benzene and free bromine, and subjecting the reaction mixture to ionizing radiation having an energy of 0.001–20 mev. at a dose rate of 0.5–100,000 rad./sec.

Surprisingly it has been found that bromination in the side chain or chains of toluene, xylene and other benzene homologs, may be advantageously activated by ionizing radiation derived from radioactive isotopes, X-ray radiation or accelerated electrons. The ionizing alpha-, beta- and gamma-radiation, the X-ray radiation and the accelerated electrons activate by interaction with the reaction mixture the substitution of the bromine radicals. Particularly good results are obtained with gamma-radiation, for instance such as may be obtained from cobalt 60 or from spent fissionable materials (fuel elements) due to their wide range, i.e. due to their ability to penetrate deeply into the reaction mass. Such deep penetration, as pointed out above, cannot be obtained with light or ultraviolet rays.

By way of example, bromination of xylene with the help of radiation proceeds in accordance with a radical-chain mechanism which can be schematically illustrated as follows:

$$Br_2 \rightsquigarrow 2Br\cdot$$

$$Br\cdot + A_1 \rightarrow A_1\cdot + HBr$$

$$A_1\cdot + Br_2 \rightarrow A_2 + Br\cdot$$

By adding these equations one obtains:

$$A_1 + Br_2 \rightarrow A_2 + HBr$$

In view of the fact that the concentration of the bromine does not substantially influence the speed of the reaction, this reaction is to be considered as a reaction of pseudo-first order. However, the concentration of the bromine in the reaction mixture will have an influence on the chain length. Thus, a higher concentration of bromine will reduce the yield of the radiation reaction and will also make possible either polar substitution in the aromatic nucleus or radical-addition at the nucleus.

The radiation bromination of xylene in the side chain is a complex reaction which comprises a series of successive reactions of the first order which may be expressed as follows:

$$A_1 \xrightarrow{Br_2} A_2 \xrightarrow{Br_2} A_3 \xrightarrow{Br_2} A_4 \xrightarrow{Br_2} A_5 \xrightarrow{Br_2} A_6 \xrightarrow{Br_2} A_7$$

In the above scheme, the symbols have the following meaning:

A_1=Xylene $H_3CC_6H_4CH_3$,
A_2=w-Monobromoxylene $BrH_2C.C_6H_4.CH_3$,
A_3=w,w'-Dibromoxylene $BrH_2C.C_6H_4.CH_2Br$,
A_4=w,w,w'-Tribromoxylene $BrHC.C_6H_4CH_2Br$,
A_5=w,w,w',w'-Tetrabromoxylene $Br_2HC.C_6H_4.CBr_2H$,
A_6=w,w,w,w',w'-Pentabromoxylene $Br_3C.C_6H_4.CHBr_2$,
A_7=w,w,w,w',w',w'-Hexabromoxylene $Br_3C.C_6H_4.CBr_3$.

Studies of the kinetics of the radiation bromination of xylene have shown that the presence of oxygen, or air as an oxygen-containing gas, will increase the reaction speed of the bromination in the side chain which is activated by the ionizing radiation. The same effect, i.e. an increase in the speed of the reaction, can also be achieved by incorporating organic peroxides, such as dibenzoyl peroxide, di-tertiary butylperoxide or ascaridol in the reaction mixture. The radiation bromination according to the present invention may be carried out either with individual isomers of xylene, i.e. ortho-xylene, meta-xylene or para-xylene, or with a technical mixture of these isomers.

In view of the high degree of development and availability of atomic energy byproducts, it is particularly advantageous to utilize ionizing radiation for activating the bromination of aromatic compounds, particularly xylene or toluene, in their side chains. The physical characteristics of ionizing radiation are suitable for carrying out the bromination reaction on an industrial scale, which appeared to be not possible with prior art side chain bromination processes. The above-described method for producing bromoxylene derivatives makes it possible to produce symmetric w,w,w',w'-tetrabromoxylene which is in great demand for producing self-extinguishing polystyrene foam and other macro-molecular compounds.

The following examples are given as illustrative only, without however, limiting the invention to the specific details of the examples.

EXAMPLE I

Radiation bromination of toluene

96 grams (0.6 mol) of bromine are dropped into 46 grams (0.5 mole) toluene. The addition of bromine is carried out at such speed that the hydrogen bromide which is formed by the reaction and which is withdrawn from the reaction vessel will not contain and will not carry along unreacted bromine, in other words, the bromine introduced into the toluene should be quickly reacted. During the addition of the bromine, the reaction mixture is treated at room temperature with radiation obtained by operation of an X-ray apparatus at 18 kv. and 30 ma. The thus obtained dose rate is 10 rad./sec. The reaction mixture is stirred with a magnetic stirring device. After the entire amount of bromine has been added, the thus obtained mixture is subjected to fractionate distillation.

The fraction boiling between 190° and 210° C. is separated and further purified by repeated fractionate distillation. The yield of benzyl bromide $C_6H_5CH_2Br$ which is obtained in this matter equals about 90% of the theoretical yield based on toluene.

EXAMPLE II

Preparation of side chain substituted mono- and di-bromoxylene

26.5 grams p-xylene (0.25 mol) are introduced into a reaction vessel which is provided with a Lenard window for the entry of electrons, and 52.5 grams bromine (0.32 mol) are slowly added thereto at room temperature. An electron accelerator with an energy of 6 mev., is used as the source of radiation. The reaction mixture is intensively mixed by means of a magnetic stirring device during the entire reaction. The dose rate equals 83,300 rad./sec. The speed of introduction of bromine is controlled by the speed with which the bromine can react in the reaction mixture. 41% w-monobromoxylene and 46% w,w'-dibromoxylene are isolated from the reaction mixture.

EXAMPLE III

Preparation of side chain substituted tribromoxylene, tetrabromoxylene, pentabromoxylene and hexabromoxylene

A reaction vessel made of glass and capable of holding 250 ml. is partly filled with 106 grams p-xylene (1 mol) and placed into a radiation chamber in which it is subjected to radiation from a cobalt 60 source of radiation. The reaction vessel is provided with a reflux cooler, heating device, conduits for introducing bromine, a dosimetric device, stirrer and conduit for withdrawing hydrogen bromide. During the course of radiation, the necessary amount of bromine, for instance 3 mols, 4 mols, 5 mols or 6 mols, plus a slight excess above the theoretically required amount, are introduced into the reaction vessel at such speed that no unreacted bromine will be carried along by the hydrogen bromide. The number of mols of bromine depends on the desired degree of bromination of the xylene. The temperature of the reaction mixture is increased during radiation in a step-wise manner from 20° to 200° C. The reaction mixture is irradiated with gamma radiation of an energy of 1.3 mev. and at a dose rate of 72 rad./sec.

The total yield of bromoxylene derivatives which is obtained thereby amounts to 99% of theoretical yield based on xylene. After isolation of individual bromine derivatives, a yield of 65–75% of the desired bromoxylene derivative, for instance tetrabromoxylene is obtained, based on the dosimetrically introduced amount of bromine.

EXAMPLE IV

106 grams of para-xylene (1 mol) having 2 grams of dibenzoyl peroxide dissolved therein are filled into a glass reaction vessel having a capacity of 250 ml. The reaction vessel is then placed inside the radiation chamber of a cobalt 60 radiation source and equipped with a reflux cooler, a bromine supply conduit, a heating device, a dosimetric device for controlling the rate of supply of bromine, a stirrer and a hydrogen bromide discharge conduit. During radiation, the required quantity of bromine is dosimetrically introduced into the reaction vessel, for instance 3 mols, 4 mols, 5 mols or 6 mols of bromine, plus a slight excess thereover in accordance with the desired degree of broination of the final product.

The temperature of the reaction mixture is gradually increased to a radiation from 20° to 200° C. The reaction mixture is radiated by a gamma source of 1.3 mev., the dose rate was 72 rad./sec.

EXAMPLE V

106 grams of para-xylene (1 mol) are filled into a glass reaction vessel of 250 ml. capacity located within the radiation chamber of a cobalt 60 radiation source and equipped with a reflux cooler, a heating device, a bromine supply conduit, a dosing apparatus for controlling the rate of introduction of bromine, a stirrer and a gas discharge conduit.

During radiation, the required amount of bromine is dosimetrically introduced, for instance 3 mols, 4 mols, 5 mols or 6 mols, plus a slight excess thereover corresponding to the required degree of bromination of the final product. At the same time, air is bubbled through the reaction mixture at the rate of 4 liters per minute, or oxygen at the rate of 1 liter per minute. The termperature of the reaction mixture is gradually increased from 20° to 200° C. The reaction mixture is radiated by a gamma source of 1.3 mev., the dose rate being 72 rad./sec.

The yield obtained according to Examples IV and V equals 99% of the theoretical yield calculated with respect to xylene. After isolating the individual bromine derivatives the yield of the desired bromoxylene derivative, for instance tetra-bromoxylene if slightly more than 4 mols of bromine were introduced, amounts to between 65 and 70% by weight based on the amount of bromine introduced into the reaction vessel.

The reaction time was shortened in all cases by the addition of organic peroxides.

Organic peroxides, for instance benzoyl peroxide, di-tert.-butyl peroxide, ascaridol, etc., preferably are added in an amount of between 1 and 10% by weight based on the amount of xylene; or organic peroxides may be produced in the reaction mixture by bubbling oxygen or air through the same during the course of radiation. The speeding up of the reaction achieved thereby amounts to between about 10 and 15% of the reaction time in the absence of organic peroxides.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. A method of brominating the side chain of an alkyl benzene, comprising the steps of forming a reaction mixture of an alkyl benzene and free bromine; and subjecting said reaction mixture to ionizing radiation having an energy of 0.001–20 mev. at a dose rate of 0.5–100,000 rad./sec.

2. A method of brominating the side chain of an alkyl benzene as defined in claim **1**, wherein said reaction mixture includes an organic peroxide.

3. A method of brominating the side chain of an alkyl benzene as defined in claim **1**, wherein during said subjecting of said reaction mixture to said ionizing radiation a gas consisting at least partly of oxygen is bubbled through said reaction mixture.

4. A method of brominating the side chain of an alkyl benzene as defined in claim **1**, wherein said alkyl benzene is a lower alkyl benzene.

5. A method of brominating the side chain of an alkyl benzene as defined in claim **1**, wherein said alkyl benzene is selected from the group consisting of toluene and xylene.

6. A method of brominating the side chain of an alkyl benzene as defined in claim **5**, wherein said alkyl benzene is toluene.

7. A method of brominating the side chain of an alkyl benzene as defined in claim **5**, wherein said alkyl benzene is xylene.

8. A method of brominating the side chain of an alkyl benzene as defined in claim **5**, wherein said reaction mixture is subjected to said ionizing radiation at atmospheric pressure.

9. A method of brominating the side chain of an alkyl benzene as defined in claim **5**, wherein said reaction mixture is subjected to said ionizing radiation at a temperature between 20 and 200° C.

10. A method of brominating the side chain of an alkyl benzene as defined in claim **5**, wherein said reaction mixture is subjected to said ionizing radiation at substantially atmospheric pressure and at a temperature of between about 140 and 150° C.

11. A method of brominating the side chain of an alkyl benzene as defined in claim **5**, wherein during said subjecting of said reaction mixture to said ionizing radiation a gas consisting at least partially of oxygen is blown into said reaction mixture.

12. A method of brominating the side chain of an alkyl benzene as defined in claim **5**, wherein said reaction mixture includes an organic peroxide.

13. A method of brominating the side chain of an alkyl benzene as defined in claim **12**, wherein said organic peroxide is present in an amount up to about 10% of the weight of said alkyl benzene.

14. A method of brominating the side chain of an alkyl benzene as defined in claim **12**, wherein said organic peroxide is selected from the group consisting of dibenzoyl peroxide, di-tert.-butyl peroxide and ascaridol.

15. A method of brominating the side chain of an alkyl benzene as defined in claim **14**, wherein during said subjecting of said reaction mixture to said ionizing radiation a gas consisting at least partly of oxygen is bubbled through said reaction mixture.

16. A method of brominating the side chain of an alkyl benzene as defined in claim **1**, wherein said alkyl benzene is selected from the group consisting of toluene and xylene, said reaction mixture includes an organic peroxide in an amount of up to about 10% by weight of said alkyl benzene, and wherein said reaction mixture is subjected to said ionizing radiation at substantially atmospheric pressure and at a temperature of between about 140 and 150° C.

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