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ALPHA-BROMOETHYLPENTACHLORO-BENZENE

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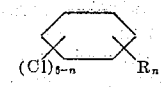
1 Claim. (Cl. 260—651)

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This invention relates to new halogenated aromatic compounds and more particularly refers to bromoethyl - pentachlorobenzene and its closely related derivatives.

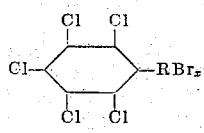
An object of this invention is to produce new alkyl substituted derivatives of polyhalogenated benzene. A further object is to produce new and useful halogenated derivatives of alkyl pentachlorobenzenes. A still further object is to produce new derivatives of ethylpentachlorobenzene by relatively simple processes. Additional objects will become apparent from the following description and claim.

These objects are attained in accordance with our invention which broadly is directed to a class of compounds conforming to the general formula:



wherein R is a bromo-alkyl group, and n is an integer from 1 to 5.

In a more restricted sense this invention is concerned with compounds conforming to the general formula:



wherein R is an alkyl group, preferably containing from two to four carbon atoms, and x is an integer from 1 to 5, preferably 1 or 2.

The following tabulation includes representative compounds embraced within the scope of this invention:

1,4 - di(alphabromoethyl) - 2,3,5,6 - tetrachlorobenzene
1,3,4-tri(bromomethyl)-2,5,6-trichlorobenzene
Betabromoethylpentachlorobenzene
Alphabromoethylpentachlorobenzene
1-bromo-1-pentachlorophenyl-propane
1-bromo-2-pentachlorophenyl-propane
2-bromo-2-pentachlorophenyl-propane
1-bromo-3-pentachlorophenyl-propane
Alpha, alpha' dibromoethylpentachlorobenzene
Alpha, beta dibromoethylpentachlorobenzene
Beta, beta' dibromoethylpentachlorobenzene
Alpha, beta, beta' tribromoethylpentachlorobenzene
Alpha, alpha', beta tribromoethylpentachlorobenzene

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Beta, beta', beta'' tribromoethylpentachlorobenzene
1,2 dibromo-2-pentachlorophenyl-propane
1,2 dibromo-1-pentachlorophenyl-propane
1,3 dibromo-1-pentachlorophenyl-propane
2,3 dibromo-1-pentachlorophenyl-propane
1,3 dibromo-2-pentachlorophenyl-propane
Pentachlorobenzyl bromide

One of the preferred embodiments of the invention concerns monobromo derivatives of ethyl pentachlorobenzene, specifically alpha-bromoethylpentachlorobenzene and betabromoethylpentachlorobenzene.

We have found that the compounds of this invention may be produced by processes which are simple and efficient. The following examples are illustrative of these processes:

EXAMPLE 1

Preparation of alphabromoethylpentachlorobenzene

278.5 grams of ethylpentachlorobenzene were heated to 90–100° C. in a three-necked flask, fitted with a dropping funnel, reflux condenser and a mechanical stirrer. A 200 watt unfrosted bulb was placed next to the flask and illuminated during the reaction. 159.8 grams of bromine were added slowly over a twelve-hour period. Hydrogen bromide was given off during the addition. The reaction mixture was poured into an evaporating dish and evacuated over potassium hydroxide and calcium chloride. The crude product thus obtained weighed 325 grams and melted at 105–115° C. This represents a 90% yield of theoretical.

Recrystallization from acetone brought the melting point of the alphabromoethylpentachlorobenzene to 121–122° C. A second recrystallization of this material brought the melting point to 123–124° C. Carbon and hydrogen analyses performed upon the pure material confirmed the empirical formula.

EXAMPLE 2

Preparation of alphabromoethylpentachlorobenzene

The procedure of Example 1 was followed with the exception that the temperature of the reacting material was maintained at about 140° C. and the time of addition was 24 hours. There was obtained a 68% yield of the alpha bromo compound.

EXAMPLE 3

Preparation of alphabromoethylpentachlorobenzene

The procedure of Example 1 was followed with the exception that the temperature was maintained at 180° C. and the bromine added over a 6-hour period. A substantial yield of the alpha bromo compound was obtained but the percentage was smaller than in Examples 1 and 2.

EXAMPLE 4

Preparation of alphabromoethylpentachlorobenzene

2 grams of methyl pentachlorophenyl carbinol, a known compound prepared by the method of Gunther Lock, Ber. 72B, 1939, pp. 300–304, and 10 grams of 48% hydrobromic acid were refluxed for two hours, with an oil bath temperature of 150° C. The reaction mixture was poured into water, filtered off and recrystallized from methanol. The first crop gave .35 gram of melting point 120–121° C. This material was recrystallized from acetone and had a melting point of 122.5–124° C. The pure material thus obtained had a mixed melting point of 99–104° C. with the starting material, and a melting point of 122.5–123.5° C. with the alpha bromo compound prepared by the method given in Example 1, which substantiates the recited structure.

EXAMPLE 5

Preparation of betabromoethylpentachloro benzene

92.5 grams (.5 mole) beta phenylethylbromide
2.5 grams $AlCl_3$
4.1 grams S_2Cl_2
404 grams SO_2Cl_2

The beta phenylethylbromide and aluminum chloride were placed in a 50 cc. three-necked flask equipped with a reflux condenser, thermometer and dropping funnel. The sulfur chloride and sulfuryl chloride mixture was run in slowly at room temperature. After a short time the aluminum chloride dissolved and the evolution of hydrochloric acid began. The color changed to yellow, then brown and the temperature began to go up but was maintained below 60° C. by means of an ice bath until approximately one-half of the chlorinating mixture had been added. The temperature was then maintained at 60–64° C. by means of a heating mantle for the rest of the addition period and for one and one-quarter hours thereafter. The reaction mixture was allowed to stand at room temperature over night and the reaction continued as evidenced by the evolution of hydrochloric acid. The next morning the mixture was heated at 70° C. for one hour at the end of which time the excess chlorinating material was removed under a water pump vacuum. The residual reaction product solidified to a yellowish green solid. Water and benzene were added to dissolve the residue. The benezene solution was washed with dilute hydrochloric acid, water, dilute sodium hydroxide and then with water. The solution was then dried with magnesium sulfate and filtered. The benezene was distilled off leaving 158 grams of light brown product melting from 88–95° C. The product was dissolved in 95% ethanol, with a separation of a small amount of tar and upon cooling crystals were deposited with a melting point of 96–98° C. Upon recrystallization from a mixture of acetone and alcohol there was obtained 84 grams of melting point 96.5–98° C. The mother liquor was worked up and a total yield of 110 grams of betabromoethylpentachlorobenzene was obtained. Three recrystallizations from acetone in alcohol brought the melting point to 98–99° C. A mixed melting point with the material of Example 1 gave a highly depressed melting point indicating that these two compounds were not the same.

EXAMPLE 6

Preparation of 1-pentachlorophenyl-1-acetoxyethane

17.9 grams of the alphabromoethylpentachlorobenzene produced in Example 1 were refluxed with 19.6 grams of potassium acetate and 275 cc. of acetic acid for 20 hours. At the end of this time most of the acetic acid was removed with a water pump and the residue taken up in benzene and water. The benzene layer was separated and dried and subjected to distillation to remove most of the benzene. The residue was dissolved in acetone and water and the product crystallized therefrom to give a melting point of 90–95° C. Upon three recrystallizations from methanol the pure acetoxy compound possessed a melting point of 101–102° C.

EXAMPLE 7

Preparation of methylpentachlorocarbinol

2 grams of the 1-pentachlorophenyl-1-acetoxyethane produced in Example 6 were refluxed for four hours with 1 gram of potassium hydroxide dissolved in 25 cc. of water and 150 cc. of acetone. At the end of this time most of the acetone was removed with a water pump vacuum and more water then added, giving a precipitate which when filtered and dried weighed 1.9 grams. This material possessed a melting point of 120.5–122° C. Upon recrystallization from methanol and water the melting point was raised to 124–125° C. A mixed melting point was made with the carbinol produced by Gunther Lock previously referred to, to give a melting point of 122–123° C., indicating that these compounds are identical.

The bromination of ethylpentachlorobenzene is generally conducted in a temperature range from about 60° C. to about 200° C., although lower temperatures may be employed when a solvent for the ethylpentachlorobenzene is employed.

The ring chlorination of beta phenylethylbromide as described previously is advisably conducted at a low temperature to minimize the condensation reactions which may occur in the presence of aluminum chloride. The temperature is generally at or below the reflux temperature of the chlorinating agents. Alternately the chlorination may be conducted with liquid or gaseous chlorine in the presence of iron.

Pentachlorobenzyl bromide may be prepared by low temperature ring chlorination of benzyl bromide or by bromination of pentachlorotoluene.

The compounds of this invention may be used as intermediates in the formation of numerous organic compounds. They possess a very high flash point and will not sustain flame per se, and above their melting points are good solvents for aromatic and chlorinated compounds. As heat transfer agents they are likewise useful. Because the aliphatic bromine is quite reactive, it is possible to use the compounds of the invention in

a large number of useful reactions such as the Friedel-Crafts reaction, with aromatic compounds; dehydrohalogenation with caustic, etc.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof except as defined in the appended claim.

What we claim is:

Alpha-bromoethylpentachlorobenzene, a solid possessing a melting point of 123–124° C.

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