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DIHALIDES FROM DIALKALI METAL HYDROCARBONS

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This invention relates broadly to the preparation of organic dihalides and, more particularly, to the preparation of certain novel organic dihalides by reaction of organometallic compounds with halogenated hydrocarbons. More specifically, the invention relates to a novel process for the production of organic dihalides by reaction of a dialkali metal hydrocarbon with an alkyl dihalide.

The present process relates to organic dihalides that are valuable as intermediates in the preparation of polysulfide polymers which, when used as fuel binding agents in solid propellants for rockets, provide numerous advantages over previously known polysulfide polymers in ballistic, physical, and processing characteristics. These include higher fuel value, increased chemical stability over a wide temperature range, improved flexibility, higher tensile strength and elongation, better adhesion, a readily controllable burning rate, and a reduced tendency toward crystallization.

The invention is based on the discovery that a dialkali metal hydrocarbon can be subjected to reaction with a dihalogenated hydrocarbon under conditions to produce organic dihalides, and, in a specific illustration, a mixture of disodiooctadiene (containing straight chain and branched chain C_8 isomers) can be reacted with ethylene dichloride under conditions whereby a reaction product is produced that contains a mixture of linear and branched chain unsaturated C_{12} dichlorides.

The process embodied herein is particularly adapted to the use of disodiooctadiene and mixtures of disodiooctadienes as the dialkali metal hydrocarbon and ethylene dichloride as the dihalogenated hydrocarbon. The process of this invention, however, is in general applicable to dialkali metal hydrocarbons and to dihalogenated hydrocarbons. For example, it is applicable to dialkali metal aliphatic hydrocarbons and some aliphatic hydrocarbons having at least one aromatic substituent on the aliphatic chain, such as dipotassiodiphenylbutane, disodiodiphenylbutane, disodiodiphenyldimethylbutane, and the like, with sodium, potassium, and lithium being the preferred alkali metal components of these compounds. In addition to ethylene dichloride, other alkyl dihalides may be employed, such as, for example, methylene chlorobromide, 1-bromo-2-chloroethane, 1,2-dichloropropane, 1,4-dichlorobutane, and others.

The present invention may be illustrated by the following equation. In this and following equations, M represents an alkali metal such as sodium, potassium, or lithium; R_1 represents a hydrocarbon diradical; Hal represents a halogen, such as chlorine, bromine, or iodine; and R_2 represents an alkyl group.

(1) $M—R_1—M+2Hal—R_2—Hal \rightarrow Hal—R_2—R_1—R_2—Hal+2MHal$

It has been found that the degree of reaction selectivity, i.e., controlled halogen replacement, and, therefore, the chain length and yield, depend upon the mode of combination of the reactants and upon the amounts of reactants employed. The desired product, that is, $Hal—R_2—R_1—R_2—Hal$, is obtained in high yields when the dialkali metal hydrocarbon is added to the alkyl dihalide and when an excess of the alkyl dihalide, is used; approximately 3 to 20 moles of the alkyl dihalide, and preferably 5 to 10 moles, are employed per mole of dialkali metal hydrocarbon. When the alkyl dihalide is added to the dialkali metal hydrocarbon or when an excess of the alkyl dihalide is not used, undesired competing reactions take place, such as

(2) $M—R_1—M+Hal—R_2—Hal \rightarrow M—R_1—R_2—Hal+MHal$

$x(M—R_1R_2—Hal) \rightarrow (M—R_1—R_2—R_1—R_2—Hal)_y+(x—y)MHal$

(3) $2M—R_1—M+Hal—R_2—Hal \rightarrow M—R_1—R_2—R_1—M+2MHal$

$M—R_1—R_2—R_1—M+2Hal—R_2—Hal \rightarrow Hal—R_2—R_1—R_2—R_1—R_2—Hal+2MHal$

Although the desired reaction can be carried out in the absence of a reaction medium, it is preferably carried out in the presence of a suitable inert diluent, such as, for example, dimethyl ether, tetrahydrofuran, or alkylate. When used, the amount of reaction medium is not critical but generally is used in an amount corresponding to about 0.5 to 10 parts of diluent to 1 part of alkyl dihalide, and preferably about 3 to 5 parts of diluent to 1 part of alkyl dihalide.

The addition of dialkali metal hydrocarbon to alkyl dihalide takes place smoothly at any temperature below the decomposition temperature of the particular reactants employed. In general, however, when substances such as disodiooctadienes and ethylene dichloride are used, the reaction temperature is preferably maintained between about −40° and +35° C.

Depending upon the starting materials, the resulting organic dihalides may be saturated or unsaturated and may contain varying proportions of linear and branched chain components. When, for example, the starting reactants are disodiooctadiene and ethylene dichloride, the product is a mixture of the unsaturated C_{12} dichlorides, 1,12 - dichlorododecadiene - 4,8, 1,10 - dichloro-3-vinyldecene-6, and 1,8-dichloro-3,6-divinyloctane.

When the crude mixed dihalides are unsaturated, such as those prepared by use of an unsaturated starting reactant or reactants, they can be converted into the saturated derivatives by hydrogenation. When the resulting product contains both linear and branched chain products, the crude mixture of isomeric products can be separated into its substantially pure linear and branched chain components. For example, from a crude mixture of C_{12} dichlorides, prepared by initially reacting a mixture of disodiooctadienes and ethylene dichloride, the dichlorides may be separated into the linear dichloride 1,12-dichlorododecadiene-4,8 and a mixture of the branched chain dichlorides 1,10-dichloro-3-vinyldecene-6 and 1,8-dichloro-3,6-divinyloctane.

The more detailed practice of the present invention is illustrated by the following examples wherein parts are given by weight unless otherwise specified. These examples are illustrative only and are not intended to limit the invention in any way except as indicated by the appended claims.

Example 1

An oven-dried, nitrogen-blanketed vessel, equipped with stirrer, thermometer, and magnetically-agitated addition tube, was charged with 54 parts (0.55 mole) of ethylene dichloride and 200 parts of alkylate. The addition tube was charged with 50 parts (0.03 mole) of 0.6 molar disodiooctadiene (mixture of straight chain and branch chain isomers) in alkylate and 50 parts of alkylate. The disodiooctadiene was added to the reaction medium over a period of about 70 minutes while the temperature was held at 30–35° C. After the completion of the addition, the mixture was stirred for 30 minutes and then allowed to stand overnight. Residual sodium or organometallic compound was destroyed by the addition of 200

parts of water. The material was then transferred to a separatory funnel, the lower aqueous layer was extracted with hexane, and the upper organic layer was combined with a single hexane extract of the lower layer. Volatile organic solvents were removed by heat and suction. The residue was distilled under vacuum to give alkylate (B.P. 35–40° C./1 mm.) and a residual oil which was flash distilled to yield 4.5 parts (64 percent, based on disodiooctadiene) of a mixture of crude unsaturated C_{12} dichlorides. Redistillation yielded a mixture comprising 1,12-dichlorododecadiene-4,8 (about 50 percent), 1,10-dichloro-3-vinyldecene-6 (about 40 percent), and 1,8-dichloro-3,6-divinyloctane (about 10 percent), B.P. 98–104° C./1 mm.

Elemental analysis	Percent C	Percent H	Percent Cl
Calculated for $C_{12}H_{20}Cl_2$	61.27	8.57	30.15
Found	62.40	8.11	29.24

Example 2

The procedure of Example 1 was repeated, except that the reaction temperature was −30° to −40° C. The yield of crude, mixed unsaturated C_{12} dichlorides was 4.6 parts (66 percent based on disodiooctadiene).

Example 3

The procedure of Example 1 was repeated, except that the ethylene dichloride was dissolved in tetrahydrofuran and the reaction temperature was −30° to −40° C. The yield of crude, mixed unsaturated C_{12} dichlorides was 4.6 parts (66 percent, based on disodiooctadiene).

Example 4

The procedure of Example 1 was repeated, except that 81 parts (0.63 mole) of 1,4-dichlorobutane was substituted for the ethylene dichloride. The semi-solid product, after distillation, consisted of 12.5 parts of a mixture of unsaturated C_{16} dichlorides comprising the straight chain 1,16-dichlorohexadecadiene-6,10 (about 45%) and the branched chain 1,14-dichloro-5-vinyltetradecene-8 (about 45%) and 1,12-dichloro-5,8-divinyldodecane (about 10%). The mixture was hydrogenated to a mixture of saturated C_{16} dichlorides, analysis of which by vapor phase chromotography indicated 44.2% of the straight chain dichloride, 44.5% of the singly branched dichloride, and 11.3% of the doubly branched dichloride. The straight chain component was isolated from the mixture by adduction with urea in ethylene dichloride and decomposition of the solid adduct with water. It mel.ed at 43–45° C. (literature value, 47° C.).

Example 5

The procedure of Example 1 was repeated, except that 86 parts (0.58 mole) of 1-bromo-2-chloroethane was used in place of the ethylene dichloride. A mixture of unsaturated C_{12} dichlorides (2.8 parts), identified by infrared spectrum, was isolated from the reaction mixture.

Example 6

The procedure of Example 1 was repeated, except that 70.5 parts (0.52 mole) of methylene chlorobromide was used in place of the ethylene dichloride. 2.7 parts of the product, boiling at 80–100° C./3 mm., was isolated. The infrared spectrum was consistent with that of a mixture of unsaturated C_{10} dichlorides comprising the straight chain 1,10-dichlorodecadiene-3,7 (about 45%) and the branched chain 1,8-dichloro-2-vinyloctane (about 45%) and 1,6-dichloro-2,5-divinylhexane (about 10%).

Example 7

A suspension of 0.1 mole of disodiodiphenylbutane in 1000 parts of a 2:1 alkylate:dimethyl ether mixture was added over 15 minutes to 248 parts (2.5 moles) of ethylene dichloride at −20° to −30° C. The dimethyl ether was allowed to evaporate, and the residue was treated with 200 parts of water. The layers were separated, and the organic phase was combined with a hexane extract of the aqueous phase. The mixture was stripped of solvent and distilled to yield 18.1 parts of liquid, B.P. 160–200° C./3 mm. On long standing, a solid which did not contain chlorine separated out of the liquid. The mother liquor was redistilled to yield 1,8-dichloro-3,6-diphenyloctane which boiled at 165–170° C./3 mm. and contained 20.69 percent Cl (theory 21.11%).

While above are disclosed but a limited number of embodiments of the invention presented herein, it is possible to produce still other embodiments without departing from the inventive concept. It is desired therefore that only such limitations be imposed upon the appended claims as are stated therein.

What is claimed is:

1. A process for preparing aliphatic organic dihalides which comprises reacting a dihalogenated hydrocarbon selected from the group consisting of ethylene dichloride, 1,4-dichlorobutane, 1-bromo-2-chloroethane, and methylene chlorobromide with a dialkali metal aliphatic hydrocarbon selected from the group consisting of disodiooctadiene and disodiodiphenylbutane at a temperature between about −40° and +35° C., about 3 to about 20 moles of said dihalogenated hydrocarbon being employed per mole of said dialkali metal aliphatic hydrocarbon.

2. The process of claim 1 wherein about 1 mole of dialkali metal aliphatic hydrocarbon is added to about 5 to about 10 moles of dihalogenated hydrocarbon.

3. A mixture comprising about 45 percent of 1,10-dihalodecadiene-3,7, about 45 percent of 1,8-dihalo-2-vinyloctane, and about 10 percent of 1,6-dihalo-2,5-divinylhexane.

4. A mixture comprising about 45 percent of 1,10-dichlorodecadiene-3,7, about 45 percent of 1,8-dichloro-2-vinyloctane, and about 10 percent of 1,6-dichloro-2,5-divinylhexane.

5. A mixture comprising about 50 percent of 1,12-dichlorododecadiene-4,8, about 40 percent of 1,10-dichloro-3-vinyldecene-6, and about 10 percent of 1,8-dichloro-3-divinyloctane.

6. A mixture comprising about 45 percent of 1,16-dichlorohexadecadiene-6,10, about 45 percent of 1,14-dichloro-5-vinyltetradecene-8, and about 10 percent of 1,12-dichloro-5,8-divinyldodecane.

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