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HALO-SUBSTITUTION OF UNSATURATED ORGANIC COMPOUNDS

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The invention relates to a process for effecting the halogenation, via substitution, of unsaturated organic compounds.

More particularly, the invention relates to a practical and economical process for halogenating, by allylic halo-substitution, an unsaturated organic compound of the class consisting of the unsaturated hydrocarbons and the halo-substituted unsaturated hydrocarbons which contain an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is of secondary character.

The process is essentially one of halo-substitution at elevated temperatures; it is executed by subjecting an unsaturated organic compound of the above-defined and hereinafter described class to a halogenation reaction, in the presence or in the absence of a halogenation catalyst, at an elevated temperature at which allylic halogen-substitution takes place but below the temperature at which substantial degradation such as cracking, splitting out of a hydrogen halide, polymerization, etc., of the organic reactant and/or product occurs.

The halo-substitution of unsaturated organic compounds of primary character, such as ethylene, and of tertiary character, such as the tertiary olefines, are not within the scope of the present invention. Since ethylene contains only two carbon atoms, it cannot be halo-substituted to form an allyl type halide, and in this respect is distinguished from the secondary olefines. In accordance with the process of the invention, the secondary olefines are halo-substituted predominantly to the readily hydrolyzable and reactive allyl type halides. If ethylene is reacted with a halogen at a sufficiently high temperature, halo-substitution can be made to occur to the substantial exclusion of the halogen-addition reaction to result in almost quantitative yields of the corresponding vinyl halide. This process for the production of vinyl halides is described and claimed in a copending application.

The halo-substitution of the tertiary olefines and halo-substitution products thereof is not within the scope of this invention. Although the principles of the invention may be applied to the halo-substitution of the tertiary olefine, such procedure may be of little advantage due to the normal tendency of these olefines to undergo halo-substitution, to the exclusion of the halogen addition reaction, at ordinary and reduced temperatures. In the case of the unsaturated compounds of primary and secondary character, the reaction of halo-substitution does not occur at all at

ordinary and reduced temperatures. At ordinary temperatures and even at considerably elevated temperatures, the normal halogenation reaction is that of halogen addition, that is, halogen adds to the olefinic linkage to saturate the same and yield a saturated polyhalide. The only halogen substitution reaction which takes place is the so-called "induced substitution", which is nothing more than halo-substitution of the saturated dihalide previously formed by the halogen addition reaction.

We have found that the high temperature halo-substitution reaction which takes place in the execution of the process of the present invention is totally unrelated to the so-called "induced substitution" reaction observed in the halogenation of ethylene and the secondary olefines at low temperatures. In accordance with the high temperature halo-substitution reaction of the invention, the halogen reacts with the secondary olefine, via halo-substitution, to result in an unsaturated halide of the allyl type. The "induced substitution" reaction which invariably accompanies the halogen addition reaction when an olefine is reacted with a halogen at low temperatures is the reaction of free halogen with the saturated product of the halogen addition reaction to form a more highly halogenated saturated product. The mechanism of this "induced substitution" reaction has been conclusively established by experimental evidence. Chlorine has been reacted with ethylene at temperatures as high as 200° C. and under conditions at which the art teaches that the "induced substitution" reaction occurs to a great extent, in fact, to such a great extent that it is impracticable to halogenate olefines by addition under such conditions. In no case could vinyl chloride be detected in the reaction products, showing that no high temperature halo-substitution occurred. However, at the low temperature the only substitution reaction which occurred was the so-called "induced substitution," that is, reaction of chlorine with ethylene dichloride to form higher chlorinated products, mostly trichloroethane.

Representative unsaturated compounds of the class which may be halo-substituted to valuable allyl type halides in accordance with the process of the invention are the secondary olefines such as propylene, the normal butylene (butene-1 and butene-2), the normal amylenes, secondary isoamylenes (isopropyl ethylene), the normal hexenes, the iso-hexenes of secondary character, the normal heptenes, the iso-heptenes of secondary character, and the straight and branched chain

secondary octylenes, nonylenes and the like; the halo-substituted normal and branched chain secondary olefines such as 1-chloropropene-1, 1-bromopropene-1, 2-chloropropene-1, 2-bromopropene-1, 1-chlorobutene-1, 1-bromobutene-1, 2-chlorobutene-1, 1,2-dichlorobutene-1, 1-chlorobutene-2, 2-chlorobutene-2, 1,2-dichlorobutene-2, 4-chlorobutene-1, 1,4-dichlorobutene-1, 1-chloropentene-1, 1-chloropentene-2, 1-chloro 3-methyl butene-1, 1-chloro 3-methyl butene-2, 2-chloro 3-methyl butene-2 and the like and their homologues and analogues. The halo-substitution of cyclic olefinic compounds of secondary character and halo-substitution products thereof is also within the scope of the invention. Suitable reactants of this type are cyclobutene, cyclopentene, cyclohexene, tetrahydrobenzene, the cycloheptenes, cycloheptadiene, the cyclooctenes and the like as well as the halo-substituted cyclic olefines. The secondary olefines, the cyclic olefines of secondary character and the halo-substitution products of such compounds of aliphatic character may be linked to one or more cycloalkyl and/or aromatic radicals. For example, compounds such as 1-phenyl propene-2, 1-phenyl 2-chloropropene-2, 1-phenyl butene-2 and the like may be halogenated by allylic halogen substitution in accordance with the process of the invention. The treated unsaturated compound may contain one or a plurality of olefinic linkages; it is only essential that at least one olefinic linkage between two secondary carbon atoms or between a secondary carbon atom and a primary carbon atom be in the allyl position to at least one carbon atom possessing a replaceable hydrogen atom. Thus, diolefinic compounds such as pentadiene-1,4, hexadiene-1,5, 2-methyl hexadiene-1,5 and the like may be advantageously halo-substituted to the corresponding allyl type halides.

The process of the invention is of particular commercial value as applied to the halogenation of the secondary olefines as propylene, the normal butylenes and the like to the corresponding allyl type halides. For example, propylene may be chlorinated, on a technical scale with perfect safety and at low cost, to the commercially valuable allyl chloride, the allyl chloride being obtained in excellent yield. The allyl type halides obtained as products in the execution of the process of the invention are of particular value because of their great reactivity. They are starting materials in the production of a wide variety of organic products such as unsaturated alcohols, unsaturated ethers, saturated polyhydric alcohols, aldehydes, cellulose ethers, resin base materials, resins and the like. In some cases, particularly at the higher temperatures, small amounts of vinylic type halides may be formed, but in all cases operation under optimum halo-substitution conditions results in a product materially predominating in an allyl type halide. In some cases, subjecting the higher olefinic compounds to the halo-substitution reaction results in a shifting of the double bond. This change of position of the double bond is not, in the cases observed, quantitative; part of the product has the double bond in the same position as in the treated unsaturated compound, while another part may have the double bond in a different position.

When the process is applied to the halo-substitution of secondary olefines, the source of the stock material is immaterial. The olefines may be obtained by the cracking of petroleum and petroleum products, by the catalytic dehydroge-

nation of paraffin hydrocarbons, by the dehydration of non-tertiary alcohols, etc. The secondary olefines may be treated individually or in admixture with each other and/or other olefines. Hydrocarbon mixtures containing one or more secondary olefines may be treated. Paraffin-olefine mixtures containing a substantial amount of one or more secondary olefines, and wherein the paraffins and olefines have the same or a different carbon content, are suitable starting materials. Technical hydrocarbon fractions, the secondary olefine content of which is conveniently halo-substituted in accordance with the process, are the propane-propene fraction, the butane-butene fraction, the pentane-pentene fraction, etc. If desired, the tertiary olefine content of any such hydrocarbon fraction may be preliminarily, selectively and substantially removed therefrom by any of the known methods. When saturated organic compounds, such as the paraffin hydrocarbons, are present in the reaction mixture during the execution of the halo-substitution reaction, they may also be halo-substituted, and the product will contain unsaturated as well as saturated halo-substitution products. In some cases, it may be desirable to form such saturated halo-substitution products as by-products of the halo-substitution process of the invention. Small amounts of water, oxygen, sulphur dioxide and hydrogen sulphide were found to exert no appreciable effect on the halo-substitution reaction of the process. From the standpoint of economics, it is desirable to execute the reaction in the substantial absence of water. Hydrogen formed due to the occurrence of the water-gas reaction may react with the free halogen present and reduce the yield of useful products from the applied halogen. The process may, if desired, be effected in the presence of an inert diluent, such as nitrogen.

The process of the invention is based on our discovery that, contrary to all expectations, an unsaturated hydrocarbon or halo-substituted unsaturated hydrocarbon of secondary character can be reacted with a free halogen, or a reactant which yields a free halogen under the conditions of operation, at an elevated temperature at which the hitherto unknown high temperature allylic halo-substitution reaction occurs together with or to the substantial exclusion of the well-known halogen addition reaction.

In the great majority of cases, the halo-substitution reaction does not occur to any substantial extent at temperatures below 100° C. The predominant reaction at temperatures below 100° C. is halogen addition. The process is preferably executed at temperatures at least equal to 200° C., but, in some cases, as when it is desired that the halogen addition reaction occur to a substantial and perhaps predominating extent, temperatures below 200° C. may be employed. The upper limit of the preferred operating temperature range is determined by the stability of the organic reactants and products under the existing conditions. For example, when optimum practical yields are desired the operating temperature should be below those temperatures, under the prevailing conditions of contact time, pressure, degree of dilution, etc., at which degradation reactions such as cracking, polymerization, splitting out of a hydrogen halide, and the like, are favored. In the majority of cases, operating temperatures of from about 200° C. to about 700° C. are suitable, and temperatures of from 200° C. to 500° C. may be used. The

optimum operating temperature in each particular case will depend upon the other operating conditions such as space velocity, pressure, the presence of catalysts, etc., as well as upon the particular unsaturated compound reacted and upon the particular halogen reacted therewith. Brom-substitution of a particular compound, other conditions being the same, can usually be effected at a lower temperature than chlor-substitution. The chlor-substitution of propylene requires a higher temperature than the chlor-substitution of the normal butylenes, and, in general, the chlor-substitution of the normal butylenes may require a higher temperature than the chlor-substitution of the secondary amylenes. The approximate observed temperature ranges within which the chlorination of various secondary olefines appears to change from chlorine addition to chlor-substitution are: propylene (200° C. to 350° C.); beta-butylene (150° C. to 225° C.) and pentene-2 (125° C. to 200° C.) When a chlorinated product materially predominating in allyl chloride is desired, we preferably effect the chlor-substitution reaction at a temperature in the range of from 350° C. to 675° C. When operating in this temperature range, the chlorine addition reaction is suppressed to such an extent that only very small amounts (less than 0.5%) of dichloropropane are obtained. Lower operating temperatures may be employed when it is desired to obtain a product containing a substantial amount of dichloropropane as well as allyl chloride. A preferred temperature range for the allylic halo-substitution of the normal butylenes is from about 200° C. to 400° C. In general, after the critical temperature is reached, the amount of halogen addition decreases and the amount of halo-substitution increases as the temperature is raised. By operating at a sufficiently high temperature, the halogen addition reaction may be almost completely suppressed.

Since the halogens and the olefinic compounds of the character herein described will react rapidly via halogen addition when brought into contact at room temperature, it is necessary, if halo-substitution to the substantial exclusion of halogen addition is desired, that the reactants be brought together at an elevated temperature so high that substantially no halogen addition can occur. Mixing the reactants at about room temperature and passing the mixture into a heated reaction zone may not suffice because the halogen addition reaction may take place to a substantial extent before temperatures at which the halo-substitution reaction occurs and the halogen addition reaction is suppressed are reached. The reactants may be brought into contact at temperatures sufficiently high to substantially obviate occurrence of the halogen addition reaction in a variety of suitable manners. The olefinic compound may be preheated and the unheated halogen added thereto at such a rate that the temperature of the mixture is maintained sufficiently high to obviate halogen addition, or the halogen may be preheated and brought into contact with the unheated olefinic compound so as to maintain a sufficiently high temperature at the point of mixing and in the mixture, or the halogen and olefinic compound may both be preheated separately and premixed or separately introduced into the reaction zone at a temperature sufficiently high to substantially obviate halogen addition. In a preferred procedure for the chlor-substitution of propylene

to allyl chloride, the propylene and chlorine are preheated separately and passed into an unheated reaction chamber wherein the exothermic chlor-substitution reaction takes place. It is not essential to the successful execution of the process that either of the reactants be preheated. In some cases, good results may be obtained by mixing the cold reactants and rapidly raising the temperature of the mixture to the desired reaction temperature.

When preheating of the reactants is resorted to, the preheating temperature or temperatures employed are usually dependent upon the reaction temperature to be used in the particular operation. One or both of the reactants is raised to such a temperature that the resultant mixture will have a temperature sufficiently high to substantially obviate the occurrence of the halogen addition reaction. In some cases, it is advantageous that the mixing temperature be substantially the same as the reaction temperature. In the chlor-substitution of propylene, preheating of the propylene alone may be resorted to, in which case, because of the much lower specific heat of chlorine it is merely necessary to preheat to a slightly higher temperature than would be necessary if both reactants were preheated. The upper limit of the preheating temperature is to a certain extent fixed by the temperature at which excessive cracking of the olefinic compound occurs. Excessive carbon formation in the preheater may be inhibited by maintaining a small amount of hydrogen sulphide in the olefinic material treated, thus permitting the use of higher preheating temperatures than would be practicable without the employment of such an agent.

When preheating of the reactants is resorted to, and there is danger of explosion and/or flaming at the mixing temperature, these difficulties may be overcome by regulating the relative velocities of the gaseous reactants. For example, when the halogen is introduced into a stream of the preheated olefinic compound, flaming may be avoided by injecting the halogen vapors into the vapors of the olefinic compound at a velocity exceeding that of flame propagation at the mixing temperature. The halogen may be introduced at a plurality of separate points along the reaction tube while the material undergoing halo-substitution is maintained within the desired reaction temperature range, and any desired degree of halo-substitution effected with safety in a single operation. In certain cases, it is desirable to make use of a high space velocity and turbulent flow of the reaction mixture through the reaction chamber to prevent the occurrence of flame and its concomitant production of free carbon, and to permit the use of higher reaction temperatures. The high velocity enables the gases to enter the reaction zone at a velocity in excess of that of flame propagation, and the turbulent flow causes intimate mixing which enables the reactants to become uniformly dispersed in each other before any substantial amount of halogenation takes place. The halo-substitution reaction is exothermic, and considerable heat is liberated during its occurrence. Overheating of the reaction chamber may be avoided by the use of conventional internal and/or external cooling means, by the use of normally gaseous diluents, or by the evaporation of an internal cooling agent so that there is substantially instantaneous dissipation of heat uniformly throughout the reaction mixture. Temperature control may be aided by employing a

relatively large excess of the olefinic compound over the halogen, such excess functioning as a diluent.

The reaction may be effected with either the halogen or the olefinic compound in excess, or with the reactants in equimolecular amounts. We, in general, prefer to employ an excess of the olefinic compound because, in such cases, the yield of the desired product based on the applied halogen is usually better and temperature control is facilitated. Olefinic compound to halogen mol. ratios of from 2:1 to 7:1 and higher have been successfully employed. When an excess of the halogen is employed, there is a greater tendency to form polyhalogenated unsaturated compounds.

The reaction tube or reaction chamber may be of any suitable material. Good results have been obtained with carbon, Hastelloy A, Hastelloy C, KA₂ steel, nickel, quartz and Monel metal reaction tubes. The formation of carbon, which is catalyzed by the metal surface of the reaction chamber or the chamber wherein the preheating of the olefinic compound is effected, may be inhibited by adding a small amount of hydrogen sulphide or an equivalent inhibiting agent to the treated olefinic compound, or by pretreating such metallic surfaces.

The space velocity or rate of passage of the reactants through the reaction zone will depend upon the design of the reaction chamber (amount of surface available), upon the temperature employed, and upon the mol. ratio of the olefinic compound to the halogen in the mixture reacted. In general, good results are obtained by employing the maximum flows that can be reacted in a given reactor. Thus, the rate of production with the given equipment, is at a maximum and the time during which the reaction products are maintained at the reaction temperature is reduced to a minimum.

The reaction may be effected in the vapor or in the liquid phase at any suitable pressure. Liquid phase operation is particularly well suited for the halo-substitution of high molecular weight secondary olefines such as are obtained by the cracking of wax.

If desired, the rate of the halo-substitution reaction may be accelerated by the use of light and/or by the use of halogenation catalysts. When photochemical accelerating means are used, suitable light-giving devices, such as incandescent bulbs, ultra-violet ray lamps, etc., may be provided around the reaction chamber which is constructed of some material, such as glass or quartz, which permits passage through its walls of the reaction-accelerating light. Suitable catalysts which may be employed are, among others, carbon, the antimony halides, the tin halides and other known halogenation catalysts. Other conditions being the same, the use of halogenation accelerating agencies such as light and/or catalysts may permit execution of the halo-substitution reaction at lower temperatures.

To avoid the occurrence of secondary reactions, such as reaction of the unsaturated reactants and/or reaction products with the hydrogen halide formed during the occurrence of the primary halo-substitution reaction, it is desirable to cool the reacted mixture and separate the hydrogen halide and unreacted halogen, if any is present, from the reaction product substantially as soon as it leaves the reaction zone. This may be achieved in a variety of suitable manners. The reacted mixture, substantially as soon as it

leaves the reaction zone, may be contacted with a suitable selective solvent for the hydrogen halide, such as water, in a conventional scrubber and the hydrogen halide absorbed and separated from the reaction product. Alternatively, the reacted mixture may be subjected to rectification immediately after it leaves the reaction zone with or without a previous neutralization treatment with a suitable base. The unreacted unsaturated compound applied may be recycled to the reactor or otherwise reutilized.

The invention is illustrated by the following examples which are presented for the purpose of showing various modes of executing the process and the results obtainable, and are not to be considered as limitative in any sense.

Example I

Chlorine and liquid β -butylene were introduced through a mixing nozzle downward into a vertical glass reaction tube of 2" diameter and about 2' long, the lower end of which widened to a 10 liter bulb which accommodated a water spray. The apparatus was not provided with any means of heating so the temperature was dependent upon the ratio of reaction heat to heat capacity of the reaction participants, i. e., the temperature could be controlled by varying the excess of hydrocarbon over the chlorine. The following table shows the influence of temperature on the composition of the product.

Reaction temperature	Percent unsaturated monochloride	Percent saturated dichloride	Percent saturated trichloride	Percent saturated chlorhydrin
Degrees				
60.....	15.7	73.4	5.6	5.3
121.....	21	63.1	7.1	7.8
140.....	41.4	45.8	8.7	4.1

The temperatures in these experiments were measured at the walls of the reaction tube, thus the true reaction temperatures may have been higher than those recorded. The chlorhydrin formed is due to the presence of water vapor or spray toward the end of the reaction zone. It is desirable that moisture be absent in the reaction system, i. e., it is preferable to operate with substantially anhydrous reactants since the presence of water vapor not only causes the formation of some chlorhydrin but catalyzes to some extent the addition reaction of hydrochloric acid to olefines, especially at elevated temperatures and/or superatmospheric pressures. Operating with dry reactants also avoids or minimizes corrosion losses.

Example II

A similar apparatus as the one described in the foregoing example was used. A longer reaction tube of 3' was used and a thermocouple well was inserted into the reaction zone. Both butylene and chlorine were introduced as gases. The results in this apparatus were similar to those obtained in Example I, but there was practically no chlorhydrin and, as expected, higher temperatures were indicated for similar products than with the previous arrangement.

Temperature, ° C.	Percent unsaturated monochloride
140.....	8
170.....	10.5
206.....	34

Example III

The chlorination was carried out in an apparatus which allowed the chlorine and the β -butylene to be preheated before mixing. The reaction zone was in a glass tube inserted in an aluminum block for heat control.

amounts of allyl chloride and dichloropropane formed.

Temperature, ° C.	Mol. ratio C_4H_8/Cl_2	Space velocity per second	Unsaturated monochloride, percent chlorine reacted	Saturated dichloride, percent chlorine reacted	Yield allyl chloride, percent chlorine basis
384-----	1.76	0.94	26.5	15.8	51.4
470-----	1.89	1.06	29.8	10.6	57.8
510-----	1.87	1.22	29.7	9.7	57.7
550-----	2.10	1.34	30.6	5.9	59.8
600-----	1.98	1.80	33.4	7.5	64.8
650-----	2.07	2.84	33.4	5.9	64.7
708-----	2.01	3.26	30.6	3.4	59.8

The unsaturated chloride formed was found to contain about 60% of a monochloride boiling around 85° C., and 40% of a monochloride boiling at 65° C. The compound boiling at 85° C. is a primary chloride as it can be hydrolyzed to a primary unsaturated alcohol, while the lower boiling one is of the secondary type.

When a mixture of α and β butylenes, containing about 20% β -butylene, was used instead of pure β -butylene, the composition of the product was practically the same as that obtained with pure β -butylene.

In the above tabulated runs, the amount of the saturated dichloride found is abnormally high. This is because the reactants were mixed at room temperature and then passed into the reactor. Considerable chlorine addition to form the saturated dichloride had taken place before the reactants were brought to the high chlor-substitution temperature. The results show that, due to side reactions, there is no increase in allyl chloride yield after a temperature of about 700° C. has been reached, and that the amount of the saturated dichloride formed decreases to a minimum as the temperature is raised.

Example IV

Propylene was chlorinated at a reaction zone temperature of 390° C. with a chlorine to hydrocarbon ratio of 0.9:1. A yield of 60% allyl chloride was obtained.

Example V

2-chlorobutene-2 was chlorinated at a temperature of 350° C. with a ratio of chlorine to chlorobutene of 0.75:1. Analysis of the product showed it to contain about 50% of an unsaturated dichloride, probably 1,2 and 2,4 dichlorobutene-2.

Example VI

Cyclohexene was chlorinated at 420° C. with 0.8

Example VIII

In the experiments, the data of which are tabulated below, both the olefinic compound and the chlorine were preheated. The preheated reactants were mixed by means of a suitable mixing jet and the hot mixture immediately passed into the reaction tube wherein the exothermic chlor-substitution reaction took place. The reaction tube and the preheaters were provided with means for accurately controlling their temperatures substantially constant at the desired value. The reaction temperature was measured by means of a jacketed thermocouple introduced into the reaction space.

Olefine	Reaction tube size (inches)		Mol. ratio olefine chlorine	Mixing temp., ° C.	Reaction temp., ° C.	Chlorine balance			Unsaturated monochloride actually recovered (mol. percent of chlorine applied)*
	Diam.	Length				Unsaturated monochloride, percent	Saturated dichloride, percent	Unsaturated dichloride, percent	
Propylene-----	3/4	14	2.05	400	595	34.2	1.9	5.8	68.5
Do-----	3/4	14	2.00	480	665	34.9	1.8	5.6	69.8
Do-----	3/4	14	6.60	600	600	39.3	0.3	3.2	78.6
Do-----	3/4	14	6.30	500	500	37.3	1.3	4.0	74.6
Do-----	3/4	14	3.60	500	582	36.9	0.3	3.7	73.8
Do-----	3/4	24	6.40	400	436	27.6	4.9	3.0	55.2
Butylene-----	5/8	27	2.40	299	445	30.9	6.1		61.9

mol. of chlorine per mol. of hydrocarbon. The product contained 63% unsaturated monochloride.

Example VII

Gaseous propylene was reacted with gaseous chlorine in a carbon reaction tube (20' x 1'). The reaction tube was surrounded by an aluminum block to which heat was supplied by means of a gas furnace. The gases, at about room temperature, were passed through a suitable mixing jet and the mixture passed immediately into the reaction tube maintained at the desired reaction temperature. The reaction temperature was measured by means of a thermocouple inserted in the aluminum block. The tabulated data show the influence of the temperature on the relative

*The actual yield of the unsaturated monohalide was considerably higher than these figures indicate. Due to use of an inefficient recovery system, not all of the formal product was recovered. The figures of line 3 of the table show that under the specified conditions the recovered unsaturated monohalide was 78.6%. When this run was duplicated using a more efficient recovery system, this figure was raised to 85.5% indicating a yield of at least 85.5%.

It is seen from the tabulated data that the chlorine addition reaction is suppressed as the reaction temperature is increased. When the preheated reactants were mixed at 600° C. and the reaction executed at the same temperature (600° C.), only 0.3% of the chlorine addition product (dichloropropane) was formed. When the reaction was effected at 665° C., more of the chlorine addition product (1.8%) was formed, but this was due to the fact that in this case the mixing

temperature was lower (460° C.), permitting the addition reaction to occur to a small extent before the mixture entered the reaction zone.

Example IX

Allyl bromide was prepared by the high temperature brom-substitution of propylene. Both the propylene and the bromine were preheated, mixed while hot, and the mixture immediately passed into the reaction tube. The allyl bromide was obtained in a yield of 71.2% based on bromine applied. The data of the experiment are tabulated below:

Reaction tube (inches)	Mol. ratio propylene chlorine	Mixing temp., ° C.	Reaction temp., ° C.	Unsaturated monobromide, percent	Saturated dibromide, percent	Yield allyl bromide, mol. percent of bro- mine applied
Diam. Length						
1½ 22	4.02	300	324	36.7	<2.5	71.2

Example X

2-chlorbutene-2 ($\text{CH}_3\text{—CCl=CH—CH}_3$) was reacted with chlorine in a mol. ratio of about 2 to 1. The preheated reactants were mixed at about 100° C. and the mixture passed into a carbon reaction tube maintained at a temperature of about 500° C. The condensed reaction product was washed with water, dried and fractionated. The main reaction products were 1,2-dichlorbutene-2 (B. P. 110° C. to 112° C.) and chloroprene (B. P. 60° C.).

The application is a continuation-in-part of our copending application, Serial No. 37,184, filed August 21, 1935.

We claim as our invention:

1. The process of predominantly halogenating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises subjecting said unsaturated organic compound to a halogenation reaction at an elevated temperature at which allylic halogen-substitution predominantly takes place but below the temperature at which substantial degradation is favored, and recovering the unsaturated allyl type halide.

2. The process of predominantly chlorinating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises subjecting said unsaturated organic compound to a chlorination reaction at an elevated temperature at which allylic chlorine-substitution predominantly takes place but below the temperature at which substantial degradation is favored, and recovering the unsaturated allyl type chloride.

3. The process of predominantly chlorinating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises subjecting said unsaturated organic compound to a chlorination reaction at a temperature between about 200° C. and 500° C., in which temperature range allylic chlorine-sub-

stitution predominantly takes place, and recovering the unsaturated allyl type chloride.

4. The process of predominantly chlorinating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises subjecting said unsaturated organic compound to a chlorination reaction with gaseous chlorine at an elevated temperature at which allylic chlorine-substitution

predominantly takes place but below the temperature at which substantial degradation is favored, and recovering the unsaturated allyl type chloride.

5. The process of predominantly chlorinating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises separately preheating said unsaturated organic compound to a temperature at which it is in the vaporous state, mixing it in that heated condition with chlorine, rapidly executing the chlorination reaction at an elevated temperature at which allylic chlorine-substitution predominantly takes place but below the temperature at which substantial degradation is favored, and recovering the unsaturated allyl type chloride.

6. The process of predominantly chlorinating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises separately preheating said unsaturated organic compound and chlorine to a temperature above 200° C., mixing them in that heated condition, rapidly executing the chlorination reaction at above 200° C., but below the temperature at which substantial degradation is favored, in which temperature range allylic chlorine-substitution predominantly takes place, and recovering the unsaturated allyl type chloride.

7. The process of predominantly chlorinating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises subjecting said unsaturated organic compound in the vapor phase to reaction with gaseous chlorine at above 200° C. but below the temperature at which substantial degradation is favored, in which temperature range allylic chlorine-substitution predominantly takes place, and recovering the unsaturated allyl type chloride.

8. The process of predominantly chlorinating by allylic substitution an unsaturated organic

compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises separately preheating said unsaturated organic compound and chlorine to a predetermined reaction temperature materially above the boiling temperature of the unsaturated organic compound and at which allylic chlorine-substitution predominantly takes place, and then mixing the heated material to be chlorinated with the heated chlorine at a velocity in excess of that of flame propagation under the conditions existing to effect the chlorine-substitution.

9. The process of predominantly chlorinating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises preheating the unsaturated organic compound to a predetermined reaction temperature at which it is in the vapor phase and then promptly injecting chlorine into said heated material at a velocity in excess of that of flame propagation under the conditions existing to effect the allylic chlorine-substitution, the reaction temperature being so high that allylic chlorine-substitution predominantly takes place but below the temperature at which substantial degradation is favored.

10. The process of predominantly chlorinating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises producing a substitution reaction between said unsaturated organic compound and chlorine at a temperature above 200° C. and for a period of time which does not favor degradation of the unsaturated organic compound, the reaction temperature being so high that allylic chlorine-substitution predominantly takes place.

11. The process of predominantly chlorinating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises injecting chlorine at a speed exceeding that of flame propagation of the reaction into a stream of the unsaturated organic compound while executing the reaction between about 200° C. and 500° C., in which temperature range allylic chlorine-substitution predominantly takes place.

12. The process of predominantly chlorinating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises injecting chlorine at a speed exceeding that of flame propagation of the reaction into the unsaturated organic compound while executing the reaction between about 200° C. and 500° C., in which temperature range allylic chlorine-substitution predominantly takes place.

13. The process of predominantly chlorinating by allylic substitution a secondary olefine which comprises subjecting it to a chlorination reaction at an elevated temperature at which allylic chlorine-substitution predominantly takes place but below the temperature at which substantial degradation is favored, and recovering the unsaturated allyl type chloride.

14. The process of predominantly chlorinating by allylic substitution propylene which comprises subjecting it to a chlorination reaction at above 200° C., at which temperature allylic chlorine-substitution predominantly takes place, for a period of time which does not favor substantial degradation of the propylene.

15. The process of predominantly chlorinating by allylic substitution a secondary butylene which comprises subjecting it to a chlorination reaction at above 200° C., at which temperature allylic chlorine-substitution predominantly takes place, for a period of time which does not favor substantial degradation of the secondary butylene.

16. The process of predominantly chlorinating by allylic substitution a secondary amylene which comprises subjecting it to a chlorination reaction at above 200° C., at which temperature allylic chlorine-substitution predominantly takes place, for a period of time which does not favor substantial degradation of the secondary amylene.

17. The process of halogenating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises subjecting said unsaturated organic compound to a halogenation reaction at any elevated temperature at which allylic halogen-substitution takes place but below the temperature at which substantial degradation is favored, and recovering the unsaturated allyl type halide.

18. The process of halogenating by allylic substitution an unsaturated organic compound of the class consisting of unsaturated hydrocarbons and halo-substituted unsaturated hydrocarbons containing an olefinic linkage between two non-tertiary carbon atoms of aliphatic character at least one of which is secondary which comprises subjecting said unsaturated organic compound to a halogenation reaction at a temperature at least equal to about 200° C. but below the temperature at which substantial degradation is favored whereby allylic halogen-substitution takes place to form an unsaturated allyl type halide, and recovering the unsaturated allyl type halide.

19. The process of halogenating a secondary butylene by allylic substitution which comprises reacting a secondary butylene with a halogen at a temperature in the range of from above 200° C. to about 400° C. whereby allylic halogen-substitution takes place to form an unsaturated allyl type halide.

20. The process of chlorinating propylene by allylic substitution which comprises reacting propylene with chlorine at a temperature in the range of from 350° C. to 675° C., whereby allylic chlorine-substitution takes place to form allyl chloride.

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