

UNITED STATES PATENT OFFICE

2,198,185

PRODUCTION OF ARYL SUBSTITUTED
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Wallington, EnglandNo Drawing. Application October 15, 1937, Se-
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5 Claims. (Cl. 260-669)

This invention relates to the production of aryl substituted olefins by condensation of aromatic hydrocarbons with unsaturated aliphatic hydrocarbons containing from 3 to 5 carbon atoms, and subsequent pyrolysis of the condensation products.

It is known that aromatic hydrocarbons such as benzene may be condensed with unsaturated aliphatic hydrocarbons by Friedel and Craft's reaction employing aluminium chloride as condensing agent and it has been proposed to use strong sulphuric acid for the purpose. A particularly advantageous method of production using strong sulphuric acid is described and claimed in the specification of our Patent No. 2,143,493.

Having obtained the alkylated aromatic hydrocarbon either by known methods or by the method of using concentrated sulphuric acid under the conditions specified in the aforesaid patent application of even date the present invention is concerned with certain novel features of conversion of the same by pyrolysis into styrene and the like as will now be explained.

It has already been proposed to prepare styrene hydrocarbons of the general formula $Ar.CH=CH_2$ by heating a hydrocarbon of at least 8 carbon atoms and at least 10 hydrogen atoms to a temperature of 450° to 700° C., the process being exemplified by the conversion of cymene into p-methylstyrene by thermal demethanation. However, we have found that in addition to styrene hydrocarbons, pyrolysis generally produces relatively large proportions of undesired substances the formation of which can be minimised, so far as we have been able to ascertain, only by observing certain operating conditions the chief of which are the following:

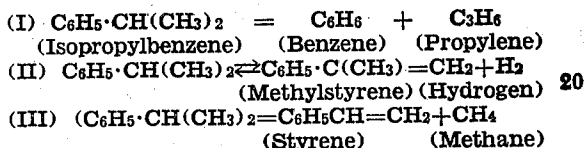
(1) Using an operating temperature lying between 600° and 800° C. preferably between 650° and 750° C., the hydrocarbon being thereby pyrolysed in the gaseous phase,

(2) Ensuring a linear gas velocity along the reaction zone in excess of the critical velocity, i. e. a velocity several times the critical velocity so as to ensure turbulence. Unless such a high velocity is maintained not only is the yield of desired products very low, but the reaction tube speedily becomes choked and renders continuous operation impossible.

(3) Controlling the character of the products of pyrolysis by adding to the main reactant one or more of the products of thermal dehydrogenation of the hydrocarbon under treatment as will now be explained. The pyrolysis according to the present invention is preferably carried out

at about atmospheric pressure or at sub-atmospheric pressure. Moderate superatmospheric pressures are not precluded,—for example up to say 5 atmospheres.

For the purpose of explanation we will refer to the pyrolysis of mono-isopropylbenzene, obtained by condensation of propylene and benzene, although the process of the present invention can be applied with due modification to such hydrocarbons as secondary butylbenzene, cymene and the like. Now, at temperatures of 600° – 800° C., the pyrolysis of isopropylbenzene has been found to occur in tubes of such varied materials as silica, pyrex glass, copper and steel, in accordance with the following reactions, all of which take place independently and simultaneously:



In addition to the above main products, considerable amounts of heavy tars may also be formed unless the working conditions hereinbefore referred to are employed.

The first of the above three reactions viz. (I) yielding propylene and benzene, is relatively unimportant under conditions of actual practice and is not greatly disadvantageous since both of the products may be partially recovered and re-used in the preparation of the starting material. When carrying out the pyrolysis of isopropylbenzene, either alone or in the presence of inert diluents such as nitrogen or steam in tubes of pyrex glass, copper or steel at 600° – 700° C., the relative proportions of the three main reaction products remain substantially the same irrespective of the material used for the reaction tubes.

In the early stages of the process Reaction II tends to predominate so that at percentage decompositions per pass up to about 20%, the molar ratio of styrene to α -methylstyrene in the reaction products is about 1:2.

However, with greater intensity of cracking, Reaction III becomes increasingly important so that at percentage decompositions per pass of 50–65%, the molar ratio of styrene to α -methylstyrene in the reaction products may exceed unity.

When operating the pyrolysis of undiluted isopropylbenzene at atmospheric pressure, the percentage of decomposition per passage is limited by the fact that the proportion of high-boiling

substances in the products tends to increase with consequent reduction in the efficiency of the process. High percentage decomposition per passage e. g. 60% of the isopropylbenzene decomposed in one treatment, may, however, be readily attained without undue formation of undesirable high-boiling by-products by effecting the pyrolysis in the presence of inert gaseous diluents, such as nitrogen or steam, the latter being preferred on account of ease of condensation and recovery of products. When steam is used as diluent, condensation of the products yields a mixture of cracked hydrocarbon product and water, from which the latter can be readily separated to give a liquid mixture rich in styrene and α -methylstyrene.

By the present invention the pyrolysis is effected in such a way that the dehydrogenation Reaction II leading to the formation of hydrogen and α -methylstyrene, is partially, or almost completely suppressed, while the competing demethanation Reaction III forming styrene is simultaneously enhanced by adding to the hydrocarbon feed material substantial proportions of one, or other, or both of the products of dehydrogenation, namely hydrogen and α -methylstyrene, this effect being undoubtedly due to the reversability of Reaction II.

The addition of hydrogen to the ingoing isopropylbenzene does tend to suppress dehydrogenation and also diminish the formation of heavy tars although it appears to increase Reaction I somewhat. Naturally when using an excess of hydrogen, the employment of other diluents is rendered unnecessary although it is not precluded. Even more satisfactory, however, in practice is the employment of α -methylstyrene itself as a means of suppressing its own formation, either alone or with hydrogen or with an inert gaseous diluent such as steam. Since α -methylstyrene is a liquid and can be readily condensed, its use alone is sometimes more convenient than the use of hydrogen since difficulties in the condensation and recovery of the liquid products of pyrolysis are minimised.

The proportion of α -methylstyrene returned with added isopropylbenzene to the cracking tubes may be varied somewhat, but satisfactory results are obtained by cracking a mixture of 15-25% by weight of α -methylstyrene and 85-75% of isopropylbenzene and using steam as diluent. Satisfactory proportions of steam are 2-10 mols. of steam per mol. of hydrocarbon feed although our invention is not restricted in this sense. Several procedures are possible in recycling the desired amount of α -methylstyrene. Thus, the crude cracked product of pyrolysis may be continuously fractionated first at atmospheric

containing 50-80% of α -methylstyrene and the residual unchanged isopropylbenzene, and (4) a residue of high-boiling materials. Fraction (2) is used in the manufacture of styrene resins by polymerisation, while fraction (3) is mixed with more isopropylbenzene and returned to the cracking operation with addition of steam.

An alternative method of procedure is rendered possible by our discovery that a mixture of styrene, α -methylstyrene and isopropylbenzene in the proportions such as are readily attained by fractionating the crude products of pyrolysis of isopropylbenzene, namely a mixture of approximately 25% styrene, 25% α -methylstyrene and 50% of isopropylbenzene can be treated in such a way as to produce resins in which most of the styrene originally present and a substantial part of the α -methylstyrene are polymerised together. Thus co-polymerisation of styrene and α -methylstyrene can be effected by heat treatment in the absence of catalysts e. g. at 130° C. for several days, or by the use of catalysts at lower temperatures. According to the proposed alternative method of procedure, therefore, the crude products of cracking or pyrolysis of isopropylbenzene are fractionated to yield a liquid mixture of styrene, α -methylstyrene and unchanged isopropylbenzene, which is then subjected to polymerisation under such conditions that nearly all the styrene and a substantial part of the α -methylstyrene are polymerised together to yield a valuable resin, the reacting mixture being then subjected to a suitable treatment (e. g. steam distillation, vacuum distillation, etc.) to separate resin and a mixture of unchanged methylstyrene and isopropylbenzene. The latter mixture is then mixed with more isopropylbenzene and returned to the cracking cycle once again.

The following examples of operating according to the present invention show various phases of the process and the effect of various factors on the results obtained at substantially atmospheric pressure.

Example 1

The results of a number of comparative tests on the pyrolysis of pure isopropylbenzene both alone and in admixture with gaseous diluents (steam and hydrogen) in small bore copper tubes at vapour velocities sufficient to ensure turbulent flow and at temperatures of 675-700° C. and percentage decompositions of isopropylbenzene per pass of 50% or over are shown in the appended table, in which the yields of products are calculated on the basis of mols. of products per 100 mols. of isopropylbenzene decomposed.

Approx. temp., °C.	Diluent, mols per 1 mol of isopropyl benzene	Approx. time of contact in secs.	Percent decomposition of isopropyl benzene per single passage	Mols of products per 100 mols isopropylbenzene decomposed			
				Benzene	Styrene	α -methylstyrene	Tars and loss
675	None.....	3.0	65	15	30	30	25
700	do.....	1.2	63	15	30	29	26
700	Steam 5.3 mols.....	1.1	50	17	31	30	22
700	Hydrogen 10.5 mols.....	0.7	70	28	30	21	21

pressure and subsequently at sub-atmospheric pressure to yield the following fractions: (1) a fraction rich in benzene (re-used in the manufacture of the raw material), (2) a fraction containing most of the styrene and some of the unchanged isopropylbenzene, and (3) a fraction

Example 2

When using a temperature of about 610° C. in copper tubes undiluted isopropylbenzene was decomposed for a time of contact of about 10 sec. whereby 30% was decomposed per passage.

Under these conditions the molar ratio of styrene to α -methylstyrene in the products was about 0.45. Under similar conditions of temperature and cracking intensity a mixture of 1 mol. of isopropylbenzene and 6 mols. of hydrogen yielded a product in which the molar ratio of styrene to α -methylstyrene was 0.7. This shows that the addition of hydrogen favours the formation of styrene.

Example 3

The following table shows the result of the pyrolysis of mixtures of isopropylbenzene and α -methylstyrene in copper tubes at high velocities and at temperatures of about 675° C., the yields of products per passage being calculated on the assumption that the α -methylstyrene fed to the cracking unit passes through substantially unaffected:

styrene and half the α -methylstyrene was polymerised. The resin was recovered by steam or vacuum distillation, giving on the one hand a valuable water-white solid resin and a distillate consisting essentially of about 20–25% of α -methylstyrene in isopropylbenzene. The latter was mixed with fresh isopropylbenzene and again passed through the cracking operation to yield further quantities of hydrocarbons capable of being polymerised in the manner described.

Example 6

In almost exactly the same way as isopropylbenzene is produced and pyrolysed, cymene can be readily produced by the combination of toluene with propylene in the presence of concentrated sulphuric acid as catalyst, and when pyrolysed at temperatures of 600–800° C. undergoes decom-

Percent by weight of α -methylstyrene in the isopropylbenzene	Diluent, mols per mol of mixed hydrocarbon feed	Approx. percent decomposition of isopropylbenzene per passage	Mols of products per 100 mols of isopropylbenzene decomposed			
			Benzene	Styrene	α -methylstyrene	Tar and loss
15	Nil	67	16	39	15	30
15	Steam 2.0 mols	61	20	41	15	24
15	Steam 4.0 mols	56	19	43	15	23
15	Hydrogen 3.5 mols	65	24	45	10	21
18	Steam 4.0 mols	61	21	45	12	22
23	Nil	66	19	43	Nil	33

Example 4

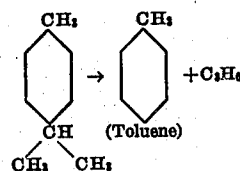
In a continuous process, a hydrocarbon mixture containing approximately 25 parts by weight of α -methylstyrene and 100 parts by weight of isopropylbenzene was vapourised and mixed with 4 times its volume of steam, the mixture being passed through a $\frac{1}{2}$ " bore Follisaind steel cracking tube at a temperature of 675° C. and at a space velocity of about 30 ft. per sec. The volume of the tube was such that the time of contact was about 1 second. The liquid products, after separation of water, were fractionated to yield about 8 parts by weight of benzene, a mixture of about 23 parts of styrene in the form of a 40–45% solution in unchanged isopropylbenzene, and a fraction containing about 25 parts by weight of α -methylstyrene admixed with some isopropylbenzene. The latter distillate was continuously returned to the cracking unit with the addition of sufficient fresh isopropylbenzene to maintain the feed concentration of α -methylstyrene approximately constant. The 40–45% solution of styrene in isopropylbenzene was used directly for the production of polystyrene resins, the isopropylbenzene being continuously recovered and re-fed to the cracking unit.

Example 5

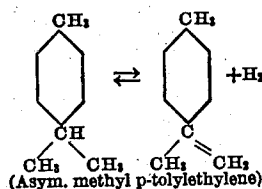
The crude liquid product derived from the pyrolysis of mixtures of isopropylbenzene and about 10% of α -methylstyrene in the presence of gaseous diluents at 650°–700° C. was topped to remove benzene and then distilled under an absolute pressure of 25 mm. to separate the main bulk of the product boiling up to about 70° C., leaving a residue of heavy oil. The main distillate containing approximately 25% of styrene and 25% α -methylstyrene and 50% of isopropylbenzene was polymerised in a stainless steel vessel in the absence of oxygen or catalysts at about 125° C. for a week, whereby practically all the

position in accordance with the following equations:

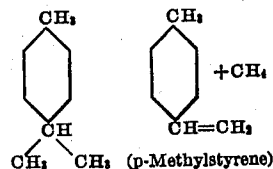
(i)



(ii)



(iii)



Reaction i is relatively unimportant, usually accounting for about 10% of the cymene undergoing decomposition. By pyrolysing cymene at atmospheric pressure in admixture with 4–5 molar proportions of steam, at temperatures of about 650–700° C. and under such conditions that 50–60% of the cymene undergoes decomposition in a single treatment, p-methylstyrene and asym.-methyl-p-tolyloethylene are produced by Reactions iii and ii respectively in amounts corresponding approximately to 30% of the theoretical in each case. However, the yield of p-methylstyrene can be increased, and that of asym.-methyl-p-tolyloethylene reduced, by conducting the pyrolysis of the cymene in the presence of excess hydrogen or of added asym.-methyl-p-tolyloethylene, or both.

What we claim is:

1. The method of producing styrene and hydrocarbons of the styrene type which comprises subjecting to pyrolysis the corresponding condensation product of an aromatic hydrocarbon and an unsaturated aliphatic hydrocarbon containing from 3 to 5 carbon atoms and controlling the character of the reaction product by adding hydrogen to the gaseous reaction material.
- 10 2. The method of producing styrene and hydrocarbons of the styrene type which comprises subjecting to pyrolysis the corresponding condensation product of an aromatic hydrocarbon and an unsaturated aliphatic hydrocarbon containing from 3 to 5 carbon atoms and controlling the character of the reaction product by adding, in the case of isopropylbenzene, α -methylstyrene to the gaseous reaction material.
- 15 3. The method of producing styrene and hydrocarbons of the styrene type which comprises subjecting to pyrolysis the corresponding condensation product of an aromatic hydrocarbon and an unsaturated aliphatic hydrocarbon containing from 3 to 5 carbon atoms and controlling the character of the reaction product by
- 20
- 25

adding hydrogen to the gaseous reaction material together with steam as diluent.

4. The method of producing styrene and hydrocarbons of the styrene type which comprises subjecting to pyrolysis the corresponding condensation product of an aromatic hydrocarbon and an unsaturated aliphatic hydrocarbon containing from 3 to 5 carbon atoms and controlling the character of the reaction product by adding, in the case of isopropylbenzene, α -methylstyrene to the gaseous reaction material together with steam as diluent.

5. The method of producing styrene and nuclear alkyl-substituted styrenes which comprises subjecting an α -alkyl-ethylbenzene, in which the α -alkyl group contains from 1 to 3 carbons, to pyrolysis whereby undesirable dehydrogenation products are formed as a side reaction and controlling the said side reaction by the addition of one of said dehydrogenation products in an amount sufficient to suppress said side reaction.

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