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METHOD OF COUPLING STYRENE WITH ALKYL AROMATICS

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This invention is a new and useful method of coupling styrene with alkyl aromatics.

The invention is applicable to the coupling of styrene with the alkyl aromatics of both the mono- and poly-aromatic nuclear types and is applicable regardless of the length of the alkyl chain attached thereto.

This application is a continuation-in-part of application Serial No. 218,703, filed March 31, 1951, now abandoned.

In the first step of the invention, there is prepared a body of the alkyl aromatic and incorporated within this material, a suspension of alkali metal which is preferably sodium. This suspension may be prepared by mechanical mixing of the alkyl aromatic and the alkali metal at a temperature above the melting point of the metal, preferably in a colloid mill or other dispersion apparatus and, preferably in the presence of agents such as sodium oleate, aluminum stearate, pyridine and the silicone oils which facilitate the forming of stable dispersions of alkali metal. Alternatively, the reaction mixture may be formed by adding to the alkyl aromatic a preformed suspension of alkali metal in a hydrocarbon solvent.

The dispersion of alkali metal and alkyl aromatic is held at a temperature between 60° C. and 200° C., and preferably at a temperature between 120° C. and 160° C., and, while so held, the styrene is added gradually and preferably continuously and at a substantially uniform rate. To promote the reaction, the dispersion should be vigorously mixed during the period while the styrene is being added. For best results the rate of addition should not exceed 0.25 moles of the styrene per hour per mole of alkali metal present in the dispersion. Preferably, the rate of styrene per hour per mole of sodium should be held below 0.15. The rate of addition of the styrene may therefore be increased by increasing the amount of alkali metal present although there does not appear to be any further advantage in maintaining more than one mole of alkali metal for each mole of free alkyl aromatic present.

The temperature, rate of addition, amount and subdivision of the alkali metal should be coordinated to insure the substantially immediate reaction of the styrene with the alkyl aromatic as it is added thereto. If the styrene does not react with the alkyl aromatics substantially completely as it is added, a polymerization of the styrene results which yields a large amount of styrene polymer rather than the desired coupled product. When operating using the critical conditions, the amount of polymer produced is negligible. In general, this result will be obtained by holding the total styrene (both free and combined) present in the system at any time to not more than one mole for each 5 moles of alkyl aromatic (free and combined) present, and preferably not more than one mole of styrene for each 8 moles of alkyl aromatic present. These values constitute the upper and lower limits of the ratio of total styrene to the total alkyl aromatics which produce satisfactory operation.

If desired, all the alkyl aromatic may be introduced at the beginning of the operation. However, since the optimum reacting conditions approach, as a limit, the presence of one mole of alkali metal for each mole of free alkyl aromatic present, this requires an excessive amount of alkali metal. It is, therefore, more efficient to start with a body of alkyl aromatic containing one mole of alkali metal for each 1 to 2 moles of alkyl aromatic present. The rate of addition of the styrene is determined by the amount of the alkali metal present, as above indicated. The critical ratio of styrene (free and combined) to the total alkyl aromatic (free and combined) present at any time is maintained by adding the styrene in solution in the amount of alkyl aromatic required to maintain 5 to 8 moles of alkyl aromatic present in the system for each mole of styrene present at any time.

The alkali metal is preferably present in a state of extremely fine dispersion, i. e., predominantly in the form of droplets or dispersed particles having a maximum diameter not in excess of 50 microns.

The reaction temperature may be maintained in any suitable way. If the particular alkyl aromatic boils within the desired temperature range, control of the temperature is accomplished by refluxing. If it boils at too low a temperature, under normal pressures, this can be corrected by the application of pressure in excess of atmospheric to the system.

The addition of the styrene is preferably discontinued when the amount of alkali metal has become reduced to one mole for each 10 to 12 moles of alkyl aromatic (free and combined) present. Otherwise, the styrene which is additionally added goes to produce the unwanted styrene polymer and no further product is formed.

At the conclusion of the reaction, any unreacted alkali metal may be destroyed by the addition of a suitable reagent. Preferably, the system is kept in quiescent state until the sodium dispersion has settled out substantially completely, whereupon the supernatant layer is decanted and distilled to separate the unreacted alkyl aromatic, following which the residue is distilled under reduced pressure to separate the various end products.

The entire reaction can be carried out continuously by the continuous addition to the system of styrene and alkyl aromatic, at substantially the same rate at which they undergo coupling reaction within the system, together with the amount of alkali metal necessary to maintain the reaction velocity, and by continuously abstracting a part of the reactants from the system, separating this into its components, withdrawing the end products and returning the remaining alkali metal and unreacted alkyl aromatic to the system.

The desired end products of the coupling reactions are valuable as chemical intermediates and may, inter alia, be sulfonated to yield highly efficient wetting agents. The polymerized material obtained as by-products is substantially useless.

The following are typical examples of the application of the invention, although it is not intended to limit the invention strictly thereto.

Example I

330 cc. (2.7 g. moles) of ethylbenzene and 23 grams (1 g. atom) of sodium were maintained at a temperature of 137° C. under an atmosphere of dry nitrogen. The sodium was present in the form of relatively small droplets suspended in the liquid. The system was vigorously stirred to maintain the velocity of the reaction and to keep the sodium in suspension. 49 grams (0.47 g. mole) of styrene in 480 cc. (3.9 g. moles) of ethylbenzene was added to the system continuously and gradually, the addition of the total amount of styrene being extended uniformly over a period of 8 hours. This corresponds to an addition rate

of .06 mole of styrene per mole of sodium per hour. At the end of this time, the mixture was refluxed for another hour.

After settling, the clear red upper layer (approximately 85% of the total volume) was siphoned into a dry flask under an atmosphere of dry nitrogen. It was then distilled to remove the excess ethylbenzene, following which the residue was distilled under reduced pressure. The following yields were obtained:

	G.
1,3-diphenylbutane	51
1,3,5-triphenylhexane	5
Polymer	1

The residue (approximately 15% of the total volume) was quenched with 60 cc. of 95% ethyl alcohol and washed free of alkali. After drying, it was distilled under reduced pressure. The following additional products were obtained:

	G.
1,3-diphenylbutane	14.7
1,3,5-triphenylhexane	2.9
Polymer	3

Example II

200 cc. (1.4 moles of α-methylnaphthalene and 18.5 g. (0.8 g. atom) of sodium dispersed in 18.5 g. of naphthalene were maintained at a temperature of 150° to 160° C. under an atmosphere of dry nitrogen. The sodium was in the form of droplets predominantly not in excess of 50 microns in diameter. The system was vigorously stirred to maintain the velocity of the reaction. 20 grams (1.9 moles) of styrene, dissolved in 200 cc. (1.4 moles) of α-methylnaphthalene, was added gradually, the rate of addition being substantially uniform over a 7 hour period. This represents an addition rate of .03 mole of styrene per mole of sodium per hour. 60 cc. of 90% ethyl alcohol was then added to quench any remaining sodium present, following which the material was washed free of alkali and distilled under reduced pressure. The following yields were obtained:

	G.
1-phenyl-3-(α-naphthyl propane)	28.5
Polymer	6

Example III

310 cc. of p-xylene and 50 g. of sodium were maintained at a temperature of 139° C. under an atmosphere of dry nitrogen. The sodium was present in the form of relatively small droplets and the system was vigorously stirred to maintain the velocity of the reaction and keep the sodium particles in suspension. 56 grams of styrene dissolved in 540 grams of p-xylene were added to the system continuously, the addition of the total amount of styrene being extended uniformly over a period of 11 hours. This is an addition rate of .023 mole of styrene per mole of sodium per hour. The mixture was refluxed for an additional hour. The remaining sodium was then quenched by the addition of water under an atmosphere of dry nitrogen. The organic and water layers were then separated and the organic layer distilled. The following yields were obtained:

	G.
1-phenyl-3-p-tolyl propane	49
Condensation product of 1 molecule of xylene with 2 molecules of styrene	27
Polymer	15

Example IV

140 grams of ethylbenzene and 25 grams of sodium in the form of a dispersion, the particles of which were predominantly not in excess of 50 microns in diameter, was maintained at a temperature of 137° C. The system was vigorously stirred to maintain the velocity of the reaction and 62 grams of styrene dissolved in 760 grams of ethylbenzene was added gradually, the rate of addition being

substantially uniform for a 17 hour period. The styrene addition was at the rate of .035 mole of styrene per mole of sodium per hour. The sodium was then quenched by the addition of water under an atmosphere of dry nitrogen. The organic and water layers were separated and the organic layer distilled. The following yields were obtained:

	G.
1,3-diphenylbutane	104.3
Condensation product of 1 molecule of ethylbenzene with 2 molecules of styrene	9.2
Polymer	1.2

Example V

120 cc. of ethylbenzene and 23 grams of sodium were maintained at a temperature of 137° C. under an atmosphere of dry nitrogen. The sodium was present in the form of relatively small droplets and the system was vigorously stirred to maintain the velocity of the reaction and to keep the sodium droplets in suspension. 49 grams of styrene, dissolved in 690 cc. of ethylbenzene, was added to the system continuously, the addition of the total amount of styrene being extended uniformly over a period of 8 hours. This styrene addition rate is .06 mole of styrene per mole of sodium per hour. The remaining sodium was then quenched by the addition of water under an atmosphere of dry nitrogen. The organic and water layers were separated and the organic layer distilled. The following yields were obtained:

	G.
1,3-diphenylbutane	65.4
Condensation product of 1 molecule of ethylbenzene with 2 molecules of styrene	8.2
Polymer	3.2

Example VI

In one experiment, styrene (62 grams), dissolved in 600 grams of ethylbenzene, was added over a 17 hour period to a stirred suspension of 6.9 grams of sodium (50 mole percent of the styrene used) in 200 grams of ethylbenzene while maintaining the temperature at 137° C. This is a styrene addition rate of .12 mole of styrene per mole of sodium per hour. The product comprised 63% of the theoretical yield of 1,3-diphenylbutane, the remainder being higher molecular weight materials.

In a second experiment, styrene (62 grams), dissolved in 600 grams of ethylbenzene, was added over a 17 hour period to a stirred suspension of 13.8 grams of sodium (equivalent to the styrene used) in 200 grams of ethylbenzene while maintaining the temperature at 137° C. This represents a styrene addition rate of .06 mole per mole of sodium per hour. The product comprised 67% of the theoretical yield of 1,3-diphenylbutane, the remainder of the product being higher molecular weight materials. Samples removed from the reaction mixture after periods of 9 and 16 hours showed less than 1% of the added styrene present in the uncombined form. The amount of uncombined styrene was determined by the iodine number.

Example VII

Styrene (62 grams) dissolved in 600 grams of ethylbenzene was added over a 7 hour period to a stirred suspension of 28 grams of sodium in 200 grams of ethylbenzene while maintaining the temperature at 137° C. This represents a styrene addition rate of .14 mole of styrene per mole of sodium per hour. The product comprises 57% of the theoretical amount of 1,3-diphenylbutane and 43% of higher molecular weight materials.

Example VIII

The following experiment was carried out to show that gradual uniform addition of styrene at controlled, critical rates is necessary to obtain the desired coupled products in satisfactory yields.

Styrene (31 grams) dissolved in 300 grams of ethyl-

benzene containing 10 grams of dispersed sodium was heated 5 hours at 137° C. Fractionation of the products yielded 2% of the theoretical 1,3-diphenylbutane; 98% of the styrene was converted to a glassy, fusible polymer.

What is claimed is:

1. A method of coupling styrene with alkyl aromatics which comprises maintaining a body of alkyl aromatics containing dispersed alkali metal in the form of suspended droplets having a diameter not greater than 50 microns, at a temperature betweein 60° and 200° C., and adding styrene thereto at a substantially uniform rate not greater than 0.25 mole of styrene per hour per mol of alkali metal present in the reacting mixture, maintaining an amount of alkali metal at all times during the reaction period of at least 1 mole of alkali metal to 10–12 moles of alkyl aromatics (both free and combined), and maintaining the mole ratio of total styrene (both free and combined) to total alkyl aromatics (both free and combined) to a ratio not exceeding 1 to about 5.

2. A method according to that described in claim 1 in which the temperature is maintained between 120° and 160° C.

3. A method of coupling styrene with alkyl aromatics which comprises maintaining a body of alkyl aromatics containing dispersed sodium in the form of particles having a diameter not greater than 50 microns, at a temperature between 60° and 200° C., and adding styrene continuously and uniformly thereto at a rate not greater than 0.25 mole of styrene per hour per mol of sodium present in the reacting mixture, maintaining an amount of sodium at all times during the reaction period of at least 1 mole of sodium to 10–12 moles of alkyl aromatics (both free and combined), and maintaining the mole ratio of total styrene (both free and combined) to total alkyl aromatics (both free and combined) to a ratio not exceeding 1 to 5.

4. A method of coupling styrene with alkyl aromatics which comprises maintaining a body of alkyl aromatics containing dispersed sodium in the form of suspended droplets having a diameter not greater than 50 microns at a temperature between 60° C. and 200° C., and adding styrene in solution in additional alkyl aromatics at a substantially uniform rate not greater than 0.25 mole of styrene per hour per mol of sodium in the reacting mixture, the rate of styrene addition at no time substantially exceeding the rate of styrene reaction, maintaining the mole ratio of sodium to total alkyl aromatics at all times during the reaction period between 1 to 1–2 and 1 to 10–12, and maintaining the mole ratio of total styrene (both free and combined) to total alkyl aromatics (both free and combined) to a ratio not exceeding 1 to 5.

5. A method according to that described in claim 4 in which the temperature is maintained between 120° and 160° C.

6. A method of coupling styrene with alkyl aromatics which comprises maintaining a body of alkyl aromatics containing dispersed sodium in the form of suspended droplets having a diameter not greater than 50 microns at a temperature between 120° and 160° C., and continuously adding styrene in solution in additional alkyl aromatics at a substantially uniform rate not greater than 0.15 mole of styrene per hour per mol of sodium in the reacting mixture, the rate of styrene addition at no time substantially exceeding the rate of styrene reaction, maintaining the mole ratio of sodium to total alkyl aromatics at all times during the reaction period between 1 to 1–2 and 1 to 10–12, and maintaining the mole ratio of total styrene (both free and combined) to total alkyl aromatics (both free and combined) to a ratio not exceeding about 1 to 5.

7. A method, as defined in claim 6, wherein the alkyl aromatic is a member from the group consisting of ethylbenzene, α-methylnaphthalene, and para-xylene.

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