United States Patent Office 3,677,914
Patented July 18, 1972

3,677,914

PROCESS FOR THE MANUFACTURE OF BUTADIENE DERIVATIVES

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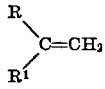
No Drawing. Filed Aug. 24, 1970, Ser. No. 66,573
Claims priority, application Germany, Sept. 1, 1969, P 19 44 278.5
Int. Cl. C09b 29/06
U.S. Cl. 204—59 R 8 Claims

ABSTRACT OF THE DISCLOSURE

Process for the manufacture of butadiene derivatives by the electrolysis of olefinically unsaturated compounds of the general formula:



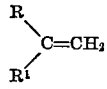
where R stands for an aromatic radical and R^1 for an aliphatic radical, in the presence of lower aliphatic alcohols and an electrolyte salt, graphite electrodes being used for effecting the electrolysis.

This invention relates to a process for the manufacture of butadiene derivatives by the electrolysis of olefinically unsaturated compounds.

Chem. Rev., 68 (1968), p. 471, discloses that the electrolysis of α-methylstyrene in the presence of methanol and sodium methylate between platinum electrodes produces 1 - phenyl - 1 - methylethylene glycol dimethyl ether, α-methoxyisopropyl benzene, acetophenone and β-methoxyisopropyl benzene.

It is an object of the invention to provide a process with which difficulty obtainable butadienes are produced in a simple manner. It is a further object of the invention to provide a process which operates with good yields.

In accordance with the present invention these and other objects and advantages are achieved in a process for the manufacture of butadienes by the electrolysis of olefinically unsaturated compounds of the general formula



where R stands for an aromatic radical and R^1 stands for an aliphatic radical, in the presence of lower aliphatic alcohols and an electrolyte salt, wherein graphite electrodes are used for effecting the electrolysis.

The process according to the invention is surprising in that the production of butadiene derivatives thereby was not to be expected, since butadience derivaties could not be observed as reaction products when platinum electrodes were used.

Preferred starting materials of Formula II are those in which R stands for a phenyl radical which may contain one or two substituents such as alkyl radicals of from 1 to 4 carbon atoms, chlorine or bromine atoms or alkoxy groups of from 1 to 4 carbon atoms, and R^1 stands for an alkyl radical of from 1 to 4 carbon atoms. Starting materials of Formula II in which R stands for a phenyl radical and R^1 stands for an alkyl radical of from 1 to 2 carbon atoms are preferred. Suitable compounds are, for example, α-methylstyrene, α-methyl vinyl naphthalene, α-ethylstyrene, p-chloro-α-methylstyrene and p-methyl-α-methylstyrene.

The electrolysis is carried out in the presence of lower aliphatic alcohol. It is preferred to use alkanols of from

1 to 3 carbon atoms, in particular methanol. Preferably, from 1 to 5 moles of alcohol is used per mole of olefinically unsaturated compound. Particularly good results are obtained when from 1.5 to 3 moles of alcohol is used per mole of olefinically unsaturated compound.

To improve conductivity electrolyte salts are employed. Preferred electrolyte salts are alkali metal iodides, alkali metal perchlorates, alkali metal methylates or mixtures thereof. We have found sodium iodide, sodium perchlorate and sodium methylate to be particularly suitable. In general, from 1 to 10% by weight of electrolyte salt is used, based on the solution to be electrolyzed. Particularly suitable amounts of electrolyte salt are from 2 to 5% by weight.

Advantageously, the electrolysis is carried out at temperatures ranging from −40° to +80° C. Particularly good results are obtained by using temperatures in the range −20° to +20° C. Preferably, anode voltages of from +0.5 to 1.8 volts and more preferably from 0.5 to 1.6 volts (against a silver/silver chloride electrode) and current densities of from 25 to 75 ma./cm.^{2} are used.

An essential feature of the invention is the use of graphite electrodes. In general, use is made of commercial graphite electrodes suitable for electrolysis purposes. We have found graphite electrodes to be particularly effective.

The process of the invention is carried out, for example, by placing an olefinically unsaturated compound of Formula II, a lower aliphatic alcohol and an electrolyte salt of the kind described above in the stated quantities in a suitable electrolysis vessel equipped with graphite electrode spaced, for example, 10 mm. apart and effecting electrolysis under the preferred conditions. The electrolysis may be carried out with or without diaphragms preferably without. We have also found it advantageous to circulate the reaction mixture during electrolysis to achieve better mixing. The electrolysis is generally carried out until from 0.1 to 0.5 Faraday has been consumed. In a suitable apparatus, the electrolysis may be carried out continuously in a simple manner. The resulting electrolyzed mixture is worked up in the usual manner, for example by fractional distillation, after extraction of the electrolyte salt with water.

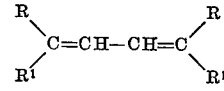
The butadiene derivatives obtained by the process of the invention are suitable as monomers for the manufacture of polymers.

EXAMPLE

A solution of 0.2 g. of sodium and 10 g. of sodium perchlorate in 120 ml. of methanol and 80 ml. of α-methylstyrene is electrolyzed at 0° C. under an anode voltage of from 1.4 to 1.5 volts and at a current density of 50 ma./cm.^{2} between graphite electrodes, until 0.201 Faraday has been consumed. After the solvent has been distilled off, 20 ml. of water is added and the mixture is extracted with ether. The ether extract is worked up by fractional distillation. There is thus obtained 10.6 g. of 1,4-diphenyl-1,4-dimethylbutadiene, B.P. 125–135° C./0.01 mm., M.P. 138–139.5° C. The current efficiency is 45%.

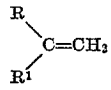
I claim:

1. A process for the manufacture of a butadiene derivative of the formula



where R is phenyl or phenyl substituted by one or two substituents selected from the group consisting of chlorine, bromine, alkyl of 1 to 4 carbon atoms and alkoxy of 1 to 4 carbon atoms and R^1 is alkyl of 1 to 4 carbon atoms, which process comprises carrying out with graphite elec-

trodes an electrolysis of an olefinically unsaturated compound of the formula:



where R and R^1 have the meanings given above, in the presence of a solvent medium consisting essentially of a lower aliphatic alcohol and an electrolyte salt.

2. A process as claimed in claim 1 wherein alkanols of from 1 to 3 carbon atoms are used.

3. A process as claimed in claim 1 wherein from 2 to 3 moles of alkanols of from 1 to 3 carbon atoms are used per mole of olefinically unsaturated compound.

4. A process as claimed in claim 1 wherein the mixture to be electrolyzed contains from 1 to 10% by weight of electrolyte salt.

5. A process as claimed in claim 1 wherein the electrolyte salt is sodium iodide, sodium perchlorate or sodium methylate.

6. A process as claimed in claim 1 wherein an anode voltage of from +0.5 to +1.8 volts is maintained.

7. A process as claimed in claim 1 wherein a current density of from 25 to 75 ma./cm.^{2} is maintained.

8. A process as claimed in claim 1 wherein a temperature of from −40° to +80° C. is used.

References Cited

Electrochemical Oxidation of Organic Compounds, by N. L. Weinberg et al., Chem. Reviews, vol. 68, 1968, p. 471.

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