United States Patent Office

3,526,672

Patented Sept. 1, 1970

3,526,672

PROCESS FOR THE MANUFACTURE OF 4-VINYLCYCLOHEXENE

Nicodemus E. Boyer, Parkersburg, W. Va., and Marvin P. Weaver, Belpre, Ohio, assignors to Borg-Warner Corporation, Chicago, Ill., a corporation of Delaware

No Drawing. Filed Jan. 14, 1969, Ser. No. 791,182

Int. Cl. C07c 3/10

U.S. Cl. 260—666

11 Claims

ABSTRACT OF THE DISCLOSURE

A process for the dimerization of 1,3-butadiene to 4-vinylcyclohexene may be practiced to produce high yields by the use of certain catalyst systems which include (1) secondary aromatic amines, or (2) metal acetylacetonates, or (3) mixtures of (1) and (2), or (4) mixtures of (2) and triphenylphosphine.

BACKGROUND AND SUMMARY OF THE INVENTION

This invention relates to a process for the production of dimers of 1,3-butadiene, specifically 4-vinylcyclohexene. More particularly, the invention is directed to an improved catalyst system which, in the presence of a conventional diluent and polymerization inhibitor, can produce 4-vinylcyclohexene with relatively high yields, for example, 84% to 91% based on the weight of reacted butadiene.

Conventional catalyst systems described in the prior art include oxides, complex carbonyl compounds, olefins, metal salts, secondary aliphatic amines, metals, as well as ultra-violet radiation. Of those listed herein, the most effective have been found to be dialkyl amines (discussed in U.S. Pat. No. 2,943,117), metal salts (discussed in U.S. Pat. No. 2,544,808), and metal, such as iron powder (discussed in German Pat. No. 949,466).

By the present invention, additional catalyst systems have been found in which the yields are consistently above 80%, are reasonably inexpensive, easy to handle, and very effective in the production of 4-vinylcyclohexene. Catalyst systems which may be employed are (1) secondary aromatic amines; (2) metal acetylacetonates; (3) mixtures of (1) and (2); or (4) mixtures of (2) and triphenylphosphine. The process is carried out in the presence of up to 60%, based on the weight of the 1,3-butadiene, or inert diluent, preferably 12 to 34% by weight, at a pressure of atmospheric to 650 p.s.i., preferably 220 to 410 p.s.i., and at a temperature of 100 to 170° C., preferably 120 to 150° C. The inert diluent may be an aromatic or halogenated aromatic solvent. A small amount of a polymerization inhibitor, such as p-tert-butylcatechol, is also conventionally used.

DETAILED DESCRIPTION OF THE INVENTION

In order to further illustrate the invention, reference will be made herein to certain specific examples which are intended to be illustrative, and not in any sense limiting.

EXAMPLE I

A one liter stainless steel autoclave, fitted with a nitrogen inlet and outlet and a thermocouple well, was charged with 5 g. (2.6% by weight based on butadiene charged) of N-phenyl-2-naphthylamine, 0.3 g. of p-tert.-butylcatechol (polymerization inhibitor) and 50 ml. (65 g., 34% by weight) o-dichlorobenzene (diluent). After being flushed with nitrogen to remove all residual air and sealed, the autoclave was cooled in a Dry Ice-acetone bath and charged with 191.7 g. of 1,3-butadiene. The charged autoclave was heated at 130–140° C. for 8 hours. During this time, the maximum internal pressure was 300 p.s.i., and, after 8 hours, dropped to 220 p.s.i. After 8 hours, the autoclave was left to cool to room temperature overnight, after which time, unreacted butadiene was vented from the autoclave. The liquid residue which remained was fractionated through a glass column (23 x 2 cm.) filled with glass helices. The yield of 4-vinylcyclohexene (B.P. 127–130° C.) was 85.2% (based on reacted butadiene).

EXAMPLE II

A one liter stainless steel autoclave, fitted with a nitrogen inlet and outlet and a thermocouple well, was charged with 10 g. (5.2% by weight) of di-2-naphthylamine, 0.6 g. of p-tert.-butylcatechol, and 32.5 g. (17% by weight) of o-dichlorobenzene (diluent). After the autoclave was flushed with nitrogen to remove residual air and sealed, it was cooled in a Dry Ice-acetone bath, and charged with 193.4 g. of 1,3-butadiene. The charged autoclave was heated at 139–141° C. for 8 hours, during which time the internal pressure ranged from 390–270 p.s.i. The autoclave was left to cool to room temperature overnight, and the unreacted butadiene removed by venting. The liquid residue which remained was fractionated as in Example I, and an 88.3% yield of 4-vinylcyclohexene was obtained.

Metal acetylacetonates alone and in combination with either secondary aromatic amines or triphenylphosphine are also effective catalysts in producing high yields of 4-vinylcyclohexene (4-VC).

By following the procedures of Examples I and II with different catalyst systems, the table below groups together additional examples.

TABLE I.—DIMERIZATION OF 1,3-BUTADIENE

Example No.	Catalyst Name	Catalyst Conc., wt. percent	Inert diluent Name	Inert diluent Conc., wt. percent	Reaction time, hours	Temp., °C.	Internal pressure, p.s.i.	Percent yield, 4-VC
III [1]	Piperidine	2.6	Toluene	16.6	8	135-140	270-420	11.9
IV	N-phenyl-2-naphthylamine	5.2	O-dichlorobenzene	13.8	8	120-150	310-370	84.8
V	Ferric acetylacetonate	5.2	do	13.8	8	138-141	220-410	85.4
VI	N-phenyl-1-naphthylamine	2.6	do	12.8	8	130-150	330-390	84.1
	Ferric acetylacetonate	2.6						
VII	Ferric acetylacetonate	2.6	do	13.8	8	130-140	270-400	91.3
	Triphenylphosphine	2.6						
VIII	N-phenyl-1-naphthylamine	7.8	do	13.8	8	130-145	240-360	83.9
IX [1]	Diethanolamine	2.6	do	24.3	8	128-138	260-330	35.8
X	N-phenyl-1-naphthylamine	3.7	do	24.3	8	134-168	340-600	88.8
XI	Di-2-naphthylamine	15.0	Toluene	60.0	48	100-120	50-220	81.5
XII	Di-1-naphthylamine	10.0			3	140-150	440-550	83.2
XIII	N-phenyl-1-naphthylamine	0.3	Chlorobenzene	15.0	12	130-150	350-450	80.5
XIV	N-phenyl-2-naphthylamine	5.0	Xylene	24.3	6	160-170	500-650	90.3

[1] Piperidine and diethanolamine belong to the class of secondary aliphatic amines which are claimed to be effective catalysts in this process in the prior art. Our experiments have shown that the yields of 4-vinylcyclohexene (4-VC) are much higher when the novel catalysts of this invention (secondary aromatic amines, triphenylphosphine, and/or ferric acetylacetonate) are used.

The examples in Table I clearly show that secondary aromatic amines are superior to secondary aliphatic amines for use in such catalyst systems. In the absence of any catalyst, no 4-vinylcyclohexene is formed from 1,3-butadiene at similar conditions.

While this invention has been described in connection with certain specific embodiments thereof, it is to be understood that this is by way of illustration and not by way of limitation; and the scope of the appended claims should be construed as broadly as the prior art will permit.

What is claimed is:

1. The process of dimerizing 1,3-butadiene to produce 4-vinylcyclohexene which comprises maintaining 1,3-butadiene in contact with a catalyst selected from the group consisting of (1) secondary aromatic amines; (2) ferric acetylacetonate; (3) mixtures of (1) and (2); and (4) mixtures of (2) and triphenylphosphine.

2. The process as defined in claim **1**, wherein the concentration of said catalyst is from 0.3 to 15% by weight, based on the weight of said butadiene.

3. The process as defined in claim **2**, wherein said reaction is maintained for at least 3 hours.

4. The process as defined in claim **3**, wherein said reaction mixture is maintained at 100° to 170° C.

5. The process as defined in claim **4**, wherein said reaction mixture is maintained at a pressure of atmospheric to 650 p.s.i.

6. The process as defined in claim **5**, wherein said reaction mixture is maintained in the presence of an inert diluent in a concentration of 0 to 60% by weight (based on the weight of said butadiene).

7. The process as defined in claim **6**, wherein said inert diluent is an aromatic or halogenated aromatic solvent.

8. The process as defined in claim **1**, wherein said secondary aromatic amine is N-phenyl-2-naphthylamine.

9. The process as defined in claim **1**, wherein said secondary aromatic amine is dinaphthylamine.

10. The process as defined in claim **1**, wherein said secondary aromatic amine is N-phenyl-1-naphthylamine.

11. The process as defined in claim **1**, wherein said catalyst is a mixture of N-phenyl-1-naphthylamine and ferric acetylacetonate.

References Cited

UNITED STATES PATENTS

2,504,016	4/1950	Foster.
2,943,117	6/1960	Gleason.
2,964,575	12/1960	Sekul.
2,991,317	7/1961	Sellers.
3,187,062	6/1965	Shechter.
3,457,319	7/1969	Olechowski.
3,446,862	5/1969	Menapace.

DELBERT E. GANTZ, Primary Examiner

V. O'KEEFE, Assistant Examiner

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,526,672 September 1, 1970

Nicodemus E. Boyer et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 49, "or" should read -- of --.

Signed and sealed this 23rd day of March 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents