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MANUFACTURE OF 1,2-BIS(ARYL)ETHYLENES

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U.S. Cl. 260—240 8 Claims

ABSTRACT OF THE DISCLOSURE

Diarylethylenes are manufactured by contacting an arylmethane with an inorganic oxidant such as arsenic pentoxide, antimony pentoxide, bismuth trioxide, manganese arsenate, or antimony tetroxide at an elevated temperature. Diarylethylenes have known utility as optical brightening agents or as active components in radiation measuring devices.

This invention relates to a novel chemical process and more particularly to a novel process for preparing 1,2-bis(aryl)ethylenes.

The 1,2-bis(aryl)ethylenes which can be prepared by the process of our invention generally are fluorescent compounds which find a wide variety of uses; e.g., as optical brighteners in the textile field, as active components in radiation measuring devices such as scintillation counters, etc.

The 1,2-bis(aryl)ethylenes are prepared in accordance with the process of our invention by contacting an arylmethane with an inorganic oxidant from the group of arsenic pentoxide, antimony pentoxide, bismuth trioxide, manganese arsenate, or antimony tetroxide at elevated temperature. If a single arylmethane is contacted with an inorganic oxidant, we obtain a symmetrical 1,2-bis(aryl)-ethylene. However, if we contact a mixture of two or more arylmethanes with the inorganic oxidant, we obtain a mixture of symmetrical and unsymmetrical 1,2-bis(aryl)ethylenes. The following general equation illustrates the process of our invention:

$$2A\text{—}CH_3 \xrightarrow{\text{Inorganic Oxidant}} A\text{—}CH{=}CH\text{—}A + 2H_2O$$

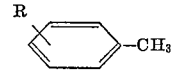
In the formulae in the preceding equation, each of the substituents A can be the same or different and is an aryl residue. The aryl residue represented by A typically has 6 to 18 carbon atoms and preferably has 6 to about 14 carbon atoms. Examples of some of the preferred aryl residues represented by A include phenyl; 4-cyanophenyl; 3-cyanophenyl; 2-cyanophenyl; 4-nitrophenyl; 3-nitrophenyl; 4-carboxyphenyl; 4-chlorophenyl; 3-chlorophenyl; 2-chlorophenyl; 4-bromophenyl; 3-bromophenyl; 2-bromophenyl; 4 - iodophenyl; 3 - iodophenyl; 2-iodophenyl; naphth-1-yl; 2-chloronaphth-1-yl; 3-bromonaphth-1-yl; 4-iodonaphth-1-yl; 5-nitronaphth-1-yl; 6-cyanonaphth-1-yl; 7 - chloronaphth-1-yl; 8-cyanonaphth-1-yl; naphth-2-yl; 1-iodonaphth-2-yl; 3-bromonaphth-2-yl; 4-nitronaphth-2-yl; 5-cyanonaphth-2-yl; 6-nitronaphth-2-yl; 7-chloronaphth-2-yl; 8-iodonaphth-2-yl; 4-(benzoxazol-2-yl)phenyl; 3-(benzoxazol - 2-yl)phenyl; 2-(benzoxazol-2-yl)phenyl; 4-(benzimidazol - 2-yl)phenyl; 3-(benzimidazol-2-yl)phenyl; 2-(benzimidazol-2-yl)phenyl; 4-(benzthiazol-2-yl)phenyl; 3-benzimidazol - 2-yl)phenyl; 2-(benzimidazol-2-yl)phenyl; etc.

Thus, included among the preferred arylmethanes for use in the process of our invention are compounds such as:

Toluene;
4-chlorotoluene;
3-bromotoluene;
2-iodotoluene;

4-cyanotoluene;
3-nitrotoluene;
4-(benzoxazol-2-yl)toluene;
4-(benzimidazol-2-yl)toluene;
4-(benzthiazol-2-yl)toluene;
3-(benzoxazol-2-yl)toluene;
2-(benzimidazol-2-yl)toluene;
3-(benzthiazol-2-yl)toluene;
1-methyl-3-chloronaphthalene;
1-methyl-2-nitronaphthalene;
1-methyl-4-cyanonaphthalene;
1-methyl-6-iodonaphthalene;
2-methyl-1-bromonaphthalene;
2-methyl-5-cyanonaphthalene;
2-methyl-8-nitronaphthalene;
2-methyl-7-chloronaphthalene;
4-carboxy toluene; etc.

Especially preferred among the arylmethanes for use in accordance with the process of our invention are the compounds of the formula:



in which R is preferably located meta or para to the methyl group and contains up to eight carbon atoms and is typically hydrogen, carboxy, cyano, alkoxycarbonyl, phenyl, amino, benzoxazol-2-yl, benzimidazol-2-yl, benzthiazol-2-yl, etc.

The process of our invention is carried out by contacting an arylmethane with an inorganic oxidant from the group of arsenic pentoxide, antimony pentoxide, bismuth trioxide, manganese arsenate, or antimony tetroxide, or with a mixture of two or more of the inorganic oxidants at elevated temperature. In general, reaction temperatures of from about 200° C. to about 600° C. are suitable. Our invention also includes the use as oxidants of inorganic or organic compounds which under the reaction conditions employed yield one or more of the aforementioned inorganic oxidants.

The process of our invention can be carried out with the arylmethane reactant in the liquid phase or in the vapor phase at the time it is contacted with the inorganic oxidant. The pressure can vary widely; e.g., from about 0.1 atmosphere or lower to about 10 atmospheres or greater. In general, the pressure selected depends upon the chosen reaction temperature, the boiling point of the arylmethane, and whether the reaction is to be carried out with the arylmethane in the liquid phase or in the vapor phase. If the reaction is to be carried out in the liquid phase, the reaction pressure should be greater than the vapor pressure of the arylmethane at the chosen reaction temperature. If the reaction is to be carried out in the vapor phase, the reaction pressure should be lower than the vapor pressure of the arylmethane at the chosen reaction temperature.

In general, reaction temperatures of about 200° C. to about 600° C. are suitable when our process is carried out with the arylmethane in the vapor phase and reaction temperatures of about 200° C. to about 450° C. are suitable when the process is carried out with the arylmethane in the liquid phase.

When the process of our invention is carried out in a batchwise manner, the arylmethane and the inorganic oxidant are contacted in a suitable reaction vessel. Stoichiometric equivalents of the arylmethane and the inorganic oxidant are often employed. However, a stoichiometric excess of either the arylmethane or the inorganic oxidant can be employed and is often preferred for reasons of economy.

When the process of our invention is carried out in a semi-continuous or continuous manner, the arylmethane is continuously passed over the inorganic oxidant. Since

the inorganic oxidant enters into the reaction and is consequently reduced during the course of the reaction, it is necessary to provide means for reoxidizing the inorganic oxidant. In a semi-continuous operation, the reaction is periodically interrupted and the inorganic oxidant is then reoxidized. In a continuous operation, means are provided for continuously reoxidizing the inorganic oxidant. For example, the inorganic oxidant can be maintained in an oxidized condition by continuously passing oxygen over the inorganic oxidant along with the arylmethane or a portion of the inorganic oxidant can be continuously or intermittently removed from the reaction zone, reoxidized, and the reoxidized inorganic oxidant can thereafter be continuously or intermittently returned to the reaction zone. The latter procedure is particularly adapted to operations in which the inorganic oxidant is in the form of a fluidized bed or a moving bed.

The inorganic oxidant can be supported or unsupported. Suitable supports for the inorganic oxidant include silica, titania, alumina, kieselguhr, etc.

Among the many valuable 1,2-bis(aryl)ethylenes which can be prepared by the process of our invention are compounds such as:

Stilbene;
4.4′-dicyanostilbene;
3,4′-dicyanostilbene;
3,3′-dicyanostilbene;
2,3′-dichlorostilbene;
2-bromo-3-chlorostilbene;
2,2′-dibromostilbene;
3,3′-dichlorostilbene;
4,4′-dinitrostilbene;
4,4′-bis(benzoxazol-2-yl)stilbene;
4,4′-bis(benzthiazol-2-yl)stilbene;
4,4′-bis(benzimidazol-2-yl)stilbene;
4-(benzoxazol-2-yl)-4′-(benzimidazol-2-yl)stilbene;
4-(benzthiazol-2-yl)-4′-(benzthiazol-2-yl)stilbene;
4-(benzthiazol-2-yl)-4′-(benzimidazol-2-yl)stilbene;
4-(benzoxazol-2-yl)stilbene;
4-(benzimidazol-2-yl)stilbene;
4-(benzthiazol-2-yl)stilbene;
4,4′-diphenyl stilbene;
1-naphthyl-2-phenylethylene;
1-(naphtha-2-yl)-2-naphthylethylene; etc.

In general, the 1,2-bis(aryl)ethylenes are obtained in accordance with the process of our invention as a mixture of the cis and trans isomers of the desired product though in some instances we obtain more of the trans isomer than the cis isomer.

The following examples illustrate the process of our invention.

EXAMPLE 1

Stilbene was prepared in a semi-continuous process from toluene according to the following procedure. Toluene was continuously contacted with bismuth oxide (Bi_2O_3) in a tubular Vycor glass reactor. The reactor was 33 inches long and had an outside diameter of 25 mm. The reactor contained 50 ml. of 4 x 20 mesh Bi_2O_3. The effluent from the reactor was collected in two receivers cooled to 10° C. and —80° C., respectively. The toluene was passed over the Bi_2O_3 at the rate of about 0.093 mole per hour for a period of about 55 minutes while the reactor temperature was held at about 505° C. by means of an electrical heater. The effluent from the reactor which was collected in the receivers comprised an organic phase and an aqueous phase. Examination of the organic phase by infrared analysis disclosed the presence of the cis and trans isomers of stilbene as well as unchanged toluene.

EXAMPLE 2

The procedure of Example 1 is repeated except that antimony pentoxide is substituted for the Bi_2O_3 and the contacting of the toluene and the inorganic oxidant is carried out at a temperature of about 450° C. Infrared analysis of the organic phase of the reaction product reveals the presence of cis and trans isomers of stilbene and unreacted toluene.

EXAMPLE 3

An intimate mixture of 2.1 g. (0.01 mole) of 4-benzoxazol-2-yl) toluene and 1.55 g. (0.0033 mole) of Bi_2O_3 was heated, under nitrogen, at 348° C. for one hour. The reaction product was extracted with benzene to remove unchanged 4-(benzoxazol-2-yl)toluene and any benezene soluble impurities. The residue remaining after extraction was dried and subjected to vacuum sublimation. Substantially pure 4,4′-bis(benzoxazol-2-yl)stilbene was obtained as the sublimate while a mixture of bismuth and Bi_2O_3 remained as the residue. The identity of the 4,4′-bis(benzoxazol-2-yl)stilbene was established by comparison of its infrared spectrum with that of an authentic sample.

EXAMPLE 4

An intimate mixture of 2.1 g. (0.01 mole) of 4-(benzoxazol-2-yl) toluene and 2.3 g. (0.01 mole) of arsenic pentoxide was heated, under nitrogen, at 297° C. for two and one-half hours. The reaction product was extracted with benzene to remove unreacted 4-(benzoxazol-2-yl) toluene and benzene soluble impurities, dried, and extracted with 10% aqueous sodium hydroxide to remove arsenic oxides. The residue was then washed with water and dried. Vacuum sublimation of the dried residue gave 4,4′-bis(benzoxazol-2-yl)stilbene.

EXAMPLE 5

A mixture of 2.1 g. (0.01 mole) of 4-(benzoxazol-2-yl) toluene and 4.4 g. (0.01 mole) of manganese arsenate is heated, under nitrogen, at a temperature of 375° C. for about three hours. The reaction product is extracted with benzene and aqueous sodium hydroxide and washed with water as described in Example 4. Vacuum sublimation of the dried residue gives 4,4′-bis(benzoxazol-2-yl)stilbene.

EXAMPLE 6

A mixture of 2.1 g. (0.01 mole) of 4-(benzoxazol-2-yl) toluene and 3.2 g. (0.01 mole) of antimony pentoxide is heated, under nitrogen, at a temperature of about 225° C. for about four and one-half hours. The residue is extracted with benzene. Vacuum sublimation of the dried residue gives 4,4′-bis(benzoxazol-2-yl)stilbene.

EXAMPLE 7

A mixture of 2.1 g. (0.01 mole) of 4-(benzimidazol-2-yl)toluene and 1.55 g. (0.0033 mole) of Bi_2O_3 is heated, under nitrogen, at about 325° C. for about two hours. The reaction mixture is extracted with benzene, dried and subjected to vacuum sublimation as described in Example 3. The sublimate is substantially pure 4,4′-(benzimidazol-2-yl)stilbene.

EXAMPLE 8

A mixture of 2.2 g. (0.01 mole) of 4-(benzthiazol-2-yl) toluene and 1.55 g. (0.0033 mole) of Bi_2O_3 is heated, under nitrogen, at about 390° C. for about one hour. The reaction mixture is extracted with benzene, dried and subjected to vacuum sublimation as described in Example 3. The sublimate is substantially pure 4,4′-bis(benzthiazol-2-yl)stilbene.

EXAMPLE 9

During a period of 60 minutes, 9.6 g. of a 25% (wt.) solution of 4-cyanotoluene in benzene is contacted with 50 ml. of 4 x 20 mesh antimony tetroxide heated to 475° C. in the Vycor reactor of Example 1. The affluent from the reactor, collected as in Example 1, comprises an organic phase and an aqueous phase. Infrared analysis of the organic phase shows the presence of cis and trans 4,4′-dicyanostilbene.

EXAMPLE 10

A mixture of 46 g. (0.5 mole) of toluene, 21 g. (0.1 mole of 4-(benzoxazol-2-yl)toluene, and 23 g. (0.1 mole) of arsenic pentoxide is charged to a 250 ml. titanium-lined autoclave. The autoclave is closed and flushed with nitrogen and the mixture is heated under autogenous pressure for a period of one hour at 300° C. At the end of the reaction period the autoclave is cooled and vented. The reaction product, consisting of a solid and an aqueous-organic liquid is extracted with aqueous sodium hydroxide to remove arsensic oxides. The remaining solid-organic liquid mixture is filtered and the filtrate contains stilbene and 4-(benzoxazol-2-yl)stilbene in addition to unchanged toluene and 4-(benzoxazol-2-yl)toluene as shown by infrared analysis. The solids collected during filtration are extracted with benzene, dried and subjected to vacuum sublimation to provide substantially pure 4,4'-bis(benzoxazol-2-yl)stilbene which is identified by infrared analysis.

EXAMPLE 11

The sample of reduced bismuth oxide from Example 1 was reoxidized in place by heating it in air and then contacted continuously with a gaseous mixture containing 0.547 mole of toluene and 6200 ml. NTP of air at a furnace temperature of 505° C. during a period of five hours and 55 minutes. A reactor effluent containing water, cis and trans stilbene, and unchanged toluene, collected and identified as in Example 1, was produced continuously throughout the entire period of operation.

We claim:

1. The process which comprises contacting an arylmethane of the formula A—CH_3 with an inorganic oxidant selected from arsenic pentoxide, antimony pentoxide, bismuth trioxide, manganese arsenate or antimony tetraoxide at an elevated temperature of about 200° C. to about 600° C. to obtain at least one 1,2-diarylethylene of the formula A—CH=CH—A in which each of the substituents A is phenyl, cyanophenyl, nitrophenyl, carboxyphenyl, halophenyl, naphthylphenyl, naphthyl, cyanonaphthyl, nitronaphthyl, halonaphthyl, naphthylnaphthyl, benzoxazolylphenyl, benzimadazolylphenyl or benzothiazolylphenyl.

2. The process of claim 1 in which the arylmethane, in the vapor phase, is contacted with the inorganic oxidant.

3. The process of claim 1 in which the arylmethane, in the liquid phase, is contacted with the inorganic oxidant at a temperature of about 200° C. to about 450° C.

4. The process of claim 1 in which the arylmethane is from the group of:

(a) toluene;
(b) 4-(benzoxazol-2-yl)toluene;
(c) 4-(benzimidazol 2 yl)toluene;
(d) 4-(benzthiazöl-2-yl)toluene; or
(e) 4-cyanotoluene.

5. The process of claim 4 in which an arylmethane, in the vapor phase, is contacted with an organic oxidant.

6. The process of claim 5 in which the arylmethane is 4-(benzoxazol-2-yl)toluene and the 1,2 - bis(aryl)ethylene is 4,4'-bis(benzoxazol-2-yl)stilbene.

7. The process of claim 4 in which an arylmethane, in the liquid phase, is contacted with the inorganic oxidant at a temperature of about 200° C. to about 450° C.

8. The process of claim 7 in which the arylmethane is 4-(benzoxazol-2-yl)toluene and the 1,2 - bis(aryl)ethylene is 4,4'-bis(benzoxazol-2-yl)stilbene.

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JOHN D. RANDOLPH, Primary Examiner

U.S. Cl. X.R.

260—465, 524, 645, 649, 669

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,476,747 Dated November 4, 1969

Inventor(s) Charles W. Hargis and Howard S. Young

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

Column 6, Claim 4, subparagraph (c), "4-(benzimidazol 2 yl) toluene" should read - - 4-(benzimidazol-2-yl)toluene - -

Column 6, Claim 5, (corresponding to original Claim 7 in the application) "organic" should read - - inorganic - -.

SIGNED AND
SEALED
MAY 26 1970

(SEAL)
Attest:

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TEC 10261