United States Patent Office

3,732,239

Patented May 8, 1973

3,732,239

4- AND 5-METHYL-1H-BENZOTRIAZOLES PREPARED FROM VICINAL TOLUENEDIAMINE MIXTURES

Sydney M. Spatz, Williamsville, Maurice E. Bailey, Orchard Park, and Francis E. Evans, Hamburg, N.Y., assignors to Allied Chemical Corporation, New York, N.Y.

No Drawing. Original application June 20, 1969, Ser. No. 835,257, now Patent No. 3,637,514, dated Jan. 25, 1972. Divided and this application Nov. 5, 1971, Ser. No. 196,239

Int. Cl. C07d *55/04;* C23f *11/14*

U.S. Cl. 260—308 B 3 Claims

ABSTRACT OF THE DISCLOSURE

Toluenediamine mixtures comprising at least about 96% by weight of vicinal toluenediamine isomers and not more than about 4% by weight of non-vicinal isomers, said mixtures being adapted for conversion to 4- and 5-methyl-1H-benzotriazoles in high yields.

This is a division of application Ser. No. 835,257, filed June 20, 1969, now Pat. No. 3,637,514.

The present invention relates to vicinal aromatic diamine mixtures. More particularly it relates to mixtures of vicinal toluenediamines which are suitable for conversion to 4- and 5- methyl-1-H-benzotriazoles in high yields.

Vicinal toluenediamines, sometimes called ortho-toluenediamines, and more specifically 1-methyl-2,3- and 1-methyl-3,4-phenylene diamines, are precursors of bz-methyl-1-H-benzotriazoles, i.e. 4- and 5-methyl-1-H-benzotriazoles, which are valuable tarnish and corrosion inhibitors. In the past, conversions of individual vicinal toluenediamines to the corresponding methyl benzotriazoles in the conventional manner, as by low temperature diazolizations at between about 0° C. and 5° C. followed by ring closure at elevated temperature of above about 50° C., have afforded yields of the triazole of no more than about 68% of theory, even when individual vicinal isomers of purities over 99% are used. Moreover, such individual isomers, even when they contain only a small fraction of a percent of non-vicinal isomers produce considerable tarry by-products, for example, as high as about 30% or more based on the weight of the triazole product.

A prior art expedient for improving product yield in the foregoing conventional synthesis, which prescribes both diazolization and cyclization at elevated temperature, requires impractically slow mixing of the reactants and generally entails addition of antioxidant to protect the labile vicinal diamine.

Vicinal toluenediamines mixtures are by-products of the manufacture of non-vicinal toluenediamines by reduction of dinitrated toluene, as described in U.S. Pat. No. 3,420,752, granted Jan. 7, 1969, and are separable therefrom by fractional distillation. However, such prior art vicinal diamine mixtures contain no more than about 90% of the ortho isomers, usually between about 70% and about 90% ortho isomers, the remainder predominantly non-vicinal toluenediamines. We have found that these mixtures, when subjected to the above conventional techniques, produce unacceptably low conversions to methyl benzotriazoles. The reason for such low conversions is not clearly understood since even vicinal toluenediamine

distillates of reduced dinitrotoluene which contain as much as about 90 weight percent vicinal toluenediamines, and even similar mixtures containing as much as about 95 weight percent vicinal isomers, give a product yield in the neighborhood of only about 60% of theory and give rise to extensive formation of by-product which appears as a tar. Moreover, methyl benzotriazoles, as conventionally prepared from such diamine mixtures, contain a colored contaminant which cannot be removed by recrystallization. Such discoloration precludes use of the product in many applications, e.g. in household detergents.

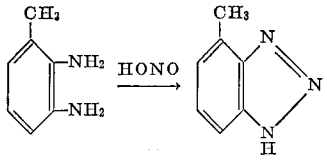
It is an object of the present invention to provide a mixture of vicinal toluenediamines suitable for conversion to bz-methyl-1-H-benzotriazoles in high yields of at least about 70% of theory and free of objectionable colored contaminants.

This and other objects and advantages are accomplished according to our invention by providing a mixture of 2,3-toluenediamine and 3,4-toluenediamine containing total vicinal toluenediamines of at least about 96% by weight and not more than about 4% by weight of non-vicinal toluenediamines, said mixtures containing 2,3-toluenediamine in amounts sufficient to provide a ratio of 2,3- to 3,4-toluenediamines between about 0.3:1 and about 1.5:1.

We have found, surprisingly, that when mixtures of vicinal toluenediamines of the purity and compositions described above are subjected to conventional diazotization and cyclization, the diamines of the invention afford mixtures of 4- and 5-methyl-1-H-benzotriazoles in yields which are about 10–30% greater than those produced in comparable reactions of mixtures of lesser proportions of vicinal toluenediamines and are at least equivalent to yields obtained with individual vicinal toluenediamines of over 99% purity. Yields from mixtures of the vicinal toluenediamines of the invention, moreover, are 10–20% greater than those produced in comparable reactions of individual toluenediamines of similar vicinal toluenediamine content. The amount of high molecular weight side product obtained on conversion of the present novel vicinal diamine mixtures to benzotriazoles is unexpectedly small, decreasing as the proportion of non-vicinal toluenediamines decreases. It is thus apparent that the mixtures of 2,3- and 3,4-toluenediamines in the proportions prescribed by the invention promote methyl benzotriazole formation whereas contamination of the diamine mixtures with higher proportions of non-vicinal toluenediamines inhibits benzotriazole formation.

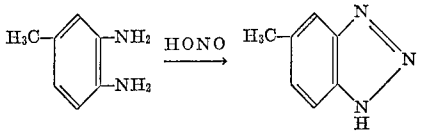
The vicinal toluenediamine mixtures of the invention can be prepared by any suitable procedure. They can be prepared, for example, by blending molten 2,3- and 3,4-toluenediamines in the proportions prescribed by the invention. More economically, the novel mixtures are obtained from the reduced aromatic dinitration product of toluene, for example by fractional distillation of the resulting toluenediamine mixtures at reflux ratios greater than about 50:1. An especially efficient production of the novel diamine mixtures is achieved by fractional distillation of the aforementioned vicinal toluenediamine distillates obtained as described in U.S.P. 3,420,752, employing a distillation column of about 15 to 30 or more theoretical plates, a still head temperature and pressure of about 150–180° C. and 20–60 mm. Hg, respectively, and a reflux ratio of about 3:1 to 10:1 or greater.

Conversion of the vicinal toluenediamines to the corresponding methyl benzotriazoles proceeds as illustrated below:



2,3-toluenediamine 4-methylbenzotriazole

and



3,4-toluenediamine 5-methylbenzotriazole

Vicinal toluenediamine mixtures of the invention suitable for conversion to methyl benzotriazoles in yields of about 70% of theory or higher should contain at least about 96% by weight of vicinal toluenediamines and should contain 2,3- and 3,4-toluenediamines in weight ratios between about 0.3:1 and 1.5:1, more preferably between about 0.6:1 and 1.2:1 and especially between about 0.65:1 to 0.85:1. The amount of non-vicinal toluenediamine in such mixtures should be no more than about 4% by weight. Vicinal toluenediamine mixtures of the invention containing about 96% by weight of vicinal toluenediamines provide yields of methylbenzotriazoles at least as high as those of highly pure, i.e. over 99% pure, individual vicinal toluenediamines, and no greater tar formation than obtained with such highly pure individual vicinal toluenediamines. Such mixtures also yield products having an off-white color, acceptable for most purposes such as epoxy resin curing. Mixtures containing about 98% by weight of vicinal toluenediamines provide yields of about 80% of theory and substantially less tar than the highly pure individual isomers and thus give an additional advantage. Mixtures containing at least about 99.5% by weight of vicinal toluenediamines and not more than about 0.5% by weight of non-vicinal toluenediamines are especially preferred since they provide methylbenzotriazoles in yields of about 90% or more having extremely low tar contents. Such methylbenzotriazoles are substantially colorless after recrystallization and, hence, are eminently suitable for use in household detergents.

The vicinal toluenediamine mixtures of the invention are effective in hardening (i.e. curing) liquid epoxy resin-forming compositions (such as the diglycidyl ether of bisphenol A) to resins having an excellent degree of cross-linking. Curing of epoxy resins employing the diamine compositions of the invention is effected in an essentially conventional manner, as disclosed in H. Lee and K. Neville "Handbook of Epoxy Resins," McGraw-Hill Book Co., New York, N.Y. 1967, Chapter 8.

In the following examples which illustrate our invention, parts, percentages and proportions are by weight, unless otherwise noted, and temperatures are in degrees centigrade.

EXAMPLE 1

Production of pure vicinal toluenediamines from a mixture high in ortho isomers

A still equipped with a forty plate Oldershaw column (1 inch diameter; 21 to 22 theoretical plates) is charged with about 3991 parts of a vicinal and non-vicinal toluenediamine mixture (distilled from the reduced aromatic dinitration product of toluene in accordance with U.S. Pat. 3,420,752) having the following composition:

72.4% 2,3- and 3,4-toluenediamines
0.63% 2,5-toluenediamine
25.85% 2,4- and 2,6-toluenediamines
1.03% "lites" (i.e. compounds more volatile than the foregoing toluenediamine isomers)

This mixture is distilled at a reflux ratio of about 10:1 to remove a distillation forecut (237 parts) containing the "lites" (collected at a still head temperature and pressure of 116–172° and 48–50 mm. Hg, respectively, and a still bottom temperature and pressure of 135–195° and 84–87 mm. Hg, respectively. The reflux ratio is adjusted to about 5:1 and 1838 parts of distillate is collected at a still head temperature and pressure of 172–173° and 49–50 mm. Hg, respectively and a still bottom temperature and pressure of 195–202° and 86–90 mm. Hg, respectively. The distilled product which is a solid (M.P. of about 56–64°) contains about 99.97% vicinal toluenediamines, i.e. 2,3-toluenediamine and 3,4-toluenediamine, the isomers being present in proportions of 2,3- to 3,4-isomers in the range of about 0.3:1 and 1.5:1 and containing no more than 0.03% non-vicinal toluenediamines, i.e. 2,4-; 2,5-; 2,6-toluenediamines.

EXAMPLE 2

Production of pure vicinal toluenediamines from a mixture low in ortho isomers

A mixture containing isomeric toluenediamines, 1.11% 2,3-; 2.06% 3,4-; 0.31% 2,5-; 21.8% 2,6- and 74.7% 2,4-isomers, corresponding to about 3.2% vicinal toluenediamines and 96.8% non-vicinal toluenediamines, obtained by reduction of the aromatic dinitration product of toluene is continuously distilled to recover a non-vicinal toluenediamine distill and following the procedure of U.S. Pat. 3,420,752 but employing a reflux ratio in the range of about 50:1 to about 60:1, i.e. a reflux ratio greater than that prescribed in the aforementioned patent. A sample (about 450 parts distillate) collected at a still head temperature and pressure of about 158° and 24 mm. Hg, respectively; a still bottom (i.e. reboiler) temperature and pressure of 214° and 80 mm. Hg, respectively, a still feed rate of 2.04×10^6 parts per hour and a distillate recovery rate of 4.77×10^4 parts per hour) has the following composition:

40.4% 2,3-toluenediamine
59.2% 3,4-toluenediamine
0.4% 2,4-toluenediamine
a trace 2,6-toluenediamine

(i.e. 99.6% vicinal toluenediamines, in the proportion of 0.68 of 2,3-isomer to 1.0 of 3,4-isomer, and about 0.4% non-vicinal toluenediamines).

EXAMPLE 3

Production of a mixture of 4- and 5-methyl-1-H-benzotriazoles (MBT) from a mixture of 2,3- and 3,4-toluenediamines

A slurry of 244 parts (containing 243 parts, 1.99 mols vicinal toluenediamines) of the toluenediamine distillate of Example 2 (containing 99.6% vicinal toluenediamines) in a mixture of 240 parts glacial acetic acid and 600 parts of water is agitated at 40–50° to dissolve the diamine mixture. The resultant solution is cooled to about 5° and charged rapidly to a solution of 154 parts (2.18 mols) sodium nitrite in 240 parts water. The temperature of the diazotized mass is allowed to rise to 90°. The reaction mixture is then agitated for about one hour while being allowed to cool to 40°. The cooled mass is allowed to stand at ambient temperature (ca. 25°) for about 16 hours. The aqueous acetic acid layer which separates on standing is decanted and extracted with 37.2 parts chloroform. The chloroform extract is washed by extraction with three 500 part portions of water and then distilled at atmospheric pressure to recover chloroform.

The resultant distilland is distilled at a still head temperature of 182–187°; a still bottom temperature of 207–231° and still head pressure of 3 mm. Hg, to recover 243 parts of crude product as distillate and 5 parts of distillation residue (a reddish brown tarry reaction by-product corresponding to only 2.04% of the distilled crude product). The reddish yellow crude is recrystallized from 580.8 parts of benzene, dried in vacuo at ambient temperature for about 16 hours and finally dried at 45–50° in vacuo. The resultant product (242 parts, 91.5% of theory based on vicinal toluenediamine charged is a white solid mixture of 4- and 5-methyl-1-H-benzotriazoles (M.P. 73–78°).

EXAMPLE 4

The procedure of Example 3 is repeated substantially as described employing the vicinal toluenediamine distillate of Example 1 (containing 99.9% vicinal toluenediamines). On distillation of the chloroform-extracted organic layer of the reaction mixture, 240 parts of distilled crude product are recovered together with 8 parts non-volatile residue (corresponding to only 3.33% of the distilled crude product). On recrystallization of the crude from 652 parts of benzene, 239 parts (90% yield of theory) of a mixture of 4- and 5-methyl-1-H-benzotriazoles (a white solid, M.P. 74–75°) is obtained.

EXAMPLE 5

When a mixture containing 98.0% vicinal and 2.0% non-vicinal toluenediamines is treated as described in Example 3 above, an 80% yield of theory, based on vicinal toluenediamine charged, of an off-white mixture of 4- and 5-methyl-1-H-benzotriazoles (M.P. 71–73°) is obtained.

EXAMPLE 6

When a mixture containing 96.6% vicinal and 3.4% non-vicinal toluenediamines is treated as described in Example 3 above, a 70% yield of theory based on vicinal toluenediamine charged of an off-white solid mixture of 4- and 5-methyl-1-H-benzotriazoles (M.P. 72–74°) is obtained.

EXAMPLE 7

The following comparative example illustrates the unsatisfactory production of bz-methyl-1-H-benzotriazoles from a vicinal toluenediamine mixture containing about 4.7% non-vicinal toluenediamines which is obtained from the reduction product of the aromatic dinitration of toluene.

A vicinal toluenediamine mixture of the following composition

39.6% 2,3-toluenediamine
55.6% 3,4-toluenediamine
1.3% 2,6-toluenediamine
3.4% 2,4-toluenediamine

(i.e. 95.2% vicinal and 4.7% non-vicinal toluenediamine) is treated substantially as described in Example 3 above. The results of this experiment are compared with those of Examples 3 and 4 in the table below.

EXAMPLE 8

The following comparative example illustrates the relatively low yield of 5-methyl-1-H-benzotriazole produced from substantially pure 3,4-toluenediamine.

The procedure of Example 3 is repeated substantially as described in treating 36.6 parts (0.3 mol) of 3,4-toluenediamine containing at least 99.5% of 3,4-toluenediamine, as analyzed by nuclear magnetic resonance spectra, dissolved in 72.3 parts glacial acetic acid and 90 parts water, with a solution of about 4 parts (0.57 mole) sodium nitrite in 65 parts water. The results of this experiment are compared with those of Examples 3 and 4 in the table below.

TABLE

Ex.	Toluenediamine charged	Distilled crude product	Distillation residue (reaction by-product)	Yield of recrystallized product (MBT) based on vicinal diamine charged
3	99.6% vicinal, 0.4% non-vicinal toluenediamines obtained in Example 2 (244 parts containing 243 parts, 1.99 mols, of the vicinal isomers).	243 parts of reddish yellow solid.	5 parts of reddish brown tar (2.02% of distilled crude product).	91.5% of white solid, M.P. 73–78° C.
4	99.9% vicinal, 0.1% non-vicinal toluenediamines obtained in Example 1 (244 parts, 2 mols vicinal toluenediamines).	240 parts of reddish yellow solid.	8 parts of reddish brown tar (3.33% of distilled crude product).	90% of white solid, M.P. 74–76° C.
5	98.0 vicinal, 2.0% non-vicinal toluenediamines	176.2 parts of reddish yellow solid.	25.7 grams reddish brown tar (14.6% of distilled crude product).	80% of off-white solid, M.P. 71–73° C.
6	96.6% vicinal, 3.4% non-vicinal toluenediamines	159.4 parts of reddish yellow solid.	46.8 grams reddish brown tar (29.3% of distilled crude product).	70% of off-white solid, M.P. 72–74° C.
7	95.2% vicinal, 4.7% non-vicinal toluenediamines distilled from the reduced product of the dinitration of toluene (256.3 parts containing 244 parts, 2 mols of the vicinal diamines).	172 parts of reddish yellow solid.	83 parts of reddish brown tar (48.3% of distilled crude product).	61.3% of brown solid, M.P. 69–70° C.
8	*3,4-toluenediamine (36.6 parts, containing at least 99.5%, 0.298 mol, of the 3,4 isomer).	27 parts of yellow solid.	8 parts of reddish brown tar (29.6% of distilled crude product).	68% of white solid, M.P. 77–78° C.

*Comparable results are obtained with 2,3-toluenediamine containing at least 99.5% 2,3-toluenediamine as with 3,4-toluenediamine.

EXAMPLE 9

Epoxy resin curing with vicinal toluenediamines

PART A—A vicinal toluenediamine mixture (3.9 parts, 0.0638 equivalents) which is obtained according to the procedure of Example 1 above and contains about 99.88% vicinal toluenediamines; 0.046% non-vicinal toluenediamines and about 0.073% "lites" as melted a about 60° and blended with 26.1 parts (0.138 equivalents) of a liquid diglycidyl ether of Bisphenol A (Epon 828) and allowed to stand in a water bath maintained at 60°±1°. The mass solidifies to an excellent epoxy resin in about 96 to 156 minutes, the maximum temperature of the mixture at gelation being about 84°.

PART B—Four bars (½ inch x ½ inch x 4 inches) of cured epoxy resin are prepared by blending Bisphenol A diglycidyl ether with vicinal toluenediamine mixture as described in Part A and heating the liquid mixture in suitable molds for 3 hours at 90° and, subsquently, for 4 hours at 150°.

The mean heat deflection temperature of the samples is 163° (as determined at 264 p.s.i. fiberstress according to the procedure of ASTM D648–56, "1965 Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 27, pp. 208–211) indicating an excellent degree of cross-linking in the cured resin.

We claim:

1. The process for preparing 4- and 5-methyl-1H-benzotriazoles and mixtures thereof which comprises diazotizing and cyclizing a toluenediamine mixture comprising at least about 96% by weight of vicinal toluenediamines consisting of 2,3- and 3,4-toluenediamines, in a weight ratio of 2,3- to 3,4-toluenediamine between about 0.3:1

and about 1.5:1, and containing not more than about 4% by weight of non-vicinal toluenediamines.

2. The process according to claim 1 wherein the vicinal toluenediamines comprise at least about 98% by weight of the mixture and non-vicinal toluenediamines comprise no more than about 2% by weight of the mixture.

3. The process according to claim 1 wherein the vicinal toluenediamines comprise at least about 99.5% by weight of the mixture and non-vicinal toluenediamines comprise no more than about 0.5% by weight of the mixture.

References Cited

UNITED STATES PATENTS

3,246,035	4/1966	Forman et al.	260—578
3,420,752	1/1969	Kirss et al.	260—582

MAYER WEINBLATT, Primary Examiner

I. GLUCK, Assistant Examiner

U.S. Cl. X.R.

252—182, 390, 401; 260—47 EN