(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 January 2017 (26.01.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/013206 A1

(51) International Patent Classification:
C07D 249/14 (2006.01)

(21) International Application Number:
PCT/EP2016/067410

(22) International Filing Date:
21 July 2016 (21.07.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10 2015 009 297.9 22 July 2015 (22.07.2015) DE

(71) Applicant: **LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN** [DE/DE]; Geschwister-Scholl-Platz 1, 80539 München (DE).

(72) Inventors: **FISCHER, Dennis**; Augsburgerstr. 17a, 86424 Dinkelscherben (DE). **KLAPÖTKE, Thomas**; Fürstenackerstr. 18, 81477 München (DE). **STIERSTORFER, Jörg**; Taubenweg 1b, 82237 Wörthsee (DE).

(74) Agents: **EHNIS, Tobias** et al.; Dr. Gassner & Partner mbB, Marie-Curie-Str. 1, 91052 Erlangen (DE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2017/013206 A1

(54) Title: PROCESS FOR PREPARING 3,3'-DINITRO-5,5'-BIS(1*H*-1,2,4-TRIAZOLE)

(57) Abstract: The invention relates to a process for preparing 3,3'-dinitro-5,5'-bis(1*H*-1,2,4-triazole) (DNBT) from 3,3'-diamino-5,5'-bis(1*H*-1,2,4-triazole) (DABT), wherein in the presence of nitrite H_2SO_4 is added to a suspension of DABT in H_2O.

Process for preparing 3,3'-dinitro-5,5'-bis(1*H*-1,2,4-triazole)

The invention relates to a process for preparing 3,3'-dinitro-5,5'-bis(1*H*-1,2,4-triazole) (DNBT) from 3,3'-diamino-5,5'-bis(1*H*-1,2,4-triazole) (DABT) and a process for preparing 3,3'-dinitro-5,5'-bis(1,2,4-triazole)-1,1'-diol.

WO 2014/086599 discloses a process for preparing 3,3'-dinitro-5,5'-bistriazole-1,1'-diol where in an intermediate step DNBT is oxidized to afford 3,3'-dinitro-5,5'-bis(1*H*-1,2,4-triazole)-1,1'-diol. The DNBT is obtained by diazotization of DABT in sulfuric acid in the presence of nitrite. However it has been shown that this can form the hazardous and highly explosive byproduct bisdiazo-bi-1,2,4-triazole.

The present invention has for its object to specify respective processes for preparing DNBT from DABT and for preparing 3,3'-dinitro-5,5'-bis(1,2,4-triazole)-1,1'-diol, where this hazardous byproduct is not formed.

The object is achieved by the process according to Claim 1 and by the process according to Claim 10. Useful embodiments are apparent from the features of Claims 2 to 9.

The invention provides a process for preparing DNBT from DABT, wherein in the presence of nitrite sulfuric acid is added, in particular slowly, to a suspension of DABT in water. This nitrite may be present in an excess of 10 equivalents. The excess sulfuric acid to be added may be 3 equivalents for example. The addition may be effected dropwise and/or continuously over several hours, for example over a period of 12 hours, for example at room temperature, with stirring. The addition of the sulfuric acid may be effected sufficiently slowly to ensure that no nitrous fumes are formed. Formation of nitrous fumes can be observed since these are typically yellow to reddish-brown. A long reaction time ensures that there is no accumulation of the hazardous bisdiazo-bi-1,2,4-triazole.

It is an essential feature of the invention that the sulfuric acid be added to the nitrite solution with DABT suspended therein rather than the nitrite solution being added to a sulfuric-acid-containing DABT suspension as is the case in the prior art. After the addition of the sulfuric acid the suspension/the solution formed in the process may be heated in order to destroy any diazonium compound potentially still present. After the heating, it is possible to boil the suspension/the solution and add to it an excess of H_2SO_4 such that the entirety of the still present nitrite is decomposed to form nitrous fumes. The end of this decomposition may be detected by the fact that no further yellow to reddish-brown fumes (nitrous fumes) are formed. Based on the nitrite the excess of sulfuric acid may be about 1.5 equivalents. The DNBT formed may be separated in the form of a precipitate from the suspension or a/the solution formed during the process. The formation of the precipitate may be brought about or at least promoted by cooling the suspension or the solution formed during the process.

In addition to avoiding the formation of a hazardous byproduct the process according to the invention has the advantage that it affords DNBT in relatively high yield.

The invention further provides a process for preparing 3,3'-dinitro-5,5'-bis(1,2,4-triazole)-1,1'-diol, wherein the DNBT produced by the process according to the invention is oxidized, in particular using $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ or another inorganic or organic peroxyacid, perborate, hydrogen peroxide or hypofluorous acid or another oxygen transfer agent, to afford 3,3'-dinitro-5,5'-bis(1,2,4-triazole)-1,1'-diol. A dihydroxylammonium salt, diguanidinium salt or ditriaminoguanidinium salt of the thus produced 3,3'-dinitro-5,5'-bis(1,2,4-triazole)-1,1'-diol may be obtained by incubation of 3,3'-dinitro-5,5'-bis(1,2,4-triazole)-1,1'-diol with hydroxylamine, hydroxylammonium ions, guanidinium carbonate, guanidinium ions, guanidine or triaminoguanidine in alcoholic solution and separation of the thus obtained precipitate.

Exemplary embodiment:

1.66 g (10 mmol) of finely ground DABT are suspended in 50 ml of H_2O. 13.8 g (200 mmol) of $NaNO_2$ are added thereto. 20 ml of 1 M sulfuric acid are added to the suspension dropwise at a constant rate over a period of 12 hours at room temperature with stirring. The long reaction time ensures that there is no accumulation of the hazardous bisdiazo-bi-1,2,4-triazole. This dropwise addition of sulfuric acid is effected no faster than is required for the reaction and in particular sufficiently slowly to ensure that no nitrous fumes are formed. Faster addition can bring about accumulation of the hazardous bisdiazo-bi-1,2,4-triazole. After addition of the sulfuric acid the resulting mixture is heated to 50° C for 1 hour to destroy any diazonium compound potentially still present. The suspension/the solution formed is subsequently boiled and about 1.5 equivalents, based on the originally employed nitrite, of a 50% sulfuric acid solution are added to decompose any nitrite that might still be present. This sulfuric acid is added until no more yellow to reddish-brown fumes (nitrous fumes) are formed. The entirety of the reaction mixture now has a volume of about 100 ml. It is allowed to cool slowly. The thus formed acicular crystalline precipitate is separated by filtration. After drying in air DNBT dihydrate is obtained with a yield of about 90%.

Claims

1. Process for preparing 3,3'-dinitro-5,5'-bis(1*H*-1,2,4-triazole) (DNBT) from 3,3'-diamino-5,5'-bis(1*H*-1,2,4-triazole) (DABT), wherein in the presence of nitrite H_2SO_4 is added to a suspension of DABT in H_2O.

2. Process according to Claim 1, wherein the suspension of DABT is basic or by addition of a base is brought to a basic pH, in particular in the range from pH 7.2 to 8.2, in particular pH 7.5 to 8.0.

3. Process according to Claim 1 or 2, wherein the H_2SO_4 is added sufficiently slowly to ensure that no nitrous fumes are formed.

4. Process according to any of the preceding claims, wherein the H_2SO_4 is added in excess.

5. Process according to any of the preceding claims, wherein the H_2SO_4 is added gradually or continuously, in particular dropwise, in particular over several hours.

6. Process according to any of the preceding claims, wherein the nitrite is present in excess.

7. Process according to any of the preceding claims, wherein after the addition of H_2SO_4 the suspension or a solution formed during the process is heated to at least 45°C, in particular at least 50°C, for at least 40 minutes, in particular at least 60 minutes.

8. Process according to Claim 7, wherein after the heating the suspension or the solution formed during the process is brought to boiling and excess H_2SO_4 is added thereto.

9. Process according to any of the preceding claims, wherein the DNBT formed is separated in the form of a precipitate from the suspension or a/the solution formed during the process.

10. Process for preparing 3,3'-dinitro-5,5'-bis(1,2,4-triazole)-1,1'-diol, wherein the DNBT produced according to any of the preceding claims is oxidized, in particular using $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ or another inorganic or organic peroxyacid, perborate, hydrogen peroxide or hypofluorous acid or another oxygen transfer agent, to afford 3,3'-dinitro-5,5'-bis(1,2,4-triazole)-1,1'-diol.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/067410

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D249/14
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 2 892 473 A1 (UNIV MUENCHEN L MAXIMILIANS [DE]) 12 June 2014 (2014-06-12) page 7, line 29 - page 8, line 7; claim 8	1-10
A	CN 103 965 125 A (XIAN MODERN CHEMISTRY RES INST) 6 August 2014 (2014-08-06) paragraph [0008]	1-10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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Date of the actual completion of the international search	Date of mailing of the international search report
11 August 2016	22/08/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Johnson, Claire

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/067410

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CA 2892473 A1	12-06-2014	CA 2892473 A1	12-06-2014
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