



Purification of Hexabenzylhexaazaisowurtzitane

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Abstract: Hexabenzylhexaazaisowurtzitane (HBIW) is produced by a condensation reaction of benzylamine with glyoxal in suitable organic solvents in the presence of protonic acid catalysts. Impurities have to be removed prior to the subsequent stages of the synthesis of CL-20. The effectiveness of HBIW purification by recrystallization from a variety of solvents has been studied here. This method was compared with a novel approach suggested for HBIW purification that consists of prolonged heating of the crude product in boiling methanol. This new purification method allows the product to be prepared in satisfactory purity, it is simple and easily performed on a large-scale.

Keywords: HBIW, CL-20, purification, differential scanning calorimetry, cryometric method

1 Introduction

Preparation of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (HBIW) is the first step in the synthesis of hexanitrohexaazaisowurtzitane (CL-20), one of the most potent high explosives. Because of the high explosive parameters of this explosive, its synthesis, properties and applications have been the subject of a great many research projects [1-4]. Successive stages in the CL-20 synthesis involve the catalytic debenylation of HBIW to acyl isowurtzitanes which are subsequently nitrated to CL-20. HBIW is formed by condensation of glyoxal with benzylamine. The reaction scheme is shown in Figure 1. Depending on the reaction conditions and the solvent used, the reaction proceeds in 60-80% yield [5-10]. A low yield is due to competitive reactions that lead to the formation of impurities in considerable quantity and these have to be removed prior to the

next stage of the synthesis. A crude product of highest purity and highest yield is obtained from the reaction conducted in acetonitrile (ACN). This solvent is very toxic; its high unit cost is responsible for a remarkable increase in the price of CL-20. Some authors [5, 6] have succeeded in replacing this expensive and toxic solvent by methanol (MeOH). The price of MeOH is about 0.3 USD/kg, and the short-term exposure limit (STEL) is 300 mg/m³. For ACN the price is 3.0 USD/kg and the STEL is 140 mg/m³. Methanol is therefore about one tenth of the cost and its STEL is double. For the synthesis when ACN was used as the solvent, the product was obtained with a melting point range of 155-157 °C, whereas when methanol was used as the solvent the m.p. range of the product was 153-157 °C.

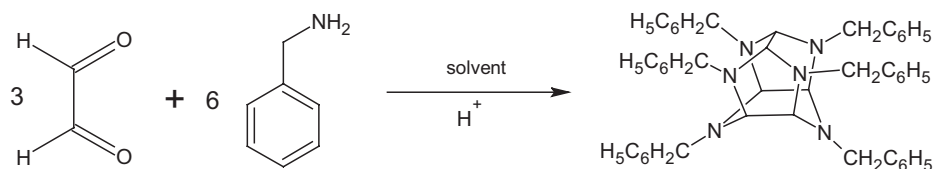


Figure 1. Synthesis scheme for condensation of benzyl amine with glyoxal.

If the impurities in HBIW are too high, the catalyst may be poisoned and the yield significantly reduced in stage two of the CL-20 process. That is why the purity of the HBIW used in the debenzilation reaction is crucial. The first HBIW purification method was recrystallization from acetonitrile [7]. This method affords a 90% yield. The author failed to specify the quantity of solvent to be used for the recrystallization. Other solvents used for HBIW purification by recrystallization, such as ethyl acetate and ethyl acetate/ethanol mixture were covered in [8]. Other approaches to produce HBIW of satisfactory purity are also available. One approach comprised varying the benzylamine to glyoxal ratio from the stoichiometric ratio (2:1) to an excess of benzylamine (3:1 or more). When benzylamine was used in excess a higher HBIW purity was achieved, but this procedure significantly increases the manufacturing cost, which makes it unattractive for large-scale applications. Another method for achieving HBIW of higher purity involves washing the crude HBIW at room temperature or at -20 °C with solvents that belong to the nitrile or alcohol groups, or with their mixtures, and also with water. Unfortunately, no details have been reported to permit repetition of the procedure described [8].

Recrystallization is the technique that allows HBIW of a satisfactory purity to be obtained. The process, however, is time-consuming and gives a low yield. In addition, it requires the use of solvents in large quantities, which makes

this technique commercially unattractive. Thus an inexpensive and effective procedure for HBIW purification continues to be an open issue.

The purpose of this work was the development of a novel HBIW purification method and comparison of this method with other purification techniques described in the pertinent literature. The parameters that were assessed included the purity of the product, the quantity of the solvents used and the yield of the purification process.

2 Experimental

2.1 Materials

Benzylamine (BASF), benzylamine content >99%, as determined by GC; glyoxal (BASF), as an aqueous solution, glyoxal content 39.5-40.5% (as determined by BASF method); perchloric acid (CHEMITEST), perchloric acid content 60%; formic acid (POCH), purity 84-87%; methanol, purity >99.5%; acetonitrile purity >99.5%; ethyl acetate purity >99.5%; sodium carbonate purity >99.5%; ethanol purity >99%.

2.2 DSC analysis

The DSC measurements were made using a heat-flow TA Instruments model Q2000 calorimeter. Indium was used as the reference in calibration. Measurements were made on ca 10 mg samples placed in tightly closed aluminium vessels at a rate of temperature rise $\beta = 2 \text{ }^\circ\text{C min}^{-1}$. The measurements were made in a nitrogen stream, flow rate $50 \text{ mL}\cdot\text{s}^{-1}$.

Liquid-crystal equilibrium was applied to analyze the purity. This equilibrium is very sensitive for impurities content in liquid phase. Small amount of impurities causes significant decrease of substance melting temperature. The following assumptions were made: the components are completely miscible in the liquid phase and completely immiscible in the solid phase, the enthalpy of melting of the components over the temperature range examined is roughly independent of temperature, the solution is dilute enough so that its properties can be described in terms of the ideal solution model. Molar concentration of impurities – purity of analyzed compound may be calculated from cryometric equation [11, 12]:

$$T_m = T_m^0 - \frac{R \cdot (T_m^0)^2}{\Delta H_m} \cdot x \cdot \frac{1}{F} \quad (1)$$

where F is the degree of sample melting, x – actual mole ratio of impurities, T_m^0 – melting point of the ideally pure substance, T_m melting point of sample, ΔH_m – enthalpy of melting. Known as the mole fraction of impurities, the purity of the sample may be found from the following equation:

$$P = (1 - x) \cdot 100\% \quad (2)$$

2.3 Synthesis of HBIW in methanol

Methanol (500 mL), water (44 mL), benzylamine (130 mL), and perchloric acid (60%, 15 mL) were added to a reaction vessel equipped with a reflux condenser, a thermocouple, a mechanical stirrer, and a heating/cooling jacket. The stirrer was turned on and the reaction mixture was cooled to 5 °C. 40% Aqueous glyoxal solution (60 mL) was adjusted to pH 6 with sodium carbonate solution in a beaker. The resultant glyoxal solution was dropped into the reaction vessel with vigorous stirring during 2 h. The vessel contents were kept at 50 °C for 24 h. The reaction mixture was then cooled to 20 °C and the solid filtered off. It was washed with methanol (400 mL). Upon drying crude HBIW (91.1 g, yield 67.6%) was obtained; m.p. 146-150 °C; cryometric purity 92.8 mol%.

2.4 Synthesis of HBIW in acetonitrile

Acetonitrile (550 mL), water (50 mL), benzylamine (60.2 mL) and formic acid (2.3 mL) were added to a reaction vessel equipped with a reflux condenser, a thermocouple, a mechanical stirrer, and a heating/cooling jacket. The stirrer was turned on and the reaction mixture was cooled to 10 °C. 40% Aqueous glyoxal solution (28.5 mL) was dropped into the reaction vessel with vigorous stirring during 1 h. The vessel contents were maintained at 25 °C for 18 h. The resultant suspension was filtered off and was washed with an acetonitrile (138 mL) and water (12.5 mL) mixture cooled to 0 °C. On drying crude HBIW (46.9 g, yield 71.9%) was obtained; m.p 146-150 °C, cryometric purity 90.5 mol%.

2.5 HBIW purification

2.5.1 Method I

The equipment for the purification process comprised a 250 mL flask, equipped with a mechanical stirrer and a reflux condenser, placed on a water bath. Methanol (50 mL), crude HBIW (5.00 g) of 92.8 mol%, cryometric purity, and sodium carbonate (0.1 g) in water (0.5 mL) were added to the flask. The whole was vigorously stirred for 5 min at the boiling temperature of methanol. The resultant suspension was then filtered off and was washed with methanol (ca 15 mL). It

was then returned to the flask for the second purification stage. Methanol (50 mL) was added to the flask and the mixture was heated to the boiling with vigorous stirring. After 5 min the HBIW was filtered off and washed with methanol (10 mL). On drying pure HBIW (4.32 g) was obtained, which corresponded to a yield for the process of 89.4%. The HBIW thus purified was snow-white and melted at 152-155 °C; the purity, determined cryometrically, was 96.0 mol%.

FTIR: ν (cm⁻¹): 3022, 2835, 1954, 1669, 1602, 1492, 1451, 1396, 1351, 1302, 1264, 1208, 1169, 1140, 1122, 1072, 1057, 1028, 1017, 986, 926, 896, 828, 792, 781, 749, 732, 698. ¹H NMR (CDCl₃, 500 MHz), δ : 7.15 to 7.42 (m, 30 H, phenyl CH), 4.18 (s, 4 H, CH₂), 4.11-4.12 (d, 8 H, CH₂), 4.06 (s, 4 H, CH), 3.60 (s, 2 H, CH). The FTIR and ¹H NMR spectra of HBIW are presented as additional information.

2.5.2 Method II

The equipment for the purification process comprised a 250 mL flask, equipped with a mechanical stirrer and a reflux condenser, placed on a water bath. Ethyl acetate (100 mL) and crude HBIW (5.00 g) of a cryometric purity of 92.8 mol% were added to the flask. The whole was vigorously stirred for 5 min at the boiling temperature of the solvent. The solution was then filtered and allowed to cool. The precipitated HBIW crystals were filtered off and dried. The snow-white HBIW (2.22 g) had a cryometric purity of 99.9 mol%, which corresponds to a process yield of 47.8%.

3 Results and Discussion

Three methods of purity determination were used during the HBIW studies: thin layer chromatography (TLC), high performance liquid chromatography (HPLC) and cryometry [5, 6, 13]. The TLC method gave the best results as the method for analysis of the reaction course, while the HBIW purity was determined most properly by cryometry. That is why this method was applied for the analysis in the purification process.

HBIW was obtained by two methods; according to the procedure disclosed in patent [8] and after the procedure described in paper [5]. In the former, acetonitrile was used as the solvent, while in the latter it was methanol. The purity of the samples was examined by DSC analysis. The DSC curves for melting of the HBIW samples obtained by both of the methods are shown in Figure 2.

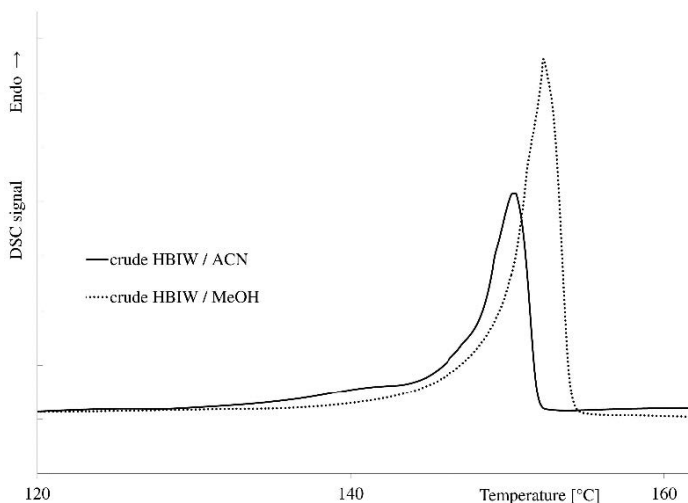


Figure 2. The DSC melting curves of crude HBIW samples obtained by reactions conducted in either ACN or MeOH.

The DSC melting curves differ significantly for the HBIW made by the procedures that employ either ACN or MeOH. The sample of HBIW produced by the ACN variant melted at $T_{\text{onset}} = 147.4$ °C, $T_{\text{max}} = 150.4$ °C. The purity as determined cryometrically was 90.9%. The low-temperature endothermic transition at $T_{\text{max}} = 146.0$ °C which relates to melting of the impurities is visible in the DSC curve. The sample of the HBIW produced by the MeOH variant melted at $T_{\text{onset}} = 149.5$ °C, $T_{\text{max}} = 152.3$ °C. The purity as determined cryometrically was 92.8%.

Crude HBIW is not suitable for use as the starting material in stage two of the CL-20 synthesis, which is the HBIW debenzoylation reaction to 2,6,8,12-tetraacetyl-4,10-dibenzyl-2,4,6,8,10,12-hexaazaisowurtzitane. The reaction occurs in the presence of palladium catalyst Pd/C* which can easily become poisoned by the impurities present in crude HBIW. For this reason it is necessary that HBIW is purified prior to it being used as a substrate in stage two of the CL-20 synthesis. The HBIW purification methods reported in the literature were compared here. The methods are based on recrystallization of HBIW from such solvents as: ACN, AcOEt or AcOEt/EtOH mixtures. The quantities of the solvents used in the recrystallizations were as reported in the literature. Samples after recrystallization were examined by DSC analysis. The results of the analyses of the purified HBIW obtained by the reaction conducted in ACN are shown in Figure 3.

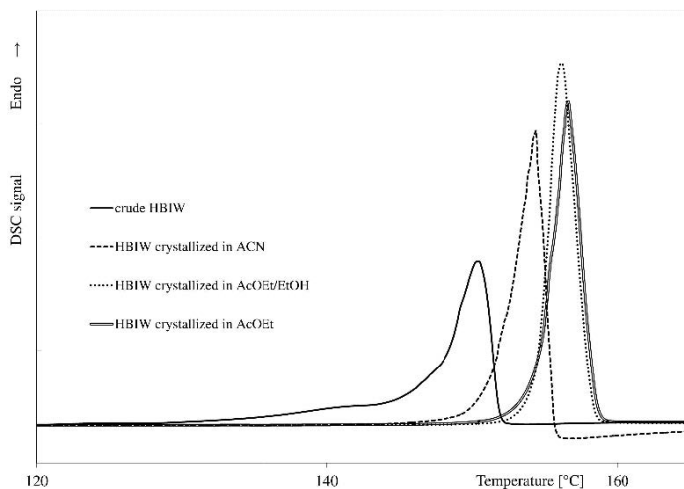


Figure 3. DSC melting curves for purified samples of HBIW obtained from a reaction conducted in ACN.

As expected, the purification process resulted in an upward shift of the HBIW melting point. The least effective of the HBIW purification methods was found to be recrystallization from ACN. A sample of HBIW thus purified melted at $T_{\text{onset}} = 153.9\text{ }^{\circ}\text{C}$, $T_{\text{max}} = 155.5\text{ }^{\circ}\text{C}$. The HBIW sample recrystallized from ethyl acetate/ethanol melted at $T_{\text{onset}} = 154.8\text{ }^{\circ}\text{C}$, $T_{\text{max}} = 155.9\text{ }^{\circ}\text{C}$. A sample with the highest melting point was obtained as a result of recrystallization of HBIW from AcOEt. This sample melted at $T_{\text{onset}} = 154.5\text{ }^{\circ}\text{C}$, $T_{\text{max}} = 157.0\text{ }^{\circ}\text{C}$. The HBIW obtained by a reaction conducted in MeOH was also taken as the product for purification by recrystallization. The results of these analyses are presented in Figure 4.

For the purification procedure and the reaction to produce HBIW conducted in MeOH, the highest melting point was observed for the sample from recrystallization of the crude product from an AcOEt/EtOH mixture. Here again, the HBIW purified by crystallization from ACN produced the lowest-melting product. The quantities of the solvents used, purification yields and the purity of the purified HBIW obtained in the reactions conducted in ACN and MeOH are reported in Table 1.

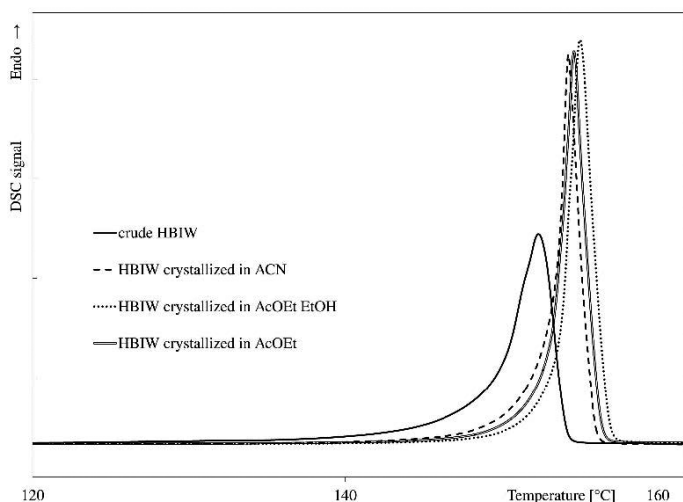


Figure 4. The DSC melting curves for purified HBIW samples obtained from a reaction conducted in MeOH.

Table 1. The quantities of the solvents used, purification yields, and the purity of the HBIW obtained in the reaction conducted in ACN or MeOH

Solvent	V solvent ^a [mL]	Purity of HBIW [%]	Yield [%]
HBIW obtained from the reaction conducted in ACN			
ACN	256	97.7	67
AcOEt	20	99.9	46
AcOEt:EtOH ^b	40	99.9	78
HBIW obtained from the reaction conducted in MeOH			
ACN	256	97.5	76
AcOEt	20	98.1	47
AcOEt:EtOH ^b	40	98.9	80

^a Volume of solvent per 1 g HBIW; ^b 1:1 (v:v).

Each of the solvents used was found to be effective in purifying crude HBIW. Samples of the purified crude product showed a purity ranging from 97.5 to 99.9 mol%. The lowest purity was observed for the product purified by recrystallization from ACN, and the highest purity was observed after recrystallization from an AcOEt/EtOH mixture. Also in the latter recrystallization variant, the yield was the highest (ca 80%). Purification by recrystallization is associated with significant HBIW losses and a considerable solvent consumption,

notably from 20 mL for AcOEt to 256 mL for ACN per 1 g of crude product. This leads to a marked increase in the manufacturing costs of the final product. This was the reason behind the search for a less expensive and simpler purification technique. While filtering using a Buchner funnel and washing the crude HBIW, MeOH was noted to dissolve the impurities well. It was checked whether a prolonged treatment with MeOH could be used to purify crude HBIW. To enhance the effectiveness of impurity removal by this approach, the process was conducted at the solvent's boiling temperature. The purification in MeOH alone or with the addition of sodium carbonate was compared, seeing that HBIW decomposes in an acid environment. The DSC melting curves for the samples of purified HBIW prepared in the reaction conducted in MeOH are shown in Figure 5. The purification yield and the purity of the purified samples of HBIW made from the reaction conducted in MeOH are collected in Table 2.

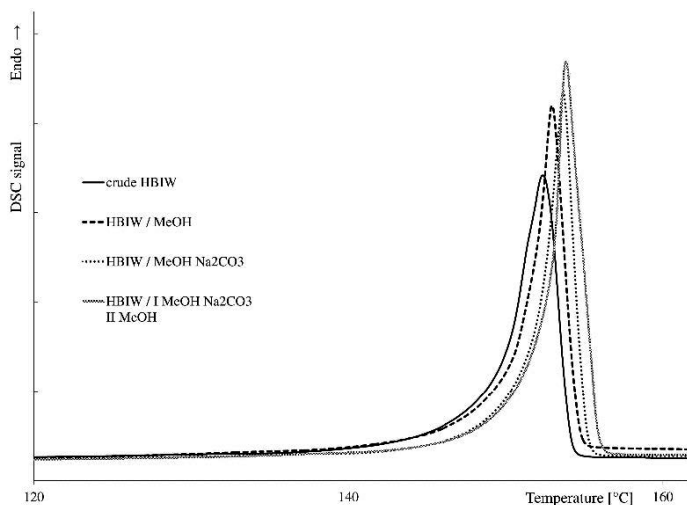


Figure 5. DSC melting curves for HBIW purified in MeOH and in MeOH with the addition of sodium carbonate, made from a reaction conducted in MeOH.

The prolonged treatment of crude HBIW in boiling methanol caused an increase in the melting temperature due to an increase in the purity of the product. A desirable influence of the addition of sodium carbonate solution in the HBIW purification process was observed. The use of carbonate accounts for the high purity of the HBIW (98.3%), 1.6% higher than when the process was run without carbonate addition. The purification process with sodium carbonate added gave a higher yield as compared with methanol alone, specifically 99% vs. 90%.

Table 2. Purification yields and purity of purified samples of the HBIW made from a reaction conducted in MeOH

Solvent	V MeOH ^a [mL]	Purity of HBIW [%]	Yield [%]
MeOH	13	94.7	90
MeOH, Na ₂ CO ₃	13	96.3	99
I MeOH, Na ₂ CO ₃ II MeOH	25	96.8	97

^a Volume of MeOH per 1 g HBIW.

A two-stage HBIW purification was also performed. Stage one involved the prolonged treatment of crude HBIW with MeOH with sodium carbonate added. Stage two consisted in a prolonged treatment of that product with boiling methanol. After stage one 96.3% purity was achieved, while after stage two the purity was 96.8%. In stage one of the purification, 3.5% of impurities were removed, while in stage two it was 0.5%. For a laboratory-scale synthesis there is no need to use the two-stage purification procedure. However, the two-stage process may prove indispensable when larger-scale syntheses are performed. For an assessment of whether the degree of HBIW purity was satisfactory, the HBIW debenzylation reaction was carried out. A high yield observed from this reaction proved the usefulness of the purification method for crude HBIW obtained from a reaction conducted in MeOH. The method involves the prolonged treatment of the crude product in boiling methanol with sodium carbonate added.

The purification method developed was also used on the crude HBIW made from a reaction in ACN. Table 3 records the results obtained.

Table 3. Purification yield and purity of crude HBIW obtained from a reaction conducted in ACN

Solvent	V MeOH ^a [mL]	Purity of HBIW [%]	Yield [%]
MeOH	13	92.5	92
MeOH, Na ₂ CO ₃	13	92.2	96
I MeOH, Na ₂ CO ₃ II MeOH	25	93.8	91

^a Volume of MeOH per 1 g HBIW.

As a result of the two-stage purification in boiling methanol, HBIW was obtained of 93.8% purity. Here the purification method involving prolonged treatment in boiling methanol proved less effective. This is due to the presence

of impurities that are only slightly soluble in methanol. A modification of the purification method was introduced which consisted in the addition of AcOEt to MeOH. Crude HBIW was purified by this modified method. Table 4 gives the purification yield and purity of the HBIW made from a reaction conducted in ACN upon purification in a boiling MeOH/AcOEt mixture.

Table 4. Yields from the purification in a boiling MeOH/AcOEt mixture and the purity of the HBIW obtained, using HBIW from a reaction conducted in ACN

Solvent MeOH + ...	V MeOH ^a [mL]	V AcOEt ^a [mL]	Purity of HBIW [%]	Yield [%]
AcOEt	13	2	92.9	90
AcOEt, Na ₂ CO ₃	13	2	93.7	95
AcOEt, Na ₂ CO ₃	13	4	95.4	94
AcOEt, Na ₂ CO ₃	13	6	96.7	89
AcOEt, Na ₂ CO ₃	13	8	96.6	88
I AcOEt II AcOEt	25	4	93.2	86
I AcOEt, Na ₂ CO ₃ II AcOEt	25	4	94.8	92
I AcOEt, Na ₂ CO ₃ II AcOEt	25	8	96.8	91

^a Volume of solvent per 1 g HBIW.

The MeOH/AcOEt mixture taken in place of MeOH for the purification of the HBIW produced from a reaction performed in ACN results in increased HBIW purity. Satisfactory results for the purification were obtained for a prolonged single-stage process where a mixture of MeOH (10 mL) and AcOEt (6 mL) mixture was taken per 1 g HBIW, and MeOH (3 mL) was used for sample washing. Comparable results were observed for the two-stage purification in which, in the first- and second-stages, MeOH (10 mL) and AcOEt (4 mL) were employed. The prolonged treatment of crude HBIW (obtained from the reaction performed in ACN) in the boiling MeOH/AcOEt mixture with sodium carbonate added allows a product of satisfactory purity, that can be used in the subsequent synthetic step, to be made.

4 Conclusions

The results of this work, along with the data reported in the literature that covers HBIW purification, indicate that recrystallization, in particular from the ethanol/ethyl acetate system, is of advantage for HBIW purification. Purification by the recrystallization approach has a number of drawbacks, *e.g.*: it is time-consuming, requires large volumes of solvents and entails substantial HBIW losses. All of these drawbacks combined significantly to raise the cost of the final product. A faster and more efficient method of purification of crude HBIW produced from a reaction conducted in methanol is the prolonged treatment of the product in boiling methanol with sodium carbonate added. An unquestionable advantage of this method is the use of a smaller amount of solvent ranging from 13 mL to 25 mL per 1 g HBIW. By this method, HBIW of ca 97% purity can be made with losses somewhere near a few percent. The solvent employed in this method can be easily recovered, which reduces the cost of CL-20 synthesis. The HBIW purification method put forward here is suitable also for the compound made from the reaction conducted in ACN. It requires, however, the use of a MeOH/AcOEt mixture in place of MeOH.

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