Asian Journal of Chemistry; Vol. 25, No. 7 (2013), 4119-4120

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14057

NOTE

Efficient Synthesis of 1,3-Adamantanedicarboxylic Acid and 1,3-Diaminoadamantane

HUA ZHU[1,*] and XIN ZHONG[2]

[1]Department of Chemistry and Chemical Engineering, Sichuan University of Arts and Science, Dazhou 635000, P.R. China
[2]Academic Affairs Office of Sichuan University of Arts and Science, Dazhou 635000, P.R. China

*Corresponding author: E-mail: zhuhua2006@163.com

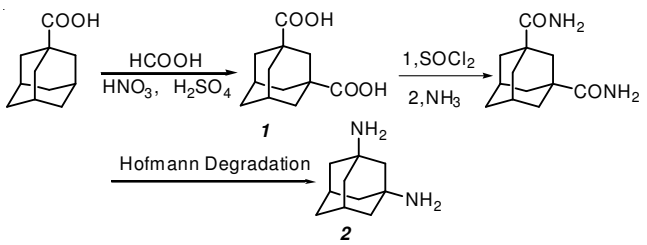
(*Received*: 14 May 2012; *Accepted*: 30 January 2013) AJC-12774

1,3-Adamantane dicarboxylic acid was efficiently synthesized from 1-adamantane carboxylic acid by one-pot method. 1,3-Diaminoadamantane was synthesized from 1,3-adamantane dicarboxylic acid *via* amidation reaction and Hofmann degradation. The structure was confirmed by NMR spectra, *etc*.

Key Words: Adamantane, 1,3-Adamantanedicarboxylic acid, 1,3-Diaminoadamantane, Synthesis.

It is well known that carboxylic acid and amino derivatives of adamantane are widely used in drug industry, polymer synthesis and fine chemicals as key intermediates. These kinds of compounds are usually used as antidepressants or anti-parkinsonic drugs in clinical practice[1-3]. In polymer manufacture, they can improve the glass transition temperatures and thermal stability of polymer[4-8]. In fine chemistry, they can be produce surfactants, rare earth complex, imprint lithography resin, *etc*.[9-11]. Due to the bifunctional structure, 1,3-adamantane dicarboxylic acid and 1,3-diaminoadamantane have great potential application value. The low production efficiencies will be the biggest hindrance in the application development. Therefore, an efficient process was sought to synthesize of 1,3-adamantane dicarboxylic acid and 1,3-diaminoadamantane.

In this paper, an efficient method for synthesis of 1,3-adamantane dicarboxylic acid and 1,3-diaminoadamantane from 1-adamantane carboxylic acid was reported. The synthetic procedure sketch is shown in **Scheme-I**.



Scheme-I: Synthesis of 1,3-adamantane dicarboxylic acid and 1,3-diaminoadamantane

The characteristic features of the involved compounds (**1, 2**) were confirmed by ^{1}H NMR and ^{13}C NMR. NMR spectra were obtained on a Varian Mercury-plus 400 spectrometer (^{1}H at 400 MHz, ^{13}C at 100 MHz) and are referenced to solvent or tetramethylsilane.

1,3-Adamantane dicarboxylic acid(1): 1-Adamantane carboxylic acid (20 g), nitric acid (65 %, 20 mL) and sulfuric acid (98 %, 160 mL) were placed in a three-necked round-bottom flask fitted with an efficient magnetic stirrer and a thermometer. Cooled to 0 ºC and held at 0 ºC, anhydrous formic acid (80 %, 70 mL) was added dropwise in 5 h and reacted for 1 h. poured to crushed ice, filtered and then washed the precipitate several times with water to give a white solid. Then the white solid was dissolved in aqueous NaOH solution and the upper clear solution was separated and acidified by HCl to pH = 3. Filtered, washed with water, dried in vacuum, recrystallized from ethanol. White solid, yield 22.9 g (92 %). m.p.: 275-276 ºC ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.616 (m, 2H), 1.691-1.727 (m, 4H), 1.759-1.791 (m, 4H), 1.850-1.882 (m, 2H), 2.059 (m, 1H), 12.062 (br, s, 2H, COOH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 27.37 (C-5, C-7), 34.98 (C-6), 37.66 (C-4, C-8, C-9, C-10), 39.78 (C-2), 39.89 (C-2, C-3), 177.76 (COOH). IR (KBr, ν_{max}, cm^{-1}) : 2913, 2851, 2636, 1691, 1451, 1410, 1344, 1249, 1103, 1084, 952, 743, 670, 528; Anal. calcd for $C_{12}H_{16}O_4$: C 64.29, H 7.14; found C 64.55, H 7.22.

1,3-Diaminoadamantane(2): 1,3-Adamantane dicarboxylic acid (12 g) was mixed with 50 mL of $SOCl_2$ and the mixture was refluxed for 3 h. Excessive $SOCl_2$ was evaporated and 1,3-adamantane dicarbonyl dichloride was obtained as

white solid, dissolved in dried benzene and added to cold ammonia solution slowly, during which a white precipitate was formed gradually filtered and then washed the precipitate several times with water to give 1,3-disaminoacyladamantane as white solid, recrystallized from ethanol. White solid, yield 10.58 g (89 %).

Put 1,3-bisaminoacyladamantane (10.58 g) and aqueous NaOH solution (10 %, 65 mL) into a 500 mL three-necked round-bottom flask fitted with an efficient magnetic stirrer and a thermometer, stirring at room temperature, a slurry was formed, cooled to 0 ºC, the fresh sodium hypobromite solution, which dissolved bromine (23 g) and sodium hydroxide (23 g) in 150 mL water was added to the slurry at 0 ºC. stirring and held at 0 ºC for 1 h, the mixture became a yellow transparent solution, then heated to 80 ºC and reacted for 1 h, cooled to room temperature, extracted by chloroform (3 × 50 mL), combined the organic layer and dried over anhydrous $MgSO_4$, after removal of $MgSO_4$ and chloroform, the crude 1,3-diaminoadamantane was purified by sublimation; white solid, yield 6.49 g (82 %). ^{1}H NMR (300 MHz, benzene-d_6) δ 1.23 (s,2H), 1.32 (m, 10H), 1.44 (NH_2, 4H), 1.95 (m, 2H); ^{13}C NMR (100 MHz, benzene-d_6) δ: 31 (C-5, C-7), 35.38 (C-6),45.3 (C-4, C-8, C-9, C-10), 49.22 (C-1, C-3), 54.7 (C-2). 1,3-diaminoadamantane is unstable and sensitive to moisture, therefore the IR and elemental analysis results did not agree with the proposed structure[6].

1,3-Adamantane dicarboxylic acid was synthesized from 1-adamantane carboxylic acid by one-pot method. In this process, the ratio of mixed acid (nitric acid and sulfuric acid) have important effect on the yield, the role of sulfuric acid not only is solvent, but also can improve the oxidate ability of nitric acid. So, within a certain range the yields raise with the increased the amount of sulfuric acid. On the other hand, the concentration of nitric acid is reduced, the oxidate ability will be decreased and the waste acid will be increased. In this study, formic acid was far in excess of 1,3-adamantane dicarboxylic acid, the optimum ratio of 1-adamantane carboxylic acid, nitric acid sulfuric acid and formic acid was 1 g: 1 mL: 8 mL: 3.5 mL, under this ratio and reacted 6 h at 0 ºC, the yield of 1,3-adamantane dicarboxylic acid was 92 %. The waste acid could be transformed to industrial salt or plaster by basified with calcium oxide, sodium hydroxide, *etc*.

The amidation reaction and Hofmann degradation had high yield without optimization, the yield was 89 % and 82 %, respectively. The total yield of 1,3-diaminoadamantane was 73 %.

Overall, each step had high efficiency and excellent yield, the energy consumption and environmental impact were low. The industrialization of this process was easily and the research of application will be promoted.

Conclusion

1,3-Adamantane dicarboxylic acid and 1,3-diaminoadamantane were synthesized from 1-adamantanecarboxylic acid successively, each step had excellent yield, this method could be industrialized and promoted the research of application of 1,3-adamantane dicarboxylic acid and 1,3-diaminoadamantane.

REFERENCES

1. R.A. Bright, D.K. Shay, B. ShuN.J. Cox and A.I. Klimov, *J. Am. Med. Assoc.*, 295, 891 (2006).
2. V.M. Deyde, X.Y. Xu, R.A. Bright, M. Shaw, C.B. Smith, Y. Zhang, Y. Shu, L.V. Gubareva, N.J. Cox and A.I. Klimov, *J. Infect. Dis.*, **196**, 249 (2007).
3. K. Pabbaraju, K.C.Y. Ho, S. Wong, S. Shokoples, X.L. Pang, K. Fonseca and J.D. Fox, *Antiviral Res.*, **79**, 81 (2008).
4. A.S. Mathews, I. Kim and C.S. Ha, *J. Appl. Polym. Sci.*, **102**, 3316 (2006).
5. A.S. Mathews, I. Kim and C.S. Ha, *J. Polym. Sci.: Part A: Polym. Chem.*, **44**, 5254 (2006).
6. Y.-T. Chern and W.-H. Chung, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 117 (1996).
7. H. Seino, A. Mochizuki and M. Ueda, *J. Polym. Sci. Part A: Polym. Chem.*, **37**, 3584 (1999).
8. A.P. Khardin, S.S. Radchenko and S.S. Novikov, *Russ. Chem. Bull.*, **21**, 2036 (1972).
9. E.V. Vashkevich, N.Y. Yurashevich, N.G. Kozlov, V. I. Potkin and T.N. Potkina, *Russ. J. Appl. Chem.*, **74**, 1892 (2001).
10. J.C. Jin, Y.N. Zhang, Y.Y. Wang, J.-Q. Liu, Z. Dong and Q.-Z. Shi, *Chem.-An Asian J.*, **5**, 1611 (2010).
11. D.Matsukawa, H. Wakayama, K. Mitsukura, H. Okamura, Y. Hirai and M. Shirai, *J. Mater. Chem.*, **19**, 4085 (2009).