

Synthesis of 1, 3, 5-Triarylbenzenes, Using CuCl_2 as a New Catalyst

Sohrab Abdollahi*, Fate meh Mostaghni

Chemistry department, Payame Noor University, I. R. of Iran, PO BOX 19395-3697, Tehran, Iran

Abstract Among the aromatic ketones, aceto phenone and its various substituted derivatives have been studied since early 20th century. This ketone can perform the self condensation reaction and produces trimer having an aromatic ring of 1,3,5-triphenyl benzene (T.P.B) with general formula of $\text{C}_{24}\text{H}_{18}$. In this research, the compounds 1,3,5-triphenyl benzene and 1,3,5-tris (2-naphthyl) benzene are synthesized via self condensation of acetophenone and 2-aceto naphthalene respectively, using Cu^{2+} (CuCl_2) as a new catalyst. Catalyst of copper(II) chloride is a very suitable catalyst and comparing to the other ones is cheaper, abundant and very facile to use in these condensation reactions for the synthesis of trimers. Since Cu^{2+} has empty p and d orbitals, therefore, CuCl_2 acts as a good Lewis acid. Further, the catalyst is a good electron transfer oxidative reagent, therefore it is very useful catalyst for self-condensation of ketones. This method seems to be general for the synthesis of other derivatives of 1,3,5-triarylbenzene using various ketone derivatives. These trigonal molecules may be converted to flexible clathrates or nano cage molecules, which are highly promising for the separation and chemical transformation.

Keywords Trimerization, Tri Aryl Benzene, Clathrate Inclusion Compounds

1. Introduction

The synthesis of 1,3,5-tris arylbenzene compounds due to self-condensation of acetophenone were reported for the first time in 1874[1]. The years later, these compounds with different substituted phenolic rings using various reagents were prepared. In 1991, the synthesis of different derivatives of this compound were conducted with high yield, using catalyst of tetrachloro silane in ethanol as a solvent at room temperature and molar ratio of 1:1 (acetophenone:catalyst) [2]. In these reactions, the central benzene ring is created by condensation of three molecules of ketones via releasing three molecules of water to produce expected trimer[3-8]. Bishop and Dance, for the first time, show that 1,3,5-triarylbenzene compound reacts with water and benzene to produce solvated crystalline molecules[9]. Later on, Weber *et al.* prepared these inclusion compounds with a number of molecules of different sizes from methanol to morpholine having properties of alicyclic, aromatic, heterocyclic and dipolar molecules with and without proton[10]. X-ray studies on the single crystal of inclusion compounds such as 1,3,5-Tris (4-carboxyl phenyl) benzene-dimethyl formamide (1:3) show that the host molecule has a propeller conformation with complete three-fold symmetry providing hydrogen bond as a donor to three DMF

molecules[3]. Therefore, in the crystalline structure the units of host-guest are arranged such as stack form in Figure 1.

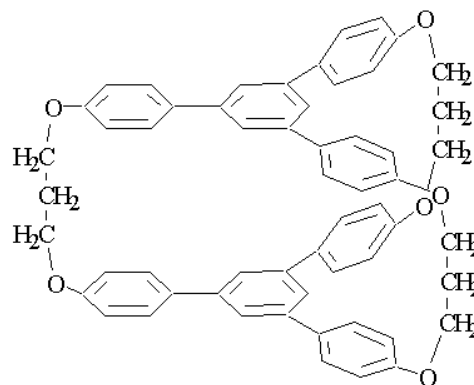


Figure 1. Inclusion molecule made of two triarylbenzene planes connected by hydrocarbon bridge and having cavity to hold different molecules

In order to study this inclusion behaviour in more detail, preparation of double-decker phanes having a cavity to include other organic molecules were attempted[3, 7, 11-17].

Other researchers reported the synthesis and characterization of a new family of star-shaped molecules and dendrimers. In these dendrimers, the structural unit of 1,3,5-triphenylbenzene acts as a fluorescent core[18]. This fluorescence core molecule, 1,3,5-triphenylbenzene, is a class of C_3 symmetry molecule which is important for electroluminescent devices and electrodes. Even for the developing of organic light emitting diodes (OLEDs)[19], the 1,3,5-triphenylbenzene core, and synthesis of dendrimers and fullerene fragments(20-24)] have been used.

* Corresponding author:

sohrab202020@yahoo.com (Sohrab Abdollahi)

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From substituted acetophenones, the synthesis of 1,3,5-triarylbenzene is possible using Suzuki cross-coupling of cyclocondensation reactions[25]. The synthesis of many chemical species, such as multimetallic pincer, star-shaped thiophenes and organic-inorganic hybrid mesoporous materials can be carried out by cyclocondensation reactions. These reactions can be conducted by triflic acid, sulfuric acid-sodium pyrosulfate, perfluorinated resins and tetrachlorosilane in ethanol (26-29).

In different syntheses, various CuCl_2 catalysts have been used. In most reactions, CuCl_2 either is supported by a solid media such as alumina[30] or is bonded to an organic groups or ligands[31-33]. Commercial catalysts are produced by impregnation of γ -alumina with CuCl (4-8 wt% Cu) following the incipient wetness method. Other chlorides, (mainly alkaline or alkaline earth chlorides) in a variable concentration are also added in order to improve the catalytic performance; making the catalyst more suitable for use in the industrial reactors[34,35]. A type of polymer- supported CuCl_2 catalyst for synthesis of dimethyl carbonate (DMC) was obtained by using π -conjugated poly (2,2'-bipyriding-5,5-diyl) as the supporting ligand. The high catalytic activity is associated with the π -conjugated conductive properties of the supporting ligand, PBpy[32]. Another type of homogeneous catalyst for dimethyl carbonate synthesis by oxidative carbonylation of methanol in the liquid-phase reaction was investigated by Jun-cheng Hu et.al.[36]. The polymer-bond monometallic PVP-CuCl catalyst (PVP, poly(N-vinyl-2-pyrrolidone) prepared by the combination of an alcoholic solution of PVP and CuCl_2 , exhibits excellent catalytic performance for the oxidative carbonylation of methanol with carbon monoxide and oxygen to DMC under 3.0 MPa pressure at temperature around 140-160°C [36].

2. Experimental

Yields refer to isolated pure center cut from column chromatography or to the main band scratched from preparative TLC plate. Products were characterized by comparison with authentic sample through IR, NMR, TLC, and mp methods. Due to the experimental limitation, the melting points are not fully accurate and determined by Mettler FP5 melting point apparatus. IR spectra were obtained on a Shimadzu IR-470. ^1H NMR data were recorded in CDCl_3 on Bruker 80 MHz and ^{13}C NMR on Bruker Advance 500-MHz spectrometer. All reagents were analytical grade and used without further purification.

2.1. Preparation of 1,3,5-tris(2-naphthyl) Benzene

For the synthesis of 1,3,5-tris(2-naphthyl) benzene, 2-acetonaphthalene and CuCl_2 are used with molar ratio of (1:15). CuCl_2 (0.03 gr, 0.19 mmole) was added to a mixture of 2-acetonaphthalene (0.4 gr 2.3 mmol) and toluene (5ml) in a 25 ml round bottom flask equipped by magnetic stirrer and reflux condenser. The mixture was refluxed in oil bath for 6

hours at temperature of 180-220°C. After completion of the reaction, the mixture was extracted by ether (3 x 10ml) and dried by magnesium sulfate. Then, the mixture components were separated by column chromatography (mp = 115-120°C). The structure of the product was analyzed by spectroscopic method such as IR, ^1H NMR and ^{13}C NMR. IR(KBr): 3050(W), 3250(m), 1418(m), 1180(s), 1145(m), 1120(s), 720(vs), 695(s) cm^{-1} . ^1H NMR(CDCl_3): δ : 6.8-7.7 (m, 24H)ppm. ^{13}C NMR(CDCl_3): δ : 131.7(s), 131.6 (s), 128.1(s), 128 (s). Anal. Calcd For $\text{C}_{36}\text{H}_{24}$ (456.396): C, 94.7; H, 5.3 Found: C, 94.7; H, 5.5.

2.2. Preparation of 1,3,5-triphenyl Benzene

For the synthesis of 1,3,5-triphenylbenzene, CuCl_2 and acetophenone are used with molar ratio of (1:15). CuCl_2 (0.03 gr, 0.19 mmole) was added to a mixture of acetophenone (0.34 gr 2.9 mmol) and toluene (5ml) in a 25 ml round bottom flask equipped by magnetic stirrer and reflux condenser. The mixture was refluxed in oil bath for 6 hours at temperature of 180-220°C. After completion of the reaction, the mixture was extracted by ether (3 x 10ml) and dried by magnesium sulfate. Then, the mixture components were separated by column chromatography (mp = 173-174°C). The structure of the product was analyzed by spectroscopic method such as ^1H NMR and ^{13}C NMR, as shown in the Figure 2 for ^1H NMR and Figure 3 for ^{13}C NMR. ^1H NMR(CDCl_3): δ_A = 7.77 ppm, δ_B = 7.68, δ_C = 7.46, δ_D = 7.37.

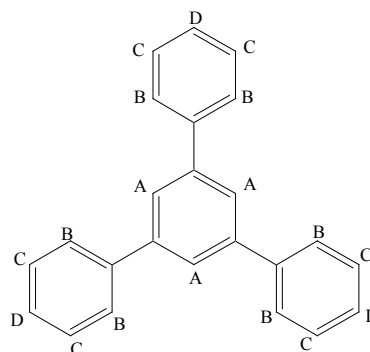


Figure 2. ^1H NMR of 1,3,5-triphenyl benzene molecule in which hydrogens are labeled by letters of A, B, C and D

^{13}C NMR(CDCl_3): δ_1 = 142.31, δ_2 = 141.13, δ_3 = 128.78, δ_4 = 127.47, δ_5 = 127.30, δ_6 = 125.11.

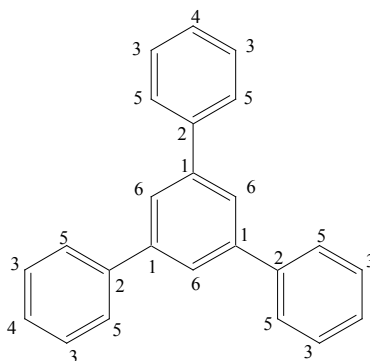


Figure 3. ^{13}C NMR of 1,3,5-triphenyl benzene molecule in which carbons are labeled with numbers 1,2,3,4,5,6

3. Results and Discussion

The goal of this research is an investigation on the self condensation reaction of aromatic ketones via CuCl_2 catalyst, considering the fact that the trisubstituted benzenes, and 1,3,5-tris(2-thienyl) compound have been synthesized previously by our group using the same catalyst[37]. Now, in this paper, CuCl_2 catalyst is used to conduct self condensation reaction of 2-aceto naphthalene to produce 1,3,5-tris(2-naphthyl)benzene. This molecule is a new one with bulky structure and trigonal symmetry that can behave as a clathrate. Substituted benzene of 1,3,5-triaryl is considered as a rich source of porous crystalline host which can provide inclusion compounds[38]. Wide spread application, specific properties of these type of compounds and also the fact that the porosity of the compounds depends on the nature, type and position of these substituents linked to it, have caused an incentive for our group to prepare 1,3,5-tris(2-naphthyl)benzene, which is shown in Figure 4. Contrary to previous syntheses by other researcher that use ligand bonded CuCl_2 catalysts, in this research the pure unhydrated powder of CuCl_2 was used as a catalyst for condensation reaction. In condensation process, CuCl_2 reduces to CuCl (Cu^{2+} to Cu^{1+}). On the other hand the produced water during reaction can oxidize in acidic solution. This oxidation reaction in turn produces more H^+ and helps the solution become more acidic. Copper cation, Cu^{2+} , contains empty orbitals such as p and d orbitals and therefore acts as a Lewis acid and attacks to free lone pairs of oxygen in carbonyl group; producing coordination bond. As a result, the oxygen of carbonyl group achieves positive charge. The positive charge at high temperature can be neutralized by α hydrogen via chloride ion which acts as a bridge in this mechanism. In this case enolate is formed and immediately attaches to protonated carbonyl group of second molecule of 2-aceto naphthalene and produces keto alcohol. At the reflux temperature, the keto alcohol releases a molecule of water. At acidic condition this ketone is protonated and reacts with third molecule of 2-aceto naphthalene via releasing two molecules of water and forms a central aromatic ring.

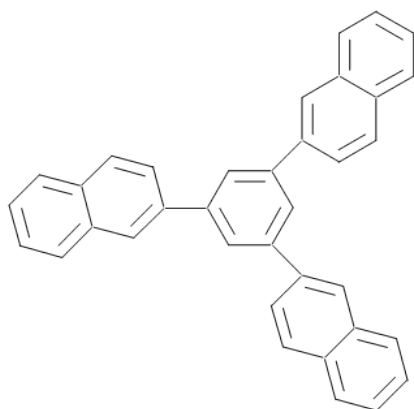


Figure 4. Molecule of 1,3,5-tris(2-naphthyl)benzene precursor of inclusion compounds

4. Conclusions

This synthesis and related product, 1,3,5-tris(2-naphthyl)benzene, can provide extensive research for the future. For example, substitution of different kinds of functional group on naphthalene ring can obtain various kinds of inclusion compounds with different sizes and inclusion behavior which may be essentially useful for the various syntheses as shown in Figure 5.

The synthesis of star like molecules such as 1,3,5-triaryl benzene ((1,3,5-triphenylbenzene and 1,3,5-tris(2-naphthyl)benzene) can be used for designing and synthesis of binary crystals via hydrogen bonds[39], halogen bonds[40], $\pi\cdots\pi$ [41] or van der Waals forces[42]. Even, the construction of ternary and higher-order cocrystals will be under considerations[43, 44].

One possible challenge to make three-component solids is host-guest design in which the host is a crystalline lattice assembled using two molecular species[45]. Usually, inclusion compounds have been synthesized by crystallizing the host and guest compounds from a solution[46]. The choice of components available for the construction of such a system is limited by the solubility of the host and the guest compounds. This limitation becomes more serious in multicomponent systems that require balancing the solubility of several molecular species.

By using these cyclization condensation reactions, via CuCl_2 as catalyst, and using heteroaromatic rings such as thiophene, pyrrole and furan, one may synthesize various molecules of star like structures with different physical and chemical properties. Many of hetero atoms such as oxygen and nitrogen that contain free lone pairs of electrons can provide an inclusion compound with interesting electrical properties in addition to separation abilities. These kinds of properties make star like molecules a good precursor for making nano cage-like compounds. By selecting proper derivatives of ketones, the cavity of the inclusion compounds can be controlled for the separation of specific molecule.

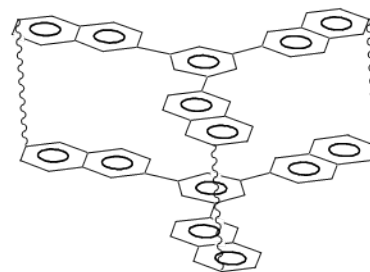


Figure 5. Proposed stack form of two molecules of 1,3,5-tris(2-naphthyl)benzene which can be used to make an inclusion compound

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REFERENCES

- [1] C. Engler, H. E. Bernthold, *ChemBer.* 7, 1123, 1874.
- [2] S. Elmorsy, A. Peter, K. Smith, *Tetrahedron Lett.*, 32, 4175, 1991.
- [3] T. Yamato, C. Hideshima, Y. Nagano, M. Tashiro, *J. Chem. Res.*, 45, 266, 1996.
- [4] U. Folli, O. Iarossi, M. Montarsi, *J. Chem. Soc. Perkin Trans I*, 537, 1995.
- [5] H. J. Lee, H. S. Kim, J. N. Kim, *Tetrahedron Lett.* 40, 4363, 1999.
- [6] T. Y. Kim, H. S. Kim, K. Y. Lee, J. N. Kim, *Bull. Korean Chem. Soc.* 20,11,1255, 1999.
- [7] N. Iranpoor,, , B. Zeynizade, *Synlett* , 1079, 1998.
- [8] Yanan Zhao, Jian Li, Chunju Li, Kun Yin, Dongyan Ye, Xueshun Jia ,*Green Chemistry - GREEN CHEM* , 12, no. 8, 2010.
- [9] R. Bishop, I. D. Dance, *J. Chem. Soc. Perkin Trans II*, 992, 1979.
- [10] E. Weber, I. Gsoresh, B. Stensland, *J. Am. Chem. Soc.*, 106, 3297, 1984.
- [11] F. Tomislav, V. Andrew, J. William, S. Motherwell, *Angew. Chem. Int. Ed.* 45, 7546, 2006.
- [12] J. Merchan, V. Lavayen, P. Jara, V. Sanchez, N. Yutronici, *J. Chil. Chem. Soc.* 53, No 2, 1498, 2008.
- [13] A. E. Christian, H. Byun, N. Zhong, M. Wanunu, T. Marti, A. Furer, F. Deiderich, R. Bittman, G. Rothblat, *Journal of Lipid Research*, 40, 1475, 1999.
- [14] T. Yamato, C. Hideshima, Y. Nagano, M. Tashiro, *ChemIn-form*, 27, 1996.
- [15] B. Peterson, F. Diederich,, . *Angew. Chem.* 33: 1625, 1994.
- [16] T. Marti, B. R. Peterson, A. Furer, T. Mordasini-Denti, J. Zarske, B. Jaun, F. Diederich, *Helv. Chim. Acta.* 81: 109, 1998.
- [17] Chi-Keung Lam, Thomas C.W Mak, *Crystal Engineering* 3, Issue 1, 33, 2000.
- [18] E.J. Juarez-Perez, C. Vinas, F. Teixidor, R. Nunez, *Organometallics*, 28, 5550, 2009.
- [19] J. Pang, E. J. P. Marcotte, C. Seward, R. S. Brown., S. Wang, *Angew. Chem., Int. Ed.*, 40, 4042, 2001.
- [20] N. Hiroyuki, M. Makoto, T. Eishun, *J. Org. Chem.*, 63, 399, 1998.
- [21] J. Brunel, I. Ledoux, J. Zyss. M. Blanchard-Desce, *Chem. Commun*, 923, 2001.
- [22] Q. He, H. Huang, J. Yang, H. Lin, F. Bai, *J. Mater. Chem.* 13, 1085, 2003.
- [23] I. A. Khotna, L. S. Lepnev, N. S. Burenkova, P. M. Valetsky, A. G. Vitukhnovsky, *J. Lumin*, 110, 232, 2004.
- [24] B. Gomez-Lor, E. Gonzalez-Cantalapiedra, M. Ruiz, O. de frutos, D. J. Cardenas, A. Santos, A. M. Echevarren, *Chem. Eur. J.* 2004.
- [25] K. Sambasivarao, K. Dhurke, L. Kakali, S. B. Raghavan, *Eur. J. Org. Chem.* 19, 4003, 2004.
- [26] H. P. Dijkstra, C. A. Kruithof, N. Ronde, R. van de Coevering, D. J. Ramon, D. Vogt, G. P. M. van Klink, G. van Koten, *J. Org. Chem.*, 68, 675, 2003.
- [27] Y. H. Kim, R. Beckerbauer, *Macromolecules*, 27, 1968, 1994.
- [28] V. V. Maxym, J. N. Ronny *Am. Chem. Soc.*, 126, 884, 2004.
- [29] Y. Takchiko, H. Chicko, N. Yoshiaki, T. MasaShi, *J. Chem. Res. Synop*, 6, 266, 1996.
- [30] VasyI Stefanyk, *CHEMISTRY & CHEMICAL TECH-NOLOG*, 6, No.1, 2012.
- [31] Jianhui Xia and Krzysztof Matyjaszewski* *Macromolecules*, 1999, 32 (8), pp 2434–2437
- [32] Y. Sato, M. Kagotani, T. Yamamoto, Y. Souma, *Applied Catalysis*, 185, Issue 2 , 219, 1999
- [33] Aizoh Sakurai, Munetaka Akita, and Yoshihiko Moro-oka, *Organometallics* , 18 (16), 3241, 1999.
- [34] M. Garilli, P. L.Fatutto, F. Piga, *La Chimica e l'Industria*, 80, 333., 1998.
- [35] W. D.Mross, *Catal. Rev. Sci. Eng.* , 25, 591, 1983.
- [36] Jun-Cheng Hu, Yong Cao, Ping Yang, Jing-Fa Deng, Kang-Nian Fan, *Journal of Molecular Catalysis A: Chemical* Volume 185, Issues 1-2, 8 July 2002, Pages 1-9.
- [37] N. O. Mahmoodi, F. Mostaghni, *J. Korean Chemical Socie-ty*, 46, 2002.
- [38] E. Weber, M. Hecker, E. Koeppe, *J. Chem. Soc. Perkin Trans II* 1251, 1988.
- [39] T. L. Nguyen, F. W. Fowler, J. W. Lauher, *J. Am. Chem. Soc.*, 123, 11057, 2001.
- [40] A. Sun, J. W. Lauher, N. S. Goroff, *Science*, 312, 1030, 2006.
- [41] J. H. Kim, S. V. Lindemann, J. K. Kochi, *J. Am. Chem. Soc.*, 123, 4951, 2001.
- [42] M. W. Hosseini, A. De Cian, *Chem. Commun*, 727, 1998.
- [43] C. B. Aakeroy, A. M. Beatty, B. A. Helfrich, *Angew. Chem.*, 113, 3340, 2001.
- [44] E. J. Cheung, S. J. Kitchin, K. D. M. Harris, Y. Imai, N. Tajima, R. Kuroda, *J. Am. Chem. Soc.* 125, 14658, 2003.
- [45] K. T. Holman, A. M. Pivovarov, M. D. Ward, *Science*, 294, 1907, 2001.
- [46] V. S. S. Kumar, F. C. Pigge. N. p. Rath, *Cryst. Growth Des.* 4, 1217, 2004.