THINK INDIA JOURNAL
ISSN: 0971-1260
Vol-22-Issue-16-August-2019

Synthesis and Characterization of 1-Naphthaldehyde Based Silanes and Silatranes.

Kanav Dhir[1], Jasbhinder Singh*[2]

[1] (Department of Chemistry, DAV College Sector-10, Chandigarh, India.160011)

[2] (Department of Chemistry, Lovely Professional University, Phagwara, India)

*Corresponding author

Abstract: The Organosilicon coordination chemistry has increased interest of scientists considerably during the last decades. The LMW organosilicon compounds are studied by the academic and the industrial individuals for many aspects of this given subject which have been defined well for their discription. Also these low weight organosilicon molecules have been widely applicable in the many many industrial as well as commercial use globally. These compounds are well characterized by the number of spectroscopic techniques which are most advanced now a days i,e. by the proton and carbon (^{1}H and ^{13}C) NMR spectroscopic technique. These compounds show a new property than the tradition compounds as they have relative more stable to moisture and air.

Keywords: organo-compounds, organo-metallics.

Introduction

Since the starting point, marked via K B Sharpless and co worker group invented that the most exclusive click chemistry has been used in the widely admired subject of matter. The Cu(I) help in the catalysis of cycloaddition of the azides and organic terminal alkynes which in the result gives triazoles designate click reaction. Click chemistry has an important benefit into the different fields for example in the research fields, which is on observation is being used in the number of every field s to cancer treatments [1, 2]. This section provides detailed synthetic aspects for the application of 'Click Silylation' and Transesterification reaction approach to organosilicon chemistry. The importance of azide–alkyne fusion to yield 1,2,3–triazole linking triethoxysilane moiety to practically any fragment has increased the utility of organosilicon compounds in many fields, such as in drug discovery,

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

bioconjugation, silica supported nano chemistry and synthetic chemistry as well. This fact is attributed to high yielding capacity of CuAAC along with their high stability [3–5].

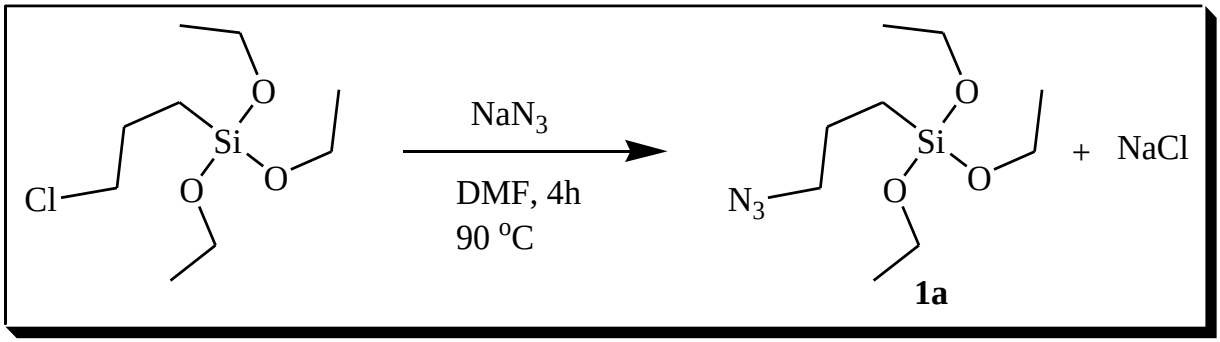
The newly advanced Silicon and atranes are compounds which are being coupled at silicon centre and they are widely diversed with the number of chelating ligands and help in various applications in the different branches in the modern era of world for all fields. The specific property of these compounds are basically arises because they have I beautiful and unique arrangement of the atoms iarrong the main silicon atom. On studying the structure of these specific types of compounds it was observed that 5^{th} bond is formed as the dative bond from Nitrogen to the Silicon atom. This happens as silicon has the empty d orbitals [6–8]. These organo silicon as silatrane compounds show hydrophilic character towards the water and they are water and air sensitive compounds[9]. The number of groups are attached and coupled in a single molecule due to which they play a important role in the number of applications.

Experimental Part

material and methods used

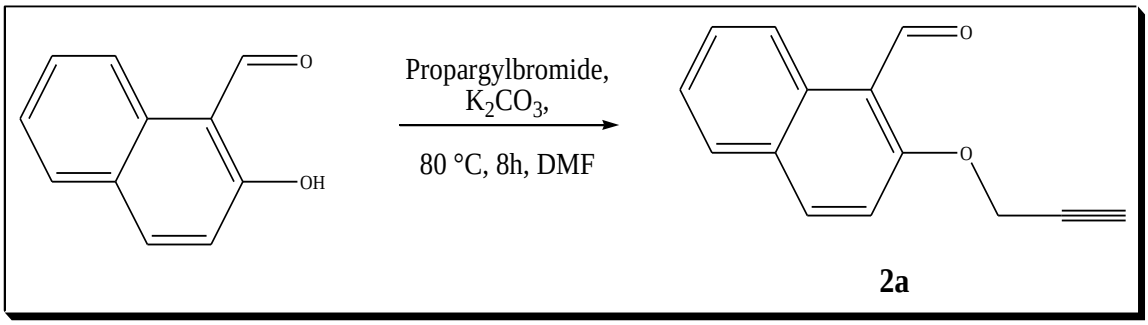
Synthesis of azidopropyltriethoxysilanes

The core compound which was used as a precursor further i.e. azidopropyltriethoxysilanes and in the presence of catalyst [10]. In this presented methdology, synthesis was done in at a at 80 ^{o}C for 5h with accurate yield in the DMF solvent [11]. This molecular compound was separated from the mixture with the help of reduced pressure in a rota evaporator as colourless oily liquid. This compound was further used as a parent molecule for the formation of triazole linked silane and silatrane.

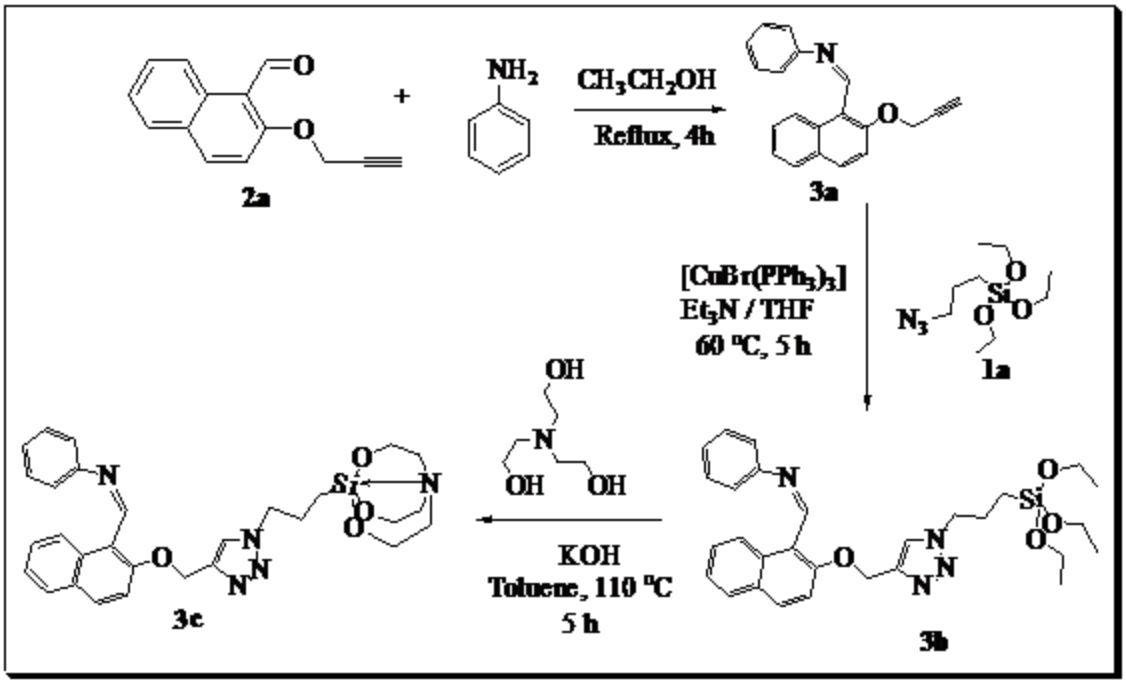


Synthesis of 1a

ISSN: 0971-1260
Vol-22-Issue-16-August-2019



Synthesis of 2a



Synthesis of 3a, 3b and 3c

Therefore, it was imperative to distil it under reduced pressure, so as to keep the boiling point below 150 ^{o}C..

Synthestic methodology of Schiff base of 1-naphthaldehyde

2-Hydroxy-1-naphthaldehyde is a very very good and useful ligand which have applications in the field of cationic, anionic, and fluorescent fileds of science[12-13].(**2a**) was synthesized by the treatment of 2-hydroxy-1-naphthaldehyde with 80% solution of propargyl bromide at 80 °C for 8 hrs in the presence of K_2CO_3 base in dimethyl formamide solution in single neck round bottom flask. The reaction mixture was then poured into ice cold water. Stable pale yellow solid (**2a** as

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

title compound) obtained was filtered on a Buchner funnel and washed with cold water and dried in excellent yield.

Synthestic methodology of 3b and 3c

Aniline group can be easily interlinked with higher coordinated silicon atom via click chemistry. So, in an effort to gain further insight into this field, commercially available Aniline was easily introduced as Schiff base into the compound **2a** resulted into Schiff based alkyne (**3a**) which further subjected to cycloaddition reaction as a terminal alkyne substrate with 1a under standard click conditions. The cyclized trialkoxysilane product i.e. compound **3b** was quantitatively converted into corresponding silatranes compounds **3c** by the aknown organic reaction named as transesterification reaction. In this well known reaction scheme the ligand which is tripodal in nature i.e. triethanolamine react with the 3c compound and in this reaction KOH is added as a catalyst to provide basic conditions and to fast the reaction. The purity of the compounds was checked by the elemental analysis, melting point, IR and NMR spectroscopy. It might be mentioned here that these techniques were reasonably good to check the purity and identification of the compounds.

Results and Discussion

For compound 1a

IR studies: An IR spectrum of AzPTES On record of Infra red spectra of 1a compound it was observed that peaks of azido goup was absorbed on 2095 cm^{-1}.

NMR studies: The proton NMR was taken of this compound 1a which shows a significant peak of triplet at $\delta = 1.17$ and a quartet $\delta = 3.842$ ppm, which are incoherence to the the tewo groups that are CH_3 and OCH_2, respectively in the molecule of 1a. The $SiCH_2$ and N_3CH_2 protons were identified at $\delta = 0.56$ ppm and $\delta = 3.21$ ppm as two triplets. In the ^{13}C NMR spectra of compound **1a**, the downfield shift from $\delta = 48.5$ ppm (due to H_2C-Cl) to $\delta = 55.7$ ppm in the signal corresponding to CH_2 carbon. This downfield shift signified the C-N_3 bond formation

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

For compound 3a

M.Pt.: Melting point of this compound 3a was recorded on meting point instrument and noted as 157 °C.

IR studies: An Infra red spectra of compound 3a was taken in the standard range of 400-4000cm^{-1} and exhibited a strong absorption band characteristic of C-C triple bond linkage at 2126 cm^{-1}. There was also missing of broad O-H band at 3390.

NMR studies: ^{1}H NMR spectra of the compound **2a** exhibited a singlet at δ = 10.35 ppm due to –CHO group. One proton of aromatic ring before the formation of alkyne was at δ = 7.55 ppm as singlet but after formation of alkyne it undergo to more downfield shift and appeared at δ = 9.25 ppm. Hump of O-H proton completely disappeared from the spectrum. Singlet of OCH_2 segment showed its signal at δ = 4.77 ppm. Strong indication of C triple bond CH given by sharp singlet at δ = 2.52ppm. Rest of the aromatic region remains at its original position at δ = 7.26- 7.55 as multiplet.

For compound 3b and 3c

IR studies: Standard range was used to record the IR peaks. In this spectra there is no peak was present at the 2100 $cm^{-1,}$which indicate that in the compound of 3b and 3c there is no azide group was present and it eas used in cyclization process for the formation of triazole ring in silanes and in silatranes. The absorption band at 3019–2789 cm^{-1} and 1660–1466 cm^{-1} gives the formation of Schiff base and presence of Schiff base in both compounds 3b abd in 3c.

NMR studies: ^{1}H When these compounds are analysed on a NMR spectroscopy then they gives the data gives a 100% confirmation that these compounds are formed and they are got in very high yield and 1005 pure. In compound **3c**–CH_2 unit of propyl was confirmed due to to a peak at δ 1.66 ppm. The –OCH_2 which is attached to the triazole was confirmed by the peak at δ 5.25–5.32 ppm. The aromatic segment was appear in the range of δ 7.16–7.55 ppm. The Schiff ─CH═N proton was came at δ 9.23 ppm. But in the 3c compound the proton that is, -OCH_2CN of silatrane ring was in tha value at δ 3.33–3.55 ppm.

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

Conclusions

With the significant fact that the silicon differs from that of all carbon family that it is not used in the field of organic chemistry but it has number of applications in different fields in life at global level. These compounds were synthesized in the inert atmosphere and they are very good reactive than the traditional compounds of this types. The basic difference in the pattern o f the reactivity of the carbon and silicon is that silicon has a unique tendency to extend or to increase its coordination number property to a more higher than the normal state coordination of silicon Atom carbon has no such kind property. So silatranes are hypercoordinated compounds of silicon and they show a very good range of applications.

References

[1] N. Moitra, J. J. E. Moreau, X. Cattoën, M. Wong, "Convenient route to water-sensitive sol–gel precursors using click chemistry" Chem. Commun., 46, 8416–8418. 2010.

[2] K. Bürglová, N. Moitra, J. Hodačová, X. Cattoën, M. W. C. Man,"Click approaches to functional water-sensitive organotriethoxysilanes", J. Org. Chem., 76, 7326–7333, 2011.

[3] V. G. Pukhalskaya, E. P. Kramarova, , L. P. Kozaeva, A. A. Korlyukov, A. G. Shipov, S. Y. Bylikin, V. V. Negrebetsky, G. V. Poryadin, Y. I. Baukov, "Synthesis, structure and muscarinic agonist activity of substituted N-(silatran-1-ylmethyl)acetamides"Appl. Organomet. Chem., 24, 162–168, 2010.

[4] A. V. Kransnoslobodtsev, L. S. Shlyakhtenko, E. Ukraintsev, T. O. Zaikova, J. F. W. Keana, Y. L. Lyubchenko, "Nanomedicine and protein misfolding diseases" Nanomed. Nanotechnol. Biol. Med., 1, 300–305, 2005.

[5] Han, L. Li, K. Qing, X. Qi, L. Hou, X. Luo, S. Shi, F. Ye," "Synthesis and biological evaluation of nucleoside analogues than contain silatrane on the basis of the structure of acyclovir (ACV) as novel inhibitors of hepatitis B virus (HBV)"Bioorg. Med. Chem. Lett., 23, 1310–1314, 2013.

[6] E. F. Belogolova, V. F. Sidorkin, "Correlation among the Gas-Phase, Solution, and Solid-Phase Geometrical and NMR Parameters of Dative Bonds in the Pentacoordinate Silicon Compounds. 1-Substituted Silatranes" J. Phys. Chem. A 117, 5365–5376, 2013.

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

[7] S. Senapati, S. Manna, S. Lindsay, P. Zhang, "Application of Catalyst-Free Click Reactions in Attaching Affinity Molecules to Tips of Atomic Force Microscopy for Detection of Protein Biomarkers"Langmuir, 29, 14622–14630, 2013.

[8] A. Bianco, M. Maggini, M. Nogarole, G. Scorrano, "Hydrolysis Rate of Functionalized Fullerenes Bearing Alkoxysilanes: A Comparative Study"Eur. J. Org. Chem. 13, 2934–2941, 2006.

[9] M. G. Voronkov, "Silatranes: Intra-complex heterocyclic compounds of pentacordinated silicon" Pure Appl.Chem. 13, 35–59, 1966.

[10] G. Lu, W. Mai, R. Jin, L. Gao, "Immobilization of dipyridyl complex to magnetic nanoparticle via click chemistry as a recyclable catalyst for Suzuki cross-coupling reactions" Synlett 9, 1418-1422, 2008.

[11] Tang, G. Cui, M. Du, Z. Chen, Y. Wang, H. Wang, "Determination of the Hydroperoxil Group Level in Polyethylene Glycols Using a Novel Mimic Enzyme Fe(III)-Mn(II)(HNAPTS)$_2$" J. Agric. Food Chem. 51, 1761, 2003.

[12] A. K. Das, S. Goswami, "Chemical sensors: definitions and classification" Sens. Actuators, B., 247, 1062, 2017.

[13] A. K. Paul, N. Guchhait, "Evidence for excited-state intramolecular proton transfer in 4-chlorosalicylic acid from combined experimental and computational studies: Quantum chemical treatment of the intramolecular hydrogen bonding interaction" J. Lumi. 132, 94, 2012.