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SYNTHESIS AND CHARACTERISATON OF NEW ASYMMETRIC TRIAZACYCLOHEXANES COMPOUNDS

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ABSTRACT: A new Asymmetric synthesis of triazacyclohexanes compound were prepared from the mixed two equivalents of 4-fluorobenzylamine and one equivalent tert-butylamine or two equivalents 4-bromoaniline and one equivalent isobutylamine with three equivalents of formaldehyde, gave solids compounds with good yields of 1,3-bis(4-fluorobenzyl)-5-tert-butyl-1,3,5-triazacyclohexane 1,3-bis(4-bromophenyl)-5-isobutyl-1,3,5- triazacyclohexane.
The identification of these compounds has been done by CCM, infrared spectroscopy IR, nuclear magnetic resonance spectroscopy of ^{1}H-NMR, ^{13}C NMR.

KEYWORDS: Triazacyclohexane, asymmetric, 4-fluorobenzylamine, tert-butylamine.

1 INTRODUCTION

The formation of 1, 3, 5-triazacyclohexane from primary amines and formaldehyde has been known for more than one hundred years [1]. The triazacyclohane was synthetised from condensation reaction with primary amines and formaldehyde (formalin) in basic solution [2].

Unsymmetrically substituted triazacyclohexanes were prepared from the condensation reaction between aromatic or aliphatic amine (1), aliphatic or aromatic amine (2) with formaline (3) [2:1:3] [3]. Triazacyclohexan are concerned with a large range of six-memberd ring compounds wich contain three nitrogen atoms in 1,3 and 5 positions [4].

Unsymmetrically subtituted 1, 3, 5-triazacyclohexane have been known for a long time and are used in a variety of ways in industrial chemistry [5]. For instance, N, N', N," - trisubstituted 1, 3, 5-triazacyclohexane can be used as adjuvant for the preparation of N-heterocyclic carbenes wich served as substantial class of ligands in homognenous catalysis [6]. Further, the interest in TAC as ligand seems to growing rapidly [7-12].

2 RESULTS AND DISCUSSION

The Unsymmetrically Substituted triazinane Such as 1,3-bis(4-fluorobenzyl) -5-tert-butyl- 1,3,5- triazacyclohexane was prepared from the condensation reaction of tert-butylamine and 4-fluorobenzylamine with formaldehyde (Scheme 1). This compound is stable at room temperature and high yield (85%) with a transparent color.

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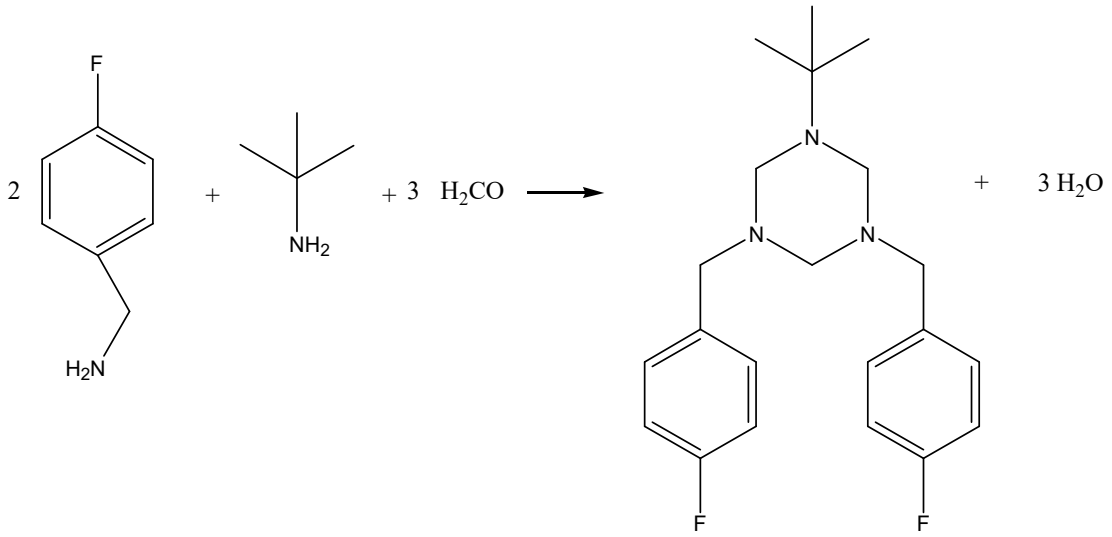
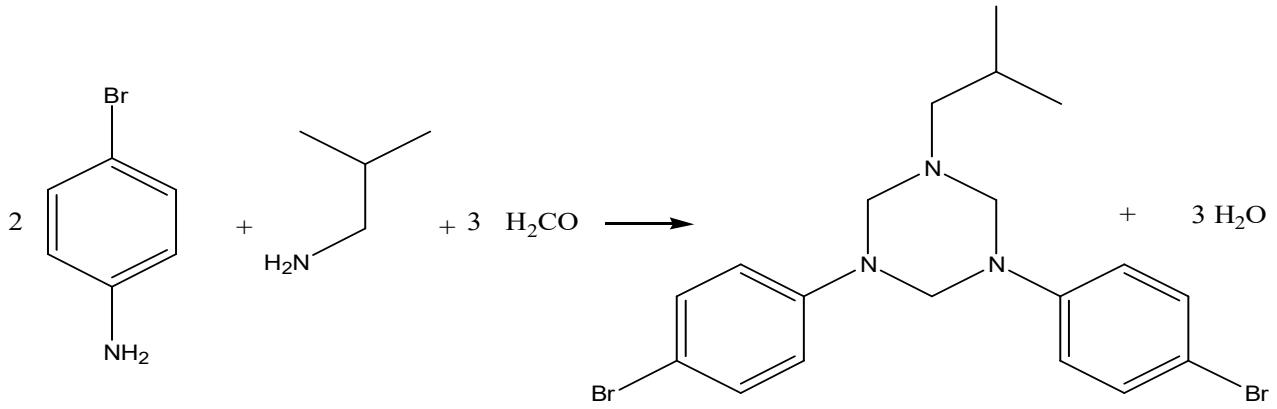


Scheme 1

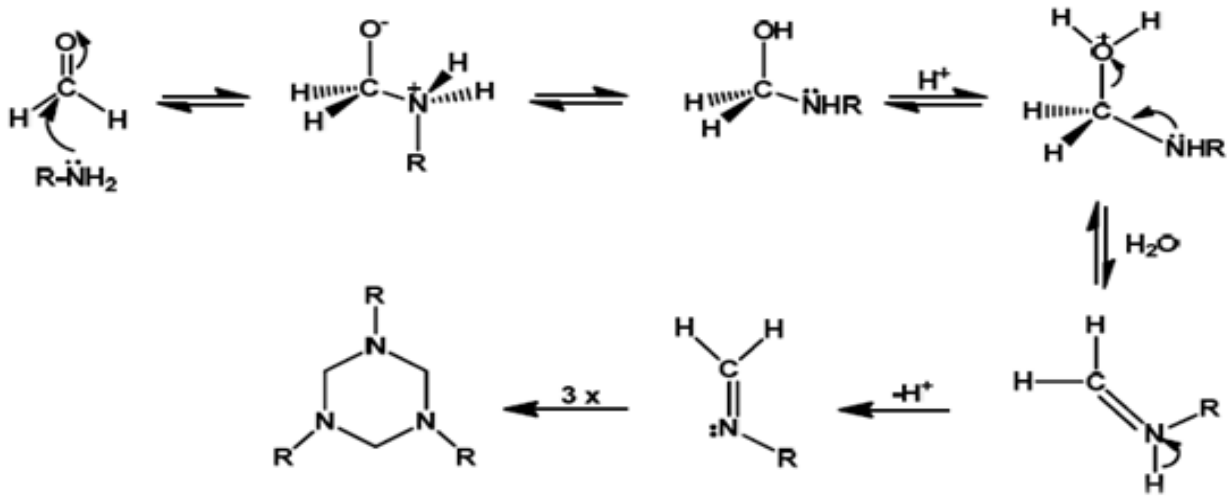
1,3-bis(4-bromophenyl)-5-isobutyl-1,3,5- triazacyclohexane was prepared from the condensation reaction of isobutylamine and 4-bromoaniline with formaldehyde (Scheme 2). This compound is stable at room temperature and high yield (89%) with a transparent color.



Scheme 2

The mechanism of interaction is the production of Schiff base, which polymerize to give:

1,3-bis(4-fluorobenzyl)-5-tert-butyl-1,3,5-triazacyclohexane or 1,3-bis(4-bromophenyl) -5-isobutyl -1,3,5- triazacyclohexane (Scheme 3).



Scheme 3

The characterization of title compound has been explained by FT-IR, ^{1}H, and ^{13}C NMR.

The infrared spectrum of the,3-bis(4-fluorobenzyl) -5-tert-butyl- 1,3,5- triazacyclohexane showed a strong band for the (C-F) group at(1202cm^{-1}), a band at (1598-1498cm^{-1}) for C=C and (753.0 cm^{-1}) for H–C- Ar .however for 1,3-bis(4-bromophenyl)-5-isobutyl -1,3,5- triazacyclohexane showed a strong band for the (C-Br) group at(1173cm^{-1}), a band at (1584.4 -1497.4 cm^{-1}) for C=C and (757.0 cm^{-1}) for H-C- Ar.

The 3-bis (4-fluorobenzyl) -5-tert-butyl- 1, 3, 5- triazacyclohexane ^{1}H NMR. The nine hydrogen atoms appear when you 1.05 ppm unilaterally, four atom of hydrogen 3.68 ppm. triazacyclohexanes ring hydrogen atoms appear when 3.38-.53 ppm and hydrogen atoms of the aryl ring appear when 6.96 -7.31 ppm multiply. However for the 3-bis (4-bromophenyl) - 5-isobutyl -1, 3, 5- triazacyclohexane ^{1}H NMR. The six hydrogen atoms appear when you 0.88 ppm and relate with one atom of hydrogen to give binary form. One atom of hydrogen 2.19 ppm attached to the 8-H to give the form of nine. Tow atom of hydrogen 2.33 ppm attached to the one H to give the doubly form. Triazacyclohexanes ring hydrogen atoms appear when 4.24-4.73 ppm unilaterally and hydrogen atoms of the aryl ring appear when 6.85-7.35 ppm multiply.

The 3-bis (4-fluorobenzyl) -5-tert-butyl- 1, 3, 5- triazacyclohexane ^{13}C NMR, The carbon atoms of the tert-butyl group appear at 26.93, 52.61 ppm, The carbon atoms of the 4-fluorobenzyl group appear at 56.59 ppm.The carbon atoms of the group appears at the 1, 3, 5 triazacyaclohexane 69.05 - 73.88 ppm And carbon atoms of the aryl group appears at 115.36, 130.7, 130.8 ppm, The carbon ring aryl which has a flurine atom appears when it is 135ppm.

However for the, 3-bis (4-bromophenyl) - 5-isobutyl -1, 3, 5- triazacyclohexane ^{13}C NMR, The carbon atoms of the isobutyl group appear at 21.17, 26.85, 60.78 ppm, The carbon atoms of the group appears at the 1, 3, 5 triazacyaclohexane 68.77 - 71.99 ppm And carbon atoms of the aryl group appears at 119.51, 132.44, 148.82 ppm, The carbon ring aryl which has a bromine atom appears when it is 113.36 ppm.

3 EXPERIMENTAL

3.1 INSTRUMENTATION

Purity of the compounds was checked by thin layer chromatography (TLC) using CH_2Cl_2: n-Hexane (2:1, v: v). FT-IR spectra were reported by a Frontier spectrometer in the region of 4000-400 cm $^{-1}$, performing KBr technique. NMR spectra were recorded on Bruker spectrophotometer ARX 500 (500 MHz for proton and 100.62 MHz for carbon). The chemical shifts (δ) are expressed in arts per million (ppm). Tetramethylsilane (TMS) is used as internal reference. The spectra are recorded in deuterated chloroform $CDCl_3$ is used as solvent ($CDCl_3$: δ 7.26 ppm, $CDCl_3$: δ 77.0 ppm).

3.2 SYNTHESIS 1,3-BIS(4-FLUOROBENZYL)-5-TERT-BUTYL-1,3,5- TRIAZACYCLOHEXANE

tert-butylamine (1 ml, 10 mmol) and 4-fluorobenzylamine (2.46 g, 20 mmol) were dissolved in ethanol (10 ml). An aqueous solution of formaldehyde in water (37%, 2.52 ml, 36 mmol) was added under stirring. The mixture was stirred for 7 hours at

25°C. The resulting solution was evaporated on a rotary evaporator to dryness. Color: Colorless. M.p.:119-121 °C. Yield: 85%. Rf (Dichloromethane: n-Hexane, 2:1, v: v): 0.66.

3.3 CHARACTERZATON OF 1,3-BIS(4-FLUOROBENZYL)-5-TERT-BUTYL-1,3,5- TRIAZACYCLOHEXANE

FT-IR (KBr,v, cm-1): 3086(Ar-H), 2955-2872 (CH_3, C),1598-1498(C=C), 1202 (C-F), 753 (Ar-H).

^{1}HNMR (500MHz, CDCl3, δ, ppm): 1.05 (s, 9H, CH_3), 3.68 (s, 4H, CH_2-Ar),3.38 (s, 2H, -N-CH_2-N-), 3.53 (s, 4H, Ar-N-CH_2-N-), 6.96-7.31 (m, 8H, Ar-H).

^{13}CNMR (75 MHz, CDCl3, δ, ppm): 26.93 ($\underline{C}H_3$-C), 52.61(CH_3-$\underline{C}$), 56.59 (Ar-$\underline{C}H_2$-N), 69.05 (-N-$\underline{C}H_2$-N-Ar), 73.88 (Ar-N-$\underline{C}H_2$-N-Ar), 115.36, 130.7, 130.8 ($\underline{C}$H=C-), 135(F- $\underline{C}$).

3.4 SYNTHESIS 1,3-BIS(4-BROMOPHENYL)-5-ISOBUTYL-1,3,5- TRIAZACYCLOHEXANE

isobutylamine (1 ml, 10 mmol) and 4-bromoaniline (3.44 g, 20 mmol) were dissolved in ethanol (10 ml). An aqueous solution of formaldehyde in water (37%, 2.52 ml, 36 mmol) was added under stirring. The mixture was stirred for 7 hours at 25 °C. The resulting solution was evaporated on a rotary evaporator to dryness. Color: Colorless. M.p.:138-139 °C. Yield: 89 %. Rf (Dichloromethane: n-Hexane, 2:1, v: v): 0.47

IR (KBr,v, cm-1): 2927.8(C-H), 1584.4 -1497.4 (C=C), 1273.8(C-N), 1137.0 (C-Br), 757.0 (H- Ar).

^{1}H. NMR (500 MHz, $CDCl_3$): 0.88 (d, 6H, CH_3), 2.19 (m, CH-C_2H_6), 2.33 (d, CH_2-CH), 4.24 (s, 4H, C_4H_9-N-CH_2-N-Ar), 4.73 (s, 2H, Ar-N-CH_2-N-Ar) 6.85-7.35 (m, 8H, Ar).

^{13}C. NMR (100 MHz, $CDCl_3$): 21.17 ($\underline{C}H_3$-CH), 26.85(C_2H_6-$\underline{C}$H-), 60.78 (CH-$\underline{C}H_2$-N), 68.77 (C_4H_9-N-$\underline{C}H_2$-N-Ar), 71.99 (Ar-N-$\underline{C}H_2$-N-Ar), 113.36 ($\underline{C}$-Br) 119.51-132.44($\underline{C}$H=C-), 148.82 (N-$\underline{C}$=).

4 CONCLUSION

We have synthesized and characterizeda new unsymmetrical 1, 3, 5-triazacyclohexane derivative. The synthesis was achieved by condensation of tert-butylamine and 4-fluorobenzylamine with formaldehyde and isobutylamine and 4-bromoaniline with formaldehyde. These compounds are very stablein air and can be a useful ligand for the preparation of new metal complexes.

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