

# Reaction of 1,1',2,2'-Tetrakis (phenylamino) Ethane with Glyoxal; Synthesis of $N^2, N^3, N^7, N^8, 1, 4, 5, 6, 9, 10$ -Decaphenyltetradecahydro-dipyrazino [2, 3-b: 2, 3-e] Pyrazine-2, 3, 7, 8-Tetraamine and 5, 6-bis (ethoxy)- $N^2, N^3, 1, 4$ -Tetraphenylhexahydro -2, 3-Pyrazinediamine

**Kakanejadifard, Ali\***<sup>+</sup>

Department of Chemistry, Faculty of Science, University of Lorestan,  
Khoramabad, I. R. IRAN

**Farnia, Sayed Morteza and Kakoiedinaki, Issa**

Department of Chemistry, Faculty of Science, University of Tehran, I. R. IRAN

**ABSTRACT:** Compound  $N^2, N^3, N^7, N^8, 1, 4, 5, 6, 9, 10$ -decaphenyltetradecahydrodipyrazino [2, 3-b: 2, 3-e] pyrazine-2, 3, 7, 8-tetraamine (4) was prepared by condensation of 1, 1', 2, 2'-tetrakis (phenylamino) ethane (1d) and glyoxal in EtOH or i-PrOH. Also, reaction of 1d with glyoxal in equimolare in EtOH resulted 5,6-bis (ethoxy)- $N^2, N^3, 1, 4$ -tetraphenylhexahydro-2, 3-pyrazinediamine (5). The natures of products are sensitive to acidity, temperature and solvent. In acidic media, 4 and 5 are unstable and degraded to diimine 6.

**KEY WORDS:** Polyazapolycyclic, Hexabenzyl-hexaaza-isowortzitane, Tetraazabicyclo [3, 3, 0] octane, 1,1', 2, 2'-tetrakis (phenylamino) ethane,  $N^2, N^3, N^7, N^8, 1, 4, 5, 6, 9, 10$ -decaphenyltetradecahydrod- pyrazino [2, 3-b: 2, 3-e] pyrazine-2, 3, 7, 8-tetraamine, 5, 6-bis (ethoxy)- $N^2, N^3, 1, 4$ -tetraphenylhexa- hydro -2, 3-pyrazinediamine.

## INTRODUCTION

Polyazapolycyclic compounds are used as initial substance for preparation of high-density, high-energy materials. These compounds are obtained by condensation of aldehydes or ketones and amines [1-10]. Also, 1,1', 2, 2'-tetrasubstituted ethane (1) were obtained by reaction of amines and glyoxal [11]. Different substituted aryl amines and alkyl amines of tetraazabicyclo

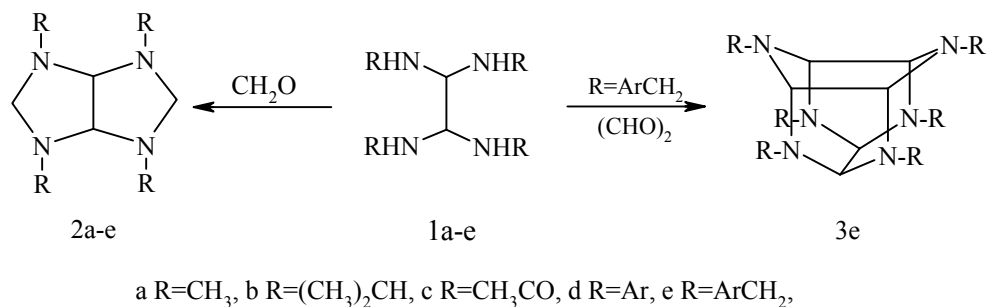
[3. 3. 0] octane (2a-e) have been synthesized by direct condensation of 1 with formal-dehyde [12-18]. Furthermore, hexabenzyl - hexaaza - isowortzitane (3e) is initial substance for preparation of hexanitro-hexaazaisowortzitane ( $Cl_{20}$ ), which is a most energetic compound. This molecule was obtained by reaction of 1,1', 2, 2'-tetrakis (benzyl amino) ethane (1e) and glyoxal

\* To whom correspondence should be addressed.

+ E-mail: kakanejadi.a@lu.ac.ir

1021-9986/05/2/39

4/\$/2.40



Scheme 1

[19]. In this work the reaction of 1,1', 2, 2'-tetrakis (phenyl amino) ethane (1d), with glyoxal was described.

## EXPERIMENTAL

All commercially available chemical reagents were used without purification. Melting points were determined with an Electro thermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu 4300 spectrometer. NMR spectra were recorded with a Bruker 80 instrument. Mass analyses of the products were conducted with a Finnigan-Matt 8430 GC-Mass instrument. Elemental analysis was carried out with a C, H, N, O Rapid-Heraeus apparatus.

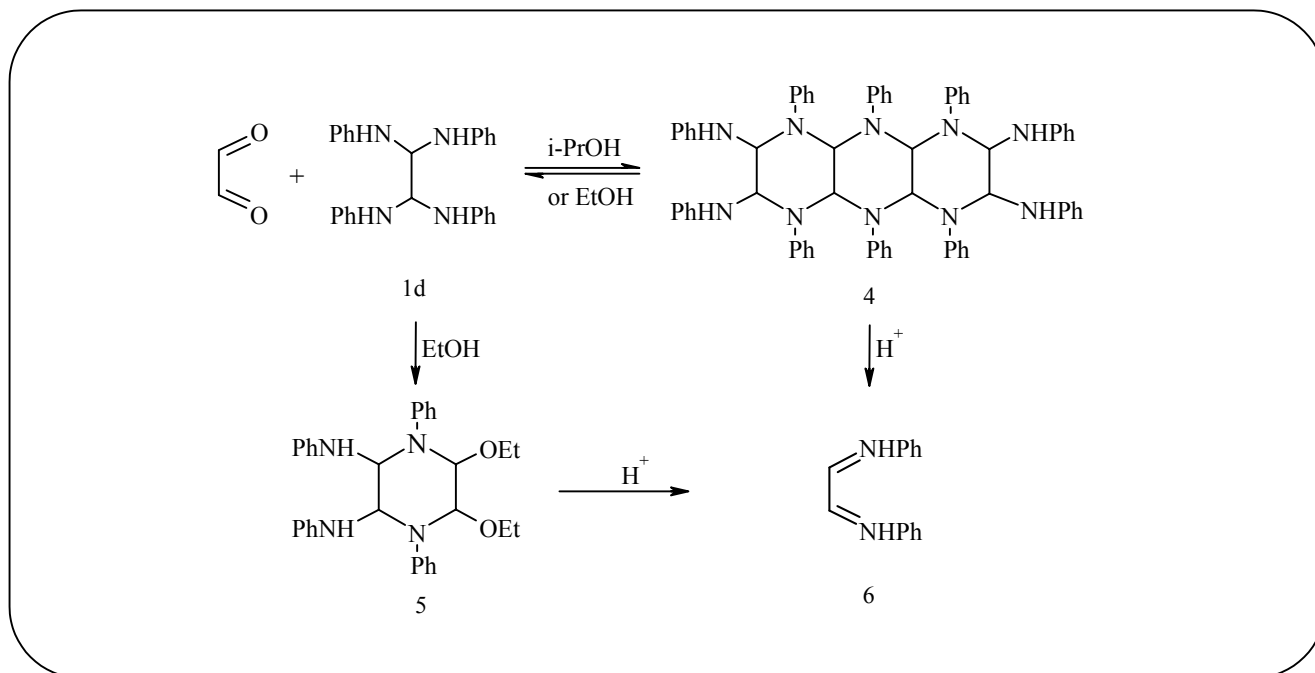
### Synthesis of N<sup>2</sup>, N<sup>3</sup>, N<sup>7</sup>, N<sup>8</sup>, 1, 4, 5, 6, 9, 10-Decaphenyltetradecahydrodipyrazino [2, 3-b: 2, 3-e] Pyrazine-2, 3, 7, 8-Tetraamine (4)

To a solution of 2.46 gr (6 mmol) of 1,1', 2, 2'-tetrakis (phenyl amino) ethane in 20 ml *i*-PrOH at 0 °C, 0.435 gr glyoxal (40% aqueous solution, 3 mmol) was added drop wise. The solution was stirred at 0-5 °C for 5 h. The precipitate was filtered and washed with cold EtOH to give, 2.88 gr (45.3% yield) of 4, mp 157.5-158 °C. IR (KBr) cm<sup>-1</sup>; 3384(NH). M/z=1018(M<sup>+</sup>), Elemental analysis, C<sub>68</sub>H<sub>62</sub>N<sub>10</sub>, calculated: C, 80.15; H, 6.09; N, 13.75, found: C, 80.24; H, 6.30; N, 13.37. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 6.63-7.49(m, 50H, CH<sub>Ar</sub>), 5.78 (s, 4H, CH) 4.95-5.08 (d, 4H, J=10 Hz, CH), 3.70-3.82 (d, 4H, J=10 Hz, NH). By addition of D<sub>2</sub>O to the NMR sample, the NH signals disappeared and doublet CH protons quickly collapsed into a singlet at 5.01. <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ:

145.40, 144.95, 144.27, 130.29, 122.71, 119.83, 119.36, 117.99, 114.33, 113.97, 76.64 (CH), 73.06 (CH). The 4 was obtained in EtOH under similar condition. Recrystallization of 4 in the hot *i*-PrOH leads to 6. But, recrystallization from EtOH gives 1.97 gr of a precipitate of 5,6-bis (ethoxy) N<sup>2</sup>, N<sup>3</sup>, 1, 4-tetraphenylhexahydro-2, 3-pyrazinediamine (5) mp 188-189 °C. IR (KBr) cm<sup>-1</sup>; 3357 (NH), M/z = 508 (M<sup>+</sup>). Elemental analysis, C<sub>32</sub>H<sub>36</sub>N<sub>4</sub>O<sub>2</sub>, calculated: C, 75.59; H, 7.08; N, 11.02, found: C, 75.60; H, 7.05; N, 11.09. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 6.69-7.37(m, 20H, CH<sub>Ar</sub>), 5.19 (s, 2H, CH), 5.19-5.30 (d, 2H, J=10.6 Hz, CH), 5.50-5.63 (d, 2H, J=10.6 Hz, NH), 3.29-3.66 (AB<sub>q</sub>, 4H, J=7.1 Hz, CH<sub>2</sub>) 1.01-1.18 (t, 6H, J=7.1 Hz, CH<sub>3</sub>). By addition of D<sub>2</sub>O to the NMR sample, the NH signal disappeared and doublet CH protons quickly collapsed into a singlet at δ 5.24. <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ: 146.31, 144.87, 130.21, 123.68, 119.61, 114.42, 114.01, 85.71 (CH), 71.59 (CH), 61.87 (CH<sub>2</sub>), and 14.53 (CH<sub>3</sub>).

### Synthesis of 5, 6-bis (ethoxy)-N<sup>2</sup>, N<sup>3</sup>, 1, 4-Tetraphenylhexahydro-2, 3-Pyrazinediamine (5)

To a solution of 2.46 gr (6 mmol) of 1,1', 2, 2'-tetrakis (phenyl amino) ethane in 20 ml EtOH at 0-5 °C, 0.87 gr glyoxal (40% aqueous solution, 6 mmol) was added drop wise. The solution was stirred at room temperature for 72 h. The precipitate was filtered and washed with cold EtOH to give 2.13 gr (67% yield) of 5, mp 180-187 °C. Recrystallization from EtOH gave a white precipitate of 5, mp 188.5-189 °C, with general properties (IR, NMR) identical with the product 5 discussed above.



Scheme 2

## RESULTS AND DISCUSSION

Condensation of 1,1', 2, 2'-tetrakis (phenyl amino) ethane (1d) with glyoxal in EtOH (or *i*-PrOH) produced N<sup>2</sup>, N<sup>3</sup>, N<sup>7</sup>, N<sup>8</sup>, 1, 4, 5, 6, 9, 10-decaphenyltetra decahydrodi-pyrazino [2, 3-b: 2, 3-e] pyrazine-2, 3, 7, 8-tetraamine (4). Also, reaction of 1d with glyoxal in equimolare of reactant in EtOH resulted in 5, 6-bis (ethoxy) N<sup>2</sup>, N<sup>3</sup>, 1, 4-tetraphenylhexahydro-2, 3-pyrazinediamine (5).

In addition, compound 5 can be obtained by recrystallization of compound 4 in EtOH. The conditions of these reaction were studied. It was found that, the nature of products is sensitive to acidity, temperature and solvent. Increasing the temperature reduces the yield of 4 and 5, but results in production to compound 6 (above 30 °C, the final product is only the compound 6).

The compound 5 is stable at room temperature; while 4 is degraded to 6 during 3 days. As was mentioned, so at pH = 5 product 4, decomposes to 6 in few minutes. In contrasted the compound 5 is more stable and decomposes in 48 h. This data show that, the compound 5 is theromo daynimal stable product. The mechanisms of formation and decomposition of polyazapolycyclic amine compounds has been studied [11, 14, 16-18]. It should be noted, that we could not produce the compound 3d from proper reactance.

## Acknowledgments

We warmly thank of Dr A. Zabardasti and Dr M. Saraji, for useful discussion.

Received : 30<sup>th</sup> July 2003 ; Accepted : 12<sup>th</sup> October 2004

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