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Short Note

2-(4-Pyridyl)-1,3-di(4-picolyl)imidazolidine

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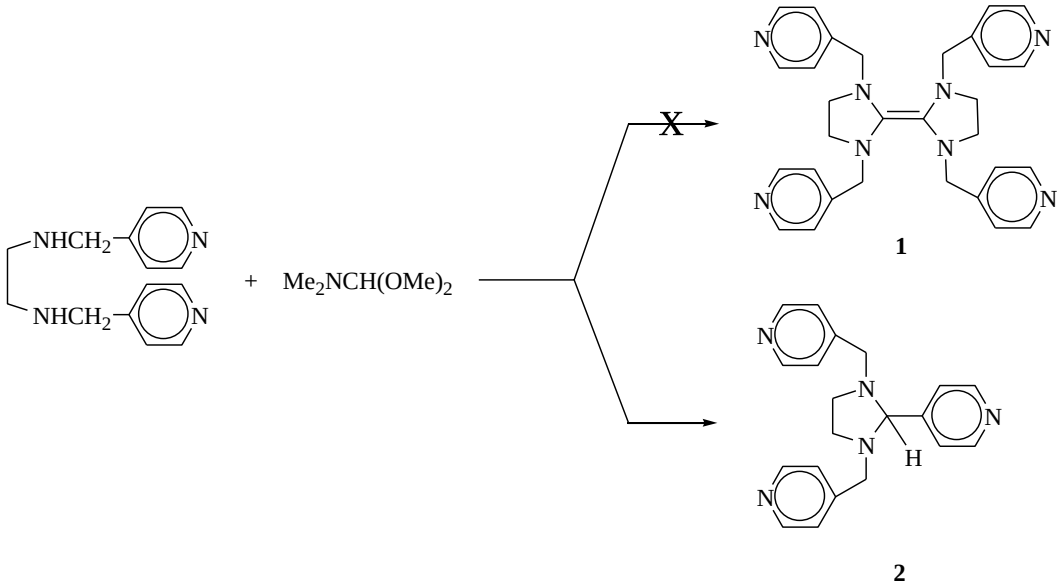
Abstract: The title compound was prepared by treatment of *N,N'*-di(4-picolyl-amino)ethane with *N,N*-dimethylformamide dimethylacetal in toluene and it was characterized by elemental analysis, ^{1}H NMR and ^{13}C NMR.

Keywords: electron-rich olefins; tetraaminoalkene; carbene

Introduction

Olefins with four electron-donating substituents react as nucleophiles and are referred to as electron-rich olefins [1,2]. These compounds have been used as strong reducing agents, precursors to carbene complexes, effective formylating agents for proton-active compounds, catalysts for benzoin-type C-C coupling reactions and chemoluminescent materials [3–7]. Carbene complexes, formed by treatment of an electron-rich olefin with metal, are air-stable and have been used for several catalytic applications including olefin metathesis, hydrogenation and hydrosilylation reactions [8–10]. Symmetric electron-rich olefins are generally prepared from an *N,N'*-disubstituted 1,2-diaminoethane with *N,N*-dimethylformamide dimethylacetal in an inert atmosphere [11]. Unsymmetric and bridged electron-rich olefins are prepared by a convenient salt elimination procedure [12]. The compound **1** was not obtained using the acetal procedure, and if formed, it would spontaneously rearrange to the compound **2**. This thermal amino-Claisen rearrangement was believed to be [3,3]-sigmatropic [13,14]. We report here on the synthesis and characterization of 2-(4-pyridyl)-1,3-di(4-picolyl)imidazolidine.

Scheme 1. Synthesis of 2-(4-pyridyl)-1,3-di(4-picolyl)imidazolidine.



Reagents and conditions: Toluene, 4 h, 90 ℃.

Experimental

Reaction for the preparation of 2-(4-pyridyl)-1,3-di(4-picolyl)imidazolidine was carried out under argon using standard Schlenk-type flasks. Solvents were dried using standard procedures and were distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H) and 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS and coupling constants (J) in Hertz. The melting point was measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and it is uncorrected. Elemental analyses was performed at TUBITAK Microlab (Ankara, Turkey).

Synthesis of 2-(4-pyridyl)-1,3-di(4-picolyl)imidazolidine (**2**)

A solution of *N,N'*-di(4-picolylamino)ethane (1.87 g; 8.5 mmol) and *N,N*-dimethylformamide dimethyl acetal (1.10 g; 9.27 mmol) in toluene (15 mL) was heated under reflux for 4 h at 90 ℃. The reaction mixture was then heated at 110 ℃ under distillation conditions, allowing the produced dimethylamine and methanol to escape. Hexane (10 mL) was added and a white solid precipitaded. The crude product was filtered off and washed with hexane (2 × 10 mL). The precipitate was then crystallized from toluene/hexane (10:10 mL). Yield: 0.93 g, 73%, m.p.: 125 ^{o}C.

^{1}H NMR ($CDCl_3$) δ: 3.3 (s, 1H, 2-C*H*), 1.71 and 2.52 (m, 4H, NCH_2CH_2N), 2.53 and 3.03 (m, 4H, CH_2C$_5$H$_4$N), 6.55 and 8.26 (d, 4H, J = 5.6 Hz, CH$_2$C$_5$$H_4$N and m, 4H, CH$_2C_5$$H_4$N), 6.88 and 8.25 (m, 4H, C$_5$$H_4$N).

^{13}C NMR($CDCI_3$) δ: 87.3 (2-*C*H), 50.8 (N*C*H$_2$*C*H$_2$N), 55.7 (*C*H$_2$C$_5$H$_4$N), 123.2, 147.2 and 150.2 (CH$_2$*C*$_5$H$_4$N), 124.1, 148.9 and 150.5 (*C*$_5$H$_4$N).

Anal. Calcd. for $C_{20}H_{21}N_5$: C, 72.50; H, 6.34; N, 21.14. Found C, 72.87; H, 6.12; N, 21.38.

References

1. Hoffman, R.W. Reactions of electron-rich olefins. *Angew. Chem. Int. Ed*. **1968**, *7*, 754–765.
2. Wiberg, N. Tetraaminoethylenes as strong electron donors. *Angew. Chem. Int. Ed*. **1968**, *7*, 766–779.
3. Bock, H.; Borrmann, H.; Havlas, Z.; Oberhammer, H.; Ruppert, K.; Simon, A. Structures of sterically overcrowded and chargeperturbed molecules. 12. tetrakis(dimethylamino) ethene an extremely electron-rich molecule with unusual structure both in the crystal and in the gas-phase. *Angew. Chem. Int. Ed*. *Engl*. **1991**, *30*, 1678–1681.
4. Cardin, D.J.; Çetinkaya, B.; Lappert, M.F.; Muir, L.J.M.; Muir, K.W. An electron-rich olefin as a source of co-ordinated carbene; Synthesis of trans-$PtCl_2[C(NPhCH_2)_2]PEt_3$. *Chem. Commun*. **1971**, 400–401.
5. Cardin, D.J.; Çetinkaya, B.; Çetinkaya, E.; Lappert, M.F.; Muir, L.J.M.; Muir, K.W. *Trans*-/*cis*-Isomerism and isomerisation of Pd(II) and Pt(II) carben complexes. *J. Organomet. Chem*. **1972**, *44*, C59–62.
6. Wanzlick, H.; Schikora, E. Ein nucleophiles Carben. *Chem. Ber*. **1961**, *94*, 2389–2393.
7. Lappert, M.F.; Maskell, R.K. A new class of benzoin condensation catalyst, the bis-(1,3-dialkylimidazolidin-2-ylidenes). *J. Chem. Soc., Chem. Commun*. **1982**, 580–581.
8. Çetinkaya, B.; Demir, S; Özdemir, İ.; Toupet, L.; Semeril, D.; Bruneau, C.; Dixneuf, P.H. First rutnenium complexes with a chelating arene carbene ligand as catalytic precursors for alkene metathesis and cycloisomerisation. *New J. Chem*. **2001**, *25*, 519–521.
9. Yiğit, M.; Yiğit, B.; Özdemir, İ.; Çetinkaya, E.; Çetinkaya, B. Active ruthenium-(N-Heterocyclic Carbene) complexes for hydrogenation of ketones. *Appl. Organometal. Chem*. **2006**, *20*, 322–327.
10. Lappert, M.F.; Maskell, R.K. Carbene-transition-metal complexes as hydrosilylation catalysts. *J. Organomet. Chem*. **1984**, *264*, 217–228.
11. Winberg, H.E.; Carnahan, J.E.; Coffman, D.D.; Brown, M. Tetraaminoethylenes. *J. Am. Chem. Soc*. **1965**, *87*, 2055–2056.
12. Çetinkaya, E.; Hitchcock, P.B.; Jasim, H.A.; Lappert, M.F.; Sypropoulos, K. Synthesis and characterisation of unusual tetraaminoalkenes (Enetetramines). *J. Chem. Soc., Perkin Trans. 1* **1992**, 561.
13. Boldwin, J.E.; Walker, J.A. Competing [1,3]- and [3,3]-sigmatropic rearrangements of electron-rich olefins. *J. Am. Chem. Soc*. **1974**, *96*, 596–597.
14. Chamizo, J.A.; Lappert, M.F. [3,3]- and [1,3]-Sigmatropic amino-Claisen rearrangements of electron-rich alkenes. *J. Org. Chem*. **1989**, *54*, 4684–4686.