

Synthesis of 1-(2-aminopyridine)-4-phenyl-1,3-butadiene and 1-(3-aminopyridine)-4-phenyl-1,3-butadiene as heterodienes for iron carbonyl complexes

A. A. Jarrahpour*, A. R. Esmailbeig and A. Adabi Ardekani

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran
Phone: +98 711 2284822, Fax: +98 711 2280926 Email: jarrah@chem.susc.ac.ir and aliasghar6683@yahoo.com

*Author to whom correspondence should be addressed

Received: 21 September 2005 / Accepted: 15 January 2006 / Published: 22 January 2006

Abstract: In this paper we propose the synthesis of 1-(2-aminopyridine)-4-phenyl-1,3-butadiene and 1-(3-aminopyridine)-4-phenyl-1,3-butadiene as new heterodienes for iron carbonyl complexes.

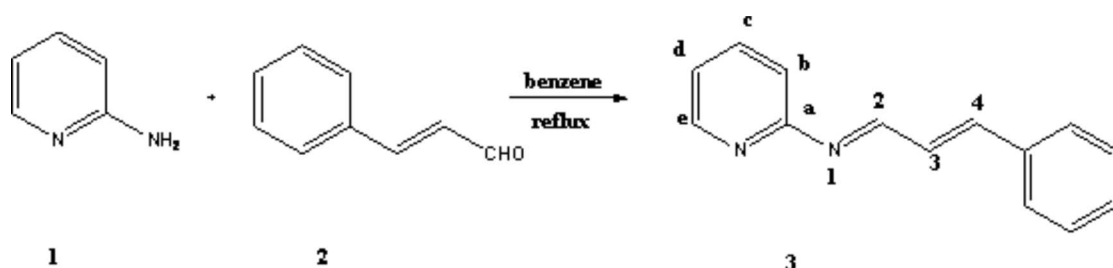
Keywords: 2-Aminopyridine, 3-aminopyridine, heterodiene, cinnamaldehyde, Schiff base.

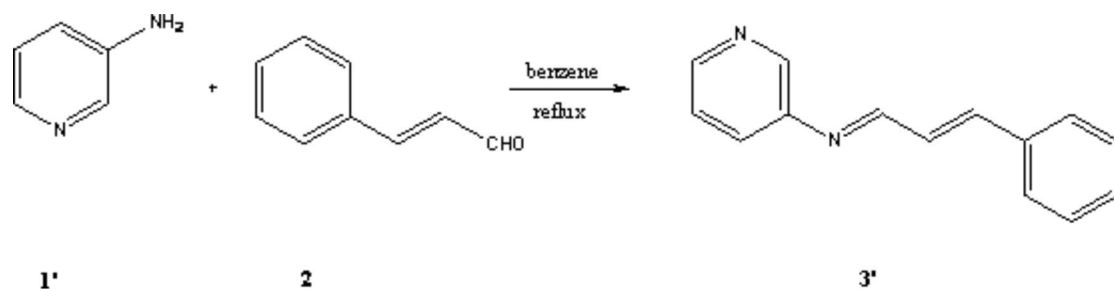
Introduction

Although a large number of p- (1,3-diene) iron tricarbonyl complexes have been reported and their reactivity investigated [1], less is known of the corresponding heterodiene compounds. In such compounds, which may be regarded as derived from the basic butadiene unit by the replacement of one or more of the carbon atoms by the oxygen or nitrogen, the possibility arises that the lone pair of electrons of the heteroatom is involved with the metal-ligand bond [2-5]. In this study we report the synthesis of two new Schiff bases derived from 2-aminopyridine, 3-aminopyridine and cinnamaldehyde. These compounds are potentially good ligands for iron carbonyl complexes.

Results and Discussion

A solution of 2-aminopyridine **1** (0.94g, 10.00mmol) in dry benzene (10mL) was added with stirring to a solution of cinnamaldehyde **2** (2.64g, 20.00mmol) in benzene (10mL). The reaction mixture was stirred at c.a. 40 °C for 4 hours. Most of solvent was removed by splash-guard adaptor attached to vessel. The residue of solvent was removed under reduced pressure. After returning to room temperature and addition of 100 mL of n-heptane, the mixture was allowed to stand overnight in a refrigerator. The upper layer was extracted and after removal of solvent, the remaining oil was allowed to stand for 2 days under hood at room temperature. The yellow crystals were separated by filtration and washed with two 3 mL portions of cold ether, yielding (1.42g, 68%) of **3**. The procedure for preparing **3'** was similar to **3**. Compound **3'** was a brown solid and its yield was 98%. Its physicochemical properties were almost the same with **3**. The IR spectrum showed the characteristic absorption of Schiff base C=N at 1580 cm⁻¹ and the C=C at 1551 cm⁻¹. The ¹H-NMR spectrum showed a multiplet for aromatic protons at 7.20-7.70 p.p.m. H^e had a doublet at 9.01 with a J= 8.80. A doublet appeared at 8.46 for H². H³ and H⁴ had a multiplet at 6.75. The ¹³C-NMR spectrum showed C=N group at 164.20. The mass spectrum showed the (M+1) peak at 209 and the M⁺ at 208. Their ability for coordination to metal ions are under study.





Melting Point: 68°C.

TLC (dichloromethane-acetone 20/1): $R_f = 0.56$

IR (KBr, ν , cm^{-1}): 1580 (s, C=N); 1551 (s, C=C).

$^1\text{H-NMR}$ (250 MHz, CDCl_3): $\delta = 9.01$ (1H, d, $J=8.8$, H^c); 8.46 (1H, d, H^2); 7.2-7.7 (8H, m, aromatic); 6.75 (2H, m, H^3 and H^4).

$^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3): $\delta = 164.2$ (C^2); 160.7 (C^a); 146.7 (C^e); 148.8 (C^3); 146.5 (C^4); 138.2 (C^c); 121.9 (C^d); 120.3 (C^b); 127.7-129.9 and 135.5 (Ph carbon atoms).

UV (EtOH; λ_{max} nm; ϵ ($\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$): 319 (18000); 226 (13000).

MS (m/z , %): 209 ($\text{M}^+ + 1$, 5.9); 208 (M^+ , 38.3); 207 ($\text{M}^+ - 1$, 50.5); 131 (100); 130 (77); 79 (87.5); 78 (54.2); 52 (49.4); 51 (52.6).

Elemental Analysis: Calculated for $\text{C}_{14}\text{H}_{12}\text{N}_2$: C, 80.77%; H, 5.76%; N, 13.46%. Found: C, 80.75%; H, 5.89%; N, 13.49%.

Acknowledgment

Authors thank the Shiraz University Research Council for financial support (Grant No.84-GR-SC-23).

References:

- Coates, G. E.; Green, M. L. H.; Wade, K. in *Organometallic Compounds*, Vol II, Methuen, London, **1969**, p 65.
- Dieck, H. T.; Bock, H. *Chem. Comm.* **1968**, 678.
- Maywald, F.; Eilbracht, P. *Synlett.* **1996**, 380-382.
- Wrackmeyer, B.; Seidel, G.; Köster, R. *Magnetic Resonance in Chemistry*, **2000**, 38 (7), 520-524.
- Kuramshin, A. I.; Kuramshina, E. A.; Cherkasov, R. A. *Russ. J. Org. Chem.*, 41 (5), **2005**, 649-655.

Sample Availability: Available from MDPI.

© 2006 MDPI. All rights reserved.