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Dipyrromethanes: Synthesis and Applications

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Abstract: *In this article we will discuss about the basics of dipyrromethanes, their synthetic methods and important applications in different fields of science and technology. Herein we will also discuss about the nature, stability and chemical properties using analytical tools. Structural investigation is one of the challenging parts of the research that we can also do in this work using different methods.*

Keywords: dipyrromethanes

I. INTRODUCTION

Dipyrromethanes is one of the nitrogen containing organic compound that is similar to half of the porphyries ring which has many biological applications.

Generally, bipyrrolic compounds are of wide interest in several areas, namely in porphyrins and related policycles, in materials, optics and medicine.

It has very important building blocks for many of the structures of interest in different fields of science and technology. The stability of dipyrromethanes towards oxidation is always a cause for apprehension during the synthetic procedure, isolation and storage of such compounds, a diversity of conditions have been established allowing good to excellent yields of dipyrromethanes to be obtained in the case when different substituents are present on the pyrrole rings. These substituents provide the stability of both the pyrrole precursors and the product.

In case of simple pyrrole rings, the dipyrromethanes are then flat to give further reactions leading to polymeric and highly reactive products, except in the specific case of some bipyrrolic cyclic compounds.

Dipyrromethane compounds are of wide interest in several areas, namely in porphyrins and related macrocycles,[1] science materials,[2] optics[3] and medicine.[4]

Dipyrromethanes are important building blocks for many of the structures of interest in the above-mentioned areas. But, the stability of dipyrromethanes from the oxidation of dipyrromethanes is always a cause for concern during the reaction, isolation and storage of such compounds; many conditions have been established for excellent yields of dipyrromethenes to be obtained in the case where different substituents are present on the pyrrole rings during dipyrromethanes synthesis. The substituents on pyrrole rings are attached for the stability of both the product dipyrromethanes and the pyrrole precursors[5,6]. Sometimes, In the case of unsubstituted pyrrole rings, the dipyrromethanes shows further reactions giving highly labile and polymeric products, except in the very few case of some polypyrrolic macrocycles.

The availability of pure pyrrole substituted dipyrromethanes is, however, of significant interest due to their importance in many building blocks and for the efforts have made during their preparation.

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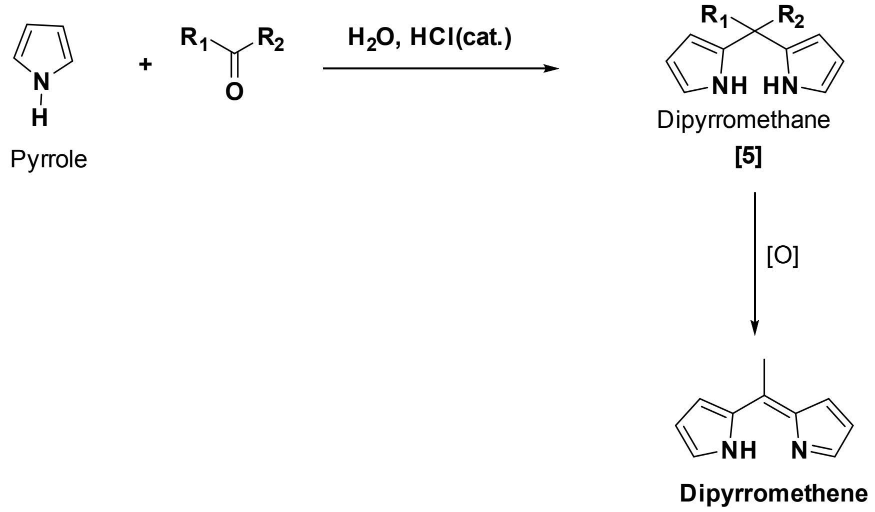

	R_1	R_2	Yield (%), with 2:1 pyrrole/carbonyl compound *(Dipyrromethanes)*
1	CH_3	C_6H_5	81
2	CH_3CH_2	CH_3CH_2	89
3	H	$(P\text{-}NO_2)C_6H_4$	36
4	H	H	27
5	H	C_6H_5	76

Scheme: Reaction scheme and the percentage yields

The above methods are based on the work of Lindsey et al.,[7] which is generally based on the acid-catalyzed condensation of the aldehydes and pyrrole, in the presence of a large excess of pyrrole, using strong acids like HCl and sometimes TFA. They must require a delicate time control to stop the reaction when the dipyrromethane concentration is at its maximum that we can identify using TLC during the reaction and involve a final workup to remove the excess unreacted pyrrole and starting materials.

Synthesis

In this experiment, we have taken a solution of 16 ml (0.14 mol) of 3-pentanone in 100 ml degassed water, 0.5 ml of 37% HCl(aq) are added, followed by the dropwise addition of 5 ml (0.7 mol) of pyrrole or substituted pyrrole and continue to refluxing at 100°C for 31 to 46 min the postponement is left for cooling up to 40–50°C and then the liquid part is transferred in to the other vessel and keep it to cool up to room temperature. The product obtained is large pale white crystals. *meso*-Phenyl-2,2-dipyrromethane 5, dipyrromethane 4 and *meso*-(4-nitrophenyl)2,2-dipyrromethane 3 gave physical data according to the literature.[7c] The product 1 and 2 are new compounds and 1 have the physical data mp: 108–110°C.

II. RESULTS AND DISCUSSION

In our experimental section, the area of porphyrin chemistry we observed that the drop-wise addition of pyrrole to the aqueous solution of required aldehydes or ketone in the presence of hydrochloric acid (HCl), gave the corresponding dipyrromethane in excellent yields up to 90 %, after 40–50 min at 100°C. In the cases where, aldehydes were used, the experiments were carried out under nitrogen atmosphere to control the oxidation of dipyrromethane to dipyrromethene shown in the scheme.

The success of our experiment is based on the fact that, the reaction between the pyrrole and the carbonyl compound occurs at the limit between the pyrrole and the acidic aqueous ketone or aldehyde solution. The separation and purification of the dipyrromethane from the aqueous layer as we observed during the reaction, forces the reaction to completion and protects the product from further reactions.[8]

The continuous TLC analysis of the reaction mixture during the course of the reactions shows the formation of the dipyrromethane in good yield in the first half hour at ~95°C in each case. When, we reflux for 3h experiment in water we observed two new compounds whose mass and fragmentation patterns related to those of the ‘*N*confused-dipyrromethane’ isomer and to the tripyrromethane.

The control the secondary products is an advantage of the method, which gives directly dipyrromethane samples of good purity. The purity of products is not only confirmed by GC–MS but also by the elemental analysis. The compounds were also detected by using several other methods of dipyrromethane or porphyrin synthesis as by-products.[9,10]

REFERENCES

[1]. Lee, C.-H.; Li, F.; Iwamoto, K.; Dadok, J.; Bothner-By, A. A.; Lindsey, J. S. *Tetrahedron* **1995**, 51, 11645–11672; (b) Shanmugathasan, S.; Edwards, C.; Boyle, R. W. *Tetrahedron* **2000**, 56, 1025–1046.

[2]. Drain, C. M.; Hupp, J. T.; Suslick, K. S.; Wasielewski, M.R.; Chen, X. *J. Porphyrins Phthalocyanines* **2002**, 6, 243– 258.

[3]. Okura, I. *J. Porphyrins Phthalocyanines* **2002**, 6, 268–270.

[4]. (a) Bonnett, R. *Chem. Soc. Rev.* **1995**, 4151–4202; (b) Sternberg, E. D.; Dolphin, D.; Bruckner, C. *Tetrahedron* **1998**, 54, 4151–4202; (c) MacDonald, I. J.; Dougherty, T. J. *J. Porphyrins Phthalocyanines* **2001**, 5, 105–129.

[5]. (a) *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed. Synthesis and preparation of porphyrin compounds; Elsevier, 1975; Chapter 2; (b) *The Porphyrins*; Dolphin, D., Ed. Synthesis of pyrroles and porphyrins via single step coupling of dipyrrolic intermediates. Academic Press, 1978; Chapter 4.

[6]. (a) Okada, K.; Saburi, K.; Nomura, K.; Tanino, H. *Tetrahedron* **2001**, 57, 2127–2131; (b) Montalban, A. G.; Herrera, A. J.; Johannsen, J.; Beck, J.; Godet, T.; Vrettou,

[7]. (a) M.; White, A. J. P.; Williams, D. J. *Tetrahedron Lett*. **2002**, 43, 1751–1753. (b) Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, 50, 11427–11440; (b) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, 64, 2864–2872; (c) Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O’Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, 64, 1391–1396; (d) Yu, L.; Lindsey, J. S. *Tetrahedron* **2001**, 57, 9285–9298.

[8]. (a) Breslow, R. *Acc. Chem. Res.* **1991**, 24, 159–164; (b) Li, C.-J. *Chem. Rev.* **1993**, 93, 2023–2035; (c) Ludwig, R. *Angew. Chem., Int. Ed.* **2001**, 40, 1808–1827; (d) Engberts, J. B. F. N.; Bladamer, M. J. *Chem. Commun.* **2001**, 1701–1708.

[9]. (a) Geier, G. R., III; Lindsey, J. S. *J. Chem. Soc., Perkin Trans.* 2 **2001**, 687–700; (b) Geier, G. R., III; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **2002**, 6, 159–185.

[10]. Ka, J.-W.; Lee, C.-H. *Tetrahedron Lett*. **2000**, 41, 4609– 4613.

[11]. (a) Jiuh, K.; Wu, J.-Y.; Chen, C.-T. *Acta Crystallogr.* **1996**, C52, 3114–3116; (b) Gallagher, J. F.; Moriarty, E. *Acta Crystallogr.* **1999**, C55, 1079–1082.

[12]. Johnson, C. K. ORTEPII. Report ORNL-5138, OakRidge National Laboratory, TN, USA, 1976.

[13]. Sheldrick, G. M. SHELXS-97 and SHELXL-97, Univ.of Go¨ttingen, Germany, 1997