

New Synthesis of 2,2'-Bipyrrole by Dimerization of Pyrroles

Jeong Soo Ahn · Hwang Hur · Dong Sul Hahn*

Dept. of Chemistry

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〈Abstract〉

Oxidative coupling of 1-benzoylpyrroles by platinum acetate in acetic acid gave the 1,1'-dibenzoyl-2,2'-bipyrrole, which was easily hydrolysed in methanol-water mixture containing HCl to give 2,2'-bipyrrole in good yield.

Pyrrole의 이합체화에 의한 2,2'-Bipyrrole의 새로운 합성법

안 정 수 · 허 황 · 한 동 설*

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〈요 약〉

1-Benzoylpyrrole을 아세트산 백금 촉매하에서 산화시켜 1,1'-dibenzoyl-2,2'-bipyrrole을 얻었고, 이 물질은 메탄올-물 혼합용매속에서 염산으로 가수분해시켜서 2,2'-bipyrrole을 좋은 수율로 얻었다.

I. Introduction

In recent years synthetic methods for polycyclic compounds containing the pyrrole ring, which are of interest in connection with existence of biologically active substances, have been extensively investigated. 2,2'-bipyrroles are of interest owing to their connection with naturally occurring compounds such as vitamin B₁₂⁽¹⁾, prodigiosin and related pigments^{(2) (3)}. However, no easy and simple method for the preparation of 2,2'-bipyrrole has been found, although Rapoport and castagnoli⁽⁴⁾ have been reported the synthesis of 2,2'-bipyrrole from 2-pyrrolidin-2-yl-pyrrole. It was already indicated from Rapoport's observations that pyrrolinylpyrrole could be converted to bipyrrole

by catalytic dehydrogenation as methods of aromatizing pyrrolynylpyrrole, the latter compound being obtained by the condensation of 1-pyrroline with pyrrole or a substituted pyrrole, but proved ineffective.

Dimerization of pyrroles as an efficient method for the preparation of 2,2'-bipyrrole has been paid little attention although coupling reactions of olefins of aromatic compounds are well known. Our present investigation was examined that 2,2'-bipyrrole is obtained by oxidation of pyrroles in good yield, and found that dimerization of 1-benzoylpyrroles by platinum acetate in acetic acid gives the corresponding 1,1'-dibenzoyl-2,2'-bipyrroles. The preparation of 1-benzoyl-pyrrole was carried out by applying the Itahara's synthetic method of 1-benzoylindole.⁽⁵⁾

*Seoul National University

II. Experimental

1. General

All reactions were run under a positive nitrogen pressure. Silica gel, Kieselgel P/UV254 (Merck) was employed for all analytical and preparative chromatograph. The following compounds were used without further purification as purchased: pyrrole (Merck), sodium hydride (Aldrich), platinum acetate (Aldrich), benzoyl chloride (Kanto), dimethylformamide (Kanto). Melting points are corrected and were taken in evacuated capillaries. UV spectra were taken in methanol on Perkin-Elmer M534 Spectrophotometer. IR spectra were taken in chloroform on Hilger and Watts' Infracgraph H 1200 MK2. NMR spectra were measured in deuteriochloroform using a Varian model A-60 spectrometer.

2. Preparation of 1-benzoylpyrrole

To a stirred solution of pyrrole (30 m mole) and sodium hydride (30 m mole) in dimethylformamide (80ml), benzoyl chloride (30 m mole) in dimethylformamide (30 ml) is added on the nitrogen atmosphere. The solution is heated as $75 \pm 3^\circ\text{C}$ for 10 hours. The reaction mixture is poured into an excess of ice-cooled water and extracted with benzene. The benzene extract is dried with sodium sulfate and evaporated to give a yellow oily residue. The residue is chromatographed on the silica gel column with petroleum ether-benzene to give 1-benzoylpyrrole.

3. Preparation of 1,1'-dibenzoyl-2,2'-bipyrrole

A mixture of 1-benzoylpyrrole and 0.30 equivalent of platinum acetate in acetic acid was heated at 120°C under nitrogen for 10 hours.

The mixture was evaporated to give a brown oily residue which was chromatographed on silica gel to give 1,1'-dibenzoyl-2,2'-bipyrrole, mp $148 \sim 150^\circ\text{C}$, in 32% yield.

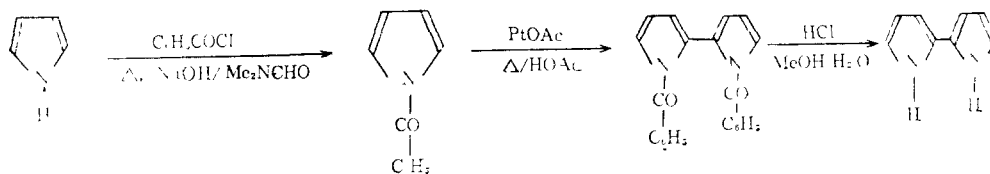
4. Preparation of 2,2'-bipyrrole

1,1'-dibenzoyl-2,2'-bipyrrole was treated in MeOH-H₂O with HCl at 60°C for 5 hours. The precipitated bipyrrole was collected, washed with hexane, and sublimed at 90° (0.2mm) to give 87% yield of pure 2,2'-bipyrrole, m. p. 190°C . (reported 187° ⁽³⁾, $189 \sim 190^\circ$ ⁽⁴⁾). Elemental analysis: calcd. for C₈H₈N₂; C, 72.7; H, 6.1; N 21.2. Found: C, 72.6; H, 6.0, N, 21.5.

III. Results and Discussion

Total synthesis of 2,2'-bipyrrole was carried out according to the general procedure used in the aromatic oxidative coupling reaction, the following reaction sequence might take place.

2,2'-bipyrrole by oxidative coupling of pyrroles was characterized spectroscopically and by elemental analysis (Table 1). Infrared spectra show strong absorption band at 3485 and 1610cm^{-1} correspond to a pyrrolic N-H and a C=N stretch, respectively. Ultraviolet absorption spectra in methanol of 2,2'-bipyrrole show 274, 278, 284 and 298nm of λ_{max} . Nuclear magnetic resonance spectra of this compound has proton peaks at 10.31(H⁽¹⁾), 6.22(H⁽³⁾) and

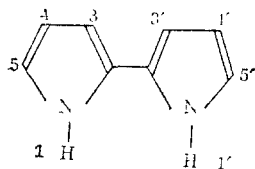


H⁽⁴⁾) and 6.46(H⁽⁶⁾) δ .

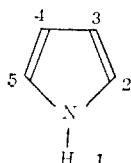
The UV absorption spectra of this material in alkali shows a bathochromic shift upon acidification. This shift is to be expected, since protonation of the imino nitrogen results in the formation of an extended π -system.

Table 1. Observed data of 2,2'-bipyrrole

UV in MeOH	λ_{\max}	298nm(ϵ 8,300)
		284 (ϵ 16,600)
		278 (ϵ 17,500)
		274 (ϵ 16,800)
IR in CHCl ₃		3485cm ⁻¹ (ν_{N-H})
		1610 ($\nu_{C=N}$)
NMR in CDCl ₃	δ 10.31	H ⁽¹⁾
	6.22	H ⁽³⁾ H ⁽⁴⁾
	6.46	H ⁽⁶⁾
Mol. Wt(Rast's method); 128 \pm 2		
Elemental anal. C, 72.6; H, 6.0; N 21.5		



2,2'-bipyrrole



pyrrole

cf. NMR spectra of pyrrole in CDCl₃;
 δ 6.22 H⁽³⁾ H⁽⁴⁾, 6.88 H⁽²⁾ H⁽⁶⁾, 8.0 H⁽¹⁾

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