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Short Note

Synthesis and Characterization of a Novel 2-Pyrazoline

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Abstract: Reaction of dibenzalacetone with hydrazine hydrate and formic acid yielded a novel 2-pyrazoline **1**, characterized by ESI-MS, FT-IR, UV, ^{1}HNMR and ^{13}CNMR data and microanalysis.

Keywords: dibenzalacetone; hydrazine hydrate; pyrazoline; 5-phenyl-3-[(*E*)-2-phenyl-vinyl]-4,5-dihydro-1*H*-pyrazole-1-carbaldehyde; fluorescence

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Introduction

Substituted pyrazolines are useful in pharmaceutical and agrochemical research. Pyrazoline derivatives with a phenyl group at the 5-position possess good film-forming properties, exhibit excellent characteristics of blue photoluminescence and electroluminescence [1]. Pyrazolines are also used as optical brighteners and whiteners. Pyrazolines display various biological activities such as antimicrobial [2], antifungal [3], antidepressant [4], immunosuppressive [5], anticonvulsant [6], anti-tumor [7], antiamoebic [8], antibacterial [9] and antiinflammatory [10] activities. Syntheses of pyrazolines by reaction of α,β-unsaturated carbonyl compounds with diazoalkanes [11] or with hydrazine hydrate [12,13] were reported in literature. N-Substituted thiocarbamoyl-3,5-diphenyl-2-pyrazoline derivatives having NS donor, their palladium II complexes [14] and hydroxyl phenyl pyrazolines have also been synthesized [15]. The reaction of *E*-arylidenes with diazomethane affords *trans*-pyrazoline while *Z*-arylidines gave *cis*-isomers [16]. 1,3-Dipolar cycloaddition of exocyclic α,β-unsaturated ketones with dibenzomethane has also been studied in detail [17–22]. The present paper deals with the synthesis of novel 5-phenyl-3-[(*E*)-2-phenylvinyl]-4,5-dihydro-1*H*-pyrazole-1-

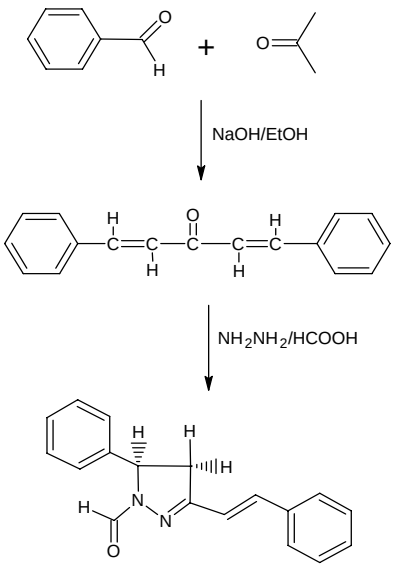
carbaldehyde from the reaction of dibenzalacetone and hydrazine hydrate with formic acid and its characterization by spectroscopic techniques.

Results and Discussion

The structure of the reaction product (Scheme 1) has been elucidated by UV, IR, ^{1}HNMR, ^{13}CNMR, ESI-MS spectroscopic techniques and the progress of reaction was monitored by TLC. The ESI mass spectrum indicated its molecular mass to be 276 (by protonated and pseudo molecular ions). The IR spectrum of compound **1** showed a strong band for the carbonyl group at 1640 cm^{-1} and a band at 1560 cm^{-1} for C=N. In the ^{1}HNMR spectra, an ABX pattern was observable, H_A, H_B and H_X appear as doublet of doublets at δ 3.1, 3.6 and 5.5 ppm with J_{AB} = 17.6 Hz, J_{AX} = 4.8 Hz, J_{BX} = 11.6 Hz. The protons of the aromatic ring were observed at δ 7.2-7.4 ppm and the formyl proton occurred as a singlet at δ 8.9 ppm. A pair of the *trans*-olefinic proton doublets appears at 6.8 and 7.1 ppm with *J* value of 16.2 Hz. The electronic spectra of the 1-formylpyrazoline (studied in the UV region) in methanol showed three absorption bands at ~ 407, 337, 321 nm assignable to n-π*, π- π* and n-σ* transitions.

Substituted pyrazolines have strong fluorescence in different solvents. They also give excellent fluorescence properties in solid state because the conjugation system contains two nitrogen atoms and one carbon atom while the other carbon atoms are sp^3 hybridized. The fluorescence spectrum of compound **1** showed an intense emission with λ_{em} = 398.3 nm and 451.9 nm at 330 nm excitation in methanol.

Scheme 1.



Experimental

Reaction of dibenzalacetone, hydrazine hydrate and formic acid afforded a crude product which was recrystallized from chloroform to give **1.** Progress of the reaction was monitored by TLC, using hexane: ethyl acetate (8:2) as mobile phase. All the starting materials were AR/GR quality of Merck.

Melting points have been recorded in open capillary with Metzer apparatus and are uncorrected. IR spectra were recorded for KBr pellets on a Perkin-Elmer FT-IR-RX-01 spectrophotometer. UV Spectra were recorded on a Perkin-Elmer double beam UV-Visible spectrophotometer (λ-25) in methanol. Fluorescence spectra were recorded on a Perkin-Elmer LS-55 spectrofluorimeter; for fluorescence, an excitation lamp (Xe, 150 W) interfaced with the computer was used. ^{1}HNMR Spectra were obtained in $CDCl_3$ on a Bruker Spectrospin DPX-300 spectrometer (300 MHz) using TMS as the internal standard.

Preparation of dibenzalacetone

30 mmol of benzaldehyde and 15 mmol of acetone were dissolved in methanol. The round-bottomed flask was placed in an ice bath and the mixture was stirred for 3 h with addition of 11% NaOH (cold solution) drop by drop. The resultant mixture was left to stand for 2 h. The yellow precipitate was crystallized from methanol to afford dibenzalacetone**.** Yield: 90%, m.p.112 °C [23–26].

Preparation of 5-phenyl-3-[(*E*)-2-phenylvinyl]-4,5-dihydro-1*H*-pyrazole-1-carbaldehyde

To a mixture of 5 mmol of dibenzalacetone in 5 ml of formic acid, 10 mmol of hydrazine hydrate in 5 mL of ethanol were added dropwise. The reaction mixture was refluxed for 24 h with constant stirring; the resultant solution was cooled and poured into crushed ice. The crude reaction product was recrystallized from ethyl acetate to afford compound **1** in 80% yield as pale yellow crystals, m.p.120–122 °C. Anal. Calc. for $C_{18}H_{16}N_2O$: C, 78.24, H, 5.84, N, 10.14; found: C, 78.13, H, 5.76, N, 10.12; UV/VIS λ_{max} nm. 407, 337, 321; IR ν_{max}: cm^{-1} 1640 (C=O), 1610 (CH=CH), 1560 (C=N), 1127 (C-N). ^{1}HNMR ($CDCl_3$) δ ppm: 3.1 (dd, J = 4.8, 17.6 Hz, 1H), 3.6 (dd, J = 11.6, 17.4 Hz, 1H), 5.5 (dd, J = 4.8, 11.5 Hz, 1H, H-5), 6.8 (d, J = 16.2 Hz, 1H, H-α), 7.1 (d, J = 16.2 Hz, 1H, H-β), 7.2-7.5 (m, 10H, 2 × Ph). ^{13}CNMR ($CDCl_3$) δ ppm: 159.82 (C=O), 141 (C=N), 138-120 (=CH, Ph), 58 (-CH), 41.3 ($-CH_2$). ESI-MS: 277 $(M+H)^+$, 299 $(M+Na)^+$, 315 $(M+K)^+$.

Conclusions

We have successfully synthesized a novel pyrazoline, namely 5-phenyl-3-[(*E*)-2-phenylvinyl]-4,5-dihydro-1*H*-pyrazole-1-carbaldehyde and characterized it by spectroscopic methods. Quantitative fluorescence studies and evaluation of the biological activity of the new compound are in progress.

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