



PHOTOCYCLISATION OF 2'-HYDROXYCHALCONES INTO 2- PYRAZOLINES UNDER IRRADIATION OF SOLAR ENERGY

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An efficient and facile reaction has been shown between 2-hydroxychalcone with hydrazine hydrate in ethanol in presence of catalytic amount of glacial acetic acid under irradiation of solar thermal energy to afford 2-pyrazoline. Cyclised product established on the basis of IR, NMR, MS, ¹³C NMR and elemental analysis.

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Introduction

Chalcones (1,3-diaryl-2-propene-1-ones) constitute an important class of naturally occurring flavonoid compounds that exhibit a wide spectrum of biological activities and are well-known intermediates for synthesizing various heterocycles.

Amongst five-membered heterocycles, pyrazolines represent a class of compounds of great importance in heterocyclic chemistry.^{1,2} Substituted pyrazolines are fluorescent compounds with high quantum yields and are used as optical brighteners and whiteners.³

2-Pyrazolines exhibit good characteristics of blue photoluminescence, electroluminescence and as fluorescence.⁴ Among the methods employed in the synthesis of 2-pyrazolines, the condensation of α,β -unsaturated carbonyl compounds with hydrazine and hydroxylamine is commonly used. Recently various modified methods for the preparation of 2-pyrazolines using mercury(II) acetate,⁵ Zn,⁶ KHSO₄.H₂O/SiO₂,⁷ tungstophosphoric acid,⁸ Lewis acid/Lewis base⁹ and porous calcium hydroxyapatite catalyst.¹⁰ The reaction combination of solvent, costly chemicals/catalyst and long reaction time makes these methods economically expensive. Thus utilization of non-toxic chemicals, renewable materials and simple reaction conditions are the key issues of synthetic chemistry.

In view of these observations, we report herein, the synthesis of 2-pyrazolines by the condensation α,β -unsaturated ketone with hydrazine hydrate in ethanol in presence of glacial acetic acid under exposure of sunlight (Scheme-1). The formation of this class of five-membered heterocyclic compounds was characterized by spectroscopic technique.¹³

Methods and Materials

Instrumentation

Reaction of chalcone, hydrazine hydrate afforded a single compound. The progress of reaction was monitored by TLC, using hexane/ethyl acetate as the mobile phase. Melting points were determined in an open capillary tube and are uncorrected. IR spectra were recorded in KBr pellets on a Perkin-Elmer FT-IR Shimadzu spectrometer. ¹H and ¹³C NMR spectra were obtained in DMSO-d₆ on Avance 300 MHz spectrometer using TMS as an internal standard. The mass spectra were recorded on EI-Shimadzu-GC-MS spectrometer. Elemental analyses were performed on a Carlo Erba 106 perkin-Elmer model 240 analyzer.

Typical procedure for synthesis of 2-pyrazolines

A mixture of 2'-hydroxychalcones **1** (0.01 mol) and hydrazine hydrate (0.02 mol) was dissolved in ethanol in 20 ml ground-glass test tube. To this reaction solution a glacial acetic acid (0.001 mmol) was added and the ground-glass test tube was closed with a ground-glass plug, and was supported in an inverted position in beaker and exposed to direct sunlight for 25-30 min. at 43 °C. The progress of reaction was monitored on TLC. After exposure to sunlight, resulting solid product was collected by filtration and recrystallized from EtOH to yield **2**.

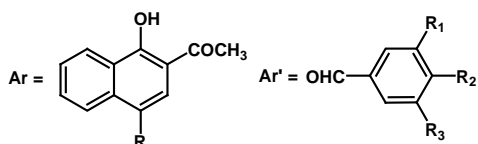
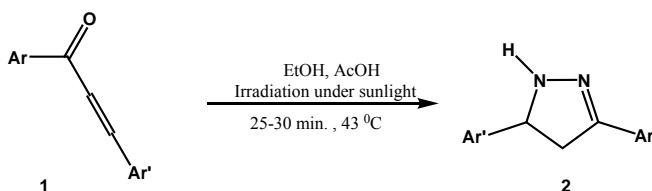
2-[5-(3,4,5-Trimethoxy-phenyl)-4,5-dihydro-1H-pyrazol-3-yl]-naphthalen-1-ol

Crystal appearance: Faint green. Yield: 92 %, M.P.: 192 °C. IR (KBr pellets): 3322 (N-H), 1589 (C=N), 1472, 1542 (C=C), 1232, 1130 (C-N) cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆) δ 12.34 (s, 1H, OH), 7.48-8.37 (m, 8H, Ar-H), 6.87 (s, 1H, NH), 3.21 (dd, *J* = 4.8, 17.5 Hz, 1H, H_A), δ 3.72 (dd, *J* = 11.8, 17.5 Hz, 1H, H_B), δ 4.89 (dd, *J* = 4.8, 11.9 Hz, 1H, H_X), δ 3.80 (s, 3H, OCH₃), 3.42 (s, 6H, OCH₃). ¹³C NMR (DMSO): 154.05 (C of Ar-OH), 153.28 (C of C=N), 148.67 (C of Ar-OCH₃), 148.42 (2C of Ar-OCH₃) 134.13 (Ar-C), 133.19 (Ar-C), 128.23 (Ar-C), 128.36 (Ar-C), 127.41 (Ar-

C), 126.30 (Ar-C), 124.97 (Ar-C), 122.71 (Ar-C), 121.28 (Ar-C), 112.65 (Ar-C), 110.86 (Ar-C), 110.32 (Ar-C), 62.39 (3C of OCH₃), 56.36 (C of CH), 42.37 (C of CH₂). MS m/z: 378 (M⁺, 80%), 377, 361, 347, 287, 231, 211, 210, 181, 168, 140, 128, 115, 109, 95, 77, 65, 51, 40. Anal. Calcd. for C₂₂H₂₂O₄N₂: C, 69.84; H, 5.82. Found: C, 70.92; H, 5.98.

2-[5-(3,4-Dimethoxy-phenyl)-4,5-dihydro-1H-pyrazol-3-yl]-4-iodo-naphthalen-1-ol

Crystal appearance: Faint green. Yield: 88 %, M.P.: 164 °C. IR (KBr pellets): 3319 (N-H), 1592 (C=N), 1468, 1546 (C=C), 1229, 1134 (C-N) cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆) δ 12.2 (s, 1H, OH), 7.22-8.23 (m, 8H, Ar-H), 6.78 (s, 1H, N-H), 3.23 (dd, *J* = 5.0, 17.5 Hz, 1H, H_A), 3.77 (dd, *J* = 12.0, 17.6 Hz, 1H, H_B), 4.92 (dd, *J* = 5.0, 12.0 Hz, 1H, H_X), 3.40 (s, 6H, OCH₃). ¹³C NMR (DMSO): 154.12 (C of Ar-OH), 153.21 (C of C=N), 148.62 (2C of Ar-OCH₃), 133.27 (Ar-C), 130.46 (Ar-C), 127.30 (Ar-C), 128.78 (Ar-C), 127.46 (Ar-C), 126.34 (Ar-C), 124.80 (Ar-C), 122.50 (Ar-C), 121.25 (Ar-C), 112.70 (Ar-C), 110.94 (Ar-C), 110.28 (Ar-C), 62.43 (2C of OCH₃), 56.39 (C of CH), 42.33 (C of CH₂). ¹³C NMR (DMSO) 146 (C=N), 139-112 (=CH, Ph), 48.62 (-CH), 40.35 (-CH₂), 52.42 (-OCH₃). MS m/z: 474, (M⁺, 65%), 443, 412, 347, 286, 228, 207, 128, 112, 77, 65, 51, 40. Anal. Calcd. for C₂₁H₁₉O₃N₂I: C, 53.16; H, 4.00; X (I), 26.73. Found: C, 50.39; H, 4.28; X (I), 26.75.



R: H, I; R₁: OCH₃, H; R₂, R₃: OCH₃.

Result and discussion

In our recent success on different methodology in organic synthesis towards the development of novel heterocyclic compounds,¹¹⁻¹⁶ in present communication we have described the photocyclisation of 2'-hydroxychalcones by the reaction of **1** with hydrazine hydrate in presence of catalytic amount of acetic acid using solar thermal energy to afford 2-pyrazolines **2**. The starting chalcones were prepared by well-known Claisen-Schmidt condensation under solvent-free conditions.¹⁵ The use solar energy can be considered as ideal green route for synthesis of 2-pyrazolines since they are easily available natural source, could be successfully used in place of toxic or expensive chemicals to overcome the activation energy in organic synthesis.

Initially we attempted the condensation of 1-(4-bromo-1-hydroxy-naphthalen-2-yl)-3-(3,4,5-trimethoxy-phenyl)-propenone **1** (0.01 mol) with hydrazine hydrate (0.02 mol) in 15 ml ethanol using glacial acetic acid in combination with solar energy irradiation. The reaction went completion

within 25 min at temperature 43 °C and corresponding product **2** obtained in 92% yield. Their IR spectra show absence of carbonyl absorption band and the appearance of characteristic absorption band for ν C=N at 1592-1588 cm⁻¹ and a band at 1130 cm⁻¹ for C-N. In the ¹H NMR spectrum, an ABX pattern was observable, H_A, H_B and H_X appear as double doublets at δ 3.10-3.30, 3.75-3.80 and 4.90-5.0 ppm with *J*_{AB} = 17.5 Hz, *J*_{AX} = 4.8 Hz, and *J*_{BX} = 11.8 Hz and singlet of 2-H pyrazolines around at δ 6.85 ppm respectively. The ¹³C NMR spectrum revealed the presence of a methylene carbon at δ 42.37 ppm, a methine carbon at δ 56.36 ppm and C=N at 153.28 ppm. The signals at δ 110.3-148.6 ppm show the presence of the aryl groups in the structure.

Conclusion

We have described efficient and simple practical procedure for synthesis of 2-pyrazoline using solar thermal energy. Present method is simple, economically cheaper and consistent with the green chemistry approach because it does not need heating.

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