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**REACTION OF HYDRAZINE HYDRATE AND HYDRAZINE HYDROCHLORIDE WITH
DIBENZOYLMETHANE AND FLAVONE: ROLE OF SOLVENT AND pH ON
FORMATION OF PRODUCTS**

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Abstract:

Selection of solvent and pH of the reaction mixture are important for the formation of desired products. Ethanol and DMF as reaction medium, pH was kept either basic (pH 10) or acidic (pH 4). Hydrazine hydrate and hydrazine hydrochloride in ethanol gave different product with dibenzoylmethane. Flavones with hydrazine hydrate in ethanol gave a product similar to that obtained by the action of hydrazine hydrate on dibenzoylmethane in ethanol. Flavones with hydrazine hydrochloride in DMF only to give flavone hydrazones. Dibenzoylmethane with hydrazine hydrate in ethanol gave pyrazole, but with hydrazine hydrochloride in ethanol gave flavone hydrazones. Flavones with hydrazine hydrochloride in DMF gave flavone hydrazones.

With hydrazine hydrate (pH 10) dibenzoylmethane and flavone gave pyrazole while dibenzoylmethane with hydrazine hydrochloride (pH 4) gave flavone hydrazone.

Key Words: Dibenzoylmethane, flavone, pyrazole, hydrazine hydrochloride, hydrazine hydrate, pH.

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Introduction:

Analysis of literature survey for the reactions of hydrazine hydrate and hydrazine hydrochloride with dibenzoylmethane and flavones reveals that the various products formed are dependent on the reaction condition. In the recent years, organic reactions carried out in aqueous media have received attention from chemists because of the concerns about the environment [1-3]. Several pyranopyrazoles are synthesized by iodine catalysed four component reactions in aqueous medium[4]. Pyrazole, pyrazole carboxamide and pyrazole carbothimide were synthesized by the reactions of substituted

prop-2-en-1-one with hydrazine hydrate, semicarbazide hydrochloride and thiosemicarbazide hydrochloride respectively[5]. Many pyrazole derivatives shows pharmacological properties and are widely used as pharmaceuticals, anesthetics, analgesics [6], antiaggregative agent [7], agrochemicals [8, 9].

Flavonoids [10] are ubiquitous group of polyphenolic substances which are present in most of the plants. Flavonoids have been shown to have antimicrobial, anti-inflammatory, antiallergic, antimatagenic, antiviral, antineoplastic, antithrombotic and vasodilatory activity. The potent antioxidant activity of flavonoids, their ability to scavenge hydroxy radicals, superoxide anion and lipid peroxy radicals may be the most important function of flavonoids. Substituted pyrazoles have been synthesized by refluxing with nucleophile such as isonicotinic acid / hydrazide/semicarbazide/ thiosemicarbazide in DMF solvent [11]. Substituted Chalcone on treatment with hydrazine hydrate in DMSO and catalytic iodine result in the formation of pyrazole[12]. Pyrazoles can also be synthesized from flavones [13] with hydrazine.

Herein author has tried to establish exact condition for the synthesis of desired product and also for the maximum yield. Selection of solvent and pH of the reaction mixture are important for the formation of desired product. After a good literature survey and exhaustive experimentation using number of solvents, the ethanol and dimethyl formamide (DMF) were selected as the reaction media, pH was kept either too basic (pH=10) or acidic (pH=4) side.

Experimental:

All melting points were determined in open capillaries on electrically heated melting point apparatus and were uncorrected. Purity of all

synthesized compounds were checked on silica gel-G plate using iodine as detecting agent.

Materials and Method:

Ethanol, p-Cresol (SD Fine), Benzaldehyde, Anisaldehyde (LOBA Chem.), Hydrazine hydrate, Hydrazine hydrochloride (E. MERK) were A.R. grade. The solvents were purified by double distilled before use.

Dibenzoylmethane **1a-b** were prepared by standard procedure as reported earlier [14].

Reactions of dibenzoylmethane with hydrazine hydrate in ethanol:

1a or **1b** (0.01mol) and hydrazine hydrate (0.01mol) were dissolved in ethanol (20ml). The reaction mixture was refluxed for 3h. Cooled and poured in cold water. The product separated was crystallized from rectified spirit to get 3-(2-hydroxy-5-methylphenyl)-5-(4-methoxyphenyl)-pyrazole, **2a** m.p. 170°C (lit.[15] 170°C); **2b** m.p. 156°C (lit.[16] 156°C). Alcoholic solution of **2a-b** gave green coloration with ferric chloride solution.

Reactions of flavones with hydrazine hydrate in ethanol:

Flavones **4a** or **4b** (0.01 mol) and hydrazine hydrate (0.02 mol) were dissolved in ethanol (20ml) and refluxed for 3h. The reaction mixture as worked out as above to get pyrazole **2a** or **2b**. (Identified by m.p., m. m. p. and Co-TLC).

Reactions of dibenzoylmethane with hydrazine hydrochloride in ethanol:

1a or **1b** (0.01 mol) and hydrazine hydrochloride (0.01mol) were dissolved in ethanol (20ml) and refluxed for 3h. The reaction mixture was poured in cold water and a solid thus separated was crystallized from ethanol to get orange color fibrous crystals of flavones hydrazone **3a**, m.p. 115°C or **3b** m.p. 109°C.

Reaction of flavones with hydrazine hydrochloride in DMF:

Flavones **4a** or **4b** (0.01 mol) and hydrazine hydrochloride (0.02 mol) were dissolved in DMF (20 ml) and refluxed for 3h. The reaction mixture was diluted with water and the solid thus separate was crystallized from rectified spirit to get orange colored compound **5a** or **5b** in 80% yields which were found to be identical with **3a** or **3b** (m.p., m.m.p. and Co-TLC).

Results and Discussion:

Hydrazine hydrate and hydrazine hydrochloride in ethanol gave different products with dibenzoylmethane. Flavones with hydrazine hydrate in ethanol gave a product similar to that obtained by the action of hydrazine hydrate on dibenzoylmethane in ethanol. Flavones reacted with hydrazine hydrochloride in DMF only to give flavones hydrazone. 2-Hydroxy-4-methyl dibenzoyl methane **1a**, with hydrazine hydrate in ethanol for 3 hours gave a light pink colored compound **2a**. Its alcoholic solution gave green color with neutral ferric chloride solution. Elemental analysis for **2a** C, 73; H, 6; N, 9.8% calculated for C₁₇H₁₆N₂O₂. C, 72.85; H, 5.8; N, 10%.

I.R.: 780s and 820s for the adjacent H of Ar-H, 900 for isolated H of Ar-H, 1380, 1470 for NH, 1600 for C=N, broad 2900 OH phenolic H-bonded and 3400 cm⁻¹s for -NH.

PMR: (in CDCl₃, tetramethylsilane as internal standard) δ 2.4 (s, 3H, Ar-CH₃), 3.83 (s, 3H, Ar-OCH₃), 6.05 (s, 1H, C-H), 6.88-7.90 (m, 7H, Ar-H). **2a** was given the structure of 3-(2-hydroxy-5-methylphenyl)-5-(4-methoxyphenyl)-pyrazole. Similarly 2-hydroxy-5-methyldibenzoylmethane **1a** gave 3-(2-hydroxy-5-methylphenyl)-5-phenylpyrazole **2b**. Flavones **4a-b** with hydrazine hydrate in ethanol on refluxing for 3h gave pyrazole identical with **2a-b** in 70% yields.

1a or **1b** with hydrazine hydrochloride in ethanol on refluxing for 3h gave **3a** or **3b**. **3a** and **3b** were orange colored fibrous compounds. **3** did not give color reaction with ferric chloride solution. Element analysis of **3a** gave C, 72.5; H, 5.8; N, 10.2% calculated for molecular wt. 280, C₁₇H₁₆O₂N₂, C, 72.85; H, 5.71; N, 10%.

I.R. 2700 (NH₂), 1640 (C=N), 1090 (asym vC-O-C), 815 (Syn nC-O-C), 800cm⁻¹ (C=CH wagging).

PMR: δ 2.34 (s, 3H, Ar-CH₃), 3.84 (s, 3H, OCH₃), 6.9-8.0 (m, 8H, Ar-H and heteroatom H), 3.5 (s, 2H, NH₂).

From the above data the compounds **3a-b** were found to be corresponding flavones hydrazones. Pyrazole was not formed at all.

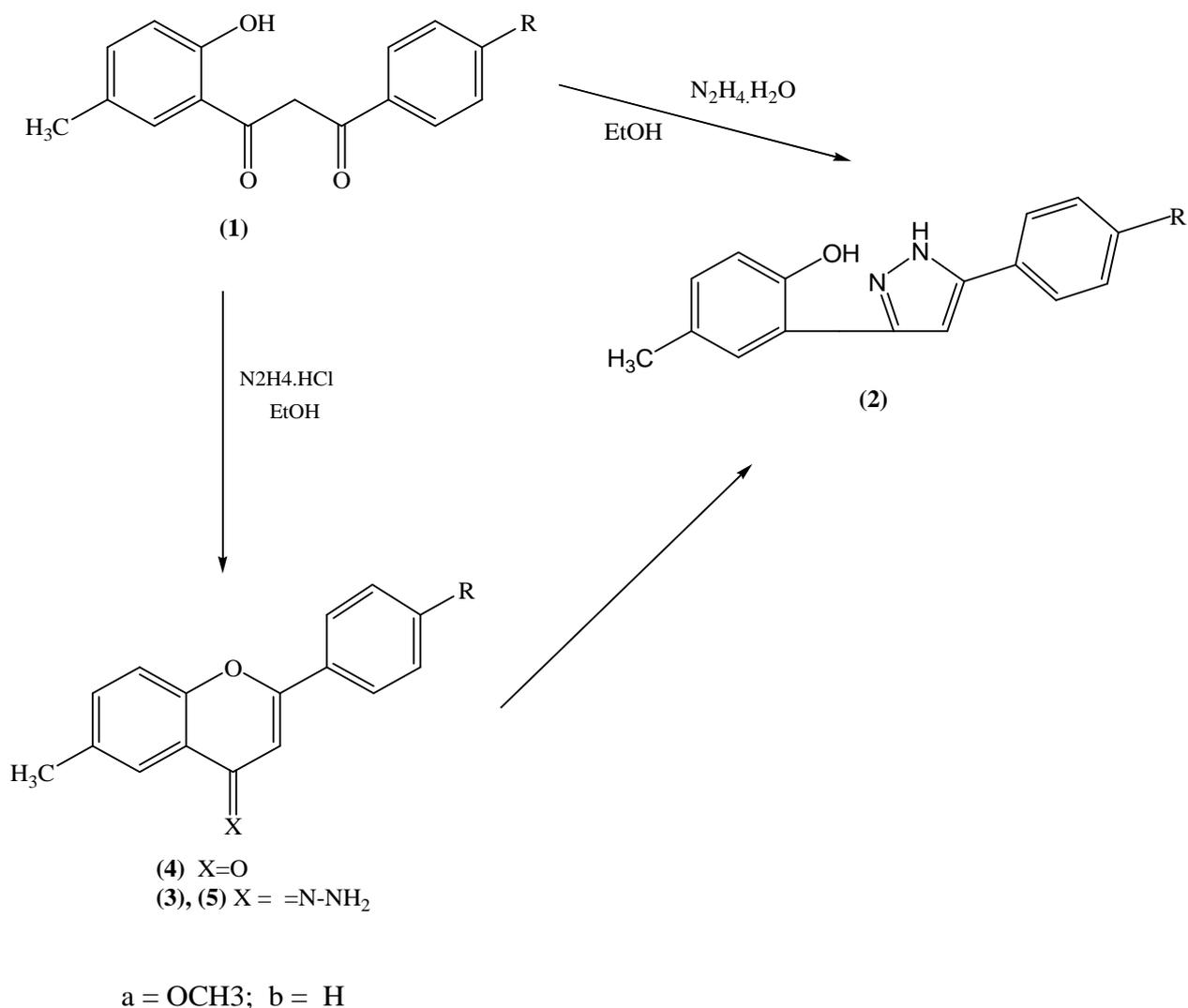
When flavones **4a-b** were refluxed with hydrazine hydrochloride in DMF for 3h. compounds **5a-b** was isolated. On the basis of spectral data and m. p., m. m. p. and Co- TLC **5a-b** were found to be identical with **3a-b**.

Conclusion:

With hydrazine hydrate (basic pH 10) dibenzoylmethane and flavones gave pyrazole while **1** with hydrazine hydrochloride (acidic pH 4) gave flavones hydrazones Further, flavones with hydrazine hydrochloride in DMF only gave flavones hydrazones but not pyrazole.

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