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# Synthesis and Characterization of some new Chalcones and Pyrazoline Compounds

**Marwa T. Mahmood** **Muneera Y. Roof**

*Department of Chemistry /College of Science/ University of Mosul*

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**corresponding author:**
**Marwa T. Mahmood**
Marwatalalmahmood@gmail.com
**Muneera Y. Roof**
mounera.yu63@gmail.com

**ABSTRACT**

An α, β-Unsaturated carbonyl compounds as presented (chalcone derivatives) (1a-d) were prepared by Claisen-Schmidt condensation reaction by coupling Pyridine-4-carboxaldehyde with acetophenone, 4-methylacetophenone and 4-aminoacetophenone in alcoholic medium in the presence 5-10% an aqueous sodium hydroxide and with stirring at room temperature gives (1a-c) compounds. While compound (1d) was prepared by coupling 2-acetyl pyridine with benzaldehyde in an aqueous medium in the presence 10% aqueous sodium hydroxide and stirring at room temperature. The other step in this research to get the target compounds is the chalcones (1a-d) have been utilized for the preparation of several pyrazoline derivatives (2a-d and 3a-d) using two different reagents either, refluxing hydrazine hydrate (99%) and glacial acetic acid to give (2a-d), or thiosemicarbazide in presence sodium acetate as base and ethanol as solvent to give (3a-d).

The chemical structures of all synthesized (1a-d, 2a-d and 3a-d) were established on the basis of some physical properties and some spectroscopy methods like, Fourier Transform-Infrared spectrum (FT-IR), Proton Nuclear Magnetic Resonance ($^{1}$HNMR) and Carbon 13- Nuclear Magnetic Resonance ($^{13}$C-NMR) spectra. Also, some of these reactions are followed by thin layer chromatography (TLC) technique and calculate the retardation factor ($R_f$) values.

**Keywords**: chalcones, pyrazolines, pyridine-4-carboxaldehyde, 2-acetylpyridine, acetophenone.

## INTRODUCTION

Pyrazolines represent an important class of two adjacent atoms and a single double bond containing heterocyclic compounds (Khan *et al.*, 2019). Many synthetic approaches to the pyrazoline nucleus are available; however, most of them fall into three broad categories. The first and most common method, involves condensation for α, β-unsaturated aldehydes and ketones with hydrazine under various reaction conditions (Dawood *et al.*, 2015; Roof *et al.*, 2019; Kumar *et al.*, 2020). The second, involves the condensation for α, β-unsaturated ketones (chalcones) with thiosemicarbazide under basic conditions (Abdel-Wahab *et al.*, 2009; Asiri *et al.*, 2011). The third, consists of a classical synthesis for reaction α, β-unsaturated ketones with diazomethane (Levai, 1997).

As the pyrazolines ring constitutes an important skeleton for many synthetic compounds (Kumar *et al.*, 2020; Khan *et al.*, 2020; Ali *et al.*, 2021), they were constituting an important skeleton for nature compounds like alkaloids, vitamins and plant cells (Shaaban *et al.*, 2012). On the other hand, these heterocyclic compounds were known to have certain biological activities such as anticancer (Moreno *et al.*, 2018; Edrees *et al.*, 2018), anti-inflammatory and analgesic (Amir *et al.*, 2008; Chandel *et al.*, 2019), and nociceptive (Kaplancikli *et al.*, 2009) and antiviral (Yar *et al.*, 2009). Away from the biological activity, pyrazolines have been widely used as optical brightening agents for textiles**,** paper and fabrics and as a hole-conveying medium in photoconductive materials (Oh *et al.*, 2004). These observations led us to synthesize a new pyrazoline derivatives from the condensation of α, β-unsaturated ketones (chalcones) with hydrazine hydrate or thiosemicarbazide.

## EXPERIMENTAL

Melting points were determined on an electrothermal Stuart melting SMP 30 and were uncorrected. Infrared absorption spectra were recorded on the (Shimadzu FT-IR) spectrophotometer from Faculty of Education, Salahuddin university, Erbil. $^{1}$H-NMR and $^{13}$CNMR spectra of some synthesized compounds were recorded on Bruker 400 mhz.FT-NMR instrument from Basra University. The chemical shifts are reported in δ values (ppm) relative to tetramethylsilane and quoted as s(singlet), d(doublet), t(triplet), br(broad) and m(multiplet).

**Synthesis of chalcone compounds(1a-d)**

**Method A** (Al-Rubay, 2017):

In a round-bottomed flask, equimolar quantities of pyridine-4-carboxaldehyde (0.025 mole, 2.7gm) and acetophenone or 4-methylacetophenone (0.025 mole) were dissolved in 10ml of methanol, the round bottom flask immersed in ice bath and cooled at (5-10) $^{o}$C. %5 Sodium hydroxide solution was added slowly with constant stirring, after completing the addition of sodium hydroxide, the mixture stirring at room temperature for (4-5 hrs.), then poured slowly onto 50ml ice water with stirring. The precipitate obtained was filtered, washed with cold water, and recrystallized from 50% aqueous ethanol gives light brown amorphous powder of compounds (1a-b).

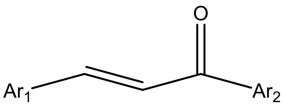
**Method B** (Marvel *et al*., 1955):

An aqueous 10% sodium hydroxide solution 40 ml and methanol 25 ml were added to a round-bottomed flask equipped with a magnetic stirrer and the mixture was cooled at (0-10) $^{o}$C surrounded the flask with ice. The stirring was started and pyridine-4-carboxaldehyde (0.023 mol, 2.5 gm) added in one portion, then 4-aminoacetophenone (0.023 mole, 3.1gm) was added in small portions over period of one hour keeping the temperature around (10-15) $^{o}$C. The mixture was stirred for (5 hrs.) and became dark in color, poured slowly onto crushed ice and neutralized with 2N hydrochloric acid until pH equal 8. The resulting solid was isolated by filtration, washed thoroughly with cold water, dried and recrystallized with 50% ethanol, giving light brown erratic solid of compound (1c).

**Method C** (Al-Bazi, 2004):

In a 250ml round-bottomed flask supplied with a magnetic bar was introduced (0.041 mole, 5 gm) of 2-acetylpyridine (0.041 mole, 4.34 gm) of benzaldehyde, and 150 ml water. The flask was immersed in ice bath at less than 15 $^{o}$C and 10ml of 10% sodium hydroxide solution was added dropwise to the mentioned mixture. Stirring was continued for an additional (4 hrs.) and the formed precipitate was filtered off, washed thoroughly with cold water, dried and recrystallized from petroleum ether (40-60) $^{o}$C giving a pale-yellow solid compound of m4. (Table 1) elucidates some physical properties of compounds (1a-d).

**Table 1: some physical properties of compounds (1a-d)**

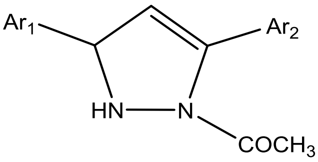



| Comp. no. | Comp.name | Ar1 | Ar2 | color | m.p.$^{o}$C | Yield % |
|---|---|---|---|---|---|---|
| 1a | (E)-1-phenyl-3-(pyridin-4-yl)prop-2-en-1-one | 4-pyridyl | phenyl | brown | 131-133 | 71 |
| 1b | (E)-3-(pyridin-4-yl)-1-(p-tolyl)prop-2-en-1-one | 4-pyridyl | 4-$CH_3$ phenyl | Light brown | 156-157 | 82 |
| 1c | (E)-1-(4-aminophenyl)-3-(pyridin-4-yl)prop-2-en-1-one | 4-pyridyl | 4-$NH_2$ phenyl | Light brown | 249-250 | 43 |
| 1d | (E)-3-phenyl-1-(pyridin-2-yl)prop-2-en-1-one | phenyl | 2-pyridyl | Pale yellow | 75-78 | 76 |

**1-(5-phenyl-3-(pyridin-4-yl)-2,3-dihydro-1*H*-pyrazol-1-yl) ethan-1-one (2a-d)( Johnson *et al*., 2007; Abdel-Karim *et al*., 2014)**

A mixture of chalcones(m1-m4) (0.001 mole), hydrazine hydrate (0.001 mole, 0.05 gm) and glacial acetic acid (10ml) was refluxed for (10 hrs.) (TLC chromatography using 20:80 n-hexane/ethyl acetate). The solution was allowed to cool, then poured into ice water, neutralized with sodium carbonate. The solid which was separated was filtered and recrystallized from absolute ethanol. (Table 2) elucidates some physical properties of titled compounds.

**Table 2: some physical properties of compounds (2a-d)**

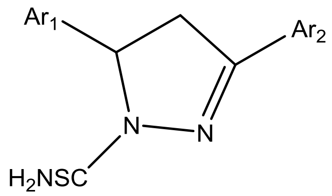



| Comp. No. | Ar1 | Ar2 | Comp. name | m.p. $^{o}$C | color | Yield % | $R_f$ values |
|---|---|---|---|---|---|---|---|
| 2a | 4-pyridyl | phenyl | 1-(5-phenyl-3-(pyridine-4-yl)-2,3-dihydro-1*H*-pyrazol-1-yl) ethane-1-one | 93-96 | Deep brown | 80 | 0.78 |
| 2b | 4-pyridyl | 4-$CH_3$phenyl | 1-(3-pyridyl-4-yl)-5-(4-tolyl)-2,3-dihydro-1*H*-pyrazol-1-yl) ethane-1-one | 112-115 | Deep brown | 40 | 0.83 |
| 2c | 4-pyridyl | 4-$NH_2$phenyl | 1-(5-(4-aminophenyl)-3-(pyridine-4-yl)-2,3-dihydro-1*H*-pyrazol-1-yl) ethane-1-one | 263-264 | Deep brown | 32 | _ |
| 2d | phenyl | 2-pyridyl | 1-(3-phenyl-5-(pyridine-2-yl)-2,3-dihydro-1H-pyrazol-1-yl) ethane-1-one | 118-120 | Deep blue | 40 | _ |

**3-phenyl-5-(pyridin-4-yl)-4,5-dihydro-1H-pyrazole-1-carbothioamide(3a-d) (Abdel-Karim *et al*., 2014)**

In a mortar, mixture of chalcones (m1-m4) (0.001 mole), thiosemicarbazide (0.001 mole, 0.091 gm.) and sodium acetate (0.001 mole, 0.082 gm) was grinding for 15min. The reaction mixture was dissolved into absolute ethanol (15 ml) and refluxed for (6 hrs.), (TLC chromatography using 20:80 n-hexane/ethyl acetate). Then the reaction mixture was cooled and poured into ice water, the precipitate was formed either directly (3a-c) or by neutralization with potassium carbonate (3d). The solid product was filtered, washed with water, dried and recrystallized from petroleum ether (40-60) $^{o}$C to get the titled compounds. (Table 3) elucidates some physical properties of these compounds (3a-d).

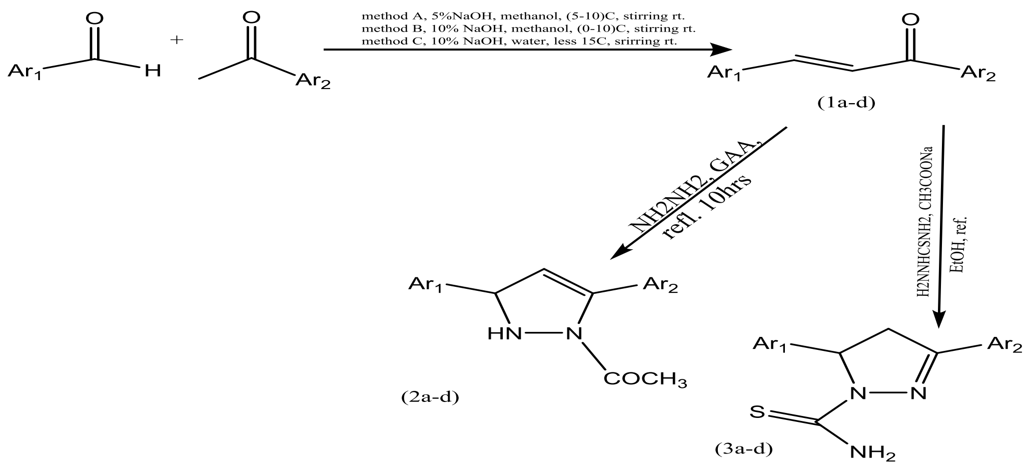
**Table 3: Some physical properties of compounds (3a-d)**




| Comp.No. | Ar1 | Ar2 | Comp.name | m.p. $^{o}$C | color | Yield % | $R_f$ values |
|---|---|---|---|---|---|---|---|
| 3a | 4-pyridyl | phenyl | 3-phenyl-5-(pyridin-4-yl)-4,5-dihydro-1H-pyrazole-1-carbothioamide | 113-116 | white | 35 | 0.54 |
| 3b | 4-pyridyl | 4-$CH_3$phenyl | 5-(pyridin-4-yl)-3-(4-tolyl)-4,5-dihydro-1H-pyrazole-1-carbothioamide | 158-160 | Deep brown | 69 | 0.53 |
| 3c | 4-pyridyl | 4-$NH_2$phenyl | 3-(4-aminophenyl)-5-(pyridin-4-yl)-4,5-dihydro-1H-pyrazole-1-carbothioamide | 104-109 | Deep brown | 77 | _ |
| 3d | phenyl | 2-phenyl | 5-phenyl-3-(pyridin-4-yl)-4,5-dihydro-1H-pyrazole-1-carbothioamide | 118-120 | Reddish brown | 38 | _ |

## RESULT AND DISCUSSION

The synthesis of compounds (1a-d, 2a-d and 3a-d) was carried out according to the steps outlined in the Scheme 1:

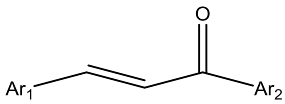



**Scheme 1**

New pyrazoline derivatives were synthesized by condensation of chalcones (1a-d) with hydrazine hydrate 99% in glacial acetic acid to give (2a-d) and with thiosemicarbazide in presence of sodium acetate to give (3a-d), as shone in Scheme 1. The chemical **st**ructures of the prepared compounds have been established by their FT-IR, $^{1}$HNMR and $^{13}$C-NMR.

Chalcones (1a-d) were synthesized by base-catalyzed claisen–Schmidt condensation of pyridine-4-carboxaldehyde and appropriate acetophenone either in methanol or water as solvent. The IR spectra of (m1-m3) showed the major absorptions at (1600-1680) cm$^{-1}$ for the C=O group and (1580-1604) for the C=C group (Al-Hamdany *et al.*, 2017, Asiri *et al*., 2011). Other absorption bands were illustrated in (Table 4).

**Table 4: FT-IR spectral data of compounds (1a-d)**

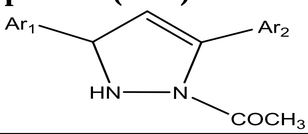



| Comp. No. | Ar1 | Ar2 | FT-IR(KBr), ν (cm$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | C-H aromatic | C-H aliphatic | C=O | C=C conjugated | C-C aromatic | others |
| 1a | 4-pyridyl | phenyl | 3061 | 2916 2895 | 1680 | 1597 | 1556 | |
| 1b | 4-pyridyl | 4-$CH_3$ phenyl | 3028 | 2918, 2897 | 1680 | 1600 | 1564 | |
| 1c | 4-pyridyl | 4-$NH_2$ phenyl | 3032 | 2926 | 1600 | 1580 | 1516 | 3392br. N-H |
| 1d | phenyl | 2-pyridyl | 3049 | 2920 | 1668 | 1604 | 1573 | |

The $^{1}$HNMR spectra of compounds (1a-c) were in agreement with the suggested structures, compound (1a) gives signals at: (7.35-7.77) ppm (m, 3H, aryl ring and 2H, pyridyl ring), (7.9-8) ppm (s-s, 2H, aryl ring, 2H, Hα and Hβ), (8.4-8.42) ppm (s-s, 2H, pyridyl ring). compound (1b) gives signals at: 2.29ppm (s, 3H, CH3 group), (7.22-7.25) ppm (m, 2H, aryl ring, 2H, pyridyl ring), (7.38-7.87) ppm (s-s, 2H, aryl ring, 2H, Hα and Hβ), (8.39-8.4) ppm (s-s, 2H, pyridyl ring). Compound (1c) gives signals at: (6.5-7.7) ppm (m, 2H, aryl ring, 2H, pyridyl ring, and 2H, NH2 group), (7.9-8.8) ppm (m, 2H, aryl ring, 2H, Hα and Hβ, 2H, pyridyl ring). The major values for $^{13}$CNMR chemical shift for (1a-b) are $C_{\alpha}$ at (128.4, 128.5) ppm and $C_{\beta}$ at (150.2, 149.8) ppm respectively (Jovanović *et al.*, 1999). Other signals are illustrated in (Table 7).

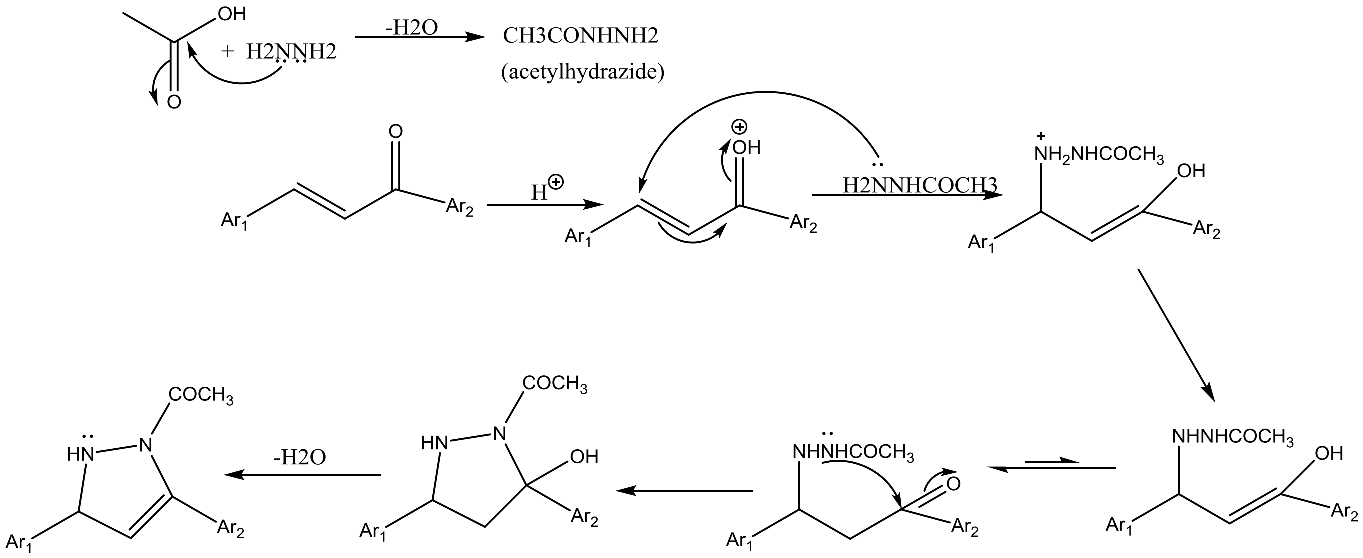
Treatment of the azachalcones (1a-d) with hydrazine hydrate under reflux in glacial acetic acid led to N-acetyl pyrazoline derivatives (2a-d). The IR spectra of compounds (2a-c) showed absorption between (1674-1683) cm$^{-1}$ for the C=O group, (1597-1602) cm$^{-1}$for the C=C group (Al-Hamdany *et al.*, 2017) and (3367-3423) cm$^{-1}$ for the NH group. Other absorption bands were illustrated in (Table 5).

**Table 5: FT-IR spectral data of compounds (2a-c)**




| Comp. No. | Ar1 | Ar2 | FT-IR(KBr), ν (cm$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | C-H aromatic | C-H aliphatic | C=O | C=C pyrazoline | C-C aromatic | C-N | N-H |
| 2a | 4-pyridyl | phenyl | 3059 3028 | 2897 | 1683 | 1597 | 1579 | 1415 | 3379 |
| 2b | 4-pyridyl | 4-$CH_3$ phenyl | 3028 | 2920, | 1680 | 1602 | 1558 | 1415 | 3367 |
| 2c | 4-pyridyl | 4-$NH_2$ phenyl | 3030 | 2899 | 1674 | 1598 | 1543 | 1323 | 3423br NH&NH2 |

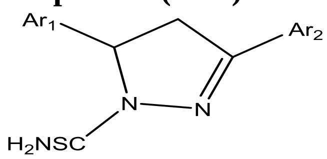
[1]HNMR spectra of compound (2a) showed signals at: (7-8.4) ppm (m, 9H, aryl and pyridyl rings), (5.3)ppm (d,1H,=CHpyrazoline ring), (3.9,3.5)ppm (br-d,2H,NH and pyrazoline ring) and 2.5 ppm (s, 3H,CH3 group) (Patel *et al*., 2011). [13]CNMR chemical shift for (2a) gives the major values at: 198.6ppm for the C=O group, (149.8, 134.9) ppm for the pyrazoline ring, other signals are illustrated in (Table 7). Scheme 2 illustrated the reaction mechanism (Kitawat *et al*., 2014), it is suggested that the reaction occurs through the nucleophilic attack by acetylhydrazide (Michail addition) followed by cyclization then a dehydration step afforded N-pyrazoline derivatives (2a-d).




**Scheme 2: Proposed reaction mechanism for synthesis N-acetyl pyrazoline derivatives**

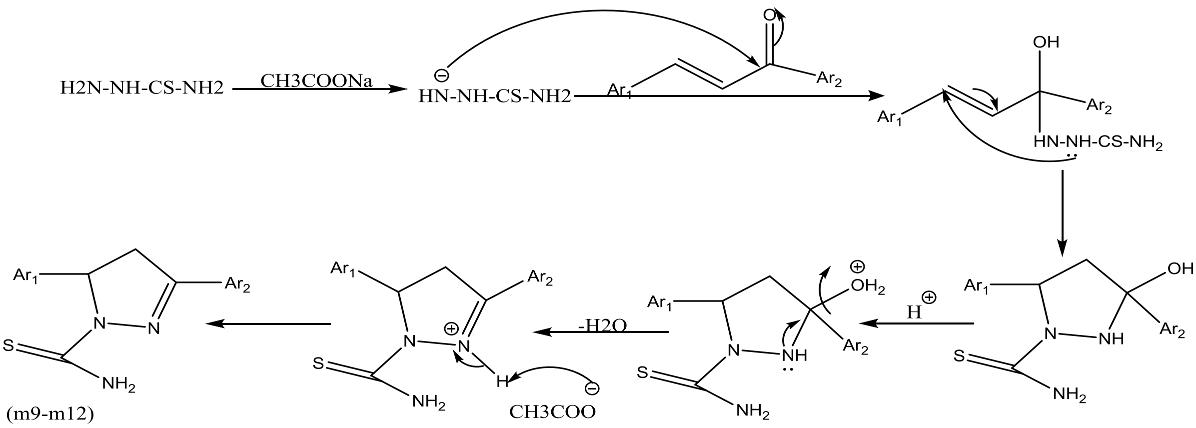
The reaction of chalcones (1a-d) with thiosemicarbazide, under reflux in the presence of base may yield the corresponding pyrazoline carbothioamides (3a-d). The structural assignments of the pyrazoline carbothioamides based on the spectral data FT-IR, [1]HNMR, [13]C NMR. The IR spectra of these compounds showed absorption between (1600-1697) $cm^{-1}$ for the C=N group (Thirunarayanan *et al*., 2013; Al-Hamdany *et al*., 2017), (1670-1674) $cm^{-1}$ for the NH bending (Kaka *et al*., 2019) and (1220-1284) $cm^{-1}$for the C=S group. Other absorption bands were illustrated in (Table 6).

**Table 6: FT-IR spectral data of compounds (3a-d)**



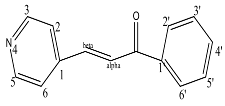
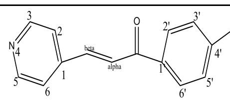
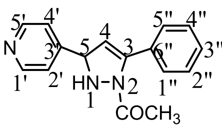
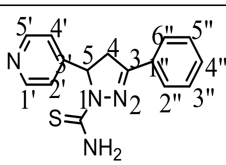

| Comp.No. | Ar1 | Ar2 | FT-IR(KBr), ν ($cm^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | C-H arom. | C-H aliph. | NH | C=N | NH bend. | C-C arom. | C-N | C=S |
| 3a | 4-pyridyl | Phenyl | 3059 | 2918<br>2852 | 3280<br>3200 | 1685 | 1674 | 1597<br>1579 | 1357 | 1284 |
| 3b | 4-pyridyl | 4-$CH_3$ Phenyl | 3028 | 2918 | 3400br. | 1683 | 1670 | 1602<br>1558 | 1350 | 1273 |
| 3c | 4-pyridyl | 4-$NH_2$ Phenyl | 3030 | 2914 | 3412br. | 1600 | _ | 1560 | 1417 | 1220 |
| 3d | phenyl | 2-pyridyl | 3057 | 2900 | 3425<br>3305 | 1697 | 1670 | 1597<br>1575 | 1336 | 1217 |

The [1]HNMR spectrum for (3a) as an example for this group of compounds, showed signals at: (7.3-8.4) ppm (m,11H, aromatic-H and NH2), (3.8-3.9) ppm (m, 1H, CH pyrazoline ring) and (3.57-3.69) ppm (dd, 2H, CH2 pyrazoline ring). [13]CNMR chemical shift for (3a) gives the major values at: 198.6 for the C=S group (Gros *et al.*, 2006) and (153.7, 43.9) ppm for the pyrazoline ring. Other signals are illustrated in (Table 7). Scheme 3 illustrated the reaction mechanism (Kaka *et al.*, 2019; Yehya *et al*., 2022), it is suggested that the reaction proceeds via Claisen addition of the anion to the carbonyl carbon followed by cyclization, dehydration and de-protonation to give pyrazoline carbothioamides (3a-d).




**Scheme 3: Proposed reaction mechanism for synthesis pyrazoline carbothioamides derivatives**

**Table 7: $^{13}$C spectral data of compounds (1a, 1b, 2a and 3a)**

| Comp.No. | Structure | 13C-δppm, DMSO |
|---|---|---|
| 1a |  | $C_{C=O}$=198.6, $C_{3(5)}$=153.7, $C_{\square}$=150.2, $C_{1}$=149.8, $C_{1'}$=137, $C_{4'}$=133.8, $C_{5'(3'),6'(2')}$=129.2, $C_{\alpha}$=128.4, $C_{2(6)}$=123.7 |
| 1b |  | $C_{C=O}$=198.2, $C_{3(5)}$=153.8, $C_{\square}$=149.8, $C_{1,4'}$=144.1, $C_{1'}$=134.5, $C_{2'(6')}$=129.7, $C_{5'(3')}$ =128.7, $C_{\alpha}$=128.5, C2(6)=123.7, $C_{CH3}$=21.6 |
| 2a |  | $C_{C=O}$ =198.6, $C_{1'(5'),3'}$ =149.8, $C_3$ =136.9, $C_{6''}$ =133.7, $C_{2''(4'')}$= 129.2, $C_{1''(5''),3''}$ = 128.3, $C_{2'(4')}$ =123.7 ,$C_5$ =43.9, $C_4$= 40.6, $C_{CH3}$=36.1 |
| 3a |  | $C_{C=S}$=198.6, $C_5$ =153.7, C $_{1'(5'),3'}$=149.8, $C_{1''}$=137, $C_{4''}$=135.8, C $_{3''(5'')}$= 129.2، $C_{2''(6'')}$ = 128.3, $C_{2'(4')}$ = 123.7, $C_3$=73.1,$C_4$ = 43.9 |

## CONCOLUSION

Two kinds of pyrazoline derivatives have been synthesized. First, N-acetyl pyrazolines which synthesized by one-pot cyclization and acetylation of azachalcone derivatives with hydrazine hydrate in presence of glacial acetic acid. Second, N-carbothioamides pyrazolines which synthesized by cyclization of azachalcone derivatives with thiosemicarbazide in presence of sodium acetate as base and ethanol as solvent. Physical and chemical properties of these compounds were established.

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# تشييد وتشخيص بعض الجالكونات ومركبات البايرازولين الجديدة

**مروة طلال محمود** **منيرة يوسف رؤوف**
قسم الكيمياء/ كلية العلوم/ جامعة الموصل

**الملخص**

تضمن البحث تحضير سلسلة من مركبات الكربونيل الفا،بيتا غير المشبعة (الجالكونات) بتفاعل كليزن- شمدت من خلال تكاثف اما بريدين-4-كاربوكسالديهايد مع الاسيتوفينون، 4-مثيل اسيتوفينون و4-امينو اسيتوفينون في وسط كحولي بوجود 5-10% محلول مائي لهيدروكسيد الصوديوم والتحريك عند درجة حرارة المختبر ليعطي المركبات (1a-c) أو بتكاثف 2-أسيتيل بريدين مع البنزالديهايد ايضا باستعمال التحريك عند درجة حرارة المختبر وبوجود 10% محلول مائي لهيدروكسيد الصوديوم ليعطي المركب (1d). الخطوة الأخرى في هذا البحث للحصول على المركبات المستهدفة هي استعمال الجالكونات (1a-d) لتحضير عدد من مشتقات البايرازولين (2a-d and 3a-d) بتفاعلها مع اثنين من الكواشف المختلفة، أما الهيد رازين المائي بتركيز 99% وبوجود حامض الخليك الثلجي واستعمال عملية التصعيد ليعطي المركبات (2a-d)، أوالثايوسيميكاربازايد وبوجود خلات الصوديوم كقاعدة والأثيل الكحولي كمذيب ليعطي المركبات ( 3a-d).

تم تشخيص الصيغ التركيبية للمركبات المحضرة بواسطة أطياف الاشعة تحت الحمراء، الرنين النووي المغناطيسي للبروتون وطيف الرنين النووي المغناطيسي كاربون-13 بالإضافة الى بعض خواصها الفيزيائية وأيضا متابعة بعض التفاعلات بتقنية كروماتوغرافيا الطبقة الرقيقة (TLC) ) وحساب قيم عامل الاستبقاء ($R_f$).

**الكلمات الدالة**: الجالكونات، البايرازولينات، بريدين-4-كاربوكسلديهيد، 2-أسيتيل بريدين، أسيتوفينون.