

Synthesis of Some Imine, From Pyrazole -1- Carbaldehyde Compound

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ABSTRACT

In this paper the synthesis of N[(1E)-1- (3,5 - disubstituted phenyl -4,5-dihydro-1H- pyrazol-1-yl) ethylidene or methylidene] substituted aniline [13-15] [17-19] and 1,1-{benzene- 1,4- or -1,3- diylbis [nitrilo (E) methylidene]} bis(4,5- dihydro -1H- pyrazole -3,5- disubstituted phenyl) [16,20] is reported. Substituted acetophenone was treated with substituted benzaldehyde to give chalcones ((2E)-1,3-disubstituted phenyl prop-2-ene-1- one) [1-4], the chalcones was treated with hydrazine hydrate in the presence of formic or acetic acid ethanol to give 1-(3,5 -disubstituted phenyl-4,5- dihydro-1H- pyrazol-1-yl) methanol or ethanone [5-12], then this products changed to imines through reaction with substituted aromatic aniline and sodium hydroxide in ethanol to give the substituted pyrazoles.

Also the substituted compounds [5-12] were converted to 1-{(1E)-1-[2-(2,4-dinitrophenyl) hydrazinylidene] methyl or ethyl} – 4,5- dihydro -1H- pyrazole-3,5-disubstituted phenyl [21-28] by reaction with 2,4-dinitrophenyl hydrazine in ethanol.

The synthetic compounds structure confirmed by IR., UV. Spectra and physical method.

Keywords: Imine, Pyrazole, Schiff bases.

تحضير عدد من اليمينات من مركبات البايرازول -1-كاربالديهايد

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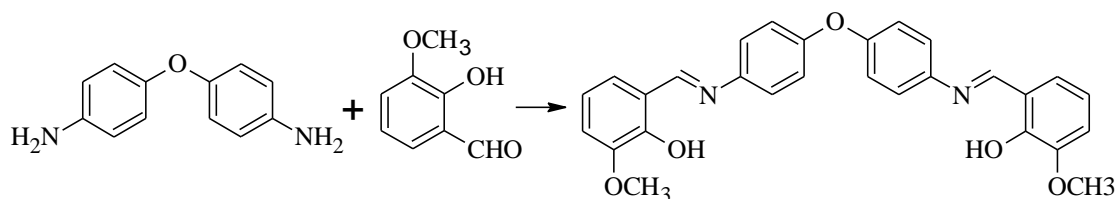
الخلاصة

تم في هذا البحث تحضير عدد من معوضات N - [(1E) - 1- (5,3) - معوضات ثنائي الفينيل -5,4- ثنائي هيدرو -H1- بايرازول -1-يل] ايثايلدين او ميثايلدين [معوضات الانيلين [13-15, 17-19] بالاضافة الى 1,1-بنزين 4,1 او 3,1 ثنائي بس [نتريلو (E) ميثايلدين] { بس (5,4) - ثنائي هيدرو -H1- بايرازول - 5,3 - ثنائي فنيل معوض) [16] و [20] حيث تم مفاعلة معوضات البنزليدهايد مع معوضات الاسيتوفينون في الوسط القاعدي لتحضير الجالكونات 3,1- ثنائي فنيل معوض بروبان -2-ين -1 - اون [4-1] ومن ثم مفاعلة الجالكونات المحضرة مع الهيدرازين المائي بوجود حامض الفورميك او حامض الخليك المذاب في الايثانول لأعطاء 1- [5,3] - ثنائي فنيل معوض - 5,4 - ثنائي هيدرو -H1- بايرازول -1-يل] ايثانول او ميثانول [5-12] الذي حول بدوره الى الامين عن طريق مفاعله مع امينات اروماتية في الايثانول بوسط قاعدي لأعطاء معوضات البيرازول. كما تم مفاعلة هذه المعوضات [5-12] مع 4,2- ثنائي نترو فنيل هيدرازين في الايثانول لأعطاء 1- [E1] - 1- [2] - 4,2) - 4,2) ثنائي نتروفنيل (هيدرازيندين] ايثايل او ميثايل) { -5,4- ثنائي هيدرو -H1- بايرازول -5,3- ثنائي فنيل معوض [21-28]. تم تشخيص المركبات المحضرة بواسطة طيف الأشعة تحت الحمراء والأشعة البنفسجية والطرق الفيزيائية.

الكلمات المفتاحية: امين, بايرازول, قواعد شيف.

Introduction

Schiff bases first reported by Schiff in 1864. The condensation of primary amines with carbonyl compounds are the main way to produce these compounds. The azomethine group with a general formula $RHC=N-R'$ was The common structural feature of these compounds, where R and R' are alkyl, aryl, cyclo., alkyl or heterocyclic groups which may be variously substituted. Compounds contain azomethine group also known as anils, imines⁽¹⁾. Schiff bases can be synthesized from an aromatic amine and a carbonyl compound by nucleophilic addition forming a hemiaminal (contain hydroxyl and amine group), then, by withdrawing of water to generate an imine. For instant, reaction, o-vanillin reacts with 4,4'-diaminodiphenyl ether⁽²⁾.



Schiff bases serve as a back bone for the synthesis of various heterocyclic compounds⁽³⁾ and Schiff base reactions are useful in making carbon-nitrogen bonds. Schiff bases look to count intermediates in a number of enzymatic reactions involving interaction of an enzyme with an amino or a

carbonyl group of the substrate⁽⁴⁾. A sequence of transition metal complexes of, Co (II), Ni (II), and Cu (II) have been synthesized from the Schiff base derived from 4-aminoantipyrine 3-hydroxy-4-nitrobenzaldehyde and o-phenylenediamine. The structural activity of the above metal complexes shows that Cu, Ni and Co complexes cleave DNA through redox chemistry⁽⁵⁾. Also Schiff Bases are insecticides, fluorescent brighteners, antitumor and other biological activities⁽⁶⁻¹⁰⁾.

Experimental

Melting points apparatuses electro thermal 9300 engineering LTD in addition, IR spectrum was recorded infrared spectrophotometer model tensor 27 Bruker Co, Germany, using KBr discs. The U.V spectrum was recorded on UV-Visible Shimadzu 1601 spectrophotometer using ethanol/ethyl acetate 1:1 as a solvent. Chemicals were purchased from Fluka and TCI Ltd.

chalcones ((2E)-1,3-disubstituted phenyl prop-2-ene-1-one)(1-4)^(11,12).

A mixture of substituted benzaldehyde (0.1mol) and substituted acetophenone (0.1mol) were dissolved in ethanol then located in cold bath after that, the reaction pot stirred for 3h. Using (10%NaOH) (cold solution) drop by drop. The mixture was gone to stand for 2hours, the solid products was filtered then dried and used ethanol for recrystallizing to afford chalcones. Table (1) scheduled physical properties and spectral data.

1-(3,5-disubstituted phenyl -4,5- dihydro -1H- pyrazol -1- yl) methanol or ethanone [5-12]⁽¹³⁻¹⁵⁾.

A solution of hydrazine hydrate (30) ml in (15) ml of ethanol was added drop wise with cooling to a solution of (15) ml of chalcones and (20) ml of acetic acid. The resultant refluxed with stirring for 24 hours. After that, the reaction left to cool to room temperature and pieces of ice through in a solution with cooling to induce the precipitation. The crud product recrystallized with ethyl acetate. Table (2) listed physical properties and spectral data.

N[(1E)-1- (3,5 - disubstituted phenyl-4,5- dihydro-1H- pyrazol-1- yl) ethylidene or methylidene] substituted aniline [13-15,17-19] and 1,1-{benzene- 1,4- or -1,3- diylbis [nitrilo (E) methylidene]} bis(4,5- dihydro -1H- pyrazole -3,5- disubstituted phenyl) [16,20]^(16,2).

pyrazoles(0.01mol) [5-12] was mixed with (0.01mol) of the proper substituted aniline(in case synthesized compound [16] and [20] we must use (0.02 mol) of proper pyrazoles) in (15 mL) of the ethanol and the combination was stirred. A solution of sodium hydroxid(0.4g in 15 mL ethanol) was added

gradually to the reaction during a period of 30 minutes and the combination was refluxed for 2h at 60c°. with continual stirring. The final mixture leaved for about 2h., poured on to crushed ice,dried, recrystallized from ethanol-water. Table (3) recorded physical properties and spectral data.

1-((1E)-1- [2-(2,4- dinitrophenyl) hydrazinylidene] methyl or ethyl} – 4,5- dihydro -1H- pyrazole - 3,5- disubstituted phenyl [21-28]⁽¹⁷⁾.

In a test tube put (0.05g) of compounds [5-12] in (0.5mL) ethanol then (5 ml) of the saturated solution of 2,4-dinitrophenyl- hydrazine in (2 M) HCl, the mixture was shacked for 10 second. The solid products (yellow- red) filtered and recrystallized by ethyl acetate-water. Table(4). listed physical properties and spectral data.

Results and Discussion

In this paper the synthesis of N[(1E)-1- (3,5 - disubstituted phenyl-4,5- dihydro-1H-pyrazol -1- yl) ethylidene or methylidene] substituted aniline [13-15,17-19] and 1,1-{benzene- 1,4- or -1,3- diylbis [nitriolo (E) methylidene]} bis(4,5- dihydro -1H- pyrazole -3,5- disubstituted phenyl) [16,20] is reported (Scheme1).

Substituted acetophenone was treated with substituted benzaldehyde afford chalcones [1-4]. The IR. spectra⁽¹⁸⁾ show absorption at $\nu(1657-1685)\text{cm}^{-1}$ (C=O) and $\nu(1602-1658)\text{cm}^{-1}$ (C=C), λ_{max} (331-400)nm. (table1)

Table (1): physical properties and spectral of compounds [1-4]

Com. No.	Yield (%)	m.p. (°C)	Colour	U.V λ max in ethanol/ ethyl acetate 1:1	I.R ν cm^{-1} (KBr)				
					C=O	C-H aromatic	C=C	C-O- C Sym. Assy m.	NO ₂ sym. assym.
1	85	159-161	Yellow	357	1658	3030	1608	-	1337, 1515
2	87	207-209	Red	354	1668	3050	1611	-	1317 , 1519
3	58	61-63	Yellow	331	1657	2959	1602	1048 1267	-
4	65	202-204	Brown	400	1685	3002	1658	1041 1248	1348 , 1528

The chalcones were treated with formic or acetic acid and hydrazine in ethanol to give 1-(3,5-disubstituted phenyl-4,5-dihydro-1H-pyrazol-1-yl) methanal or ethanone (5-12). The IR shifts⁽¹³⁾ of compounds [5-12] show absorption at $\nu(1649-1698)\text{cm}^{-1}$ (C=O) and $\nu(1606-1657)\text{cm}^{-1}$ (C=N), λ_{max} (331-360)nm. (Table 2).

Table (2): physical properties and spectral of compounds [5-12]

Com. No.	Yield(%)	m.p. (°C)	Colour	U.V λ_{max} in ethanol/ ethyl acetate 1:1	I.R ν cm^{-1} (KBr)				
					C=O	C-H aromatic	C=N	C-O-C Sym. Assym	NO ₂ sym. assym.
5	60	115-116	Orange	332	1680	3076	1657	-	1345 1514
6	75	144-146	Orange	332	1676	3081	1630	-	1318 1522
7	58	105-107	Yellow	338	1661	3051	1607	1055 1272	-
8	64	264-266	Brown	329	1697	3045	1620	1053 1250	1320 1528
9	63	151-153	Yellow	329	1649	3041	1610	-	1350 1518
10	69	99-101	Yellow	333	1653	3050	1606	-	1348 1528
11	71	83-82	Yellow	329	1699	3044	1652	1047 1285	-
12	55	112-114	Orange	331	1698	3043	1654	1045 1285	1314 1530

The pyrazols were changed to imines by reaction with substituted aromatic aniline in presence of sodium hydroxide in ethanol to give the compound[13-20]. The IR spectra⁽¹⁶⁾ of [13-20] show absorption at $\nu(1605-1681)\text{cm}^{-1}$ for (C=N) and $\nu(1161-1180)\text{cm}^{-1}$ for (N-N), λ_{max} (329-333)nm. (Table 3).

Table (3): physical properties and spectral of compounds [13-20]

Com. No.	Yield (%)	m.p. (°C)	Colour	U.V λ max in ethanol/ ethyl acetate 1:1	I.R ν cm^{-1} (KBr)				
					C=N	C-H aromatic	C-N	C-O-C Sym. Assym.	NO ₂ sym. assym
13	83	292-294	Yellow-red	333	1650	3014	1180	-	1335 1520
14	78	119-121	Brown	333	1674	3080	1178	-	1309 1521
15	80	289-291	Yellow	329	1647	2995	1168	1051 1240	-
16	86	249-251	Brown	329	1681	3040	1168	1194 1254	1317 1529
17	83	250-253	Yellow	329	1647	3041	1180	-	1334 1521
18	79	154-156	Brown	332	1628	3035	1179	-	1302 1528
19	78	104-106	Yellow	332	1605	3058	1178	1051 1260	-
20	75	142-144	Brown	329	1651	3083	1161	1040 1258	1315 1529

The presence of carbonyl group in the pyrazol ring have been proved by using the chemical reagent 2,4- dinitrophenylhydrazine which yield the hydrazone product [21-28] which identified through I.R spectra⁽¹⁹⁻²⁰⁾ which indicate the disappear of carbonyl group and the appearance of imines group at ν (1602-1675) cm^{-1} for (C=N) ; ν (1317-1348) cm^{-1} symmetric and ν (1515-1530) cm^{-1} asymmetric for (NO₂) and ν (3421-3448) cm^{-1} for (N-H), λ_{max} (236-329)nm.(table 4).

Table(4): physical properties and spectral of compounds [21-28]

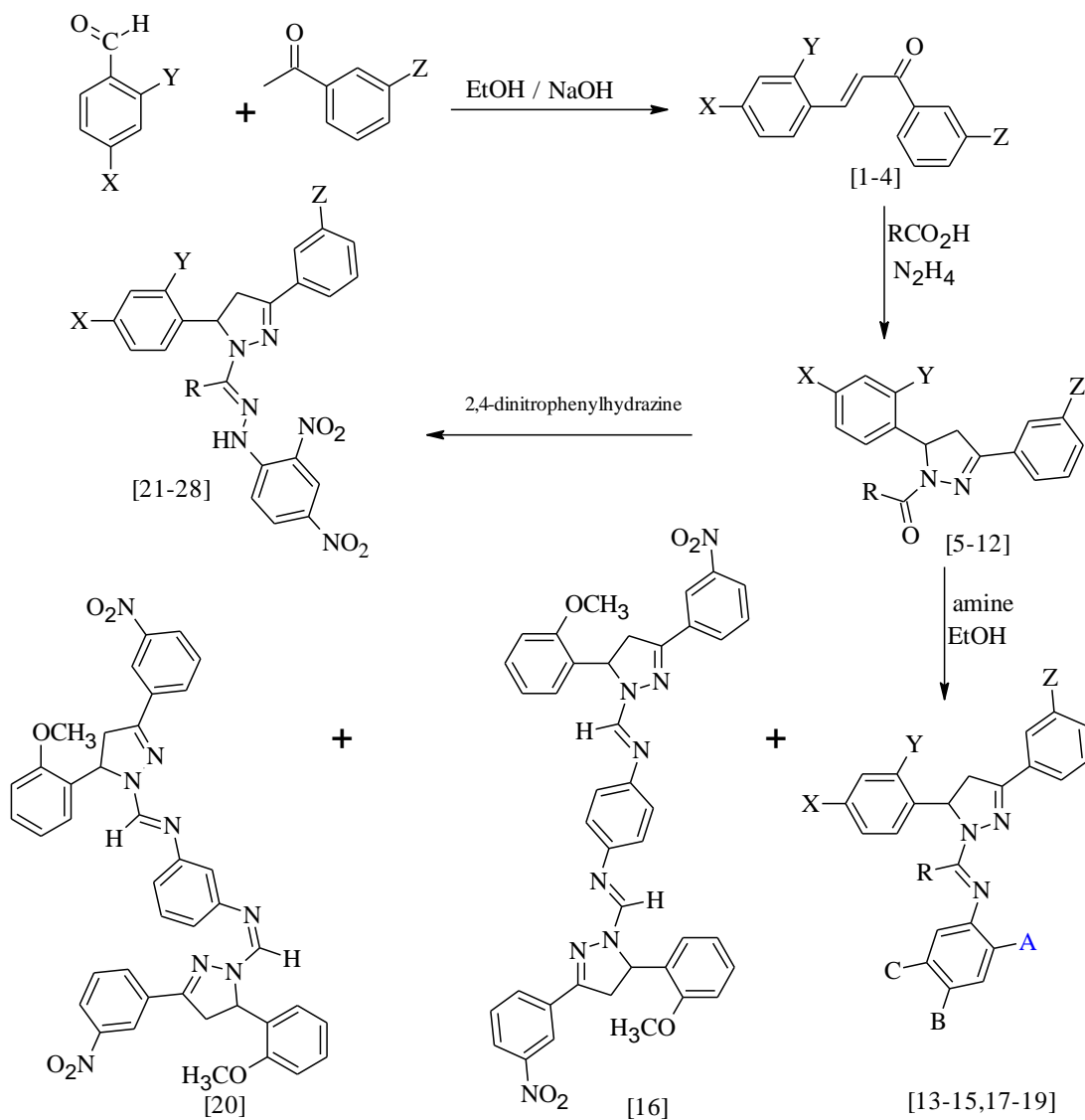
Com. No.	Yield(%)	m.p. (°C)	Colour	U.V λ max in ethanol/ ethyl acetate 1:1	I.R ν cm^{-1} (KBr)			
					C=N	N-H	NO ₂ sym. assym	C-O-C Sym. Assym.
21	85	118-120	Red	329	1664	3448	1339 1515	-
22	78	150-149	Yellow-red	329	1675	3443	1319 1520	-
23	79	108-110	Orange	329	1640	3435	1320 1525	1055 1250
24	77	135-137	Orange	329	1621	3422	1317 1522	1057 1280
25	82	191-193	Orange	329	1602	3423	1334 1520	-
26	80	260-262	Yellow-red	329	1617	3422	1347 1519	-
27	73	61-63	Orange	332	1620	3420	1325 1520	1045 1247
28	80	106-108	Yellow	332	1618	3421	1348 1518	1041 1267

Table(5): groups of compound [1-12]

No.	X	Y	Z	R	No.	X	Y	Z	R
1	NO ₂	H	H	-	9	NO ₂	H	H	CH ₃
2	H	H	NO ₂	-	10	H	H	NO ₂	CH ₃
3	H	OCH ₃	H	-	11	H	OCH ₃	H	CH ₃
4	H	OCH ₃	NO ₂	-	12	H	OCH ₃	NO ₂	CH ₃
5	NO ₂	H	H	H					
6	H	H	NO ₂	H					
7	H	OCH ₃	H	H					
8	H	OCH ₃	NO ₂	H					

Table (6): groups of compound[13 – 28]

No.	X	Y	Z	R	A	B	C	No.	X	Y	Z	R
13	NO ₂	H	H	H	H	CH ₃	H	21	NO ₂	H	H	H
14	H	H	NO ₂	H	H	NO ₂	H	22	H	H	NO ₂	H
15	H	OCH ₃	H	H	CH ₃	H	H	23	H	OCH ₃	H	H
16	H	OCH ₃	NO ₂	H	H	NH ₂	H	24	H	OCH ₃	NO ₂	H
17	NO ₂	H	H	CH ₃	H	CH ₃	H	25	NO ₂	H	H	CH ₃
18	H	H	NO ₂	CH ₃	H	NO ₂	H	26	H	H	NO ₂	CH ₃
19	H	OCH ₃	H	CH ₃	CH ₃	H	H	27	H	OCH ₃	H	CH ₃
20	H	OCH ₃	NO ₂	CH ₃	H	H	NH ₂	28	H	OCH ₃	NO ₂	CH ₃



Scheme (1)

Note: see table (5,6) for substituted group

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