Synthesis of 4-Methyl-1,2,3,4-tetrahydronaphtho [1,2-c]-5-aryl-2`-pyrazolines

A.KH. Ahmad
Department of Chemistry, College of Education, University of Mosul
Mosul, Iraq

(NJC)

(Received on 16 /1 /2006) (Accepted for publication on 15/ 11/2006)

Abstract

A number of new heterocyclic tetrahydronaphtho [1,2-c]- 2`-pyrazolines were synthesized from the reaction of aryl aldehydes with 4- methyl- 1-tetralone. The structures of these compounds were confirmed by some spectroscopic methods.

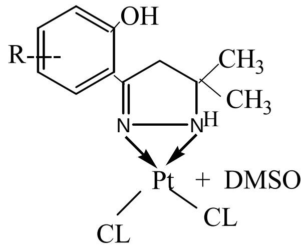
الخلاصة

تم تحضير عدد جديد من مركبات رباعي هايدرونفثو - (1، 2، ج)-2-` بايرازولين الحلقية غير المتجانسة من تفاعل مركبات أريل الدهيد مع 4- مثيل -1- تترالون. شخصت هذه المركبات بواسطة بعض الطرق الطيفية.

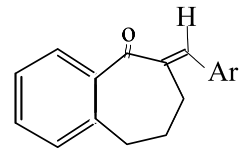
Introduction

The compounds of type 2-arylidene-1-tetralone (5) represents an intriguing goal for the development of new heterocyclic compounds, since there are many compounds of this structural type prepared from the reaction of chalcones with hydrazine derivatives[1-7].

As a continuation of previous studies[8] on the synthesis of some platinum (II) complexes of 3- aryl-5,5-dimethyl-2-pyrazolines (1)a procedure is described here for the preparation of 4-Methyl-1,2,3,4-tetrahydronaphtho[1,2- c] -2-pyrazolines(6) from the corresponding 2- arylidene -1- tetra lone (5).A considerable attention has been concentrated on 2- pyrazolines,due to their interesting activity of variously substituted pyrazolines as biological agents .These compounds reflect a pharmaceutical importance which lies in the fact that they can be effectively afforded as; antibacterial [9] , antiviral [10], antiparasitic [11], antitubercular [12], antimicrobial agents [13] and insecticidal agents[14]



(1)



(2)

. R= 4`-MeO$C_6H_5$ , 4`,5`-and 4`,5`- $(MeO)_2C_4H_3$, 3`,4`,5`-$(MeO)_3C_6H_2$, 3`,4`-3`,5`-, 4`,6`- and 4`,5`-$Me_2C_6H_3$

Experimental

Melting points were determined on a kofler Hot Plate and uncorrected. The I.R. absorption spectra were recorded with Perkin-Elmer Model 127 spectrophotometers. The ^{1}HNMR spectra were measured on a Bruker WH 90 and Varian 60 MHz with a deuterium internal lock.

General procedure for the preparation of 2- arylidene -4-methyl -1-tetralone [15] (5a- g)

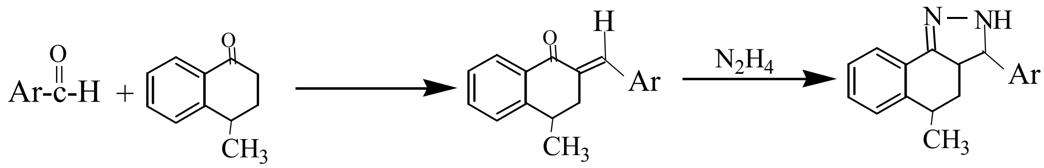
Equimolar amounts of the aldehydes 3 a-g (0.05 mole) and 4-methyl -1- tetra lone(0.05 mole) (4) were dissolved in 100 ml ethanol. The mixture was treated with 1.5 g of potassium hydroxide and stirred for 3 hours at room temperature. The product was filtered and recrystallized from ethanol to give the pure title compounds (5 a-g). The physical properties and spectral data were listed in the (Tables 1 and 2).

General procedure for preparation of 4-Methyl-1,2,3,4-tetrahydronaphtho [1,2-]-5-aryl-2`-pyrazolines [15] (6a-g)

A solution of 2- arylidene -4-methyl -1- tetra lone (5 a-g) (0.2 mole) and hydrazine hydrate (2g , 0.4 mole) in absolute ethanol (50 ml) was refluxed for 4-5 hours . The ethanol and unreacted hydrazine were removed at 100C°/ 25mm. The residue crystallized to a solid mass on cooling. This was recrystallized from ethanol to give the title compounds (6a-g). The physical properties and spectral data were listed in the (Table 3)

Results and Discussion

Generally, the synthetic method[15] followed to obtain the corresponding 2- arylidene -1-benzosuberones (2) has been employed to prepare 2- arylidene-4-methyl -1-tetralones (5). The appropriate aromatic aldehyde (3) was condensed with 4-methyl-1-tetralone (4) and the corresponding chalcones (5) were reacted with hydrazine to provide the desired tetrahydronaphtho [1,2-c]-2`-pyrazolines (6).



(3) (4) (5) (6)

a; Ar = C6H5
b; Ar = 4- OCH3C6H4
c; Ar = 2- OH.C6H4
d; Ar = 3, 4- OCH2O.C6H3
e; Ar = 3,4-CL2.C6H3
f; Ar = 1-naphthyl
g; Ar = 9-anthracenyl

The structure (5) was deduced from the ^{1}H NMR. spectrum, in particular, the position of the lower field singlet at 8.0- 8.2 which showed the arylidene group to occupy the 2-position. The signals of the sp^3 protons H-3, H-4 and CH**3** are readily assigned from the observed spin- spin coupling. As expected, the signals due to the H-3 and H-4 occur at somewhat lower field as a doublet and triplet and absorb in region δ 2.8-3.2, respectively as a multiplet, while CH**3** is found at higher field as doublet. The infra red spectra of these compounds (5a-g) show absorption bands in the regions 1660-1680 cm^{-1} and 1600- 1615 cm^{-1}attributed to C=O and C=C , respectively (Table 2).

The chalcones (5a-g) were condensed with hydrazine in an attempt to prepare the corresponding final product (6a-g). According to the IR and ^{1}H NMR. data (Table 3) the coupling products exist predominantly in the pyrazole form. The NMR–spectra of (6a-g) revealed the presence of one signal in the range of δ 3.5-3.8 ppm for N-H protons, which disappeared upon deuteration.The benzylic protons appeared as multiplets in the region δ 4.15-4.6 ppm (J =12 Hz). The cyclohexyl protons and methyl group appeared as multiplets in the range of 2.1-2.4 ppm for the former and at 1.0-1.5 ppm for the latter (Table 3).

Table (1). Physical and Analytical Data of Compounds 5a-g

Compd.No.	Formula	M.P. (C°)	Yield (%)	Analysis(Calc./Found)	
				C	H
5a	C**18**H**16**O	114-117	90	87.09 87.31	6.45 6.51
5b	C**19**H**18**O**2**	54-55	92	82.20 82.24	6.47 6.32
5c	C18H**16**O**2**	141-142	89	81.81 81.73	6.06 6.13
5d	C**19**H**16**O**3**	118-120	95	78.08 78.40	5.47 5.63
5e	C**18**H**14**CL2O	90-92	93	68.35 68.54	4.43 4.80
5f	C**22**H18O	100-101	87	88.59 88.31	6.04 6.16
5g	C**26**H**20**O	>300	97	89.65 89.83	5.74 5.81

Table (2). Spectral Data of Compounds 5a-g

Compd.No.	I.R.(KBr), ν cm^{-1} C=O	C=C	^{1}HNMR δ (ppm) solv. $CDCl_3$
5a	1600	1610	1.4 (d, 3H, CH_3) 3.0-3.2 (m,3H, H-3 ,H-4) 7.2-8.3 (m,10H, Ar-H, C=C-H)
5b	1670	1600	1.3 (d,3H, CH_3) 3.0-3.2 (m,3H,H-3, H-4) 4.0 (s, 3H, OCH_3) 7.0 -8.2 (m, 9H, Ar-H, C=C-H)
5c	1680	1610	1.35 (d,3H, CH_3) 2.7-2.9(m, 3H, H-3,H-4) 7.0-8.0 (m, 9H ,Ar-H, C=C-H) 10.2 (s, 1H, OH)
5d	1680	1615	1.2 (d, 3H, CH_3) 3.0-3.2(m,3H ,H-3 ,H- 4) 6.0 (s, 2H, OCH_2O) 7.0-8.2 (m, 8H, Ar-H, C=C-H)
5e	1670	1600	1.2 (d, 3H , CH_3) 3.0-3.2 (m, 3H , H-3,H-4) 7.2-8.3 (m, 8H , Ar-H , C=C-H)
5f	1675	1600	1.1 (d, 3H , CH_3) 2.9-3.1 (m,3H, H-3, H-4) 7.1- 8.6 (m, 12H, Ar-H , C=C-H)
5g	1680	1610	1.1(d, 3H, CH_3) 2.9-3.1 (m,3H, H-3,H-4) 7.1-8.9(m, 14H,Ar-H,C=CH)

Table (3). Physical and Spectral Data of Compounds 6a-g.

Compd.No.	M.P.(Ċ)	Yield (%)	I.R.(KBr), ν cm^{-1} N-H	C=C	^{1}HNMR δ (pmm)solv.CDCL**3**
6a	88- 90	70	3340	1625	1.3(d,3H, CH**3**) 2.0-2.2(m,4H, CH2,2CH) 2.7(s,1H, N-H) 4.3(m,1H, Benzylic proton) 7.1-8.2(m, 9H,Ar-H)
6b	150- 154	75	3345	1610	1.4(d,3H, CH3) 2.1-2.3(m,4H, CH2,2CH) 3.8(s, 1H, N-H) 4.0(s, 3H, ,OCH**3**) 4.4(m,1H, Benzylic proton) 6.9- 8.0(m,8H,Ar-H)
6c	120 -123	60	3360	1610	1.5(d, 3H, CH**3**) 2.1-2.3(m, 4H, CH2,2CH) 3.6(s, 1H, N-H) 4.3(m, 1H, Benzylic proton) 7.1-8.2(m,8H, Ar-H) 10.1(b, 1H, OH)
6d	150- 152	80	3360	1615	1.3(d,3H, CH**3**) 2.1-2.3(m,4H, CH2,2CH) 3.5(s,1H, N-H) 4.15(m,1H, Benzylic proton) 6.1(s,2H, OCH**2**O) 7.0-8.1(m, 7H, Ar-H)
6e	156- 160	70	3365	1617	1.2(d,3H, CH**3**) 2.3-2.5(m,4H, CH2,2CH) 3.8(s, 1H, N-H) 4.5(m,1H, Benzylic proton) 7.0-8.0(m,7H, Ar-H)
6f	156- 158	65	3380	1615	1.3(d, 3H, CH**3**) 2.0-2.2(m,4H, CH2,2CH) 3.6(s, 1H, N-H) 4.4(M, 1H, Benzylic proton) 7.0- 8.1(m, 11H, Ar-H)
6g	108- 110	60	3350	1620	1.0(d, 3H, CH**3**) 2.2-2.4(m, 4H, CH2,2CH) 3.7(s, 1H, N-H) 4.6(m, 1H, Benzylic proton) 7.1- 8.5(m,13H, Ar-H)

References

1- N.R. EL-Rayyes, G.H. Hovakeemian and H.Hammoud, ***J. Chem.Eng***.Data, 1984, **29**, 225
2- N.R. EL-Rayyes and N.J. AL-Johary, ***ibid***.,1985, **30**,500
3- N.R. EL-Rayyes and N.A. AL-Awadi, ***Synthesis***, 1985,1028,
4- N.R. EL-Rayyes and A. AL-Jawhary, ***J. Heterocyclic Chem***.,1986, **23**, 135
5- N.R. EL-Rayyes and H.M. Ramadan, ***J. Heterocyclic Chem.***,1987, **24**, 589
6- A. Lè vai, ***J.Heterocyclic Chem***.,2002, **39**, 1
7- A.J. AL-Hamdany, Ph. D. Thesis, Mosul Univ. (2002)
8- T.A.K. AL-Allaf. M.T. Ayoub and R.I. H. AL- Bayati, ***Inorg. Chim. Acta***, 1988, 147-185.
9- S.G.Roelfvan; C.Amold; K.Wellnga, ***J.Agric. Food Chem.,*** 1979, **84**,406
10- R.M. Kedar ; N.N.Vidhale and M.M.Chincholkar, Orient ***J. Chem.***, 1997, **13**, 143
11- A.Singh; S. Rathod; B.N.Berad and A.G. Dosh, Orient, ***J. Chem.,*** 2000, **16**, 315
12- H.Z.Katri; S.A.Vunii, ***J.Ind.Chem*.Soc.,** 1981,**58**,168
13- D.Azarifar and M.Shaebanzadeh, ***Molecules,*** 2002, **7**,885
14- N.B.Das and A.S.Mittra, ***J.Ind.Chem.,*** 1978,**16B**,638
15- N.R. EL- Rayyes and N.H. Bahtiti, ***J. Heterocyclic Chem.***, 1989, **2, 6**, 209.