

Synthesis of Some New Substituted 1,3,5-Triaryl Pyrazolines

Mowafaq Y. Shandala and Aws M. Hamdy

Department of Chemistry, College of Science, Mosul University

(NJC)

(Received on 26/2/2007)

(Accepted for publication on 24/3/2008)

Abstract

A series of substituted chalcones were synthesized by the Calaisen-Schmidt condensation of substituted benzaldehydes and acetophenones. The reaction of these chalcones with phenyl hydrazine were studied under phase transfer catalysis (PTC) conditions employing tetrabutyl ammonium iodide (TBAI) as a catalysed to synthesize 1,3,5-pyrazolines. The structures of all products were elucidated by physical and spectroscopic methods.

(-)

-5,3,1

Introduction

As a part of an investigation of the reaction of phenyl hydrazine with different chalcones give pyrazoline⁽¹⁻³⁾. Recently the reaction of chalcones with phenyl hydrazine under phase transfer catalysis (PTC) technique employing tetrabutyl ammonium iodide (TBAI) as a catalyst in 50% aqueous sodium hydroxide as a base and benzene as a solvent⁽⁴⁾.

In present work the reaction of phenyl hydrazine with exocyclic α,β -unsaturated cyclic ketones under phase transfer catalysis was undertaken.

Thus different aromatic aldehydes were condensed with different acetophenone derivatives to give the corresponding chalcones (1-9)⁽⁵⁾.

Then the title compound (1,3,5-triazolines) (11-19) were synthesized by

the reaction of chalcones (1-9) with phenyl hydrazine⁽⁶⁾.

Experimental

1. Preparation

Preparation of the starting materials (chalcone):

The compounds under investigation were prepared by standard method⁽⁴⁾, where the corresponding substituted benzaldehydes and acetophenones are condensed in aqueous ethanolic sodium hydroxide.

2. Instrumental and Apparatus

Melting points were measured on Electrothermal IA 9000 Series Digital Melting Point Apparatus and are uncorrected. IR spectra (cm^{-1}) were recorded by a Pye Unicam

SP 2000 Spectrophotometer in KBr disk. NMR spectra were recorded on Hitachi Perkin-Ekmer NMR Spectrophotometer (60 MHz), using TMS as internal reference. Elemental analysis were performed on a Carlo Erba type 1106, CHN Spectrophotometer UV-1650PC using chloroform as solvent. All measurements were carried out in University of Mosul. Physical and spectral data of the products (1-9) are listed in Table (1).

Condensation of chalcones with phenyl hydrazine⁽³⁾

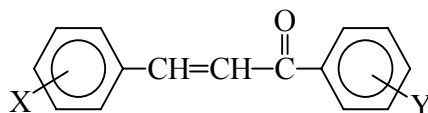
In a 50 ml round-bottomed flask fitted with a mechanical stirrer, was introduced phenyl hydrazine (0.005 mole), aqueous sodium hydroxide (6 ml-50%), benzene (25 ml) and tetrabutyl ammonium iodide (TBAI) as a catalyst (0.00055 mole). The mixture

was stirred for (15 min) and the corresponding chalcone (0.005 mole) was added while stirring was continued. The reaction mixture was kept at 50 °C in water bath until no color change of the reaction mixture was observed, about two hours.

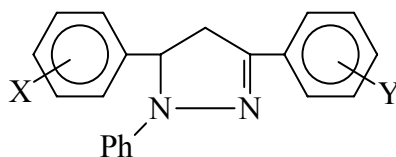
The reaction mixture was transferred into a separating funnel and the aqueous layer was separated. The benzene layer unless otherwise stated was worked up by washing it several times with water to remove rid of the base and the catalyst, dried over anhydrous magnesium sulphates filtered and then evaporated under reduced pressure using rotatory evaporator.

The residue obtained was dissolved in boiling ethanol, decolorized by activated charcoal and filtered. The filtrate gave after cooling crystalline product compounds (11-19).

Table (1): Physical and spectral data for chalcones (1-9)



Comp. No.	X	Y	m.p. °C		Yield %	IR (KBr) ν cm^{-1}		UV (CHCl_3) λ_{max} (nm)
			Found	Lit. ⁽⁷⁾		C=C	C=O	
1	H	H	56-58	53-55	90	1619	1665	328
2	2-Cl	H	45-47	-	85	1585	1627	318
3	4-Cl	H	110-112	112-115	80	1601	1656	315
4	2,4-diCl	H	98	-	70	1606	1627	325
5	H	4-Cl	102-103	100-101 ⁽⁸⁾	75	1620	1656	314
6	2,4-diCl	4-Me	97	-	85	1600	1627	332
7	3,4-diCl	4-Me	122-124	-	78	1606	1627	320
8	H	4-Me	78-80	80-81 ⁽⁸⁾	90	1606	1665	325
9	2-Cl	2-OMe	54-56	-	90	1601	1649	345

Table (2): Some physical data for compounds (11-19)

Cmp. No.	X	Y	m.p. °C	Yield %	Molecular formula	Molecular weight (g/mole)	Analysis calc./found		
							%C	%H	%N
11	H	H	132-134	78	C ₂₁ H ₁₈ N ₂	298	84.41	5.14	9.28
							84.56	5.24	9.39
12	2-Cl	H	99	80	C ₂₁ H ₁₇ ClN ₂	332	75.53	5.23	8.63
							75.78	5.11	8.42
13	4-Cl	H	125-127	75	C ₂₁ H ₁₇ ClN ₂	332	76.06	5.24	8.29
							75.78	5.11	8.42
14	2,4-Cl	H	179-180	78	C ₂₁ H ₁₆ Cl ₂ N ₂	366	68.74	4.52	7.74
							68.66	4.35	7.62
15	H	4-Cl	149-150	70	C ₂₁ H ₁₇ ClN ₂	332	75.58	5.25	8.32
							75.78	5.11	8.42
16	2,4-Cl	4-Me	150-151	80	C ₂₂ H ₁₈ Cl ₂ N ₂	380	69.39	4.84	7.22
							69.29	4.72	7.34
17	3,4-Cl	4-Me	175-177	75	C ₂₂ H ₁₈ Cl ₂ N ₂	380	69.35	4.85	7.25
							69.29	4.72	7.34
18	H	4-Me	155-157	60	C ₂₂ H ₂₀ N ₂	312	84.22	6.62	8.69
							84.61	6.41	8.97
19	2-Cl	2-OMe	139	58	C ₂₂ H ₁₉ ClN ₂ O	362	72.92	5.44	7.83
							72.82	5.24	7.72

Results and Discussion

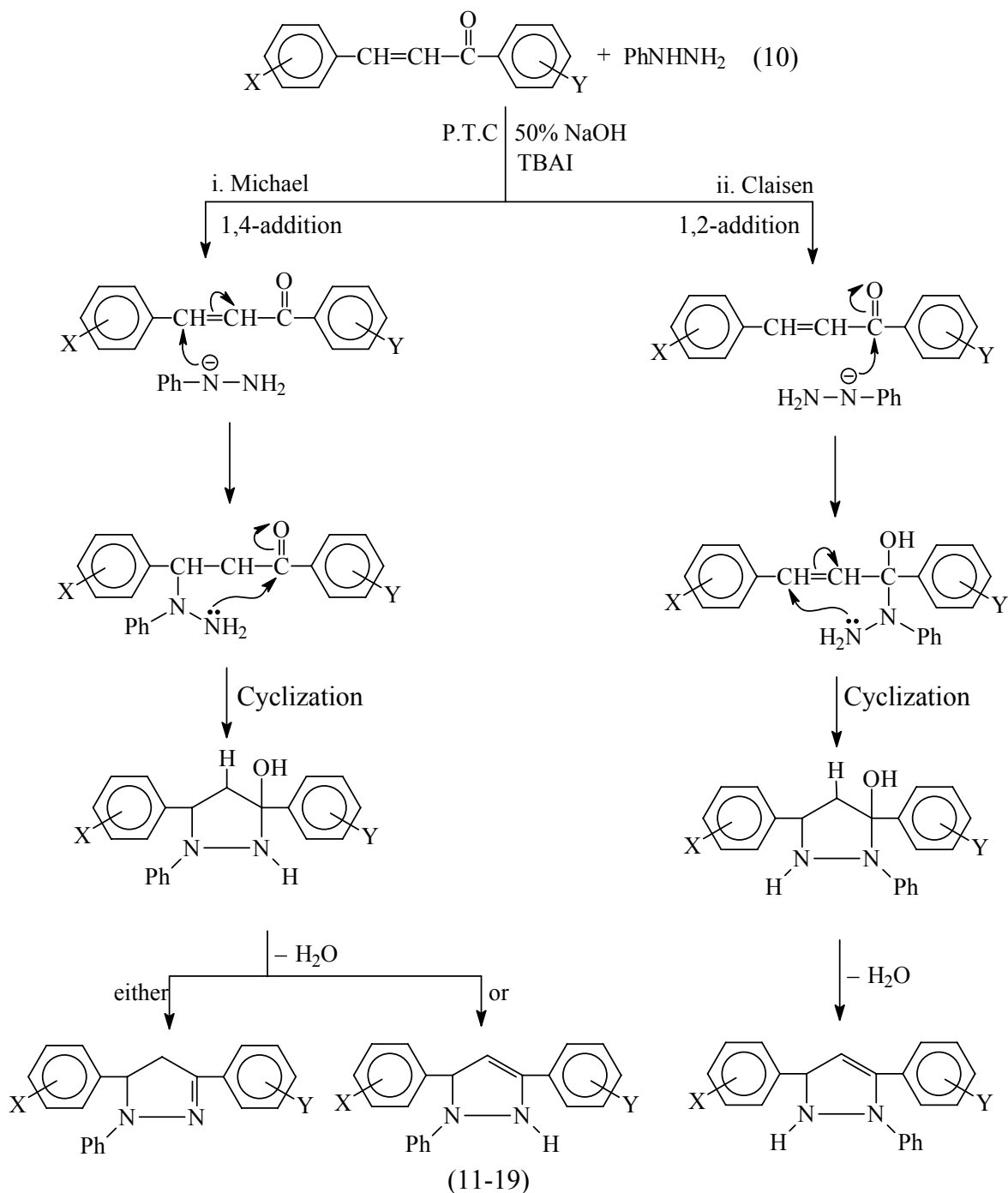
The reaction of phenyl hydrazine with chalcones (1-9) under phase transfer catalysis (PTC) conditions in presence of tetrabutyl ammonium iodide (TBAI) as a catalyst in 50% aqueous sodium hydroxide and benzene (liquid-liquid system), yielded the corresponding 1,3,5-triaryl pyrazolines (11-19).

The reaction pathway could be described by either route (i) or (ii)^(9,10). Route (i) Scheme (1) proceed by

Michael addition of (carbanion ion) (PhN⁻NH₂) to the chalcones (1,4-addition) followed by cyclization via Claisen addition and spontaneous dehydration.

Route (ii) proceed by Claisen addition of amide (H₂NNPh) to the chalcones (1,2-addition) followed by cyclization via Michael addition with spontaneous dehydration.

Both routes give the corresponding 1,3,5-triaryl pyrazolines (11-19).



Scheme (1): Reagent of chalcone with phenyl hydrazine

Table (3) shows the UV, IR and ^1H NMR spectral data for the products. The data are in quite good agreement with the proposed structure. Due to the similarity in the structures of the

products (11-19)⁽¹¹⁾. compound (12) will be used as a representative model for elucidation of the structures of the proposed products by the analysis of the spectral data.

Table (3): Spectral data for compounds (11-19)

Comp. No.	UV (CHCl ₃) λ_{\max} (nm)	IR (KBr) ν (cm ⁻¹) C=N	¹ HNMR				
			OCH ₃	CH ₃	CH ₂	CH	Ar-H
11	228	1607	*	*	*	*	*
12	230	1588	-	-	2.7 (d)	4.6 (tb)	6.0-7.6 (m)
13	235	1592	-	-	2.7 (d)	4.6 (tb)	6.1-7.6 (m)
14	252	1597	-	-	2.8 (d)	4.7 (tb)	6.2-7.5 (m)
15	237	1595	-	-	2.6 (d)	4.5 (tb)	6.0-7.1 (m)
16	259	1603	-	2.8 (s)	2.6 (d)	4.7 (tb)	6.2-7.4 (m)
17	252	1598	*	*	*	*	*
18	245	1601	*	*	*	*	*
19	259	1593	3.5 (s)	-	2.7 (d)	4.6 (tb)	6.1-7.4 (m)

* ¹HNMR spectra are not performed due to the lack of solvent.

The abbreviations of the proton signal description are s: singlet, d: doublet, m: multiplet, b: broad, t: triplet.

The IR spectral data⁽¹¹⁾ for compounds (11-19) show an absorption bands at 1588-1607 cm⁻¹ which correspond to C=N. The ¹H-NMR spectral data for compounds show a doublet at 2.7 ppm for CH₂ group and a triplet at 4.6 for CH group and a multiple for ring system 6.0-7.6 (9H) aromatic hydrogen.

The UV spectral data for the products show an absorption band trend at 228-259 nm indicating a blue shift (bathochromic shift) for the absorption of chalcones⁽¹²⁾.

References

1. J. Elguero, In Comprehensive Heterocyclic Chemistry, A.R. Katritzky, C.W. Rees and E.F. Scriven, Eds., *Pergamon Press, Oxford*, 1996, **3**, 1.
2. M.A. El-Maghray, A.K. Khalafalla, M.E. Hassan and H.A. Soleiman, *J. Indian Chem. Soc.*, 1986, **LXIII**, 910.
3. A. Levai, *J. Heterocyclic Chem.*, 2002, **39**, 1.
4. E.B. Krein and Z. Aizenshat, *J. Org. Chem.*, 1993, **58**, 6103.
5. A. Vogel, "Practical Organic Chemistry", Longmans, 2nd Ed., pp. 676, 681, (1951).
6. M.T. Ayub, S.A. Said and M.M. Zakarya, *Raf. Jour. Sci.*, 2001, **12**, 1, Chemistry Special Issue, 53.
7. F. Toda, H. Takumi, M. Naggmi, K. Tanaka, *Heterocyclic*, 1998, **47**, 471.
8. A. Yousif, M.Sc. Thesis, Mosul Univ., p. 32, (1999).
9. Coispeau and J. Eguero, *Bull. Soc. Chim. Fr.*, 7, 2717, (Fr) (1970); *Chem. Abst.*, 73, 109713t, (1970).
10. A.J. Al-Hamdany, A.M. Hamdy, *J. Edu. Sci.*, 2006, **18**, 2, 48.
11. D.H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry", 2nd Ed., McGraw-Hill, England, pp. 51-64, (1973).
12. V.M. Parikh, "Absorption Spectroscopy of Organic Chemistry", Addison-Wesley Pub Co., pp. 62, 245, (1974).