## Synthesis of Some Cyclohexene Derivatives by Diels-Alder Reaction

Jasim A. Abdullah Omar Th. Ali Yaser S. Al-Jawharji

Department of Chemistry, College of Education, University of Mosul, Mosul-Iraq (Received 17 / 2 / 2008, Accepted 11 / 6 / 2008)

#### Abstract

In this study a compounds of 1-(4-chlorophenyl)-5-phenyl-4-methyl-2,4-pentadiene-1-one (1) and 1-(4-methoxyphenyl) -5- phenyl-4-methyl-2,4-pentandiene-1-one (2) were prepared by reaction of  $\alpha$ -methyl cinnamaldehyde with substituted acetophenones.

Also1,3-diphenyl-2-chloropropene-1-one (3) was synthesized from reaction of benzaldehyde with 2-chloroacetophenone through Claisen - Shmidt condensation. The substituted cyclohexene (4,5) were prepared by reaction of (1,2) with (3) through Diels-Alder reaction. Compounds (4,5) were reacted with some of amino derivatives to synthesize compounds (6-11).

The structures of all synthesized compounds were confirmed by available physical and spectral data.

Key words: Cyclohexene, Diels-Alder Reaction

#### Introduction

The Diels-Alder reaction is one of the most important and useful method in organic synthesis because it is efficiently provide a various ring structures which are present in many natural products<sup>(1)</sup>. The Diels-Alder reaction, in which a conjugated diene and substituted alkene-the dienophile–react to form a cyclohexene.



This is an example of cycloaddition, reaction in which two unsaturated molecules combine to form a cyclic compound, with  $\Box \pi$  electrons being used to form two new  $\sigma$  bonds. The Diels-alder reaction is a (4+2) cycloaddition, since it involves system of  $4\pi\Box$  electrons and a system of  $2\pi$  electrons. This reaction take place very easily, often spontaneously, and at most requires moderate application of heat<sup>(2)</sup>.In Diels-Alder reaction a double bond adds 1,4- to conjugated diene a (4+2) cycloaddition<sup>(3)</sup>, so that the product is always a sixmembered ring. The double bond compound is called adienophile. The reaction is easy and rapid and of very broad scope. Most dienophiles are of the form (-C=C-Z), where (Z) is: CHO, COR, COOH, COOR, COCl, COAr, CN,NO<sub>2</sub>, CH<sub>2</sub>OH, Ar, CH<sub>2</sub>Cl, CH<sub>2</sub>NH<sub>2</sub>, CH<sub>2</sub>CN, CH<sub>2</sub>COOH, C=C and halogen<sup>(4,5,6)</sup>. In the latter case the dienophile is itself a diene .it is now well established that 1-aryl-5-phenyl-4-methyl-2,4-pentadiene-1-

ones(1and2)are useful precursors to dienes.<sup>(7)</sup>. The carbonyl group has been used as a control element in the Diels-Alder reaction<sup>(8)</sup>. In addition to the compound(3) contain halogen (Cl) electron withdrawing group It make compound(3) a good dienophile<sup>(9)</sup>. The Diels-Alder reaction of compounds(1,2) with dienophile (3) to form compounds (4,5) respectively, will be studied<sup>(10)</sup>.

#### Experimental

**Chemicals and instrumentation:** 

All chemicals were purchased from Flucka and BDH Chemical Ltd. The melting points were measured on an Electrothermal 9300 Engineering LTD and were uncorrected. IR spectra were recorded on Infrared Spectrophotometer Model Tensor 27, Bruker Co., Germany, using KBr discs. UV spectra were recorded on Shimadzu Double-Beam Spectrophotometer UV-210 A using chloroform as a solvent.

The theoretical calculations were computed using semiempirical AM1 module in the CS ChemOffice molecular modeling package. The data obtained from the minimized geometry were used for the theoretical calculations.

#### Preparation of 1-aryl-5-phenyl-4-methyl-2,4pentadiene-1-ones (1,2)<sup>(11)</sup>

Substituted acetophenone (0.0166 mole) was mixed with  $\alpha$ -methyl cinnamaldehyde (0.0166mole) in (25ml) of absolute ethanol, the mixture was stirred in a bath of crushed ice, a solution of (15ml) of sodium ethoxide (the instant preparation from (0.75g) of sodium with (15ml) of absolute ethanol) was added to the mixture. The bath was removed while a vigorous stirring was continued for (1-2hr) at room temperature, the product was filtered, washed with cold ethanol, dried and recrystallized from (1:1-benzene-ethanol) to give greenish yellow crystals, (Table 1).

# **Preparation of 1,3-diphenyl-2-chloropropene-1-one(3)**<sup>(12)</sup>

A solution of (22g) of sodium hydroxide in (200ml) of water and (125g) of ethanol was placed in a flask provided with a mechanical stirrer, the flask was immersed in a bath of crushed ice. (0.43mole) of pure 2-chloro-acetophenone and (0.43g) of pure benzaldehyde were added with stirring. The temperature of the mixture was maintained at  $(25^{\circ}C)$  while a vigorous stirring was continued for (15min). The product was filtered, washed with cold water until be neutral to litmus, then washed with ice-cold rectified spirit and finally recrystallized from ethanol to give white solid product (3).

 Table (1): Some physical properties and spectral data for compound (1-3)

Comp. No X m.p °C Yield	I IR(KBr), $v(cm^{-1})$	U.V (CHCl <sub>3</sub> )
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			%	С=О	C=C-C=C	C=C	Ar-C=C	$\lambda_{max}(nm)$
1	-Cl	143-144	95	1652	1562,1587	-	1500,1600	326
2	-OCH <sub>3</sub>	118-120	60	1653	1569,1576	-	1500,1600	325
3	-	78-80	95	1686	-	1640	1500,1600	302

## Preparation of 1-methyl-5,6-diphenyl-4-chloro-4benzoyl-3-(4-chloro benzoyl) cyclohexene(4) and 1-methyl-5,6-diphenyl-4-chloro-4-benzoyl-3-(4methoxybenzoyl) cyclohexene (5) <sup>(13)</sup>

A mixture of (0.31 mole) of (1or2) with (0.31 mole) of 1,3-diphenyl-2-chloropropene-1-one in benzene (50 ml) was refluxed for (24 hr),then benzene evaporated and the product was recrystallized from petroleum ether to give (4or5) as a pale yellow crystals.

## Preparation of 1-methyl-5,6-diphenyl-4-chloro-4benzoyl-3-(4-chlorobenzoyl phenyl hydrazone) cyclohexene(6,7)<sup>(14)</sup>

(0.02mole) of compounds (4or5) was added to solution of phenyl hydrazine (0.02mole) in (25ml)of ethanol and(5drops)of conc. HCl. The mixture was refluxed for (30 min.), after cooling the solid was filtered, washed with methanol and recrystallized from (1:2-waterethanol) to give compounds (6 or 7).

#### Preparation of 1-methyl-5,6-diphenyl-4-chloro-4benzoyl-3-(4-

chlorobenzoylsemicarbazone)cyclohexe (8) and 1-methyl-5,6-diphenyl-4-chloro-4-benzoyl-3-(4-

## methoxy benzoyl semicarbazone) cyclohexene (9)

A solution of semicarbazide hydrochloride (0.005mole) in (20ml) of water and anhydrous sodium acetate (0.5gm) was heated till to be clear solution, then (0.005mole) of compounds (40r5) was added ,the mixture was refluxed for (2 hr). After cooling, the solid was filtered and recrystallized from ethanol to give compounds (8 or 9).

#### Preparation of 1-methyl-5,6-diphenyl-4-chloro-4benzoyl-3-(4-chlorobenzoyloxime) cyclohexene(10) and 1-methyl-5,6-diphenyl-4-chloro-4-benzoyl-3-(4methoxy benzoyloxime) cyclohexene(11)<sup>(16)</sup>

A mixture of (0.02mole) of hydroxyl amine hydrochloride in (20ml) of ethanol and (0.8g) of sodium hydroxide, was immersed in bath of crushed ice. Then(0.02mole) of compounds (4 or 5) was added gradually with stirring. The temperature was maintained at (15°C), after the addition was completed, the mixture was left in a refrigerator for (1h),the product was filtered, washed with water and recrystallized from ethanol to give compounds (10 or 11).

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Comp. No	X	m.p °C	Color	Yield %
4	-Cl	108-111	Pale yellow	75
5	-OCH <sub>3</sub>	75-77	Yellow	93
6	-Cl	153-155	green	65
7	-OCH <sub>3</sub>	109-112	green	70
8	-Cl	186-170	Light gray	70
9	-OCH <sub>3</sub>	127-129	Light gray	75
10	-Cl	133-135	Brown	87
11	-OCH <sub>3</sub>	117-119	Light brown	82

Table (2): physical properties for compounds (4-11)

## **Result And Discussion**

In this study, compounds (1,2) were prepared by section (1), the structure of compound (2) was elucidated by ultra violet and infrared spectra (Table 1), which showed sharp peak at  $(1652 \text{ cm}^{-1})$  due to carbonyl group. The range of bands at (1562-1600cm<sup>-1</sup>) due to the conjugated diene system (C=C-C=C). Compound (3) was prepared by (clasin-shmidt) reaction in section (2), the spectral informations showed a sharp peak at (1686cm<sup>-1</sup>) due to carbonyl group, a medium peak at (1640 cm<sup>-1</sup>) due to (C=C) double bond, the IR spectrum for carbonyl group appeared at a higher frequency than that in compounds (1,2) from their rates<sup>(16,17)</sup>. The U.V spectra of compounds (1- 3) showed  $\lambda_{max}$  at (302-326 nm) which indicates that conjugation was found between the (C=O) group and (C=C) group causing bathochromic shift (red shift) comparing with those which have no conjugation (starting materials).

The reaction of each compounds (1,2) with (3) produced compounds (4,5) respectively. The calculations of the heat of formation for the products showed that the suggested structures are the possible structures because they have a low energy of heat of formation (Table 3).

The structures of compounds (4,5) showed sharp peaks at (1686, 1690 cm<sup>-1</sup>) respectively, due to the two interfered carbonyl groups, another bands at (1589,1599 cm<sup>-1</sup>) respectively, due to the double bonds. The IR spectra which appeared higher than their values indicates that conjugation was disappeared. The U.V spectra which showed a  $\lambda_{max}$  at (284,292 nm) for compounds (4,5) respectively indicates that conjugation was decreased so that the absorption appeared at shorter wave length (blue shift).

Compounds (6,7) were synthesized from the reaction of compounds (4,5) with phenyl hydrazine, one carbonyl group reacted with the reagent and the other one did not because of the value of the steric effect which was calculated theoretically showed that unreacted carbonyl group has a very high steric effect. The proposed structures for these compounds are in a good agreement with spectral data and the direct products<sup>(19)</sup>, compound (6) had a low heat of formation ( $\Delta$ H). One carbonyl group absorbed at (1686,1690cm<sup>-1</sup>) region (1650, 1654 cm<sup>-1</sup>) due to (C=N) group and (3446,3442cm<sup>-1</sup>) due to (NH) group for compounds (6,7) respectively.

Compounds (8,9) were synthesized by the reaction of (4,5) with semicarbazide hydrochloride, the IR spectra showed in addition to peaks for (C=O,C=N and NH) new peaks for amide carbonyl (CONH<sub>2</sub>) near the electron donating group that reduces the stretching vibration of carbonyl<sup>(20)</sup>. The new peaks absorbed at (1651,1653 cm<sup>-1</sup>) due to (CONH<sub>2</sub>) for compounds (8,9) respectively.

Compounds (10,11) were synthesized by the reaction of compounds (4,5) with hydroxyl amine hydrochloride respectively. IR spectra showed a sharp bands at (1686, 1690 cm<sup>-1</sup>) due to carbonyl group for compounds (10,11) respectively, a medium peaks at (1651,1653cm<sup>-1</sup>) due to (C=N) group and abroad peaks at (3250,3274 cm<sup>-1</sup>) due to (OH) groups.

Comp. No X	\$7			IR (KB)	U.V(CHCl <sub>3</sub> )					
	А	C=O	C=C	Ar- C=C	C=N	N-H	C=O amide	0-Н	$\lambda_{max}(nm)$	
4	-Cl	1686	1579	1600, 1500	-	-	-	-	284	51.82
5	-OCH <sub>3</sub>	1690	1590	1600, 1500	-	-	-	-	292	20.10
6	-Cl	1686	1579	1600, 1500	1650	3446	•	•	346	157.20
7	-OCH <sub>3</sub>	1690	1590	1600, 1500	1654	3442	-	-	306	125.40
8	-Cl	1686	1579	1600, 1500	1578	3444	1651	-	312	91.41
9	-OCH <sub>3</sub>	1690	1590	1600, 1500	1586	3443	1653	-	344	87.48
10	-Cl	1686	1579	1600, 1500	1651	-	-	3250	338	84.47
11	-OCH <sub>3</sub>	1690	1590	1600, 1500	1653	-	-	3274	302	53.48

Table (3): IR.	<b>ILV</b> and AF	I data for co	mnounds (	4-11)
$\mathbf{I}$ and $(\mathbf{J})$ , $\mathbf{I}$	$\mathbf{O}$	$\mathbf{I}$ uata ivi $\mathbf{U}$	mpounus i	<b>T I I I I</b>



Scheme (1)

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- الحسين خضير شربة، جاسم محمد على الراوى ومحمد احمد

تحضير بعض مشتقات الهكسين الحلقي بوساطة تفاعل ديلز –ألدر جاسم علي عبد الله و عمر ذنون علي و ياسر شكيب الجوهرجي قسم الكيمياء ، كلية التربية ، جامعة الموصل ، الموصل ، العراق ( تاريخ الاستلام: ١٧ / ٢ / 2008 ، تاريخ القبول: ١١ / ٦ / 2008 )

#### الملخص

تم تحضير المركبات ١- (٤- كلوروفنيل) -٤- مثيل -٥- فنيل-٤،٢- بنتادايين-١- أون (١) و ١- (٤- ميثوكسي فنيل)-٤- مثيل-٥- فنيل-٤،٢-بنتادايين-١- أون (٢) من تفاعل المركب ألفا- مثيل- سينمالديهايد مع معوضات ألاسيتوفينون.

حضر المركب ٣،١- ثنائي فنيل-٢- كلوروبروبين-١- أون (٣) من تفاعل البنزالديهيد مع ٢- كلوروأسيتوفينون بوساطة تكاثف (كليزن-شمدت). حضرت معوضات الهكسين الحلقي (5,4) من خلال تفاعل المركبان (١ و ٢) مع المركب (٣) بوساطة تفاعل ديلز – ألدر. تم الحصول على المركبات (6-11) من خلال تفاعل المركبين (٥,٤) مع بعض مشتقات الأمينات.

> شخصت المركبات الناتجة بوساطة الطرائق الفيزياوية والتحليلات الطيفية المتوفرة (U.V,IR) بالاضافة إلى بعض الكشوفات المختبرية. ا**لكلمات المفتاحية**: الهكسين الحلقي، تفاعل ديلز – الدر