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## Reaction of $\alpha$ , $\beta$ -Unsaturated Carbonyl Compounds with Ethyl Phenylacetate Carbanions. A Synthesis of Substituted Cyclohexanones

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**ABSTRACT.** The Michael acceptors (chalcones II) react with the ethyl phenylacetate carbanion I in the presence of sodium hydride at room temperature and yield the corresponding Michael products:  $\gamma$ -aroylbutyrates III (from one mole each of I and II), the corresponding acids IV, or 2,4-diaroyl-cyclohexanones V (from one mole I and two moles of II). The nature of these products depends on the reaction conditions. The mechanism of the formation of the cyclohexanone derivatives (Va-g) as well as the regression of the Michael reaction are discussed. The structure of all products were inferred by chemical and spectroscopic methods.

In a previous publication (Baddar *et al.* 1976), the reaction of acetylenic ketones with compounds containing an active methylene group was reported. The present investigation was intended to study the reaction of different types of  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds II with ethyl phenylacetate, and to elucidate the structure of the products by chemical and spectral methods.

### Results and Discussion

The chalcones (IIa-c) were reacted with ethyl phenylacetate using sodium hydride (2 molar) as a base. The products proved to be a mixture of the esters (IIIa-c) and the acids (IVa-c). The structure of all products was substantiated by chemical and spectral methods (*cf.* Table 1, 2). Thus, the infrared spectra of the esters III (*cf.* Table 2), show two absorption bands in the region 1730-1740  $\text{cm}^{-1}$  and 1680-1684  $\text{cm}^{-1}$  which can be ascribed to  $\nu_{\text{C}=\text{O}}$  of the ester and aryl ketones, respectively (Bellamy 1958). The electronic spectra (*cf.* Table 2) of the esters reflect their structural analogy and agree with the proposed structure (Adembri *et al.* 1966). The nmr-spectra (*cf.* Table 2) lend further support to their structure and show

**Table 1.** Melting points and analyses of compounds III-VI.

Compound	Molecular formula	M.P. °C	Found (%)					required (%)				
			C	H	N	Cl	S	C	H	N	Cl	S
IIIa	C <sub>25</sub> H <sub>24</sub> O <sub>3</sub>	158	80.42	6.35				80.61	6.49			
b	C <sub>25</sub> H <sub>23</sub> O <sub>3</sub> Cl	108	73.53	5.71		8.63		73.79	5.69		8.71	
c	C <sub>26</sub> H <sub>26</sub> O <sub>4</sub>	144	77.42	6.33				77.58	6.51			
IVa	C <sub>23</sub> H <sub>20</sub> O <sub>3</sub>	177	80.13	5.81				80.21	5.85			
b	C <sub>23</sub> H <sub>19</sub> O <sub>3</sub> Cl	193	72.71	4.73		9.13		72.92	5.05		9.35	
c	C <sub>24</sub> H <sub>22</sub> O <sub>4</sub>	196	76.65	5.71				76.98	5.92			
Va	C <sub>38</sub> H <sub>30</sub> O <sub>3</sub>	264	85.17	5.41				85.36	5.65			
b	C <sub>38</sub> H <sub>28</sub> O <sub>3</sub> Cl <sub>2</sub>	186	75.43	4.83		11.84		75.62	4.67		11.74	
c	C <sub>38</sub> H <sub>28</sub> O <sub>3</sub> Cl <sub>2</sub>	212	75.31	4.51		11.66		75.62	4.67		11.74	
d	C <sub>40</sub> H <sub>34</sub> O <sub>5</sub>	209	80.63	5.45				80.78	5.76			
e	C <sub>30</sub> H <sub>22</sub> O <sub>4</sub> S <sub>4</sub>	275	64.41	3.81			22.72	64.48	3.97			22.95
f	C <sub>34</sub> H <sub>26</sub> O <sub>3</sub> S <sub>2</sub>	258	74.53	4.47			11.61	74.69	4.79			11.73
g	C <sub>36</sub> H <sub>30</sub> O <sub>5</sub> S <sub>2</sub>	247	71.08	4.76			10.42	71.26	4.98			10.57
VIa	C <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>2</sub> O	276	76.00	4.55	4.53	11.80		76.12	4.70	4.67	11.82	
b	C <sub>34</sub> H <sub>26</sub> N <sub>2</sub> OS <sub>2</sub>	249	75.30	4.71	5.22		11.63	75.24	4.82	5.16		11.81

chemical shifts which can be attributed to the hydrogens of the esters in their different environments (Al-Hajjar *et al.* 1979).

The structure of the acids (IVa-c) was also supported by chemical and spectral analysis. Thus, the infrared spectra of these acids show absorption bands in the regions 1675-1690  $\text{cm}^{-1}$  and 1690-1697  $\text{cm}^{-1}$  (*cf.* Table 2) which can be ascribed to the  $\nu\text{C}=\text{O}$  of the aryl ketones and carboxylic acids, respectively (Bellamy 1958). The acids absorb also in the region 3050-3100  $\text{cm}^{-1}$  which can be correlated to the

**Table 2.** Infrared, electronic spectra and nmr data of compounds III, IV and VI.

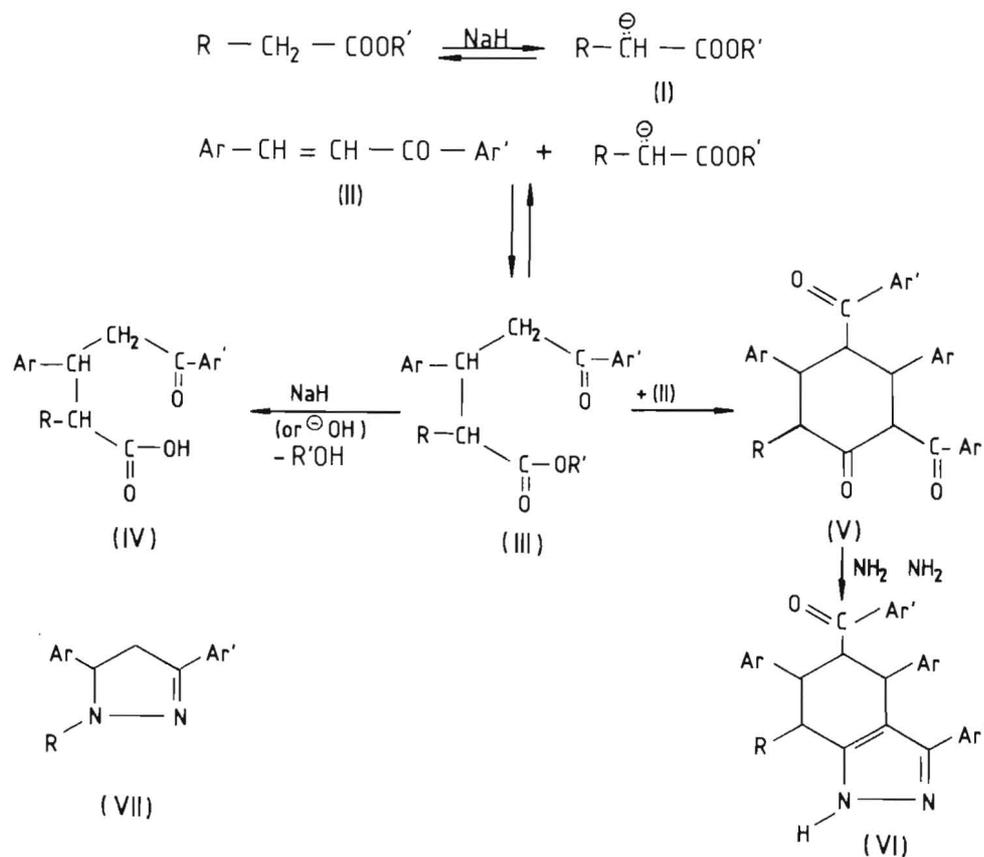
Compd	$\text{cm}^{-1}$	$\nu$	$\lambda_{\text{max}}$ (nm)	$\epsilon$	$\delta$	(No. of H) Assignment		
IIIa	1684 (s)	C=O	242	10290	7.7-7.07 (m)	(15) Ar-H		
	1732 (s)	C=O			5.2-3.0 (m)	(6) CH-CH-CH <sub>2</sub> + OCH <sub>2</sub>		
					1.0 (t)	(3) CH <sub>3</sub>		
b	1682 (s)	C=O	254	18600	7.71-6.85 (m)	(14) Ar-H		
	1730 (s)	C=O			5.1-3.0 (m)	(6) CH-CH-CH <sub>2</sub> + OCH <sub>2</sub>		
c	1680	C=O	228	20100	0.85 (t)	(3) CH <sub>3</sub>		
	1740	C=O			245	13300	7.7-6.7 (m)	(14) Ar-H
							3.7 (s)	(3) OCH <sub>3</sub>
IVa	1684 (s)	C=O	244	39820	5.1-3.0 (m)	(6) CH-CH-CH <sub>2</sub> + OCH <sub>2</sub>		
	1693 (s)					0.97 (t)	(3) CH <sub>3</sub>	
	3050 (br)				OH	7.9-7.03 (m)	(15) Ar-H	
b	1690 (s)	C=O	252	13440	5.15-3.45 (m)	(4) CH-CH-CH <sub>2</sub>		
	1696 (s)	C=O			7.9-7.1 (m)	(14) Ar-H		
c	3050 (br)	OH	229	16150	5.15-3.3 (m)	(4) CH-CH-CH <sub>2</sub>		
	1675 (s)	C=O			242	11700	7.9-6.65 (m)	(14) Ar-H
	1690 (s)	C=O					5.2-3.4 (m)	(7) CH-CH-CH <sub>2</sub> + OCH <sub>3</sub>
VIa	2990-3100 (br)	OH	227	21060				
	1600 (m)	Ar			252	16065	7.2-6.9 (m)	(18) Ar-H
	1680 (s)	C=O					7.5 (br)	(1) N-H
b	3400 (s)	NH	244	20340	4.9 (d)	(1) -N=C-C-H (J = 5 Hz)		
							4.4-3.4 (m)	(3) -CH-CH-CH
	1600 (m)	Ar					7.2 (s)	(10) Ar-H
VIa	1672 (s)	C=O	244	20340	6.8-6.4 (m)	(6) Thioph-H		
	3400 (s)	NH					5.8 (br)	(1) N-H
							5.35 (d)	(1) N=C-C-H (J = 5 Hz)
					4.6-4.0 (m)	(3) -CH-CH-CH-		

OH stretching vibrations (free) (Bellamy 1958). The electronic spectra of these acids are almost identical; this reflects their structural analogy (*cf.* Table 2). The nmr-spectra of the acids (IVa-c) reveal two multiplets in the regions  $\delta$  7.9-6.97 ppm and  $\delta$  5.15-3.3 ppm which are ascribed to the aryl and the adjacent (CH-CH-CH<sub>2</sub>) hydrogen, respectively. The mass spectra lend further support to the structure of these acids. Thus, the spectrum of the acid IVa showed a molecular ion peak at *m/e* 344 (0.84%). The base peak at *m/e* 105 (100%) stands for the benzoyl ion [C<sub>6</sub>H<sub>5</sub>-C=O]<sup>+</sup>. The relatively intense peak at *m/e* 209 (13.78%) stands for the ion [C<sub>6</sub>H<sub>5</sub>-CH-CH<sub>2</sub>-CO-C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>. The intense peak at *m/e* 118 (30.81%) represents the ion [HC-CO-C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>. The spectrum of the acid IVc revealed a molecular ion peak at *m/e* 374 (4.14%). The base peak at *m/e* 135 (100%) stands for the *p*-methoxy-benzoyl ion [*p*-OCH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-C=O]<sup>+</sup>, and the rest of the molecular ion shows a peak at *m/e* 239 (7.49%). The prominent peak at *m/e* 150 (32.95%) corresponds to the *p*-methoxyacetophenone ion.

**Table 3.** Infrared, electronic spectra of cyclohexanones Va-g.

Compd	cm <sup>-1</sup> (KBr)	$\nu$	cm <sup>-1</sup> (CHCl <sub>3</sub> )	$\nu$	$\lambda_{\max}$ (nm)	$\epsilon$
Va	1597 (m)	C=O	1600 (s)	C=O	248	28405
	1658 (s)		1685 (s)			
	1685 (s)		1722 (s)			
	1723 (s)					
b	-		-		227	32560
					246	26205
c	1605 (m)	C=O	-		222	14850
	1660 (s)		242		10800	
	1682 (s)		310		4500	
	1740 (s)					
d	1600 (s)	C=O	-		228	29800
	1660 (s)		242		24680	
	1680 (s)					
	1738 (s)					
e	1632 (s)	C=O	-		242	20585
	1668 (s)		263		17050	
	1730 (s)		290		15470	
f	1595 (m)	C=O	1600 (s)	C=O	245	58090
	1660 (s)		276		31435	
	1690 (s)		1685 (s)			
	1728 (s)		1723 (s)			
g	1600 (s)	C=O	1600 (s)	C=O	223	28520
	1653 (s)		277		37010	
	1680 (s)		1680 (s)			
	1722 (s)		1720 (s)			

Closely associated with the foregoing is the condensation of the chalcones (IIa-g) with ethyl phenylacetate in presence of excess base to give the substituted cyclohexanones (Va-g). The structure of these products was elucidated by chemical and spectral methods (*cf.* Table 3). The infrared spectra revealed absorption bands in the regions  $1632\text{--}1668\text{ cm}^{-1}$ , and  $1722\text{--}1740\text{ cm}^{-1}$  which can be ascribed to the  $\nu_{\text{C}=\text{O}}$  of the 2-aryl substituent (Bellamy 1958) and the cyclohexanone (Bellamy



Compound	Ar	Ar'	Compound	Ar	Ar'
II-V, VII a	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	II, Ve	C <sub>4</sub> H <sub>3</sub> S	C <sub>4</sub> H <sub>3</sub> S
II-V, VII b	C <sub>6</sub> H <sub>5</sub>	p-Cl-C <sub>6</sub> H <sub>4</sub>	II, Vf, VIb	C <sub>4</sub> H <sub>3</sub> S	C <sub>6</sub> H <sub>5</sub>
II-Vc	C <sub>6</sub> H <sub>5</sub>	p-OCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	II, Vg	C <sub>4</sub> H <sub>3</sub> S	p-OCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>
II, Vd, VIa	p-Cl-C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>			

IIIa-c : (R' = C<sub>2</sub>H<sub>5</sub>), III-VII : (R = C<sub>6</sub>H<sub>5</sub>)

Scheme 1.

1958). The low absorption in the region  $1595\text{--}1605\text{ cm}^{-1}$  may be due to aromatic ring vibrations or to chelated 1,3-dicarbonyl group. In the latter case, this absorption arises from a carbonyl group which has had its double bond character reduced by resonance (Bellamy 1958).

The absorption bands in the region  $1668\text{--}1690\text{ cm}^{-1}$  are due to the  $\nu\text{C}=\text{O}$  of the 4-aryl substituent (Bellamy 1958). It is noteworthy to mention, in this respect, that the absorption bands in the region  $1653\text{--}1660\text{ cm}^{-1}$  disappeared when the spectra were run in chloroform.

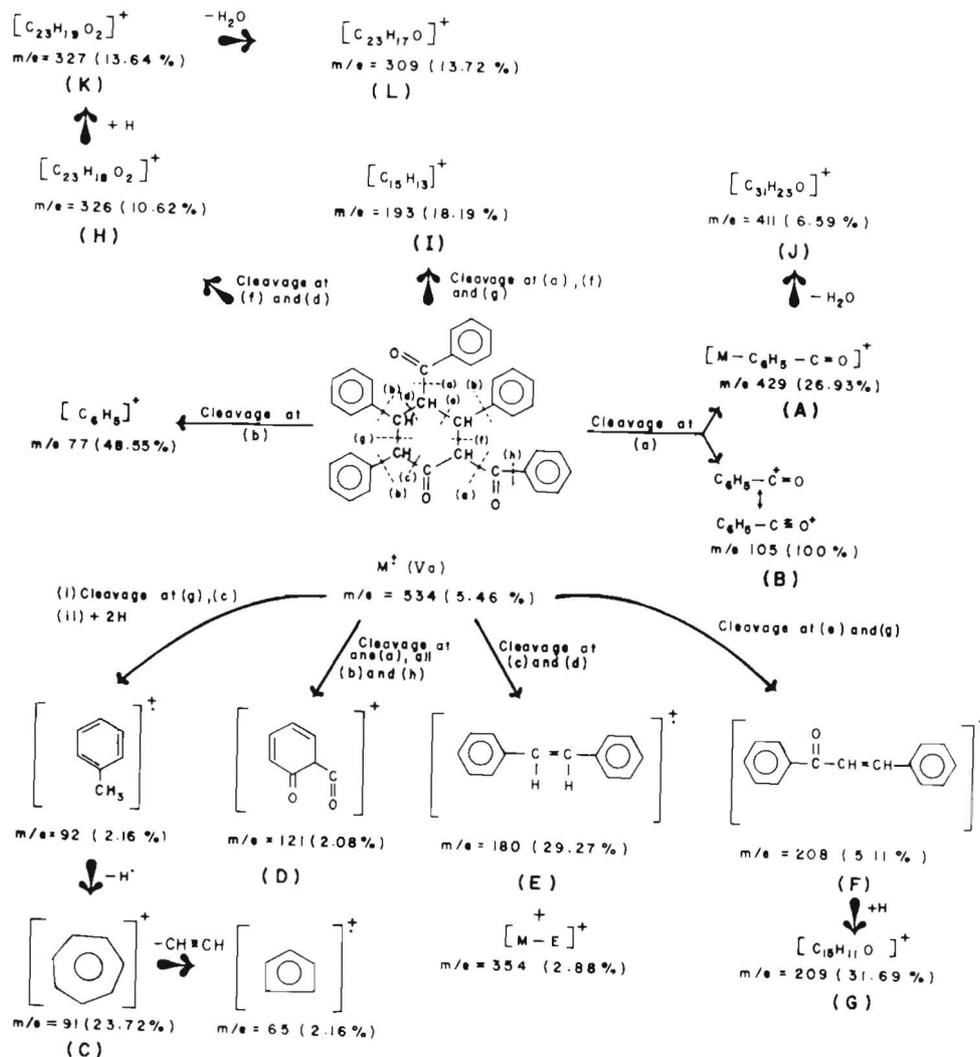
The electronic spectra of the cyclohexanone derivatives (Va-g) lend further support to their structure. They show absorption bands which can be ascribed to aryl moieties (Gencarelli *et al.* 1970). Compelling evidence to the structure of the cyclohexanones (V) can be obtained from their mass spectra. The spectrum of (Va) showed a molecular ion peak at  $m/e$  534 (5.46%). The other peak at  $m/e$  535 (2.40%) is due to the natural abundance of  $^{13}\text{C}$ , taking into account that Va has 38 carbon atoms. The base peak corresponds to the benzoyl ion  $[\text{C}_6\text{H}_5\text{--C}=\text{O}]^+$ , and appears at  $m/e$  105 (100%). The intense peak at  $m/e$  429 (26.93%) originates from the molecular ion after cleavage at one (a) position (*cf.* Scheme 2) to give the ion (A). Other fragment ions are represented in Scheme (2). The spectrum of Vc reveals a molecular ion peak at  $m/e$  594 (2.0%). The base peak at  $m/e$  105 stands for the benzoyl ion, and the ion with  $m/e$  489 (17.20%) corresponds to  $[\text{M}-105]^+$ . The peaks at  $m/e$  121 (17.85%) and  $m/e$  238 (20.14%) stand for the ions  $[\text{C}_7\text{H}_5\text{O}_2]^+$  and  $[\text{C}_{16}\text{H}_{14}\text{O}_2]^+$ , respectively (*cf.* ions D and 'methoxy-F' in Scheme 2). The ion at  $m/e$  161 (16.06%) corresponds to  $(p\text{--OCH}_3\text{--C}_6\text{H}_4\text{--CH}=\text{CH}\text{--C})^+$ .

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The spectrum of the cyclohexanone derivative (Vf) showed a molecular ion peak at 546 (12.68%). The base peak at  $m/e$  105 (100%) can be assigned to the benzoyl ion. The ion  $[\text{M}-105]^+$  peaks at  $m/e$  441 (47.76%), and the ion  $[\text{M}-\text{H}_2\text{O}]^+$  peaks at  $m/e$  528 (13.43%). The prominent peak at  $m/e$  186 (35.82%) stands for the ion  $[\text{C}_4\text{H}_3\text{S--CH}=\text{CH--C}_6\text{H}_5]^+$  which resembles the ion (E) (*cf.* Scheme 2). The spectrum of Vg revealed a molecular ion at  $m/e$  606 (22.95%) with an intense isotopic peak at  $m/e$  135 (100%), corresponding to the ion  $[p\text{--OCH}_3\text{--C}_6\text{H}_4\text{--C}=\text{O}]^+$ , an intense peak at  $m/e$  588 (32.78%) standing for the ion  $[\text{M}-\text{H}_2\text{O}]^+$  and a peak at  $m/e$  244 (55.73%), corresponding to the ion of the chalcone  $[\text{C}_4\text{H}_3\text{S--CH}=\text{CHCO--C}_6\text{H}_4\text{--OCH}_3]^+$ .

Chemical evidence can also be adduced in favour of the proposed structure of the cyclohexanone (V). Thus, the reaction of (Vd) and (Vf) with hydrazine led to the formation of their pyrazole derivatives (VIa, b). The structure of these pyrazoles is evident from their chemical and spectral data. Their infrared spectra (KBr) (*cf.* Table 2) show strong absorption bands at  $1660\text{ cm}^{-1}$  and  $1670\text{ cm}^{-1}$ ,

respectively, which can be correlated to the  $\nu\text{C}=\text{O}$  of the aroyl substituents. They also show broad absorption bands which can be ascribed to the NH. Their infrared spectra in chloroform revealed the strong absorptions of the aroyl carbonyl groups, in addition to a strong band at  $3480\text{ cm}^{-1}$  for each of them, which is due to the NH stretching absorption (Bellamy 1958). The electronic spectra (*cf.* Table 2) of both compounds show absorption bands which can be ascribed to the aroyl and the substituted pyrazoles (Dal Monti Casoni *et al.* 1956, Kost and Grandberg



Scheme 2.

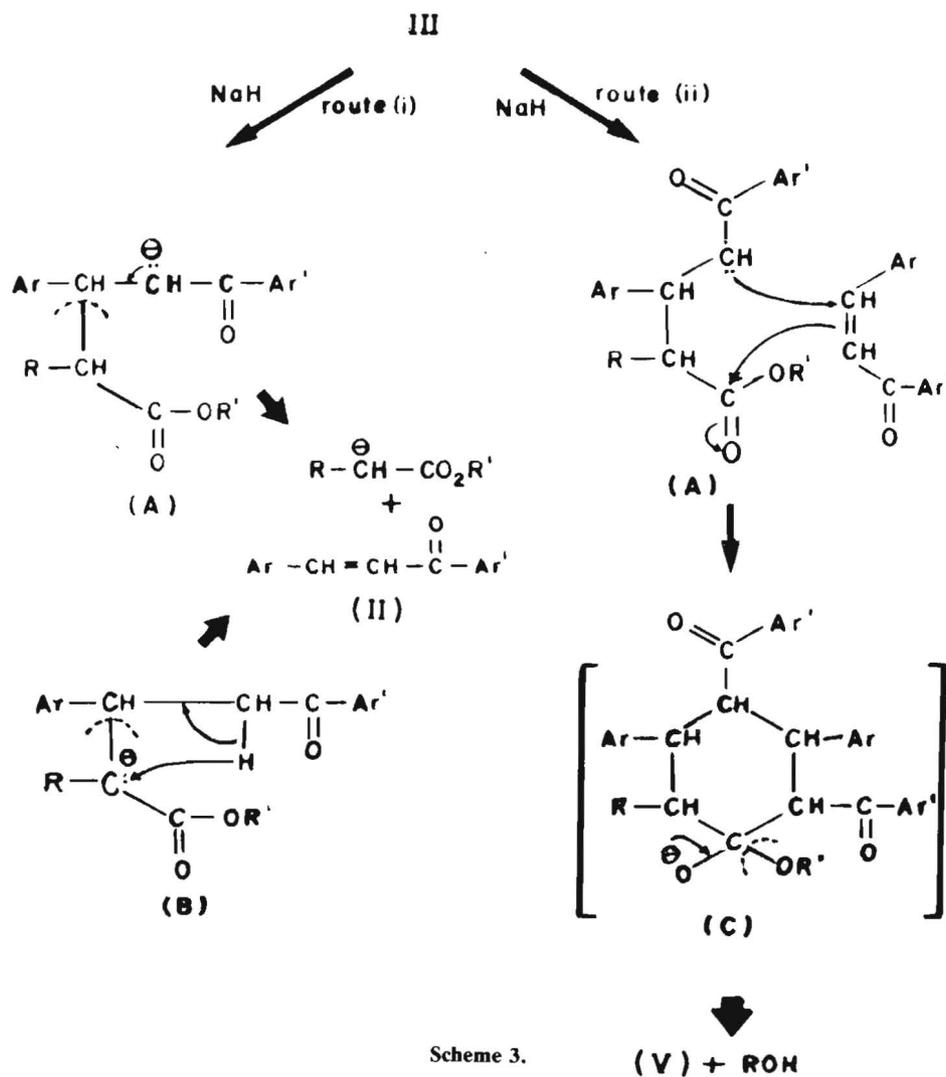
1966). The nmr-spectra of these compounds show signals which can be correlated to the (N-H) and the cyclohexanone protons. The signal assigned to the (N-H) disappears upon treatment with  $D_2O$ . The mass spectrum of (VIa) lends further support to its structure and shows a molecular ion peak at  $m/e$  598 and, in addition, isotopic peaks due to  $^{37}Cl$  at  $m/e$  600 (8%) and 602 (6%). The base peak at  $m/e$  105 (100%) stands for the benzoyl ion  $[C_6H_5-C=O]^+$ . The spectrum of (VIb) revealed a parent peak at  $m/e$  542 (17.6%) which stands for the molecular ion  $[M]^+$ . The base peak at  $m/e$  105 (100%) represents the benzoyl ion  $[C_6H_5-C=O]^+$ .

Based on the above considerations, one may infer that the formation of the esters III is due to the Michael reaction of the carbanions (I) with the chalcones (II) (*cf.* Scheme 1). The presence of extra base in the reaction medium might affect these esters in two different ways leading to the formation of different products. Thus, it can be envisaged that this base can lead to the hydrolysis of the esters (III) to produce the corresponding acids (IV). The base shows another, rather more subtle influence on the ester, by abstracting one of the labile hydrogens, to give the carbanion (A) or (B) (*cf.* Scheme 3). This will lead to a reversed Michael reaction or regression to produce the chalcone (II) and the alkyl aryl ester (or acid). The regression of (B) might take place through a four-membered transition state (Grob and Baumann 1955). This mechanism was supported by chemical reactions. Thus, the reaction of the esters (IIIa, b) with phenylhydrazine produced the pyrazolines (VIIa, b). One might argue, in this respect, that the formation of the pyrazolines (VII) is the result of such a regression, where the phenylhydrazine acted as the base. This will lead to the formation of the chalcone which can react with phenylhydrazine to form the pyrazolines (VII) (El-Rayyes and Hamoud 1983).

On the other hand, one may predict that the carbanion (A) can undergo a second Michael reaction (route (ii), Scheme 3) to produce the intermediate (C), which is the precursor of the substituted cyclohexanones (Va-g). All the above considerations can be adduced in favour of the proposed structures of (V) and (VI), compared to those claimed by other authors (Al-Hajjar *et al.* 1979) who have later on corrected their previous results (Al-Hajjar personal communication, 1983).

### Experimental

Microanalyses were performed by Prof. H. Malissa and G. Reuter, Analytisches Laboratorium, BRD. The infrared (KBr) or ( $CHCl_3$ ) and electronic spectra (ethanol) were measured on a Perkin-Elmer 520B and Pye Unicam SP8000 spectrophotometer, respectively. The nmr-spectra were run on a Varian T-60A spectrophotometer in  $CDCl_3$  with TMS as internal standard. The mass spectra were recorded using Varian MAT 311A mass spectrometer.



*Preparation of 1,3-diaryl-2-propen-1-ones IIa-g*

These chalcones were prepared by the method previously described (El-Rayyes 1982).

*Reaction of 1,3-diaryl-2-propen-1-ones II with ethyl phenylacetates (I)*

*a) Preparation of  $\gamma$ -aroyl- $\alpha, \beta$ -diarylbutyrates IIIa-c*

A mixture of ethyl phenylacetate (I) (0.1 mol), 1,3-diaryl-2-propen-1-one (II)

(0.1 mol) and sodium hydride (0.2 mol, 50% dispersion in oil) in dry benzene was stirred at room temperature. A few drops of methanol were added to initiate the reaction and the mixture was left for 8 hr. The reaction mixture was then poured on cold water. The benzene layer was separated, dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was distilled off. The remaining product was crystallized from the proper solvent to give the ester (III) from cyclohexane. (Yield: 40-45%). Acidification of the aqueous alkaline layer with dil. HCl gave a small amount of a solid product, which was isolated and crystallized from the proper solvent to give the acid (IV) from benzene, (Yield: 15-20%).

*b) Preparation of 2,4-diaroyl-3,5,6-triaryl-cyclohexanones (Va-g)*

A mixture of ethyl phenylacetate (I) (0.1 mol), 1,3-diaryl-2-propen-1-one (II) (0.2 mol) and sodium hydride (0.4 mol, 50% dispersion in oil) in dry benzene was stirred at room temperature. A few drops of methanol were added and the mixture was left for 8 hr, and worked up as above. The organic layer gave a product which was crystallized from the proper solvents (acetone or acetone-benzene), and proved to be the substituted cyclohexanone (V) (Yield: 40-45%). The aqueous alkaline layer gave, after acidification, the corresponding  $\gamma$ -aroyl- $\alpha$ ,  $\beta$ -diarylbutyric acids (IVa-c), (Yield: 30-35%).

*Hydrolysis of the Esters (III) to the Acids (IV)*

A mixture of the ester (III) (1.0 g) and 30% methanolic KOH (20 ml) was refluxed on a water-bath for a period of one hour. The acid was isolated and crystallized from the proper solvent to give the corresponding  $\gamma$ -aroyl- $\alpha$ ,  $\beta$ -diarylbutyric acid IV as colorless crystals, which proved to be identical to the above corresponding acid.

*Reaction of the Esters III with Phenylhydrazine*

A mixture of the esters (IIIa, b) and phenylhydrazine was refluxed for two hours. The solid product was isolated and crystallized from hexane to yield the 3,5-diaryl-1-phenylpyrazolines (VIIa, b).

*Reaction of the Cyclohexanone Derivatives (V) with Hydrazine Hydrate*

A mixture of the substituted cyclohexanones (Vd or f) in ethanol (20 ml) and 5 ml of hydrazine hydrate was refluxed for 1 hr. and left to cool. The solid product was crystallized from benzene to give 1,4,5,6,7-pentahydro-5-benzoyl-4,6-di-(*p*-chlorophenyl)-3,7-diphenyl indazole (VIa) and 1,4,5,6,7-pentahydro-5-benzoyl-4,6-di- $\alpha$ -thienyl-3,7-diphenyl indazole (VIb), respectively, in about 80% yield.

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## تفاعلات المركبات الكربونيلية - ألفا، بيتا - غير المشبعة مع الكربانيونات . اصطناع مركبات الهكسانون الحلقي المستبدلة

نزار رباح الريس

قسم الكيمياء - جامعة الكويت - الكويت

تفاعل مستقبلات ميخائيل (٢) مع كربانيون إثيل أسيتات  
فيل (١) في وجود هيدريد الصوديوم وعند درجة حرارة  
الغرفة، لتتكون نواتج ميخائيل المقابلة وهي: أوميجا -  
بوتيرات أرويل (٣) (الناجمة من تفاعل جزيء من كل  
المركبين (١، ٢) أو الأحماض المقابلة (٤) أو مركبات ٢، ٤ -  
ثنائي أرويل حلقي هكسانون (٥) (الناجمة من تفاعل جزيء  
من المركب (١) مع جزيئين من المركب (٢).

إن طبيعة هذه النواتج تعتمد على ظروف التفاعل .  
لقد تم مناقشة آلية تكوين مشتقات الهكسانون الحلقي (٥)  
وكذلك انعكاس تفاعل ميخائيل . أما تركيب النواتج فلقد  
تم إثباتها بالطرق الكيميائية والطيفية .