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Synthesis and Correlation of Spectral Properties of Some Substituted 1,3-Diphenyl-2-Propen-1-Ones

M. Giasuddin Ahmed,[a] U. K. R. Romman,[a] S. Mosaddeq Ahmed,[b] Kawsari Akhter,[a] and Md. Ershad Halim[a]

[a]Department of Chemistry, University of Dhaka, Dhaka-1000 and
[b]Faculty of Science, American International University-Bangladesh (AIUB), Banani, Dhaka-1213, Bangladesh

Abstract

Seven arylideneacetophenones: 1-(4-chlorophenyl)-3-phenyl-2-propen-1-one **(1a)**, 1-(4-nitrophenyl)-3-phenyl-2-propen-1-one **(1b)**, 1-(4-methoxyphenyl)-3-phenyl-2-propen-1-one **(1c)**, 1-(4-methylphenyl)-3-phenyl-2-propen-1-one **(1d)**, 1-(4-chlorophenyl)-3-(4-methoxyphenyl)-2-propen-1-one **(1e)**, 1-(4-methylphenyl)-3-(4-methoxyphenyl)-2-propen-1-one **(1f)** and 1,3-di(4-methoxyphenyl)-2-propen-1-one **(1g)** were synthesized from the corresponding substituted acetophenones and benzaldehydes in presence of sodium hydroxide in aqueous ethanol. The structures of the compounds **1a-g** were confirmed by their UV, IR, ^{1}H NMR, ^{13}C NMR spectral data.

Introduction

There has been tremendous interest in the application of Claisen-Schmidt reaction (Conrad and Dolliver, 1943; Russel and Kenyon, 1955; Auerbach and Crumrine, 1988; Wittigand and Hesse, 1988) for a long time for the synthesis of α,β-unsaturated ketones commonly known as chalcones where aromatic aldehydes condense with aliphatic or mixed alkyl-aryl ketones in the presence of alkali in aqueous ethanol. In such reactions where acetophenone is used as the ketone, single condensation reaction occurs giving arylideneacetophenones as the final dehydrated products. From these reactions the arylideneacetophenones were obtained in good yields. Later on a number of workers (Hathawa, 1987; Nelson, 1990) made improvements on the types of the catalysts used in the condensation reaction for better yields and convenient procedures.

The basic skeleton of chalcones figures widely in natural products which are known to have multi-pronged activity (Winterniz *et. al.,* 1986). Many of the chalcones are used as the precursors for the synthesis of pyrimidine

derivatives (Deli, *et. al.*, 1984) and as agrochemicals and drugs (Misra, *et. al.*, 1973).

Having this background, in continuation to our work (Ahmed, *et. al.*, 1998; Ahmed *et. al.*, 2005) on the α,β-unsaturated ketones, we synthesized seven arylideneacetophenones **1a-g** with different substituents on the benzene ring. Since the spectral data of these compounds do not seem to be available in the literature, we would like to herein report the spectral behaviour of these compounds in addition to their syntheses.

Materials and Methods

The UV spectra were run in ethanol using SHIMADZU, UV-160A ultraviolet spectrophotometer. The IR spectra were recorded as KBr pellet using SHIMADZU IR-470 infra-red spectrophotometer in the range of 4000-400 cm^{-1}. The ^{1}H NMR spectra were recorded on a Bruker 400 MHz NMR spectrophotometer. The solvent used was deuterated CDC_{l3}. The reactions described in the present paper were carried out primarily following a general procedure (Conrad and Dolliver, 1943) and by changing the reaction conditions whenever necessary.

General procedure

A mixture of benzaldehyde (0.05 mol) and acetophenone (0.05 mol) was dissolved in 50 ml rectified spirit in a 250 ml round-bottomed flask equipped with a magnetic stirrer. Then 50 ml NaOH solution (5g in 50ml H_2O) was added dropwise to the reaction mixture on vigorous stirring for 30 minutes when solution became turbid. The reaction temperature was maintained between 20-25^{O} C using a cold water bath on the magnetic stirrer. After vigorous stirring for 4-5 hours the reaction mixture was neutralized by 0.1-0.2N HCl whereby the precipitaton occurred. On filtering off, the crude chalcone was dried in air and recrystallized by rectified spirit.

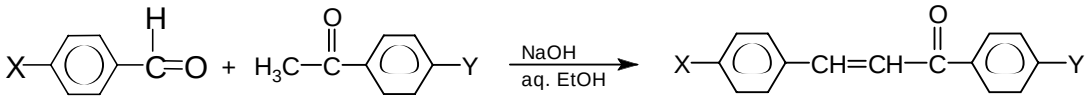
Results and Discussion

Arylideneacetophenones **1a-d** were prepared by carrying out reactions of benzaldehyde

Table I. Physical constants of the compounds 1a-g

Compound	m.p. (^{O} C)	Yield %	R_f value in tlc	Eluting solvent
1a	89-91	86.5	0.75	EtOAc:$CHCl_3$, 10:1
1b	140-141	57.0	0.25	Pet-ether 60-80^{O} C:$CHCl_3$, 4:1
1c	96-98	78.0	0.55	$CHCl_3$
1d	69-71	98.0	0.89	Pet-ether 60-80^{O} C:$CHCl_3$, 1:4
1e	114-115	84.3	0.63	EtOAc:MeOH, 10:1
1f	91-92	97.0	0.65	Pet-ether 60-80^{O} C:$CHCl_3$, 1:4
1g	93-94	87.0	0.78	EtOAc:MeOH, 10:1

with *p*-chloroacetophenone, *p*-nitroacetophenone, *p*-methoxyacetophenone, and *p*-methylacetophenone; and **1e-g** by the reactions of *p*-methoxybenzaldehyde with *p*-chloroacetophenone, *p*-methylacetophenone and *p*-methoxyacetophenone in aqueous ethanol using sodium hydroxide as catalyst. A general experimental procedure was followed which was based on a known method.[1] The duration of experiment and temperature of reaction were modified as required. The assignment to the structures of the com pounds **1a-g** was made on the basis of their UV, IR, ^{1}H NMR and ^{13}C NMR.



1a-g

Substituents at *p*-positions	1a	1b	1c	1d	1e	1f	1g
X	H	H	H	H	OMe	OMe	OMe
Y	Cl	NO_2	OMe	CH_3	Cl	CH_3	OMe

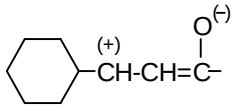
Table II. IR and UV spectral data of compounds 1a-g

Compound	IR ν_{max} in cm^{-1}			UV, λ_{max} (nm)	
	>C=O in conjugation with C=C	>C=C< in conjugation with C=O	>C=C< aromatic	$\pi\rightarrow\pi^*$ of C=C-C=O	$\pi\rightarrow\pi^*$ of C=C of phenyl
1a	1648	1590, 1555	827, 792, 760, 727, 690	311	227, 206
1b	1650	1585, 1560	820, 800, 782, 770, 740, 700, 680	318	269, 209
1c	1645	1598, 1560	828, 762, 727, 695	317	228, 206
1d	1642	1585, 1555	819, 760, 720, 690	305	226, 207
1e	1652	1592, 1560	820, 760, 740, 705, 665	345	243, 206
1f	1642	1585, 1555	820, 805, 785, 740, 730, 670	342	237, 206
1g	1650	1590, 1560	822, 810, 750, 670	346	243, 206

In the compounds **1a-g** the conjugated keto-carbonyl stretching frequencies were observed between 1652-1642 cm^{-1} (Table II). It is well known that in a conjugated carbonyl system the better the conjugation the lower will be the stretching frequency for carbonyl group. The stretching frequency of C=O is 1642 cm^{-1} in the case of the compound **1d** and is the lowest in the series indicating that *p*-CH_3 group makes the conjugation best among these compounds. This may be rationalized by the fact that carbon being the least electronegative among the bonded atoms of substituents to the ring in these compounds, the -CH_3 group is better conjugated to the ring and extended upto C=O. The relatively lower values of ν_{max} for C=O at 1645 cm^{-1} in the case of compound **1c** and 1642 cm^{-1} for compound **1f** also reflect better stretching of the CH=CH-C=O system. The values of nmax for C=O in the rest of the compounds are comparable (~ 1642 cm^{-1}) showing similar conjugation among them. The absorption bands for C=C of the α,β-unsaturated carbonyl system and C=C of aromatic rings in the compounds **1a-g** are in good agreement with the standard values reported in the literature for these types of structures (Dinwiddie, *et. al.,* 1962; De Jongh and Wynberg, 1965).

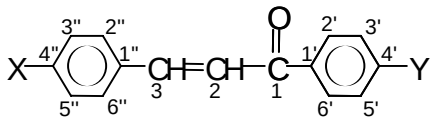
The UV spectral data of the compounds **1a-g** showed a number of absorption bands (Table II) in the range of 346-305 nm which may be attributed to the π→π* transition of the extended α,β-unsaturated carbonyl conjugated system. These observed values correspond well to the expected λ_{max} values for these compounds applying Woodward and Fieser rules for α,β-unsaturated ketones. The remaining absorption bands at 269-206 nm may be accounted for the π→π* transition of the disubstituted benzene rings considering CH=CH-C=O structural unit as a substituent (Fleming and Williams, 1966).

In ^1H NMR spectra, for assigning chemical shifts to vinylic protons, the structures **1a-g** were considered as 3-substituted vinyl ketones. In these compounds vinylic protons, α (at 2-H) and β (at 3-H) give two sets of doublets at δ 7.53-7.32 and 7.81-7.75 respectively having the coupling constant J around 16 Hz and thus showing the trans (E) configuration of the carbon-carbon double bonds of α,β-unsaturated carbonyl system (Table III). In the case of each of these compounds the β-protons were more deshielded than the α-protons. The charge density on β-carbon is reduced by its dispersal through conjugation with the adjacent phenyl group (A). Moreover, -OCH_3, the *p*-substituted implies this effect by its electron releasing tendency and thus neutralizes the (+)ve charge further of *p*-carbon. Perhaps the proximity of adjacent phenyl ring could be attributed to the considerable downfield shift of β-proton.



A

Table III. ^{1}H NMR spectral data of the compounds 1a-g. [(d) in ppm and (J) in Hz]

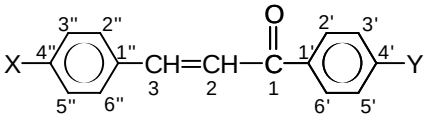


1a-g

Compound	3-H	2-H	Aromatic	X	Y
1a	7.78 (d, J=15.68)	7.45 (d, J=15.85)	7.63 (d, J=8.46, 2H, 2´and 6´ -H) 7.55 (d, J=8.50, 2H, 3´and 5´ -H) 7.41 (d, J=7.61, 2H, 3´´and 5´´ -H) 7.14-7.0 (m, 3H, 2´´, 4´´and 6´´ -H)	---	---
1b	7.81 (d, J=15.70)	7.47 (d, J=15. 71)	8.31 (d, J=8.41, 2H, 3´and 5´ -H) 8.11 (d, J=8.46, 2H, 2´and 6´ -H) 7.64-7.63 (m, 2H, 3´´and 5´´ -H) 7.44-7.43 (m, 3H, 2´´, 4´´and 6´´ -H)	---	---
1c	7.79 (d, J=15.66)	7.53 (d, J=15.65)	8.03 (d, J=8.83, 2H, 2´and 6´ -H) 7.63 (d, J=7.50, 2H, 3´´and 5´´ -H) 7.41-7.39 (m, 3H, 2´´, 4´´and 6´´ -H) 6.97 (d, J=8.82, 2H, 3´ and 5´ -H)	---	3.88 (s, Ar-OC$\underline{H}_3$)
1d	7.81 (d, J=15.70)	7.53 (d, J=15.69)	7.94 (d, J=7.98, 2H, 3´´and 5´´ -H) 7.63 (d, J=7.08, 2H, 2´and 6´ -H) 7.41-7.40 (m, 3H, 2´´, 4´´and 6´´ -H) 7.29 (d, J=7.90 , 2H, 3´ and 5´ -H)	---	2.43 (s, Ar-C$\underline{H}_3$)
1e	7.75 (d, J=15.58)	7.32 (d, J=15.58)	7.91 (d, J=8.50, 2H, 2´´ and 6´´ -H) 7.55 (d, J=8.64, 2H, 2´ and 6´ -H) 7.42 (d, J=8.48, 2H, 3´ and 5´ -H) 6.89 (d, J=8.66, 2H, 3´´ and 5´´ -H)	3.81 (s, Ar-OC$\underline{H}_3$)	---
1f	7.76 (d, J=15.61)	7.40 (d, J=15.60)	7.91 (d, J=8.02, 2H, 2´´ and 6´´ -H) 7.57 (d, J=8.64, 2H, 3´ and 5´ -H) 7.27 (d, J=7.97, 2H, 2´ and 6´ -H) 6.91 (d, J=8.61, 2H, 3´´ and 5´´ -H)	3.82 (s, Ar-OC$\underline{H}_3$)	2.41 (s, Ar-C$\underline{H}_3$)
1g	7.75 (d, J=15.56)	7.40 (d, J=15.55)	8.00 (d, J=8.55, 2H, 2´´ and 6´´ -H) 7.56 (d, J=8.26, 2H, 2´ and 6´ -H) 6.94 (d, J=8.44, 2H, 3´´ and 5´´ -H) 6.89 (d, J=8.22, 2H, 3´ and 5´ -H)	3.84 (s, Ar-OC$\underline{H}_3$)	3.81 (s, Ar-OC$\underline{H}_3$)

The ^{1}H NMR spectral data of the aromatic protons in the compound **1a-g** were assigned by considering them as monosubstituted and disubstituted benzenes. The CH=CH-C=O moiety in all these compounds serve as an electron withdrawing substituent. Correlation

Table IV. ^{13}C NMR spectral data of the compounds 1a-g. [(d) in ppm]

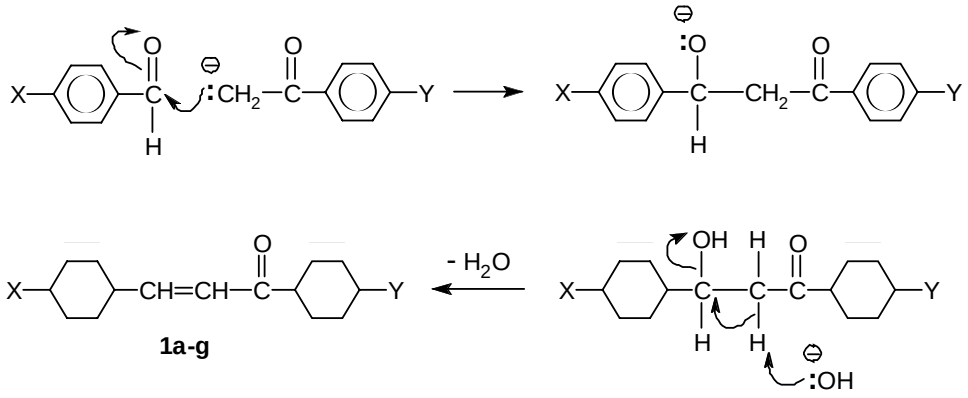


1a-g

Compound	C=O	2-C	3-C	Aromatic	X	Y
1a	189.04	121.43	145.25	139.14 (1′), 136.45 (4′), 135.11 (1′′), 134.64 (4′′), 130.68 (3′, 5′), 129.85(3′′, 5′′), 129.49 (2′, 6′), 128.65 (2′′, 6′′)	---	---
1b	188.94	121.27	146.72	150.03 (4′), 142.99 (1′), 134.27 (4′′), 131.19 (1′′), 129.37 (2′, 6′), 129.08 (3′′, 5′′), 128.67 (2′′, 6′′), 123.80 (3′, 5′)	---	---
1c	188.71	121.92	143.94	163.44 (4′), 135.10 (1′′), 131.11 (1′, 2′, 6′), 130.81 (3′′, 5′′), 130.31 (2′′, 6′′), 128.35 (4′′), 113.85 (3′, 5′)	---	55.48 (Ar-O<u>C</u>H$_3$)
1d	189.89	122.04	144.29	143.56 (1′′), 135.58 (4′), 134.95 (1′), 130.35 (2′′, 6′′), 129.27 (2′, 6′), 128.87 (3′, 5′), 128.59 (3′′, 5′′), 128.34 (4′′)	---	21.60 (Ar-<u>C</u>H$_3$)
1e	188.96	119.02	145.06	161.00(4′′), 138.81 (1′), 136.72 (4′), 130.25 (1′′), 129.73 (3′, 5′), 128.76, 128.40 (2′′, 6′′), 128.40, 127.34 (2′, 6′), 114.34 (3′′, 5′′)	55.31 (Ar-O<u>C</u>H$_3$)	---
1f	189.92	119.72	144.15	161.00 (4′′), 143.28 (1′), 135.86 (4′), 130.10 (1′′), 129.21 (2′′, 6′′), 128.50 (3′, 5′), 127.67 (2′, 6′), 114.34 (3′′, 5′′)	55.32 (Ar-O<u>C</u>H$_3$)	21.58 (Ar-<u>C</u>H$_3$)
1g	188.59	119.46	143.67	163.19 (4′), 161.44 (4′′), 131.27 (4′), 130.60, 130.02 (1′, 1′′), 127.72 (2′, 2′′, 6′, 6′′), 114.30 (3′, 5′), 113.71 (3′′, 5′′)	55.36 (Ar-O<u>C</u>H$_3$)	55.29 (Ar-O<u>C</u>H$_3$)

charts for the ring protons shifts relative to benzene, for monosubstituted benzenes (Scheinmann, 1970) and disubstituted benzenes (Scheinmann, 1970) are available in the literature. In the cases of present compounds **1a-g** these ^{1}H NMR correlation charts were considered as the basis for assigning the chemical shifts and coupling constant values for the aromatic protons.

In the compounds **1a-g** the chemical shifts of carbonyl carbons were found to be at δ (189.92-188.59) (Table IV). These values are in good agreement with the ^{13}C NMR



chemical shifts of carbonyl carbons in α,β-unsaturated ketones (Grutzner, *et. al.*, 1970; Stothers and Lauterbur, 1964; Marr and Stothers, 1965). In these compounds the vinylic carbons, α (2-C) and β (3-C), showed the chemical shifts at δ (122.04-119.02) and (146.72-143.67) respectively. These values correlate well with the olefinic chemical shifts in α,β-unsaturated ketones (Spiesecke and Schneider, 1961). Shifts are at somewhat down field, particularly for the β-carbons (3-C) which may be explained with the help of resonance forms A. Similar deshielding was also observed for the β-hydrogens as shown in their ^{1}H NMR spectral data.

The ^{13}C shifts of the carbons of the aromatic ring were assigned on the basis of the correlation chart of ^{13}C spectral data available in the literature (Lauterbur, 1961). The chemical shifts observed for the different carbons in the ring in the compounds **1a-g** are found to be consistent with the effects of different substituents (Spiesecke and Schneider, 1961; Lauterbur, 1961; Maciel and Natterstad, 1965; Dhami and Stothers, 1967).

A plausible reaction mechanism for the formation of α,β-unsaturated ketones **1a-g** is shown below:

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