SPECTROSCOPIC STUDIES
OF SOME ENOL LACTONES

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FAGR ABDEL SAYED ISMAIL YOUNES

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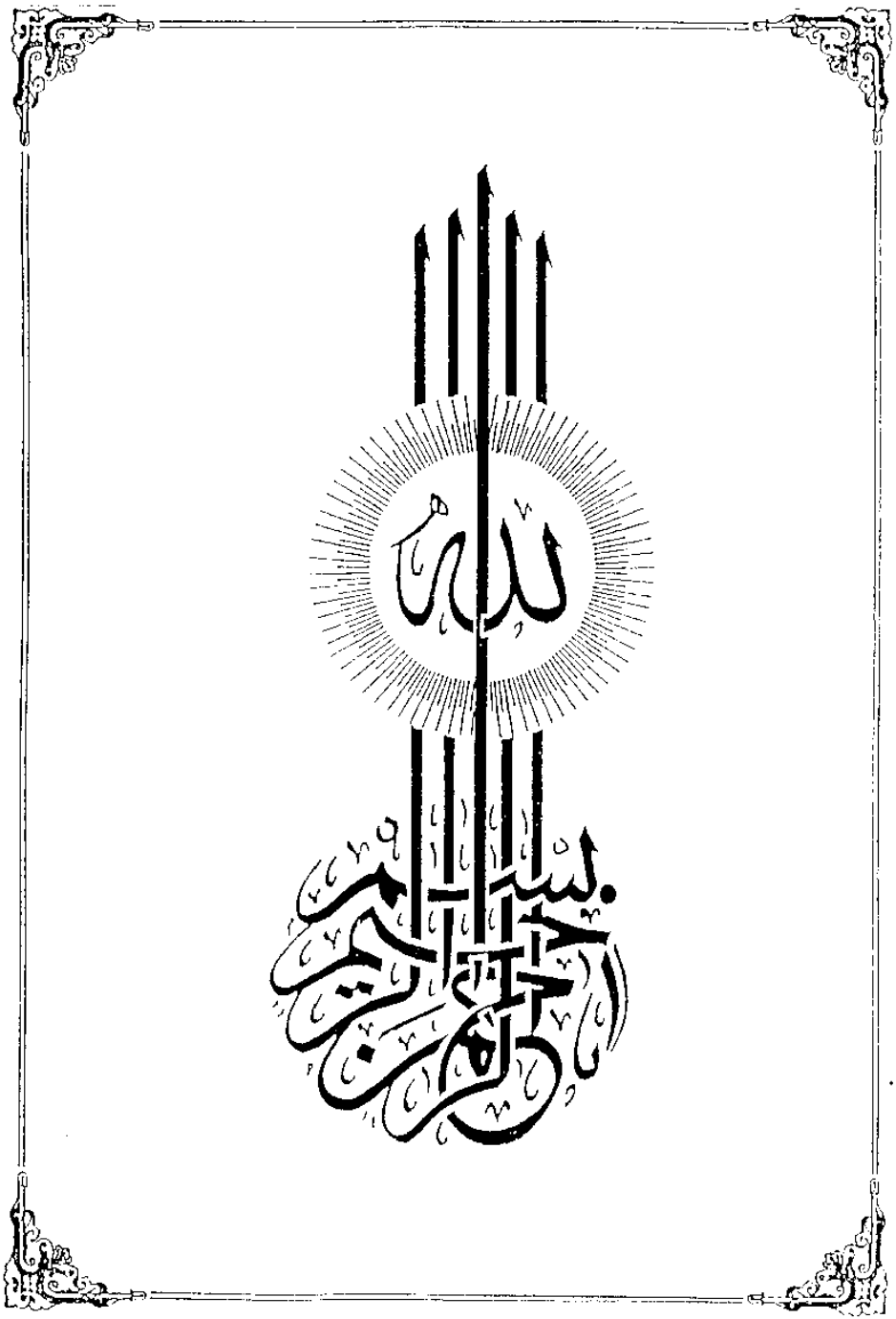

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SOME ENOL LACTONES

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NOTE

The candidate has attended postgraduate courses for one year, covering the following topics:

I. Spectroscopy.

II. Microanalysis.

III. Instrumental Analysis.

IV. Photochemistry.

V. Heterocyclic Compounds.

VI. Organometallic Compounds

VII. Chemical Kinetics.

VIII. Quantum Chemistry.

IX. Thermodynamic.

She has successfully passed written examination in these courses.

Vice Dean
for Graduate Studies Research

Prof. Dr. N.A. Eleish

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SUMMARY

SUMMARY

Condensation of benzaldehyde or substituted benzaldehyde **1** with B-aroylpropionic acid **2** under Perkin conditions yielded the enol lactones, **3a-d - 7a-d.**

The structural assignment of the enol lactones **3-5a-d** and **6a-c** could be determined by high-resolution ^{1}H NMR (400 MHz) spectroscopy.

The enol lactones **6d** and **7a-d** were difficult to dissolve in a suitable solvent for ^{1}H NMR measurements.

Mass, infrared and ultraviolet spectroscopy of the enol lactones, **3-7a-d** were also studied.

Assignment of the ^{1}H NMR (400 MHz) spectroscopy of lactones, 3-6:

The ^{1}H NMR (90 MHz) shows only complex multiplets, but at 400 MHz, the well separated signals allow the complete assignment of the major and the minor isomers.

The spectra of the pure or crude lactones **3a-d** are only (E)-isomers and there are no detectable amounts of the (Z)-isomers. The spectra of the enol lactones **3a-c** show two singlets for protons H-4 and H-5 at δ = 7.47, 6.95 (**3a**), 7.58, 7.37 (**3b**), 7.38, 6.81 (**3c**). The spectra of the enol lactone **3d** shows a singlet at δ = 7.48 for proton H-4 and a doublet at δ = 6.94 (J = 2Hz) for proton H-5. The singlet olefinic proton H-4 of lactones **3a-d** is remarkably deshielded due to the adjacent carbonyl group. The δ -values of the two singlets of the lactone **3b** are very similar due to a large solvent effect with D_6-DMSO, (Figs. 1-4).

The spectra of the pure or crude enol lactone **4a** is unseparated mixture of (E) and (Z)-isomers with a ratio (E):(Z) = 10 : 1. It shows for the (E)-isomers a downfield singlet at δ = 7.43 for proton H-3 and an upfield singlet at δ = 6.93 for proton H-4.(Z)-**4a** showed two singlets at δ = 6.48 and 7.10 for protons H-3 and H-4, respectively, it is obvious that the δ-value of proton H-3 of the (E)-isomer is deshielded due to the adjacent carbonyl group in comparison to the δ value of proton H-3 of the (Z)-isomer.

The spectra of the enol lactones **4b-d** are only (E) isomers and it showed downfield singlets for proton H-3 at δ = 7.37, 7.34 and 7.68, respectively,(Figs. 5-8).

The enol lactones **5a-d** are only (E)-isomers. It showed singlets for proton H-5 at δ = 7.42, 7.37, 7.34 and 7.66, respectively. It also showed singlets for proton H-6 at δ = 6.93, 6.87, 6.79 and 7.42, respectively. The δ values of H-5 and H-6 of the enol lactone **5d** are very similar due to a large solvent effect with D_6-DMSO,(Figs. 9-12).

The analysis of the spectra of lactones **6a-c** proved that all lactones are only (E)-isomers and it showed for proton H-5 a singlet at δ = 7.60 (**6a**), a doublet at δ = 7.58 (J = 2Hz) (**6b**), and a singlet at δ = 7.51 **6c**). Proton H-6 of the enol lactone **6a** showed a doublet at δ = 7.50 (J = 2Hz), and that of **6b** and **6c** showed singlets at δ = 7.52, 7.46, respectively, (Figs. 13-15).

The aryl (A) protons and the aryl (B) protons of all enol lactones **3-6** showed a well separated signals and all protons could be assigned,(Figs. 1-15).

Mass spectra evidence:

The electron impact induced fragmentation of the enol lactones **3-7a-d** are qualitatively similar to each other. In general all lactones exhibit relatively intense molecular ion peaks, M^{+} (a). Aroyl ion $R^{1}C_{6}H_{4}C{\equiv}O^{+}$ (b), and aryl ion $R^{1}C_{6}H_{4}^{+}$ (c), are major fragment ions in the mass spectra of all studied enol lactones,(Figs. 16-35).

Infrared spectra evidence:

The structure of the enol lactones **3-7a-d** was supported by the study of their I.R. absorption spectra which showed absorption bands characteristic of carbonyl group ($\rangle C{=}O$), of γ-lactones conjugated with an olefinic bond, (Figs. 36-55).

Electronic spectra evidence:

The U.V. absorption spectra curves showed similarity in its skeletal pattern to 1.1.4.4-tetraphenylbutadiene, Figs. (56 - 75).

INTRODUCTION

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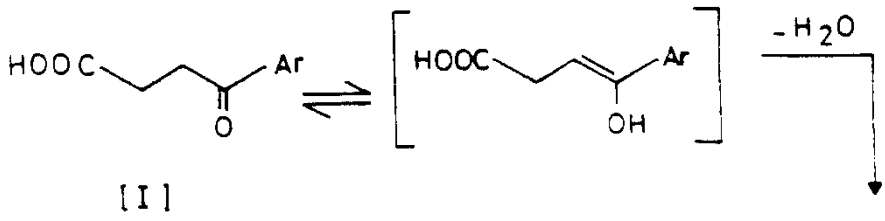
The Perkin's condensation[1] of aromatic aldehydes with B-aroyl propionic acids[2-8] to give the corresponding enol lactones [4] was described by several investigators[9-18] (scheme 1). Borsche[9] suggested that condensation had occurred by intermediate formation of the γ-aryl-but-γ-enoic acid lactones[19-22] [2] derived from the enolisation at the α-position of the keto acid [1], followed by their direct lactonisation under the influence of warm acetic anhydride.

El-Assal et al[23] confirmed Borsche[9] suggestion by synthesizing several lactones of type [2] and converted them under the conditions of the original condensation to the lactones [4]. The structure of the lactones [2,4] were confirmed by infrared spectroscopy.[24]

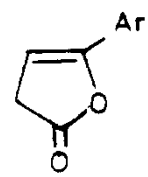
The same authors[23,25-27] also recommended a modified condition for the direct preparation of the enol lactones [4] by heating the mixture of B-aroyl propionic acid [1], aromatic aldehyde [3] and sodium acetate in acetic anhydride up to 70-80°C during 2 hours, kept thereat for further 5 hours and the enol lactones of type [4] were obtained in satisfactory yields.

Isomerization[16,25,28] of the enol lactones of type [4] with glacial acetic acid in the presence of conc. hydrochloric acid led to the 4-aryl-2-naphthoic acids [5].

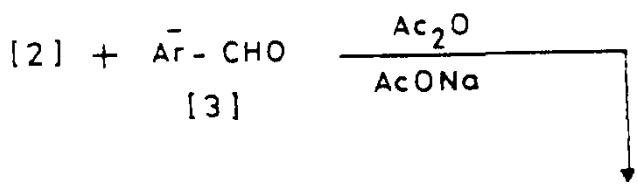
Scheme (1)

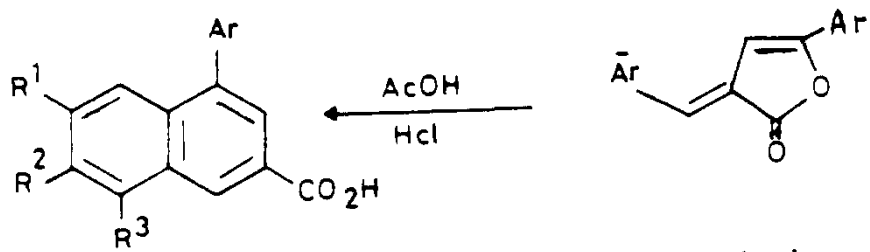


[1]



[2]





[5] [4]

Ar = phenyl, *p*-tolyl, *p*-anisyl, o,p-dimethoxyphenyl, p-chlorophenyl or m,p-dichlorophenyl.

R^1 = H, OMe or O-CH_2-O.

R^2 = H, Me, OMe, O-CH_2-O or NO_2.

R^3 = H or OMe.

As an extension to the previous investigation, El Wahhab and El-Assal[29] have prepared other new enol lactones of type [4] by condensation of 5-membered heterocyclic aromatic aldehyde such as thiophen-2-carbaldehyde [6] with p-substituted-B-benzoyl-propionic acids[2-4] [7a-d] under Perkin conditions[1] (scheme 2).

The structure of the obtained enol lactones [8a-d] were confirmed from their isomerization[16,25,28] to the corresponding 4-aryl-benzo[b]-thiophene-6-carboxylic acids [9a-d] and also from their infrared spectroscopy.[24]