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CHARACTERIZATION AND STEREOCHEMISTRY OF ALKYL 2-CHLORO-3-FORMYLACRYLATES: EXPERIMENTAL NMR AND THEORETICAL DFT STUDIES© 2010 T.M. Barhoumi-Slimi^{1*}, M.T. Ben Dhia¹, M. Nsangou², M.M. El Gaied¹, M.R. Khaddar¹¹Laboratory of Structural Organic Chemistry: Organic Synthesis, Faculty of Sciences of Tunis, 1060 Tunis, Tunisia²Department of Physics, Faculty of Science, University of Ngaoundere, Cameroon

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The synthesis of alkyl 2-chloro-3-formylacrylates **1** from alkyl pyruvates was carried out using Vilsmeier reaction. The reaction is highly stereoselective and leads to a 95:5 mixture of *Z* and *E* stereoisomers. Both stereoisomers were characterized by ¹H and ¹³C NMR. In CDCl₃ solution, the NMR data, particularly the NOEDIFF experiments, show that the major species formed is the *Z* stereoisomer. Heating compound **1** in THF at reflux afforded the cyclic product **2** in 90 % yield. The interpretation of the experimental data were further supported by DFT/B3LYP calculations.

Keywords: synthesis, Vilsmeier reaction, stereoisomerism, stereoselectivity, cyclization, NMR, NOEDIFF, B3LYP.

INTRODUCTION

α,β -Unsaturated carbonyl systems form part of the most interesting synthons in organic synthesis [1]. When other functions are present together with these systems, a large variety of supplementary reactions may take place leading to interesting molecules. For instance, the ethyl 3-formylprop-2-enoate is a useful precursor for the synthesis of natural products such as fruity flavours [2] used in food industry, natural insecticides [3] and hypoglycins [4].

The Vilsmeier reaction is widely used for the synthesis of many heterocyclic compounds [5, 6], particularly for the synthesis of substituted β -chloroacrylaldehydes [6–8] which are much less reported in the literature. Surprisingly, very few authors have reported the synthesis of the chlorinated derivative of ethyl 3-formylbut-2-enoate, the alkyl 2-chloro-3-formylacrylate **1** [9] which could be used as a precursor for the synthesis of heterocyclic molecules and biomolecules. Fariña et al. [9a] have reported the synthesis of methyl 2-chloro-3-formylacrylate starting from pseudoesters in several steps.

In this paper, we describe the synthesis of compound **1** through a one-pot Vilsmeier reaction on alkyl pyruvates and investigate its stereochemistry using both experimental NMR technique and theoretical DFT calculations.

EXPERIMENTAL*General experimental procedure*

DMF and alkyl pyruvates were distilled and DMF was kept over molecular sieves (Union Carbide Type 3 Å). POCl₃ was used as purchased. IR spectra were recorded in CHCl₃ on a Perkin-Elmer Spectrometer Pargon 1000 PC. ¹H and ¹³C NMR spectra were recorded on Bruker AC 300.130 (MHz) spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane in CDCl₃. Coupling

* E-mail: b.sthouraya@yahoo.com

constants (J values) are given in Hz. Mass spectra were obtained with a Hewlett-Packard 5890 II instrument.

Preparations

Alkyl 2-chloro-3-formylacrylate (1): Anhydrous N,N -dimethylformamide (6.3 g; 86.25 mmol, 2.5 eq.) was cautiously added to phosphorus oxychloride (13.22 g; 86.25 mmol, 2.5 eq.) maintained in a nitrogen atmosphere at 0 °C. The reaction mixture was then stirred at room temperature for 30 min after which time a solution of alkyl pyruvate (4 g; 1 eq.) was added dropwise. Stirring at room temperature was continued for 24 h and then a solution of sodium hydrocarbonate in water (20 ml) was added cautiously. The mixture thus obtained was stirred at room temperature for an additional 1 h and the product was extracted into diethyl ether, dried over magnesium sulfate and concentrated. The crude product was purified by chromatography on silica gel using diethyl ether — petroleum ether (2:98) as the eluent.

1a: Methyl 2-chloro-3-formylacrylate: Yield 30 %, IR: 1738, 1690, 1610 cm^{-1} . *Anal.* Calcd. for $\text{C}_5\text{H}_5\text{Cl}_3$: C 40.4, H 3.4, Cl 23.9. Found: C 40.9, H 3.7, Cl 24.2.

Z-1a: NMR ^1H : δ 3.94 (s, 3H, H_e), 7.05 (d, 1H, H_b , $J = 6.8$ Hz), 10.20 (d, 1H, H_a , $J = 6.8$ Hz). ^{13}C NMR: δ 54.0 (C_e), 132.1 (C_b), 139.6 (C_c), 161.9 (C_d), 190.5 (C_a).

E-1a: ^1H NMR: δ 3.96 (s, 3H, H_e), 6.61 (d, 1H, H_b , $J = 6.6$ Hz), 10.14 (d, 1H, H_a , $J = 6.6$ Hz). ^{13}C NMR: δ 54.0 (C_e), 132.5 (C_b), 137.0 (C_c), 161.9 (C_d), 189.0 (C_a).

1b: Ethyl 2-chloro-3-formylacrylate: Yield 50 %; IR: 1740, 1685, 1605 cm^{-1} . M.S. m/Z : (165,163) ($M+3$, $M+1$) (9, 25 %), (135, 133) (100, 34 %), 127 (53 %), (119, 117) (23, 70 %), 71 (40 %), 61 (96 %), 53 (84 %).

Z-1b: ^1H NMR: δ 1.3 (t, 3H, $J = 7.2$ Hz), 4.23 (q, 2H, $J = 7.2$ Hz), 7.03 (d, 1H, $J = 6.8$ Hz), 10.15 (d, 1H, $J = 6.8$ Hz). ^{13}C NMR: δ 13.9 ($\underline{\text{C}}\text{H}_3$), 63.6 ($\underline{\text{O}}\underline{\text{C}}\text{H}_2$), 131.9 ($\underline{\text{C}}\text{Cl}$), 140.2 ($\underline{\text{C}}\text{H}=\text{$), 161.5 ($\underline{\text{C}}\text{O}$), 190.7 ($\underline{\text{C}}\text{H}\text{O}$).

E-1b: ^1H NMR: δ 1.27 (t, 3H, $J = 7.2$ Hz), 4.17 (q, 2H, $J = 7.2$ Hz), 6.81 (d, 1H, $J = 6.8$ Hz), 10.14 (d, 1H, $J = 6.8$ Hz). ^{13}C NMR: δ 15.6 ($\underline{\text{C}}\text{H}_3$), 62.0 ($\underline{\text{O}}\underline{\text{C}}\text{H}_2$), 137.2 ($\underline{\text{C}}\text{Cl}$), 141.3 ($\underline{\text{C}}\text{H}=\text{$), 161.5 ($\underline{\text{C}}\text{O}$), 189.3 ($\underline{\text{C}}\text{H}\text{O}$).

2: 3-chloro-5-alkoxy-2(5H)-dihydrofuran-2-one: A solution of the aldehyde **1a,b** (**Z**) (100 mg) in anhydrous THF (5 ml) was introduced in a heating tube (~ 100 cm^3). The latter was sealed and heated in an oil bath at 80 °C for 24 h. Then the sealed tube was cooled and opened, and the reaction mixture was concentrated *in vacuo* to remove solvent. The crude product was purified by chromatography on silica gel to afford 90 mg of the expected compound **2a,b**.

2a: 3-chloro-5-methoxy-2(5H)-dihydrofuran-2-one: Yield 90 %; IR: 1625, 1790 cm^{-1} . ^1H NMR: δ 3.61 (s, 3H, H_e), 5.86 (d, 1H, H_a , $J = 1.4$ Hz), 7.10 (d, 1H, H_b , $J = 1.4$ Hz). ^{13}C NMR: δ 52.4 (C_e), 103.2 (C_a), 128.5 (C_c), 138.5 (C_b), 166.8 (C_d). *Anal.* Calcd. for $\text{C}_5\text{H}_5\text{ClO}_3$: C, 40.4; H, 3.4; Cl, 23.9. Found: C, 40.7; H, 3.5; Cl, 24.1.

2b: 3-chloro-5-ethoxy-2(5H)-dihydrofuran-2-one: Yield 90 %; IR: 1625, 1790 cm^{-1} . ^1H NMR: δ 1.27 (t, 3H, CH_3 , $J_{\text{CH}_3-\text{H}_a} = 7.1$ Hz), 3.76 (qd, 1H, H_a , $J_{\text{H}_a-\text{H}_b} = 9.4$ Hz, $J_{\text{H}_a-\text{CH}_3} = 7.1$ Hz), 3.93 (qd, 1H, H_b , $J_{\text{H}_b-\text{H}_a} = 9.4$ Hz, $J_{\text{H}_b-\text{CH}_3} = 7.1$ Hz), 5.91 (d, 1H, H_a , $J = 1.4$ Hz), 7.08 (d, 1H, H_b , $J = 1.4$ Hz). ^{13}C NMR: 14.5 ($\underline{\text{C}}\text{H}_3$), 66.5 ($\underline{\text{O}}\underline{\text{C}}\text{H}_2$), 101.5 (C_a), 130.5 (C_c), 142.5 (C_b), 166.0 (C_d). M.S. m/Z : M^+ 162 (0.03), 147 (0.18), [133(36), 135(12)], [117(100), 119(34)], 118(20), 120(7)], [89(27), 91(9)], 83(84).

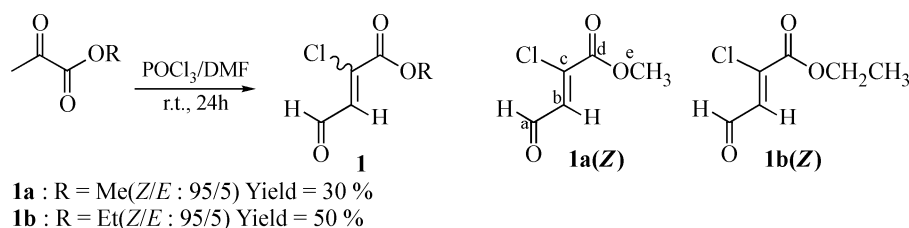
Computations

Density functional theory (DFT) calculations were carried out on compounds **1** (in both *E* and *Z* forms) and **2** using the suite of programs Gaussian 03W [10], with the non-local hybrid functional denoted as B3LYP [11, 12]. The basis set used was of three Zêta 6-311++G** type of McLean and Chandler [13] doubly polarized with diffuse functions on all the atoms. The geometries were optimized using analytical gradient. The harmonic vibrational frequencies of the different stationary points of the potential energy surfaces (PES) have been calculated at the same level of theory in order to identify the local minima as well as to estimate the corresponding zero-point vibrational energy (ZPE).

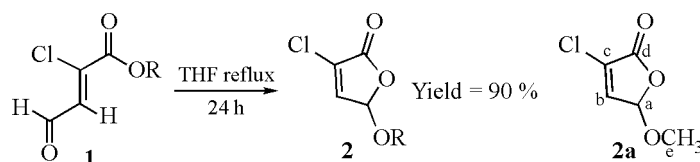
RESULTS AND DISCUSSION

Synthesis

The subjection of ketones bearing methyl or methylene groups in α position to a Vilsmeier reaction leads generally to a mixture of *Z/E* stereoisomers with variable ratios and yields depending on the stability of the obtained products [5, 14]. In our case, the reaction of the Vilsmeier reagent (POCl_3/DMF) with the methyl or ethyl pyruvates at room temperature for 24 hours is highly stereoselective and affords a 95/5 mixture of the *Z/E* stereoisomers in 30 % yield for **1a** and 50 % yield for **1b** (Scheme 1).



On the other hand, it is observed that aldehyde **1** (*Z+E*: 95/5) may be entirely converted into the furanone **2** when standing for few months. In the experimental conditions, the furanone **2** is obtained by heating aldehyde **1** at reflux in THF during 24 h (Scheme 2).



The formation of the furanone **2** results manifestly from cyclization of the *E*-stereoisomer. To explain the high stereoselectivity of the Vilsmeier reaction and the formation of furanone **2**, therefore, NMR studies and DFT calculations were performed.

NMR studies

The ^1H NMR spectra of compounds **1** in CDCl_3 at 25 °C show the doubling of all signals with markedly different intensities. The aldehyde proton appears as two doublets: the major doublet is at 10.18 ppm and low intensity one is at 10.14 ppm. On the basis of the chemical shift range known for the proton of unsaturated aldehydes, the major lower field doublet (*i.e.* the predominant species) is assigned to the *Z* isomer. Furthermore, the vicinal H—H coupling between aldehyde and vinylic protons, 3J, is in line with this assignment, showing values of 6.60 and 6.80 Hz for the *E* and *Z* stereoisomers, respectively. Interestingly, the NOE difference experiments performed on the major species observed show that the predominant isomer does exist in the *Z* configuration (*see* Table 1). The irradiation of the ester proton (methyl protons) signals of the major species showed in the ^1H NMR spectra an enhancement of 9 % and 7 % for the peaks related to the vinylic and aldehydic protons, respectively. This indicates that the interaction of the ester group with the vinylic proton is more important than that with the aldehydic proton, suggesting that the major species present is in the *Z* form. Unfortunately, the very small amount of the *E* stereoisomer (5 %) did not allow the measurement of the NOEDIFF.

When the ^1H and ^{13}C NMR spectra were measured after heating product **1** in THF at reflux, an interesting spectral feature was observed. The ^1H NMR spectra showed the absence of signals in the region of aldehydic protons and significant changes in the ^{13}C chemical shifts, in particular of the C_a atom (Table 1).

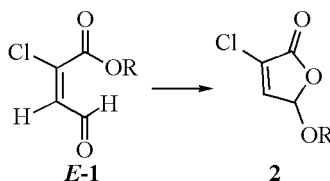
These interesting observations in the NMR spectra can be rationalized by considering the equilibrium of **1**, at high temperature, between the major *E* and minor *Z* forms. It can be proposed that the structure of **1** in the *E* form would allow full and spontaneous cyclization to the furanone **2** (*see*

Table 1

¹H and ¹³C NMR chemical shifts for compounds **1a** and **2a** in CDCl₃

Compound	δ _{Ha}	δ _{Hb}	δ _{He}	δ _{Ca}	δ _{Cb}	δ _{Cc}	δ _{Cd}	δ _{Ce}
Z-1a	10.18	7.05	3.94	190.5	132.1	139.6	161.9	54.0
E-1a	10.14	6.61	3.96	189.0	132.5	137.0	161.9	53.8
2a	5.86	7.10	3.61	103.2	138.5	128.5	166.8	52.4

Scheme 3), while in the *Z* form the unfavorable position of the aldehyde group prevents such a cyclization. This may explain the stability of **2** as compared to the *E* form of **1**.



Theoretical calculations

In order to confirm the NMR data obtained for the studied compounds, the molecular geometries of **1** in the *Z* and *E* forms and **2** were fully optimized at the DFT/B3LYP level of theory using 6-311++G** basis set. The structures have been identified as local minima on the singlet potential energy surfaces (PES) (Fig. 1). Optimized values of selected geometrical parameters are listed in Tables 3 and 4. Calculations show that the geometries of the *E*-isomer of **1a** and **1b** are the least stable among all the compounds. As can be seen from Table 2, the *Z*-isomer of **1a** is the most stable. The potential energy difference between the two isomers of **1a** is 2.57 kcal/mol (see Table 3). This difference is in good agreement with the experimental NMR data (95 % for *Z* and 5 % for *E*).

As for the structure of **2**, **2a** is 2.32 kcal/mol more stable than *E-1a*. The same trend is observed for the ethylated compounds **1b** and **2b**. The Compound **2b** is 0.18 kcal/mol less stable than compound *Z-1b*. In the same way, compound *E-1b* is 2.63 kcal/mol less stable than compound *Z-1b* (see Table 2).

As shown in Tables 3 and 4, the shortest C—C bond lengths calculated at the DFT/B3LYP level of theory are those of C(2)—C(3) (1.342 Å) in **1** and C(3)—C(4) (1.328 Å) in **2** which correspond to a C—C double bond. In addition, the angle C(3)—C(4)—H(9) is smaller in the *E*-isomer as compared to the *Z* form, indicating possible existence of some hydrogen bond interactions which would be more favoured in the *E* than in *Z* isomers (see Fig. 1).

The analysis of all the possible space structures of the *Z* and *E* isomers shows that the distance between the methylic protons of the ester group and the vinylic proton is shorter in the *Z* forms as compared to the *E* ones [(d_{C11H8})_Z = 4.23 Å vs. (d_{C11H8})_E = 6.02 Å]. On the other hand, the distance between the methylic protons of the ester group and the aldehydic proton is larger for *Z* than that for *E* stereoisomers: [(d_{C11H9})_Z = 6.61 Å, (d_{C11H9})_E = 4.98 Å] (Tables 3 and 4). Interestingly, in the *Z* form of **1a**, the

Table 2

Calculated electronic energy *E*, ZPE, corrected electronic energy including the energy of level zero *E*₁ (in a.u.) and dipole moment μ (in Debye) of the studied molecules

Parameter	Compound					
	<i>E-1a</i>	<i>Z-1a</i>	2a	<i>E-1b</i>	<i>Z-1b</i>	2b
<i>E</i>	-879.5294	-879.5335	-879.5331	-918.8593	-918.8635	-918.8632
ZPE	0.0950	0.0951	0.0974	0.1232	0.1232	0.1255
<i>E</i> ₁ = <i>E</i> + ZPE	-879.4344	-879.4384	-879.4358	-918.7361	-918.7403	-918.7377
μ	2.6974	4.2228	4.6941	3.0327	4.6185	4.8754

Table 3

Selected bond lengths (Å) and angles (deg.) for compound 1

Parameter	Stereoisomer 1a		Stereoisomer 1b		Parameter	Stereoisomer 1a		Stereoisomer 1b	
	Z	E	Z	E		Z	E	Z	E
Bonds lengths					Bond angles				
C1—C2	1.508	1.512	1.510	1.514	C1—C2—C3	119.4	118.2	119.4	118.3
C2—C3	1.341	1.344	1.341	1.344	C2—C3—C4	126.2	128.5	126.2	128.6
C3—C4	1.475	1.479	1.474	1.479	C3—C4—O10	122.0	126.3	122.1	126.4
C4—O10	1.212	1.210	1.212	1.210	C3—C4—Ha	116.9	113.3	116.8	113.3
C4—Ha	1.103	1.108	1.103	1.108	C1—C2—Cl	117.6	117.8	117.6	117.7
C3—Hb	1.085	1.085	1.085	1.085	C2—C3—Hb	117.3	115.4	117.2	115.3
C2—Cl	1.745	1.728	1.746	1.728	C2—C1—O5	112.9	112.9	112.9	112.9
C1—O5	1.334	1.333	1.332	1.331	C2—C1—O6	122.3	122.5	122.0	122.3
C1—O6	1.207	1.208	1.208	1.209	C1—O5—C11	115.9	115.9	116.3	116.5
O5—C11	1.444	1.443	1.456	1.455	Dihedral Angle				
					Ha—C4—C3—Hb	180.0	0.0	180.0	0.0

Table 4

Selected bond lengths and angles for compound 2

Parameter	2a	2b	Parameter	2a	2b
Bonds lengths			Bond angles		
O1—C2	1.368	1.367	O1—C2—C3	106.6	106.7
C2—C3	1.499	1.499	C2—C3—C4	109.8	109.8
C3—C4	1.328	1.328	C3—C4—C5	108.5	108.5
C4—C5	1.503	1.504	C4—C5—O1	104.9	104.8
C5—O1	1.452	1.453	O1—C2—O8	124.0	124.0
C5—O6	1.318	1.380	C2—C3—Cl	121.2	121.2
O6—C7	1.432	1.442	O1—C5—O6	111.6	111.7
C2—O8	1.193	1.193	Dihedral angle		
C3—Cl	1.717	1.718	C2—O1—C5—O6	119.3	119.3
C4—H10	1.080	1.080			

distance between H(8) and C(11) carrying the methyl protons is 4.88 Å while that between H(9) and C(11) is 6.44 Å. This is consistent with the results obtained with NOE difference experiments giving an enhancement of 9 % and 7 %, respectively.

It is worth noting that the cyclization proposed in Scheme 3 is in good agreement with the theoretical calculations which show that, on the one hand, the structure of **2a** is more favoured than that of the stereoisomer *E*-**1a** and, on the other hand, it is very close in energy to that of *Z*-**1a** (Scheme 4). The *E* isomer can thus be considered as an intermediate in the conversion from *Z*-**1a** to **2a** when the former is heated. The aldehydic group of *E*-**1a** is considerably twisted with the C(1)—C(2)—C(3)—C(4) dihedral angle of 0.56° (see Table 3).

Despite the fact that we did not calculate the transition states in these systems, it can be considered that the difference in energy between the two isomers of **1a** represents a major part of the activation enthalpy ΔH^* for the conversion which is at least 2.57 kcal/mol.

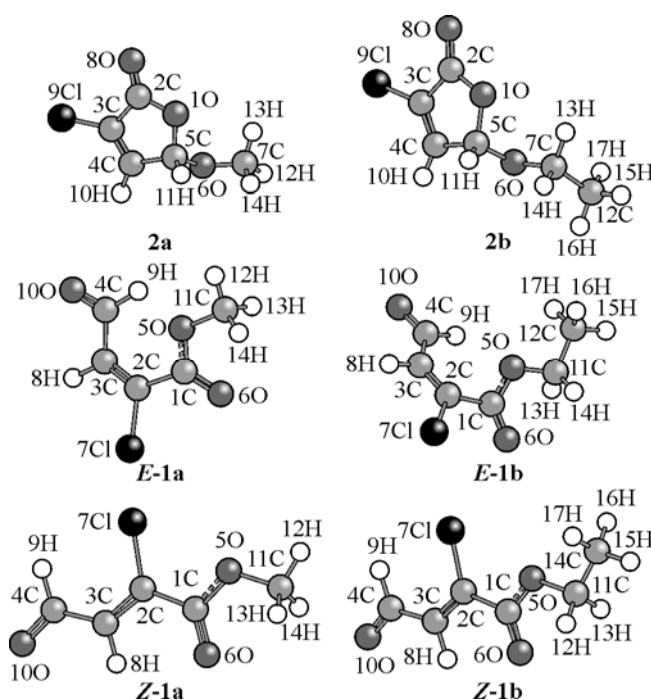
CONCLUSION

We have reported a new method for synthesizing substituted β -chloroacrylaldehydes. In addition to its great reactivity, this precursor is obtained in a high stereoselectivity (*Z/E* = 95/5). The results of

DFT(B3LYP)/6-311++G** optimized geometries of **1** and **2**

the various investigations by NMR and those of the theoretical study are in favor of assigning *Z*-stereochemistry to the major isomer present under the conditions used. On the basis of the experimental and theoretical data, we have also shown that the predominant stereoisomer, *Z*-**1**, is converted at high temperature to *E*-**1** which in turn is readily cyclized to furanone **2**. This may be used as a one-pot preparation of furanone **2** from β -chloroacrylaldehydes **1**.

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