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(*E*)-, (*Z*)-Interconversion in 3-Aroylmethyl-5-arylmethylene-2,4-dioxo-1,3-thiazolidines

Mohamed T. Omar*, and **Aly M. Youssif**

Chemistry Department, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt

Summary. The (*E*)-, (*Z*)-interconversion in 3-aroylmethyl-5-arylmethylene-2,4-dioxo-1,3-thiazolidines is simply achieved upon treating with phenylhydrazine in acetic acid solutions. Configurational assignments are based on ^{1}H-NMR spectral data.

Keywords. 3-Aroylmethyl-5-arylmethylene-2,4-dioxo-1,3-thiazolidines; Configurational assignments; Isomerization; Phenylhydrazine.

(*E*)-, (*Z*)-Interkonversion von 3-Aroylmethyl-5-arylmethylen-2,4-dioxo-1,3-thiazolidinen

Zusammenfassung. Die (*E*)-, (*Z*)-Interkonversion in 3-Aroylmethyl-5-arylmethylen-2,4-dioxo-1,3-thiazolidinen wird durch Behandlung mit Phenylhydrazin in essigsaurer Lösung erreicht. Die Zuordnung von Konfigurationen basiert auf ^{1}H-NMR-Daten.

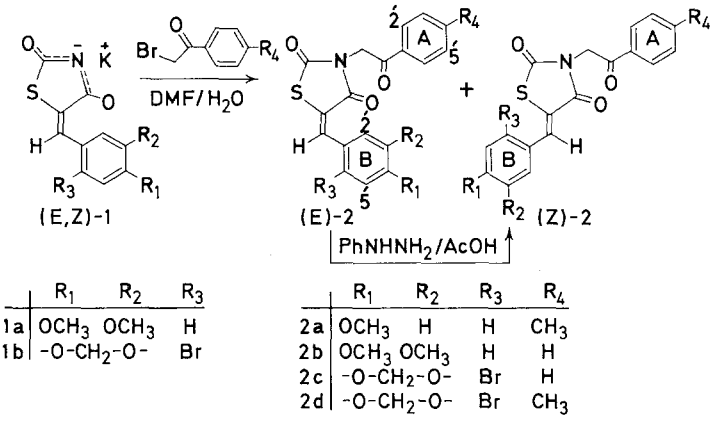
Introduction

The chemistry of 4-thiazolidinones has been a subject of our continuing interest [1–8] over the last 20 years. The aim of the present work is to study the (*E*)-, (*Z*)-interconversion in a series of 3-aroylmethyl-5-arylmethylene-2,4-dioxo-1,3-thiazolidines **2**. Our intent is to use the potential ability of the exocyclic α,β-unsaturated enone system of compounds **2** to add nucleophiles [8–10] on the one hand, and the easy decomposition of the formed adducts upon heating [9] on the other hand; both are elements of our new method for (*E*)-, (*Z*)-interconversion.

Results and Discussion

A series of 3-aroylmethyl-5-arylmethylene-2,4-dioxo-1,3-thiazolidines **2** has been synthesized via treating the potassium salts of respective 2,4-dioxo-1,3-thiazolidines **1** with aroylmethyl bromides using a modified method of Lo et al. [11]. For the interconversions we used phenylhydrazine in glacial acetic acid solutions. The use of acetic acid as a solvent is advantageous as it facilitates the decomposition of the phenylhydrazine adducts [12] which are supposed to be formed at first in the reaction, and further it supresses the nucleophilicity of phenylhydrazine, thus preventing formation of cleavage products [7, 8].

Compounds **2** are shown by ^{1}H-NMR spectroscopy to be mixtures of the (*E*)- and (*Z*)-isomers. Two distinct sets of signals are arising for aromatic, $N-H_2CO\mathit{Ar}$



	R_1	R_2	R_3
1a	OCH_3	OCH_3	H
1b	$-O-CH_2-O-$		Br

	R_1	R_2	R_3	R_4
2a	OCH_3	H	H	CH_3
2b	OCH_3	OCH_3	H	H
2c	$-O-CH_2-O-$		Br	H
2d	$-O-CH_2-O-$		Br	CH_3

and exocyclic olefinic protons, the most explicit signals being due to protons of ring "A" as well as the olefinic protons. The shifts of H-2′,6′ and H-3′,4′ of ring A, which are observed in one of the isomers indicate an interaction between the aryl moieties A and B. Inspection of molecular models shows that this interaction is possible especially in the (*E*)-configurated isomers. A special conformation about the single bonds joining the aryl groups (A and B) with the neighbouring C = O and C = C systems allows to minimize unfavourable interactions. This is evidenced by the deshielding observed for the chemical shift values of protons of ring A in the (*Z*)-configurated, rather than the (*E*)-configurated isomers. This configurational assignment is in accord with the configurations which would be obtained upon comparing the observed chemical shift values of the exocyclic olefinic protons with the incremented values [13]; the olefinic protons of the (*Z*)-isomers are relatively deshielded as compared with the (*E*)-counterparts. Peak area intensities of the crude products showed that in compounds **2** the (*E*)-isomer is predominating.

It has been observed that, upon treating (*E*, *Z*)-**2a**–**c** with phenylhydrazine in glacial acetic acid solutions, the ratios of the (*Z*)-isomers are increased at the expense of the (*E*)-isomers. Table 1 shows the ratios of isomers before and after isomerization.

The (*E*)-, (*Z*)-interconversion occurs most likely via the formation of the phenylhydrazine adducts which upon decomposition yield the less sterically crowded more stable (*Z*)-isomers. Isolation of a similar phenylhydrazine adduct has been

Table 1. (*Z*)/(*E*) ratio before and after isomerization

Compound	(*Z*)/(*E*) ratio[a]	
	Before isomerization	After isomerization
2a	15/85	≈100/0
2b	10/90	80/20
2c	20/80	≈100/0
2d	30/70	≈100/0

[a] (*Z*)/(*E*) ratio of the crude products

Table 2. Characteristic ^{1}H-NMR data[i] of compounds **2a–d**

Compound	Solvent	=CH s(1H)	CH_2CO*Ar* s(2H)	Aromatic hydrogens									OCH_3 s(3H)	CH_3 s(3H)	$-O-CH_2-O-$ s(2H)
				Ring A					Ring B						
				H-2′	H-6′	H-4′	H-3′	H-5′	H-2′	H-6′	H-5′	H-3′			
(*E*)-**2a**	$CDCl_3$	7.82	5.08	7.80[a]		–	6.90[a]		7.42[b]		7.25[b]		3.80	2.40	–
(*Z*)-**2a**	$CDCl_3$	7.90	5.05	7.82[a]		–	6.95[a]		7.42[b]		7.25[b]		3.80	2.40	–
(*E*)-**2b**	$CDCl_3$	7.80	5.00	7.95[c]		7.35		7.55[d]	6.80[c]	6.98[g]	6.90[f]		3.88[h]	–	–
(*Z*)-**2b**	$CDCl_3$	7.92	5.20	8.20[b]		7.40		7.70[d]	6.95[e]	7.20[g]	7.02[f]		3.95[h]	–	–
(*E*)-**2c**	$CDCl_3$	8.00	5.15	7.90[b]		7.25		7.40[d]	7.15[e]	–	7.05[e]		–	–	6.10
(*Z*)-**2c**	$CDCl_3$	8.20	5.20	8.00[b]		7.45		7.70[d]	7.15[e]	–	7.05[e]		–	–	6.10
(*E*)-**2d**	*DMSO*	7.93	5.26	7.90[b]		–	7.36[b]		7.37[e]	–	7.00[e]		–	2.40	6.15
(*Z*)-**2d**	*DMSO*	7.98	5.22	8.05[b]		–	7.50[b]		7.40[e]		7.05[e]		–	2.42	6.18

[a] d(2H, J=7.5 Hz)
[b] d(2H, J=7.0 Hz)
[c] dd(2H, $J_{2',3'}$=7.0 Hz, $J_{2',6'}$=1.5 Hz)
[d] m(3H)
[e] s(1H)
[f] d(1H, $J_{5',6'}$=6.0 Hz)
[g] dd(1H, $J_{5',6'}$=6.0 Hz, $J_{2',6'}$=1.5 Hz)
[h] Corresponding to 6H
[i] Carried out on a Varian EM 390, 90 MHz instrument using *TMS* as an internal reference

Table 3. Physical characteristics of compounds **1** and **2**

Compound	Yield [%]	M.p. [°C]	Molecular formula	IR [cm^{-1}][a] C=O	UV [nm][b]	
					λ_{max}	ε_{max}
1a	75[d]		$C_{12}H_{10}NO_4SK$ (303)	1670, 1610	–	–
1b	80[d]		$C_{11}H_5BrNO_4SK$ (366)	1665, 1610	–	–
(*E,Z*)-**2a**	≈78[e]	238–240	$C_{20}H_{17}NO_4S$ (367)	1730, 1670 (br)	244	14850
					343	21670
(*Z*)-**2a**[c, h]	80[f]	225–226	$C_{20}H_{17}NO_4S$ (367)		248	14800
					340	22500
(*E,Z*)-**2b**	≈75[e]	204–207	$C_{20}H_{17}NO_5S$ (383)	1728, 1667 (br)	238	13505
					355	13300
(*E,Z*)-**2b**[c]	85[g]	197–200	$C_{20}H_{17}NO_5S$ (383)		238	22100
					355	24450
(*E,Z*)-**2c**	≈80[e]	176–178	$C_{19}H_{12}BrNO_5S$ (446)	1730, 1665 (br)	240	22600
					312	8540
					355	15980
(*Z*)-**2c**[c]	80[f]	169–171	$C_{19}H_{12}BrNO_5S$ (446)		240	23500
					312	10100
					355	23300
(*E,Z*)-**2d**	≈80[e]	161–163	$C_{20}H_{14}BrNO_5S$ (460)	1728, 1670 (br)	240	25500
					312	11000
					357	16500
(*Z*)-**2d**[c]	82	180–182	$C_{20}H_{14}BrNO_5S$ (460)		245	30100
					312	12100
					357	20800

[a] Carried out on a Unicam. Sp 1200 spectrometer as KBr discs
[b] Carried out on a Perkin Elmer Lambda 3 B spectrometer in ethanol solutions
[c] Isomerization product
[d] From ethanol
[e] From glacial acetic acid
[f] From ethanol–benzene mixture
[g] From methanol
[h] MS *m/e* (%): 367 (M^+: 47.2). 164 (51.3). 149 (32.6). 119 (100). 91 (52.7), 65 (17.5). The spectrum was recorded on a Mattauch-Herzog geometry double focusing model Jeol JMS-O1SG-2 operating at 75 e.v.

reported in a previous publication from this laboratory [8] upon treating 3-benzyl-5-phenylmethylene-2,4-dioxo-1,3-thiazolidine with phenylhydrazine in ethanol solutions.

The structures of compounds **2** are based on microanalysis, infrared spectra showing the stretching absorptions of the olefinic and aromatic C–H bonds as well as the coupled carbonyl pattern of the 2,4-dioxo-1,3-thiazolidine ring system and electronic spectra showing two intense peaks assignable to the *Ar*CO and *Ar*CH–C(S)–C=O chromophoric systems. Furthermore the ^{1}H-NMR spectra show the olefinic, aromatic and the aroylmethyl methylene protons in accord with

the proposed structure (Table 2). The structure of (*Z*)-**2 a** is further supported by MS spectroscopy by its molecular ion and a fragmentation pattern consistent with the proposed structure.

Experimental

Potassium Salts of 5-(3,4-Dimethoxyphenylmethylene)-**1 a**, *and 5-(6-Bromo-3,4-methylenedioxyphenylmethylene)*-**1 b**-*2,4-dioxo-1,3-thiazolidines*

These salts were synthesized either by treating the respective 5-arylmethylene-2,4-dioxo-1,3-thiazolidines following the method of Lo et al. [11], or by treating the respective 2-piperidyl-4-oxo-2-thiazolines [3, 14] (synthesized previously in our laboratory) with methanolic potassium hydroxide solutions [6].

(E,Z)-3-Aroylmethyl-5-arylmethylene-2,4-dioxo-1,3-thiazolidines **2**

A suspension of each of the potassium salts (50 mmol) in water (3 ml) was added to a solution of aroyl methyl bromide (55 mmol) in dimethylformamide (50 ml) and the whole mixture was refluxed for 5 h. The reaction mixture was concentrated, poured into ice cold water and the precipitated solid was filtered off and recrystallized from the proper solvent to give the title compounds (cf. Table 3).

Procedure of Isomerization

Phenylhydrazine (0.5 ml) was added to a solution of each of (*E,Z*)-**2 a–d** (0.5 g) in glacial acetic acid (20 ml) and the whole mixture was refluxed for 6 h, concentrated, cooled and poured into water (250 ml). The precipitated solid was filtered off, washed successively with water and left to dry overnight. The crude product was recrystallized from the proper solvent to give the isomerized product (cf. Table 3).

The microanalytical data (C, H, N) for compounds **1 a**, **1 b**, (*E, Z*)-**2 a**, (*Z*)-**2 a**, (*E, Z*)-**2 b**, isomerized (*E, Z*)-**2 b**, (*E, Z*)-**2 c**, (*Z*)-**2 c**, (*E, Z*)-**2 d**, and (*Z*)-**2 d** were determined and found to be in very good agreement with the calculated values.

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