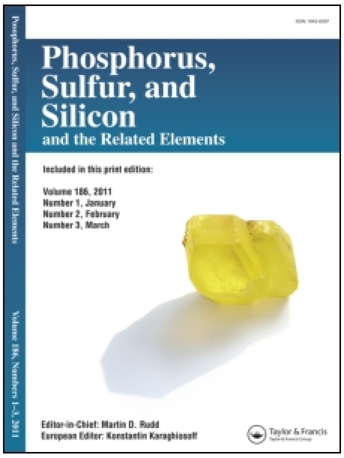

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THE STEREOSPECIFITY OF THE CYCLOADDITION OF 5-ARYLIDENE-2-THIAZOLIDINONE-4-THIONE DERIVATIVES TO ELECTRON-DEFICIENT OLEFINS

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The cycloadditions of 5-arylidene-2-thiazolidinone-4-thiones and their 3-phenyl derivatives **1a–d** to maleic and fumaric acid esters have been investigated. The stereochemistry of the reaction products indicates a concerned mechanism.

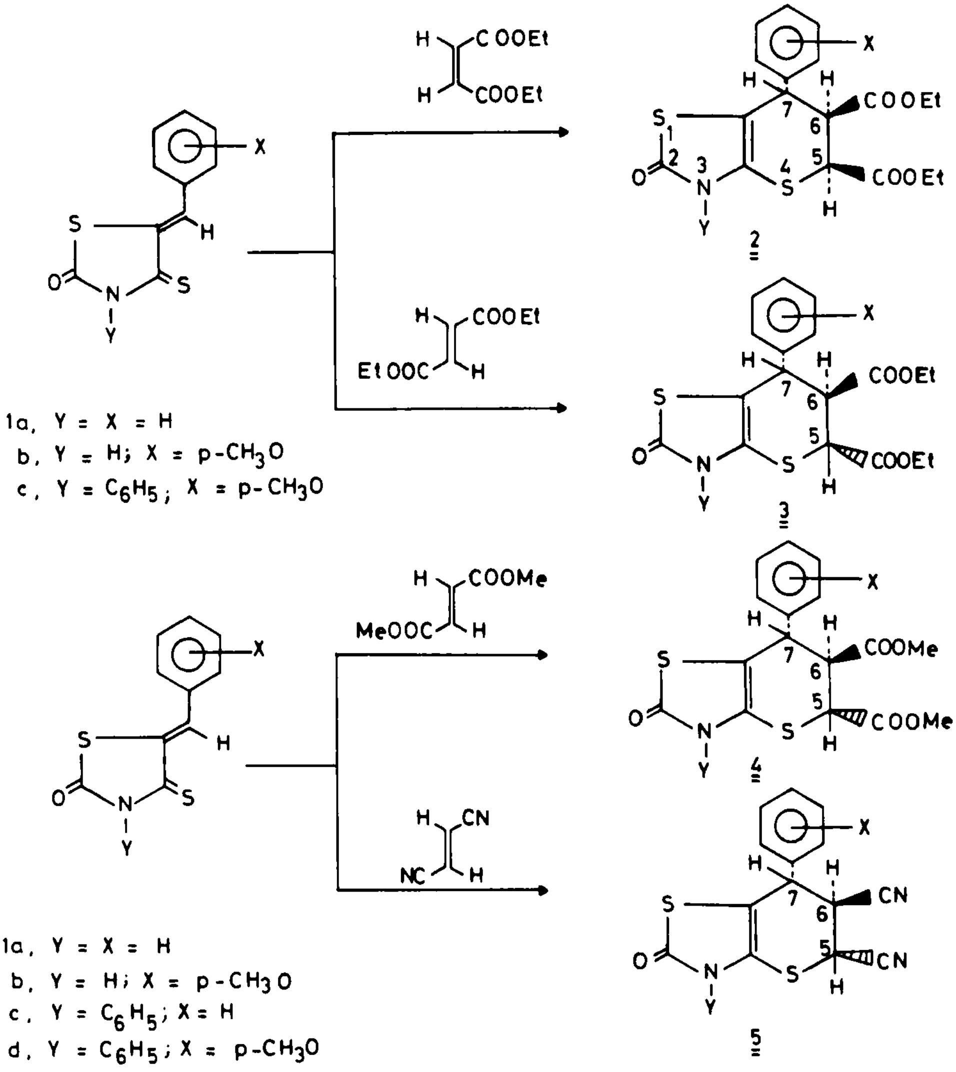
Key words: Stereochemistry; cycloaddition; 5-arylidene-2-thiazolidinone-4-thiones.

INTRODUCTION

Previous work from our laboratory and others dealt with the [4 + 2]-cycloaddition of different electron deficient dienophiles **1** to 5-arylidene thiazolidonone derivatives **2**.[1–5] However, in all previous reports the stereochemistry of this cycloaddition reaction was not discussed. This was probably due to the fact that the configuration of both reactants (**1** and **2**) used were not defined. In this paper we wish to report the results of our investigation on the stereochemistry of the reaction of a series of E-5-arylidene thiazolidinones (**2a–c**) with fumaronitrile, diethylmaleate, diethyl fumarate and dimethylfumarate.

RESULTS AND DISCUSSION

Three compounds of type **1** were prepared as previously described.[6] Only one isomer was obtained in each case as indicated by TLC and ^{1}H NMR spectroscopic analyses. Usually the Z or E configuration can be assigned to α,β-unsaturated cyclic carbonyl compounds by means of ^{1}H-NMR spectroscopy. On the basis of the chemical shift value of 8.30 ppm observed for the vinylic proton, the compounds **1a–c** were assigned the Z-configuration. This is because in this configuration the vinylic proton is expected to be more deshielded by the thione group than in the E-configuration. This rationalization is an accepted assumption in the elucidation of the configuration of arylidene derivative of azlactone,[7] piperazine,[8] indol-2-one,[9] succinimide[10] and 2-pyrazolin-5-one.[11] Reaction of **1a,b** with diethyl maleate yielded a 1:1 adduct which can be formulated as **2a,b** or its isomeric **3a,b**. ^{1}H NMR of **2** showed $J_{5,6}$ values of 9 Hz which is in accordance



with a cis-isomer. In order to support this conclusion the reaction of **1a–c** with diethyl fumarate was examined. The products obtained from the latter reaction were different from those obtained from **1** and maleate (m.p. and mixed m.p.). The ^{1}H NMR spectra of **3a–c** were characterised by the presence of a doublet ($J = 4$ Hz) near δ 3.75 and a dd* at δ 3.6 ppm assignable to H-5 and H-6, respectively. Thus, the cycloadducts **3a–c** could be assigned the indicated trans-configuration.[6]

The reaction of **1a–d** with dimethyl fumarate and **1c,d** with fumaronitrile, when carried out in a similar manner gave the corresponding thiopyrano[2,3-d]thiazolidine-2-one derivatives **4a–d** and **5c,d**, respectively. ^{1}H NMR spectra of **4a–d** and **5c,d** exhibit in each case signals at δ 4.7 (d, $J = 4$ Hz, 1 H), 3.55 (dd, $J = 4$ Hz, 1 H), and 4.3 (d, $J = 4$ Hz, 1 H) assignable to H-5, H-6 and H-7,

TABLE I

Physical and IR data of cycloadducts **2–5**

Compd.	M.P. °C	Yield %	Mol. Formula*	IR (cm^{-1})
2a	158–60	85	$C_{18}H_{19}NO_5S_2$	3220 (NH); 1680 and 1730 (ring and ester C=O).
2b	200–1	80	$C_{19}H_{21}NO_6S_2$	3200 (NH); 1680 and 1730 (ring and ester C=O).
2c	152–3	85	$C_{25}H_{25}NO_6S_2$	1680, 1740 (ring and ester C=O)
3a	136–7	80	$C_{18}H_{19}NO_5S_2$	3200 (NH); 1690 and 1730 (ring and ester C=O).
3b	130–1	80	$C_{19}H_{21}NO_6S_2$	3220 (NH); 1680 and 1740 (ring and ester C=O).
3c	144–5	85	$C_{25}H_{25}NO_6S_2$	1680, 1730 (ring and ester C=O)
4a	194–6	75	$C_{16}H_{15}NO_5S_2$	3200 (NH); 1690 and 1730 (ring and ester C=O).
4b	182–3	85	$C_{17}H_{17}NO_6S_2$	3220 (NH); 1680 and 1730 (ring and ester C=O).
4c	156–7	70	$C_{22}H_{19}NO_5S_2$	1680 and 1740 (ring and ester C=O).
4d	135–7	75	$C_{23}H_{21}NO_6S_2$	1680 and 1730 (ring and ester C=O).
5c	220–2	75	$C_{20}H_{13}N_3OS_2$	1680 (C=O) and 2220 (CN).
5d	187–9	80	$C_{21}H_{15}N_3O_2S_2$	1690 (C=O) and 2220 (CN).

* Satisfactory analytical data were obtained.

TABLE II

^{1}H NMR data of cycloadducts **2–5**

Compd.	H-5	H-6	H-7	CH_3OAr	NH	CH_3CH_2OCO CH_3OCO
2a	4.8 (d)	3.8 (dd)	4.1 (d)		10.8 (s)	1.2 (t) 4.4 (q)
2b	4.8 (d)	3.7 (dd)	4.2 (d)	3.7 (s)	10.7 (s)	1.2 (t) 4.2 (q)
2c	4.7 (d)	3.8 (dd)	4.0 (d)	3.7 (s)		1.2 (t) 4.3 (q)
3a	4.3 (d)	3.5 (dd)	4.1 (d)		10.2 (s)	1.2 (t) 4.3 (q)
3b	4.4 (d)	3.5 (dd)	4.1 (d)	3.7 (s)	10.1 (s)	1.2 (t) 4.2 (q)
3c	4.3 (d)	3.5 (dd)	4.0 (d)	3.7 (s)		1.2 (t) 4.2 (q)
4a	4.7 (d)	3.5 (dd)	4.3 (d)		10.1 (s)	3.7 (s)[1]
4b	4.6 (d)	3.5 (dd)	4.2 (d)	3.8 (s)	10.2 (s)	3.7 (s)[1]
4c	4.7 (d)	3.5 (dd)	4.2 (d)			3.6 (s)[1]
4d	4.6 (d)	3.5 (dd)	4.2 (d)	3.7 (s)		3.6 (s)[1]
5c	4.6 (d)	3.6 (dd)	4.3 (d)	3.7 (s)		
5d	4.7 (d)	3.5 (dd)	4.3 (d)	3.7 (s)		

For **2a–c**, $J_{5,6} = 9$ Hz, $J_{6,7} = 5$ Hz and for **3a–c** and **4a–d**: $J = 4$ Hz, $J_{6,7} = 5$ Hz. All compounds exhibit also aromatic proton multiplet signals in the region 7.0–7.7 ppm.

respectively. On the basis of the foregoing results it is reasonable to conclude that the reaction studied proceeds with retention of the configuration of the reacting dienophile. This suggests that the examined mechanism would be expected to lead to an isomeric mixture regardless of the stereochemistry of the dienophile used.

EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded on a Pye Unicam SP-1100 spectrophotometer using KBr disc. ^{1}H NMR spectra were recorded on a Varian EM-390 90 MHz spectrometer using DMSO-d_6 as a solvent and TMS as an internal standard. Chemical shifts are expressed as ppm Units. The microanalyses were performed by the microanalytical center at Cairo University.

Synthesis of tetrasubstituted 7H-tetrahydrothiopyrano[2,3-*d*]*thiazolidine-2-one derivatives* **2–5**. To a solution of the appropriate 5-arylidene derivative **1** (0.01 mole) in benzene (30 ml) was added the appropriate dienophile (0.01 mole). The mixture was refluxed for 4 h and then left overnight at room temperature. The colourless solid that precipitated was collected and crystallization from ethanol gave the corresponding cycloadduct. The reaction products **2–5** together with their physical constants are listed in Tables I and II.

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