

Isomerisation of Methyl (E) 2-Bromo-3-(4- XC_6H_4)-propenoates

Mercedes A. Badajoz,* Rosana S. Montani and Mercedes Cabaleiro

INIQO, Universidad Nacional del Sur, Av. Alem 1253, (8000) Bahía Blanca, Argentina

Tel/Fax: +54 (291)-459-5187, E-mail: mbadajoz@criba.edu.ar

* Author to whom correspondence should be addressed.

Abstract: The geometric isomerisation of the title compound induced by bromine or chlorine appears to involve ionic pair species resulting from the nucleophilic attack of the halogen.

Keywords: isomerisation, propenoates.

Introduction

The title compounds show geometrical isomerisation when subjected to the action of halogen (chlorine or bromine) Since these systems are involved in addition reactions [1,2], the examination of the nature of the isomerisation is required to define the details of the whole process. We here report on a study on the reaction of



induced by chlorine or bromine in various solvents.

Experimental

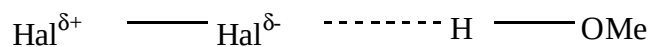
The isomeric pure acids were obtained by fractionated reprecipitation from the E and Z isomers mixture. Then, the E-esters were prepared from the corresponding acids. Finally, the α - β unsaturated esters were treated either with chlorine or with bromine in a series of solvents. The isomerization reaction was followed measuring the E/Z ratio by glc.

Results and Discussion

From inspection of the data summarised in the Table, some general conclusion can be drawn.

1. The halogen participates in the rate determining stage
2. The observed reactivity of the substrates increases with decreasing dielectric constant of the solvent which is related to a transition state involving the action of molecular halogen.

For the polar medium, the rate seems to be disfavoured by the protic nature of the solvent. This might be attributed to solvation of the halogen exerted by the latter which leads to a reduction of its actual concentration.



3. The influence of the aromatic substituent appears to depend on the nature of the solvent. Thus, a decrease in the reactivity occurs with increasing electron release when the reaction is carried out in benzene or in methanol. The former observations can be reconciled with an halogen attack which, though molecular in nature, proceeds through its nucleophilic end. This would lead to an intermediate with an olefinic bond weak enough to allow the molecule isomerise to the more stable form.

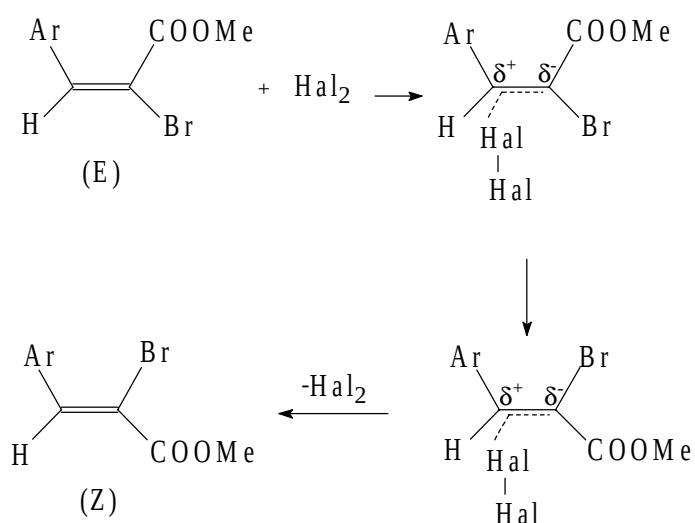


Table. Rate coefficients for the isomerisation (E→Z) of (E) 4-XC₆H₄CH=CHBrCOOMe [dm³mol⁻¹min⁻¹] promoted by halogen at 30°C.

<i>Hal</i>	<i>X</i>	<i>MeOH</i>	<i>MeCN</i>	<i>Benzene</i>
<i>Br</i> ₂	<i>H</i>	0,307 ^a	1,16 ^a	39,98 ^b
	<i>Me</i>	0,103 ^a	1,74 ^a	27,52 ^b
	<i>Cl</i>	0,342 ^c	0,25 ^c	66,59 ^b
<i>Cl</i> ₂	<i>H</i>	0,0127 ^a	0,017 ^a	18,1 ^b
	<i>Me</i>	0,0090 ^a	0,102 ^a	6,33 ^b
	<i>Cl</i>	0,0212 ^a	0,038 ^d	20,80 ^b

^a [Hal₂] = 0,2 mol dm⁻³; ^b [Hal₂] = 0,006 mol dm⁻³;

^c [Hal₂] = 0,03 mol dm⁻³; ^d [Hal₂] = 0,4 mol dm⁻³

When acetonitrile is used as solvent the reactivity sequence appears to be the opposite. On the basis of the available evidence, it is difficult to draw a full explanation of the observed results and additional evidence will be required to establish the mechanism of the whole reaction.

References and Notes

1. Badajoz, M.A.; Montani, R.S.; Cabaleiro, M.C. Triethylamine-induced Reactions of Methyl 2,3-Dibromo-2,3-diarylpropanoates in Methanol. *J.Chem.Res.(S)* **1998**, 124.
2. Badajoz, M.A.; Montani, R.S.; Cabaleiro, M.C. Methyl 2,3-dibromo-2,3-diarylpropanoates. De-bromination and dehydrobromination reactions. *J.Chem.Soc., Perkin Trans. 2* **1996**, 1717.