Isomerization of *cis*-1,2-Diarylethylenes. Catalysis by Selenium, Methanesulphonic Acid, and Potassium t-Butoxide

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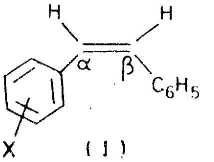
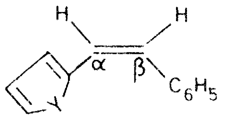
Second-order rate constants and activation parameters for the isomerization of *cis*-X-substituted-diphenylethylenes (X = *p*-OCH_3, *p*-CH_3, H, *p*-Cl, *m*-Cl, or *p*-NO_2), *cis*-2-styrylfuran, and *cis*-2-styrylthiophen have been measured in decahydronaphthalene using selenium (Se), methanesulphonic acid (MSA), and potassium t-butoxide (PTB) as catalysts. The catalyst effectiveness decreases in the order Se > MSA > PTB. Acid-catalysed isomerization is enhanced by electron-donating substituents, base-catalysed one is favoured by electron-withdrawing groups, and selenium-catalysed isomerization is not affected by substituents. The heterocyclic derivatives react faster than stilbene with all catalysts. A stepwise mechanism including addition and elimination of the catalysts is proposed.

THE kinetics of isomerization of *cis*-stilbene have been widely investigated using selenium,[1] sulphuric acid,[2] boron trifluoride,[3] iodine,[4] platinum,[5] and potassium t-butoxide[6] as catalysts. Theoretical[7] and spectroscopic[8] studies prove that in *cis*-stilbene the aromatic rings are twisted with respect to the ethylene plane by *ca.* 30°, and it is well known that *trans*-stilbene is the energetically more stable isomer owing to its planar configuration.



(I)

X = *p*—OCH_3, *p*—CH_3, H, *p*—Cl, *m*—Cl or *p*—NO_2



(II)

Y = O or S

We have been interested in the kinetics and mechanism of isomerization of *cis*-diarylacrylonitriles by selenium (Se),[9] methanesulphonic acid (MSA),[10] and potassium t-butoxide (PTB)[10] as catalysts. We now report the rate constants and activation parameters for the isomerization of *cis*-diarylethylenes (I) and (II) in decahydronaphthalene using the same catalysts as in the reaction of diarylacrylonitriles, with the aim of providing structure–reactivity relationships and details of the isomerization mechanism.

RESULTS AND DISCUSSION

The kinetics of isomerization of *cis*-diarylethylenes (I) and (II), followed by g.l.c. analysis of the *cis*- and *trans*-isomers, obeys a first-order rate law to at least 90% completion. The pseudo-first-order rate constants increase linearly on increasing the catalyst concentration, as shown in Figure 1.

The intercepts of the log k_1 against catalyst concentration plots (Figure 1) are almost zero, indicating the lack of non-catalysed thermal isomerization. The second-order rate constants, obtained from the slopes of these plots, are reported in Tables 1 and 2, together with the activation parameters calculated at 170 °C. Selenium is the most effective catalyst, the relative rates for the isomerization of *cis*-stilbene at 190 °C being in the ratio 734 : 20.6 : 1, for Se, MSA, and PTB, respectively.

A comparison between the isomerization kinetics of diarylethylenes and diarylacrylonitriles[9,10] shows remarkable differences. In fact, the higher electron density on the double bond of diarylethylenes favours acidic (electrophilic) isomerization, whereas base-catalysed isomerization is faster for diarylacrylonitriles, in which the electron-withdrawing cyano-group favours initial attack of the nucleophile and stabilizes the negative charge in the carbanionic intermediate.

As in diarylethylenes there are two centres for catalyst attack (C_α or C_β); these reactions have the difficulty that changing the substituent in the aryl ring can change the regiochemistry of addition, so that non-linear Hammett plots may be expected, as found in the bromination of diarylethylenes.[11] In fact, two lines meeting at the stilbene points are found in the Hammett plots of the isomerization by MSA (Figure 2).

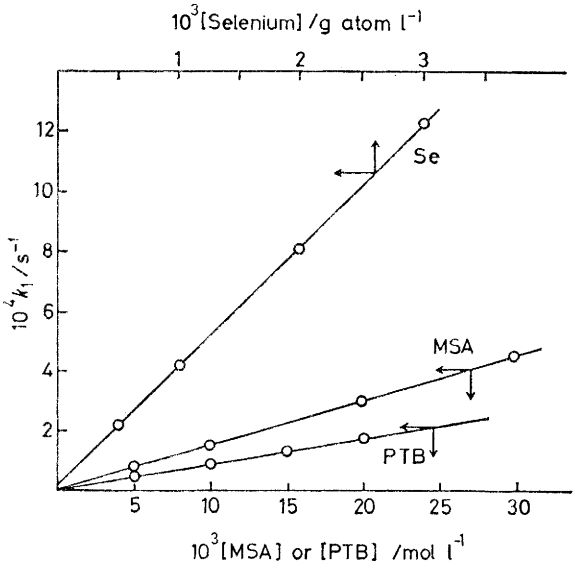


FIGURE 1 Plots of pseudo-first-order rate constants at 190 °C *versus* catalyst concentration for the isomerization of *cis*-2-styrylthiophen

The satisfactory linear correlation between log k_2 and the σ^+ values of the electron-donating substituents (ρ^+ -0.92 ± 0.07 at 170 °C) suggests that the acidic hydrogen atom of MSA is transferred to the C_β atom of the substituted ring with formation of an incipient positive change at the C_α atom. This transition state (α-carbocation) can be quickly converted into a *trans*-olefin by fast rotation around the single bond and by loss of a β-proton.

TABLE 1

Second-order rate constants and activation parameters for the selenium-catalysed isomerization of *cis*-$XC_6H_4CH{=}CHC_6H_5$ and *cis*-2-$C_4H_3YCH{=}CHC_6H_5$

	10^3k_2/l mol^{-1} s^{-1}			$\Delta H^\ddagger$/	$\Delta S^\ddagger$/
	150 °C	170 °C	190 °C	kcal mol^{-1}	cal mol^{-1} K^{-1}
X = *p*-OCH_3	1.99	8.49	38.0	27.8	−5.9
p-CH_3	1.73	7.67	36.7	28.8	−3.8
H	2.55	12.2	39.5	25.9	−9.9
m-Cl	1.26	6.06	31.6	30.5	−0.6
p-Cl	1.88	8.62	37.5	28.3	−5.0
p-NO_2	2.56	15.0	69.9	31.3	3.0
Y = O	16.0	85.2	293	27.5	−2.5
S	11.6	81.0	397	33.6	11.3

The ' mean ' standard deviations of the estimated activation parameters are ±1.0 kcal mol^{-1} for $\Delta H^\ddagger$ and ±3.0 cal mol^{-1} K^{-1} for $\Delta S^\ddagger$.

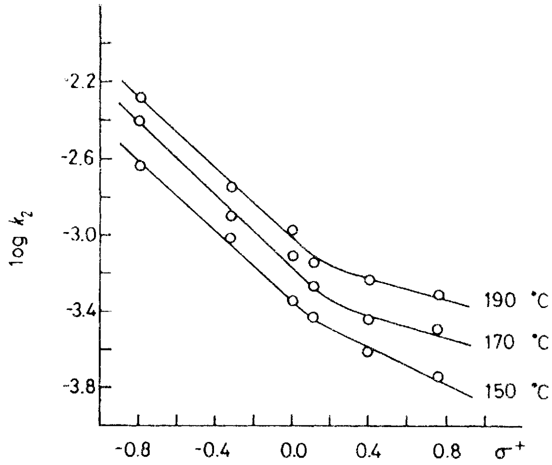
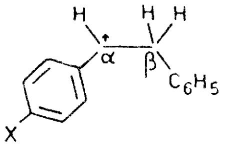
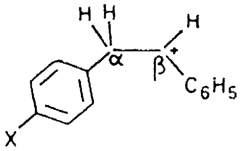


FIGURE 2 Hammett plots for the isomerization of *cis*-$XC_6H_4CH{=}CHC_6H_5$ by methanesulphonic acid

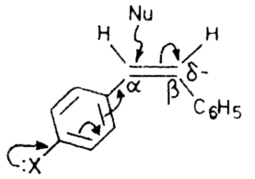
The electron-withdrawing groups reverse the mode of addition and a β-carbocation is formed; the relative slopes in the Hammett plots (Figure 2) are less negative (ρ^+ -0.35 ± 0.12 at 170 °C), because the substituents are insulated by a methylene group from the carbonium ion centre.

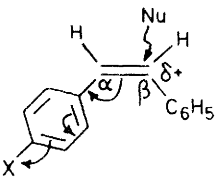
Nucleophilic attack on diarylethylenes by PTB follows different regiochemistry depending on the substituent effects, as shown by the curvilinear Hammett plot (Figure 3). Electron-withdrawing groups favour





the isomerization rate in a different manner from acidic isomerization. Initial attack of the alkoxide group on the C_α or C_β atoms seems to be the rate-determining step.





The insensitivity of the selenium-catalysed isomerization to substituent effects (Figure 3) could be explained by a free radical mechanism, as in the corresponding isomerization of diarylacrylonitriles.[9] Nevertheless, the diagnostic tests for a free radical reaction were un-

TABLE 2

Second-order rate constants (10^3 k_2/l mol^{-1} s^{-1}) and activation parameters for the isomerization of *cis*-$XC_6H_4CH{=}CHC_6H_5$ and *cis*-2-$C_4H_3Y{-}CH{=}CHC_6H_5$ catalysed by methanesulphonic acid and potassium t-butoxide

	Methanesulphonic acid					Potassium t-butoxide
	150 °C	170 °C	190 °C	$\Delta H^\ddagger$/ kcal mol^{-1}	$\Delta S^\ddagger$/ cal mol^{-1} K^{-1}	190 °C
X = *p*-OCH_3	2.26	3.95	5.19	7.3	−54.1	0.0125
p-CH_3	0.998	1.27	1.85	5.1	−61.0	0.0315
H	0.453	0.789	1.11	7.9	−55.9	0.0538
p-Cl	0.380	0.560	0.730	5.5	−61.9	0.0654
m-Cl	0.244	0.369	0.602	7.9	−57.1	0.102
p-NO_2	0.183	0.313	0.503	9.0	−55.0	0.216[a]
Y = O	1.32	1.67	2.75	6.2	−57.8	0.119
S	3.28	6.06	15.1	13.9	−37.8	8.93

[a] 10^3k_2 0.0480 (150°), 0.111 (170°) l mol^{-1} s^{-1}; $\Delta H^\ddagger$ 13.8 kcal mol^{-1}; $\Delta S^\ddagger$ −46.3 cal mol^{-1} K^{-1}. The ' mean ' standard deviations of the estimated activation parameters are ±1.0 kcal mol^{-1} for $\Delta H^\ddagger$ and ±3.0 cal mol^{-1} K^{-1} for $\Delta S^\ddagger$ values.

successful. In fact various kinetic runs carried out in the presence of dibenzoyl peroxide (radical initiator) or of hydroquinone (radical inhibitor) provide the same k_2 values as under the standard conditions, within the range of experimental error. The lack of sensitivity to the substituent effects requires that complex formation involves the vinyl group specifically in a rate-determining step. As selenium has a remarkable ability in interacting with the π-electron of olefins,[1,10] enhanced reactivity occurs. This fact could justify the poor selectivity with regard to substituent effects, according to the reactivity–selectivity principle.[12]

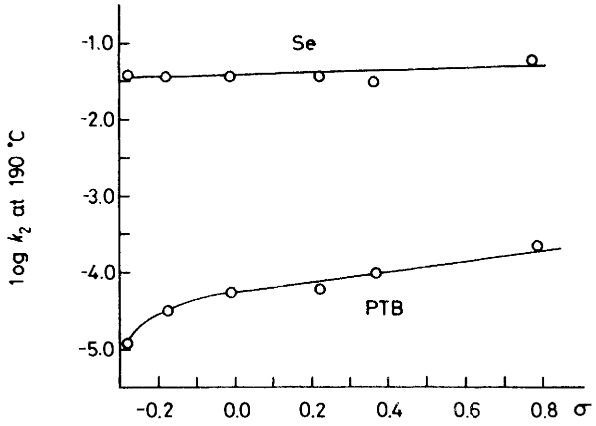
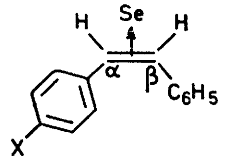


FIGURE 3 Hammett plots for the isomerization of *cis*-$XC_6H_4CH=CHC_6H_5$ by selenium and potassium t-butoxide



The isomerization rates of *cis*-2-styrylfuran and *cis*-2-styrylthiophen are faster than that of *cis*-stilbene with all catalysts, because of the ability of the heterocyclic nuclei to stabilize both positive and negative charges better than benzene ring.[13]

The reaction rates depend largely on activation entropies. The selenium-catalysed isomerization is faster in spite of high $\Delta H^\ddagger$ values, whereas the acidic isomerizations show lower $\Delta H^\ddagger$ and highly negative $\Delta S^\ddagger$ values, in agreement with the polar structure of the transition state.[14]

EXPERIMENTAL

Materials.—*cis*- and *trans*-Diarylethylenes were prepared by a Wittig reaction between equimolar amounts of benzyltriphenylphosphonium chloride and the appropriate arenecarbaldehyde in the presence of EtONa in EtOH. The separation of the isomers was carried out by column chromatography on alumina: *cis*- and *trans*-$XC_6H_4CH=CHC_6H_5$ (X, m.p. or b.p./mmHg), *cis*-*p*-OCH_3, 98—100°/2;[15] *trans*-*p*-OCH_3, 136—137°;[16] *cis*-*p*-CH_3, 110—112°/2;[15] *trans*-*p*-CH_3, 119—120°;[15] *cis*-H, 105°/2;[15,16] *trans*-H, 124°;[17] *cis*-*p*-Cl, 90°/0.05;[18] *trans*-*p*-Cl, 129°;[15,16] *cis*-*m*-Cl, 92°/0.06;* *trans*-*m*-Cl, 73—74°;[16] *cis*-*p*-NO_2, 62—63°;[17] *trans*-*p*-NO_2, 156—157°;[15] *cis*- and *trans*-2-$C_4H_3YCH=CHC_6H_5$ (Y, m.p. or b.p./mmHg), *cis*-O, 79—80°/0.05;[19] *trans*-O, 54—55°;[19] *cis*-S, 92°/0.3;[20] *trans*-S, 111°.[20]

Decahydronaphthalene, black selenium powder, methanesulphonic acid, and potassium t-butoxide (commercial products; AnalaR grade) were used without further purification.

Kinetic Procedure.—The reaction medium was homogeneous in all cases. In particular, selenium is completely soluble in the substrate, owing to the rapid formation of an adduct between the olefin and selenium (π-complex).[1,10]

To *cis*-isomer solution in decahydronaphthalene (5 ml; *ca.* 0.15 mol l^{-1}), placed in a glass-stoppered bottle and maintained at constant temperature, catalyst solution (5 ml) was added (for catalyst concentration see Figure 1). At suitable intervals, portions were removed by a microsyringe and analysed by g.l.c., using the procedure previously described.[1,10]

All kinetic measurements were carried out in duplicate; less than 6% deviation between the two rate constants values was observed.

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* This work. Satisfactory combustion analytical data (C and H) were found.

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