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KINETICS AND MECHANISM OF SELENIUM-CATALYZED ISOMERIZATION OF SOME *cis*-DIARYLACRYLONITRILES†

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Abstract—The kinetics of the *cis–trans* isomerization of some α,β-diarylacrylonitriles has been investigated in decahydronaphthalene at 150–190° with selenium as a catalyst. The reaction is first order with respect to olefin and 1/2 apparent order with respect to catalyst. Isomerization rate is increased by electron donating groups in the α-phenyl and by electron withdrawing ones in the β-phenyl. Satisfactory correlations between log k and substituent σ^+ values are observed. Evidence is obtained for a free radical mechanism. The results are consistent with a reaction path involving the formation of a σ-complex between the α-C atom and selenium diradical, followed by a free rotation around the single bond and removal of the catalyst. The effects of heteroaromatic nuclei linked to α-C atom on the isomerization rate (phenyl > 2-furyl > 2-thienyl) indicate the lack of conjugation from heteroatom to the side chain in the rate determining step.

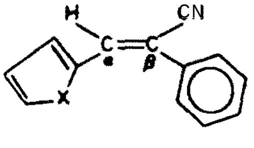
During recent decades, *cis–trans* isomerization of α,β-substituted ethylenes has been extensively investigated for its theoretical interest and possible application.[1] The interconversion of both isomers to equilibrium mixtures originates from π-bond rupture followed by free rotation of adjacent groups around the σ-bond. The π-bond rupture can be induced thermally[2] and photochemically[3] or by paramagnetic compounds[4] which determine the formation of free radical intermediates in the reaction path; moreover, the action of protic[5] or Lewis acids,[6] bases,[7] some metals[8] or positive ions[9] favour a mechanism which proceeds through ionic transition states.

Selenium has also been used as catalyst in the isomerization of oleic acid,[10] *cis*-stilbene[11] and some cyclic dienes;[12] however, in this case, the proposed mechanism had not been developed sufficiently because of the lack of suitable experimental information.

Following previous work on the isomerization of *cis*-α,β-diarylethylenes,[13] we report the kinetic results for the isomerization of some *cis*-α,β-diarylacrylonitriles 1 and 2 in decahydronaphthalene at 150–190°, with selenium as catalyst.

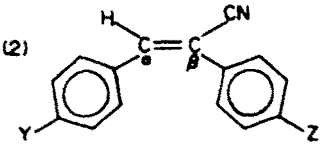
This study, which involves substituent effects in both phenyl ring systems, was undertaken to investigate the selenium-catalyzed isomerization mechanism. Moreover we hope to contribute to the knowledge of the electronic effects of the furan and thiophene cycles to the adjacent double bond, in connection with the studies on side chain reactivity of 5-membered heterocycles.[14]

(1)



X = O, S

(2)



Y = H; Z = OMe, Me, H, Cl, NO_2
Y = OMe, Me, Cl, NO_2; Z = H

RESULTS AND DISCUSSION

Pure samples of each *cis*-isomer in decahydronaphthalene were treated with different amounts of selenium at constant temperature. The reaction medium was homogeneous, selenium being completely soluble in the substrate, owing to the fast formation of an adduct between the olefin and selenium (π-complex), as suggested by Fitzpatrick and Orchin.[10,11]

Quantitative analysis of both isomers was carried out by gaschromatography (Experimental), which was preferred to other techniques for accuracy and reproducibility of results and for its general applicability to the examined compounds.

The reactions gave *trans*-isomers by excellent pseudo first order kinetics with respect to the substrate.‡ Table 1 reports k_1 values at different catalyst concentrations for the isomerization of α,β-diphenylacrylonitrile at 170° and 190° and of α-(2-thienyl), β-phenylacrylonitrile at 170°.

To calculate the reaction order with respect to selenium, it was necessary to know the molecular species in solution. Selenium has the hexagonal structure and dissolves as an 8-membered species (presumed to be

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‡Preliminary experiments have confirmed that: (i) the thermal isomerization, in the absence of selenium, is negligible; (ii) the *trans*-isomers undergo selenium-catalyzed isomerization giving only 3-4% of *cis*-isomers (equilibrium mixture); (iii) the reaction is always homogeneous and after cooling the catalyst ppts in the red modification.

Table 1. Dependence of the pseudo first order rate constants on the selenium concentration and apparent order with respect to catalyst

Selenium (10^3 g atom l^{-1})	10^3 k_1 (min^{-1}) $C_4H_3SCH{=}C(CN)C_6H_5$ 170°C	$C_6H_5CH{=}C(CN)C_6H_5$ 170°C	$C_6H_5CH{=}C(CN)C_6H_5$ 190°C
1.52		2.53	
2.22		2.78	
2.44	1.94	2.82	7.89
3.61		3.77	
4.67		4.11	
5.01	3.14	4.14	11.9
7.28	3.32	5.07	14.2
Reaction Order	0.52±0.13	0.47±0.03	0.54±0.02

rings) as shown by cryoscopic and ebullioscopic measurements.[15] By increasing the temperature these molecules dissociate; particularly, the diatomic molecule is paramagnetic and able to induce a free radical chain.[16]

The logarithmic plot between pseudo first order rate constants, for isomerization of α,β-diphenylacrylonitrile at 170°, and selenium stoichiometric concentration (g atom l^{-1}) is linear with a slope near to 1/2 (Fig. 1). The same fractional order was found for the isomerization of α,β-diphenylacrylonitrile at 190° and of α-(2-thienyl), β-phenylacrylonitrile at 170°.

The values of pseudo first order rate constants at various temperatures, obtained with 5.01×10^{-3} g atom l^{-1} selenium, are reported in Table 2, together with the activation parameters calculated at 170°. The substituents can produce opposite effects on the reaction rate: the isomerization is in fact favoured by electron donating groups in the β-phenyl and by electron withdrawing ones in the α-phenyl ring.

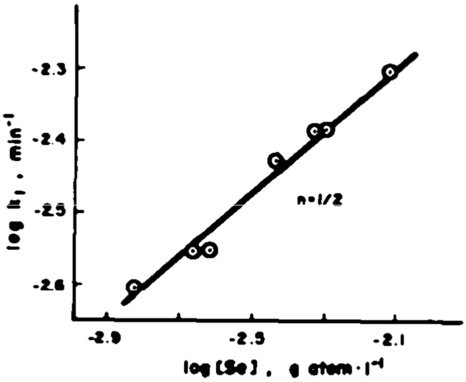
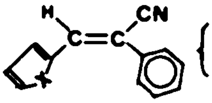
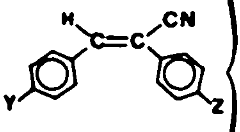


Fig. 1. Apparent order with respect to selenium concentration for the isomerization of *cis*-α,β-diphenylacrylonitrile in decahydronaphthalene at 170°C.

Table 2. Pseudo first order rate constants at 5.01 g atom l^{-1} of selenium and activation parameters at 170°C of some *cis*-α,β-diarylacrylonitriles in decahydronaphthalene

			10^3 k_1 (min^{-1}) 150°C	170°C	190°C	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal $mol^{-1}K^{-1}$)	$\Delta G^{\neq}$ (kcal mol^{-1})
	X=O		0.244	1.43	4.81	28.2	-8.9	32.1
	S		0.0881	0.938	3.14	34.1	3.1	32.7
	Y=H;	Z=OCH_3			20.2			
	H	CH_3			13.3			
	H	H	0.748	4.14	11.9	26.2	-11.5	31.3
	H	Cl			11.5			
	H	NO_2	0.271	1.15	6.28	29.7	-5.5	32.2
	OCH_3	H	0.339	2.18	5.72	26.8	-11.6	31.9
	CH_3	H	0.492	3.24	9.00	27.5	-9.0	31.5
	Cl	H	0.780	3.42	11.6	25.4	-13.3	31.3
	NO_2	H	2.01	6.88	25.6	23.9	-15.2	30.6

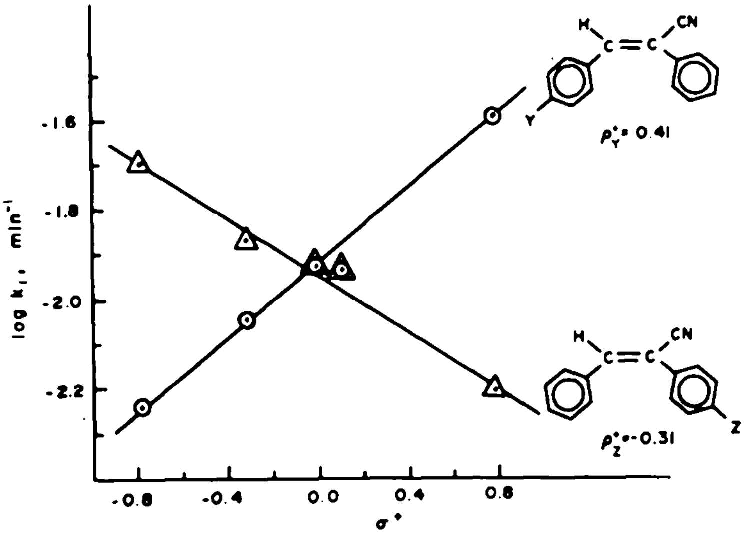


Fig. 2. Dependence of log k_1 on σ^+ values for the isomerization of *cis*-α-p-Y-phenyl,β-phenylacrylonitrile (⊙) and of *cis*-α-phenyl,β-p-Z-phenylacrylonitrile (Δ) in decahydronaphthalene at 190°C.

Figure 2 shows the good correlation between log k_1 at 190° and σ^+ values of the substituents. Analogous plots are obtained at the other temperatures.

The significance of the activation parameters values on the *cis–trans* isomerization mechanism had been discussed.[17] Particularly, the values of the preexponential factor (A) are diagnostic for isomerization *with* or *without* change in electron multiplicity at the transition state (respectively *triplet* or *singlet* states). The A values of about 10^{12} min^{-1} observed for the examined acrylonitriles could be associated with a mechanism which proceeds by singlet state.

The probable existence of paramagnetic molecular species in non polar solvent at high temperatures, the fractional reaction order and small ρ^+-values suggest a reaction mechanism via free radical intermediates.[18] However, in order to check this hypothesis some diagnostic kinetic runs were carried out; the addition of small amounts of radical inhibitor (hydroquinone) to the reaction solution brings a remarkable lowering of the isomerization rate constant values; moreover the reaction is inhibited in strongly polar solvent (ethylene glycol) which does not allow the free radical formation. These results support the above hypothesis.

In comparison with the isomerization of α,β-diarylethylenes,[13] the isomerization of the α,β-diarylacrylonitriles show some features indicating different reaction paths. In fact, the reactivity order for heterocycles-containing compounds, with respect to diphenyl derivative, is: *phenyl* > 2-*furyl* > 2-*thienyl*, whilst for diarylethylenes is: 2-*furyl* > 2-*thienyl* > *phenyl*; at comparable experimental conditions the isomerization is kinetically less favoured owing to remarkable differences in the activation parameters (about 12–16 kcal mol^{-1} for $\Delta H^{\neq}$ and about 10^5–10^6 min^{-1} for preexponential factor).

In the diarylethylene isomerization, selenium is probably bonded at β-C atom, as it bears the most of π-electron density, as indicated by electrophilic reaction data for these compounds.[19,20] The C_β–Se bond formation induces on the α-C atom an unshared electron, which can be delocalized on the π-orbital of the adjacent heterocycle (Fig. 3a). The observed reactivity order is in fact in excellent accord with electrophilic σ^+ values for the heteroatoms obtained from extended selectivity treatment.[21]

3a 3b

Fig. 3. Probable structures of σ-complex intermediates: (a) in diarylethylenes; (b) in diarylacrylonitriles.

In diarylacrylonitriles, instead, the electronic distribution in the double bond differs from that of diarylethylenes because the CN group makes the β-C atom less electron-rich than the α-C atom. On the latter atom, then, selenium preferably would be bonded. Moreover, the C_α–Se bond making, is preferred not only for the lower steric hindrance but also since the unshared electron is placed on the energetically more stable tertiary β-C atom (Fig. 3b).

Figure 4 reports the reaction path for the selenium-catalyzed isomerization, according to the experimental results. This mechanism implies the fast formation of a *cis*-π-complex between olefin and the diradical selenium, followed by σ-complex formation. The free rotation around the simple σ bond and the consecutive formation of *trans*-π complex yields the *trans*-isomer, with removal of the catalyst which initiates again the reaction chains.

The observed substituent effects are consistent with a mechanism involving an intermediate complex, since the rate determining step depends on the position of substituents in the α- or β-phenyl rings. Electron donating groups, in both cases, would promote the C–Se bond making and would oppose the C–Se bond breaking; opposite effects would be predicted for the electron withdrawing groups.

If the substituted phenyl ring is adjacent to the α-C atom bonded to selenium, the rate limiting step could be associated with the transformation of the *trans*-σ-complex in *trans*-π-complex (step 5), since the electron

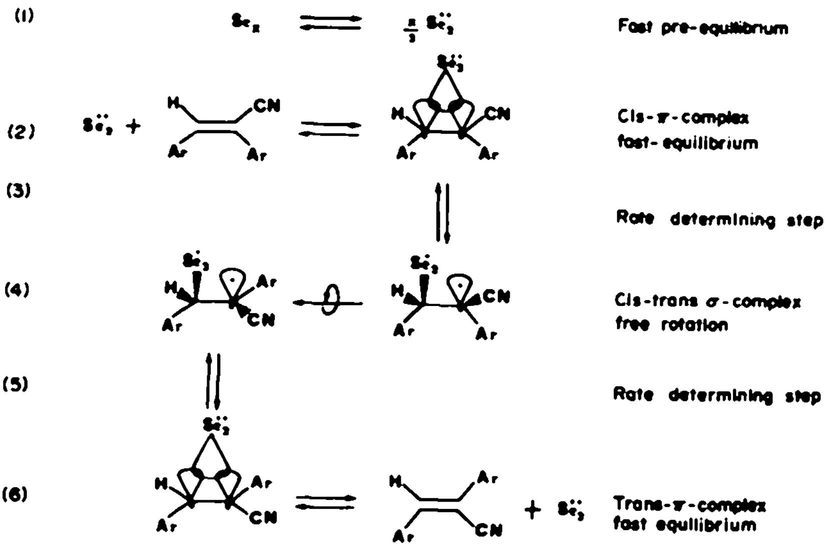


Fig. 4. Scheme of the reaction mechanism.

withdrawing groups increase the isomerization rate. If however the substituent is in the β-phenyl ring, the σ-complex is stabilized by electron donating groups. In this case the kinetic control is determined by σ-complex formation (step 3).

A further support to the proposed mechanism is given by the sign of ρ^+ values (Fig. 2). Positive ρ_Y^+ values indicate that conjugation in the transition state is less important than in the initial state,[22] according to the formation of a σ-complex bearing a saturated C atom. Negative ρ_Z^+ values indicate, instead, the greater conjugation in the σ-complex with respect to the initial state. Negative ρ^+ values have been found in several free radical reactions, as the halogenation of substituted toluenes and the benzoylperoxides decomposition.[23]

The reactivity sequence of heteroaromatic nuclei (*phenyl* > 2-*furyl* > 2-*thienyl*) can be explained in terms of side chain electron demand. Analogous sequence to that here found has been observed for the reactions of arylsulphonyl chlorides with aniline[24] and for the acid hydrolyses of arylanilides.[25] These reactions are kinetically controlled by conjugative effects of the heteroatom in the ground state rather than in the transition state, since a saturated atom is bonded to the heterocycle. In this case a standard model-process, which measure the conjugative effects of the heteroatoms in the ground state, can be given by σ^+ values obtained from IR stretching frequency of cyano-derivatives.[26] Figure 5 shows the satisfactory correlation. Instead, in the isomerization of diarylethylenes, in which

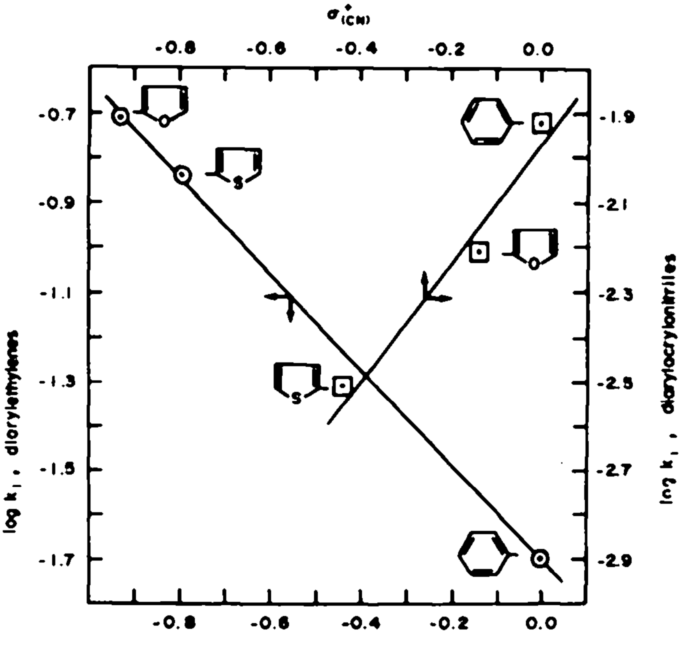


Fig. 5. Correlation of log k_1 at 190°C for the isomerization of diarylethylenes with σ^+ electrophilic values, (⊙); correlation of log k_1 at 190°C for the isomerization of diarylacrylonitriles with σ^+ (ArCN IR stretching) values, (⊡).

the adjacent C atom is electron deficient, a greater conjugation in the transition state is possible, and reactivity follows the order of the σ^+ electrophilic values (Fig. 5).

EXPERIMENTAL

Materials. The *cis*-α,β-diarylacrylonitriles were obtained by the method of Codington and Mosettig,[27] by the following reactions series: (i) Condensations of the appropriate arylcarboxaldehydes with phenylacetic acids, in Ac_2O with Et_3N as catalyst,[28] afford the *cis*-phenylcinnamic acids; (ii) Reactions of their corresponding acid chlorides with 33% NH_3 yield amides; (iii) *cis*-diarylacrylonitriles were obtained by dehydration of amides with P_2O_5 in xylene.

The *trans*-α,β-diarylacylonitriles were prepared by condensations of the appropriate arylacetonitrile and arylcarboxaldehyde in EtOH with NaOEt.[29]

Physical constants, analytical C, H, N data, UV and PMR spectra, conformational studies on the *cis* and *trans* isomers here investigated, and on the parent compounds, are reported in a separate paper.[30]

Se powder black and decahydronaphthalene (commercial products) were used without further purifications.

Kinetic procedure. To appropriate amounts of *cis*-isomer in 10 ml of decahydronaphthalene (0.01 0.07 mol l^{-1}), placed in a glass-stoppered bottle and maintained at constant temp., were added with stirring calculated quantities of Se (for catalyst concentration see Table 1). At suitable intervals, aliquots were removed by a Hamilton microsyringe and analyzed by glc.

Gas-chromatographic analyses were performed on a Carlo Erba Fractovap/C instrument. The following column was used: 0.80 m × 4 mm stainless steel containing 25% methylsilicone polymer Se 30 on a Chromosorb P (60–80 mesh) at 220°. Helium was used as gas carrier. The chromatographic areas are proportional to the relative concentrations of both isomers, being the area correction factors near to 1.0.

All kinetic measurements were carried out in duplicate to at least 75–80% isomerization; less than 6% deviation between the two rate constants values was observed.

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