Selenium-Catalyzed Thermal Isomerization of
cis-2-Styrylfuran and cis-2-Styrylthiophene

Giuseppe Scarlata and Michele Torre

Institute of Industrial Chemistry of the University, Viale Andrea Doria, 8, Catania, Italy

The rate of selenium catalyzed cis-trans isomerization of stilbene, 2-styrylfuran and 2-styryl-thiophene in decahydronaphthalene has been studied in the temperature range 170-190° by gas chromatographic analysis. Rate constants were pseudo first order and gave the following reactivity order: cis-stilbene < cis-2-styrylthiophene < cis-2-styrylfuran. In all cases the reaction orders with respect to selenium are temperature dependent. For catalyzed cis-stilbene isomerization the activation energy is ca. 15 kcal. mole^{-1} lower than for thermal isomerization. The hypothesis that cis-2-styrylfuran isomerizes through a triplet state is proposed.

Following earlier studies on the stereoisomerism of 1,2-diarylethylenes (I) (1-8), in this paper we report the kinetics of selenium-catalyzed isomerization of cis-2-styrylfuran ([II] Ar = 2-furyl) and cis-2-styrylthiophene ([II] Ar = 2-thienyl) in decahydronaphthalene, in comparison with that of cis-stilbene under the same experimental conditions.

Z   -CH=CH-, O, S.
Y   H, COOH.
X   H, Cl, CH₃, NO₂.
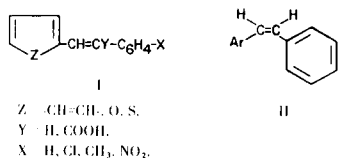
Pure samples of each cis isomer in decahydronaphthalene were treated with different concentrations of selenium at constant temperature; at suitable intervals aliquots of this solution were removed and the isomer percentage determined by gas chromatography (see Experimental).

This procedure was preferred for accuracy and reproducibility of results and for its general applicability to all members of the series. The use of the solvent prevented side reactions of olefin decomposition. In all cases we operated in homogeneous media, selenium being completely soluble in the substrate.

Results and Discussion.

The isomerization reactions of the three substrates follow first order kinetics.

In Table I are collected the rate constants of the pseudo first order reactions of the cis-diarylethylenes II at various
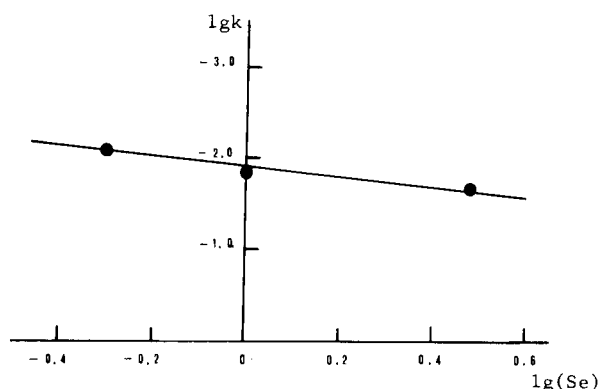
Figure 1. Dependence of rate reaction of cis-stilbene on the catalyst concentration (T = 190°).

selenium concentrations. Fitzpatrick and Orchin (9,10), studying the selenium catalyzed isomerization of cis-stilbene in the temperature range 190-210°, found that the reaction follows first order kinetics and that the rate increases with the concentration of the catalyst.

They found a reaction order about three with respect to selenium and postulate the following process:
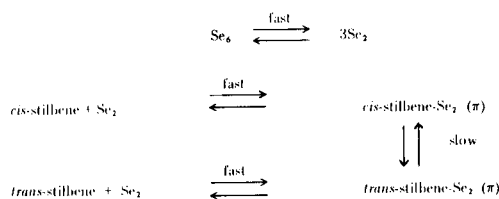
Table I

Pseudo First Order Rate Constants (k. 10^3 min^{-1}) for the Isomerization of the cis-Diarylethylenes II at Various Selenium Concentrations

T % Se Ar =	190° C			180° C			170° C
	0.5	1	3	0.5	1	3	3
(benzene)	8.05	14.74	21.45	2.02	8.69	10.76	6.21
(thiophene)			146.0	20.14	47.56	64.34	47.73
(furan)			197.2			148.6	106.0

where cis(or trans)stilbene-Se$_2$ (π) indicates π complex between the olefin and the catalyst and involves the π bonding orbital of the olefin and the anti-bonding orbital of selenium.

Our results, although obtained under different experimental conditions, are in good agreement with those of Fitzpatrick and Orchin (9,10), but the reaction orders with respect to selenium are lower and depend on the temperature (see Table II and Figure 1).

It is likely that the lower temperatures affected the dissociation equilibrium of the selenium or that the solvent modified the aggregation state, as already pointed out by Gmelin (11) from ebullioscopyc data.

The influence of the aryl (Ar) group on the rate of isomerization of the ethylenes II is evident by an inspection of the Table I; the increase is in the order: cis-stilbene < cis-2-styrylthiophene < cis-2-styrylfuran.

The activation parameters are listed in Table III, as well as the λ max values of the uv spectra referring to the K-band together with the corresponding energies of the electronic transition (E$_T$ kcal. mole^{-1}) and the values of the infrared stretching vibration of the ethylenic C=C bond.

A comparison between the activation energy for the purely thermal isomerization of cis-stilbene (12,13) and that catalyzed by selenium shows that the latter is ca. 15 kcal. mole^{-1} lower. The catalytic effect of this element is therefore comparable with that of molecular iodine on the same reaction in n-hexane (14).

The influence of the aromatic nucleus on the activation energy is evident; this decreases in the order: stilbene > styrylthiophene > styrylfuran.

This sequence is in excellent agreement with the results of recent dipole moment measurements (8) and uv spectroscopic data (5,7).

A plot of activation energies of isomerization (Δ E‡) against the electronic transition energy E$_T$(K-band) show a sufficient linearity (Figure 2) and suggest that on increasing the degree of conjugation (benzene compound < thiophene < furan derivative), the π electrons of the
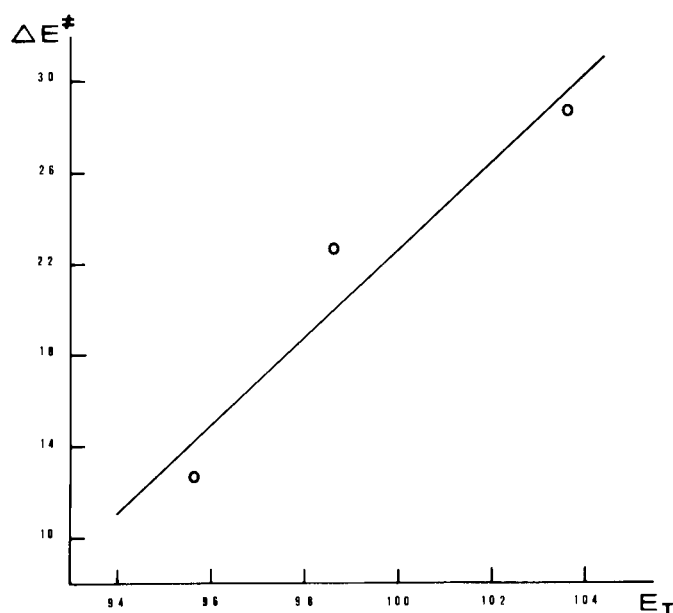

Figure 2. Plot of ΔE‡ against E$_T$ (K-band).

Table II

Reaction Order (n) with Respect to Catalyst for Isomerization of cis-Stilbene and cis-2-Styrylthiophene

	T (°C)	n
cis-stilbene	190	1.89
	180	1.15
cis-2-styrylthiophene	180	1.63

ethylenic bond are delocalized with consequent reduction of double bond character and therefore of the energy barrier to rotation. Further evidence for the diminished character of the ethylenic double bond in 2-styrylfuran may be taken from the values of the ν C=C stretching

Table III

Spectroscopic Data and Activation Parameters for Isomerization of the *cis*-Diarylethylenes II

Ar =	$\Delta E^{\ddagger}$ (kcal. mole^{-1})	A (min.$^{-1}$)	log A (min.$^{-1}$)	λ max (nm)	E_T (kcal. mole^{-1})	ν C=C (cm^{-1})
	25.22	1.73 x 10^{10}	10.23	276	103.62	
	22.69	6.76 x 10^9	9.83	290	98.62	1624
	12.65	1.86 x 10^5	5.27	299	95.65	1595

frequencies in the infrared spectrum (see Table III).

The significance of the preexponential factor value (A) on the mechanism has been discussed (15); A values of 10^{12} and 10^5 orders of magnitude have been associated, respectively, with different mechanisms of isomerization, depending on a singlet or triplet state of the substrate in the transition state.

In the case of thermal isomerization of stilbenes, Calvin and Alter (16) find intermediate A values (10^{10}-10^8) and suggest that both mechanisms coexist.

On increasing the conjugation (4-amino-4'-nitrostilbene), the frequency factor decreases to 10^5, corresponding to a pure triplet mechanism. This mechanism is frequently observed for heavy metal catalyzed *cis-trans* isomerizations.

The frequency factors in the present study seems to suggest that *cis*-2-styrylfuran, in contrast with the *cis*-2-styrylthiophene, isomerizes through a triplet mechanism which is also shown by the low value of the activation energy.

EXPERIMENTAL

cis- and *trans*-Diarylethylenes.

The synthesis of the *cis* and *trans* styryl compounds was carried out by the Wittig reaction between **equimolecular** amounts of the appropriate benzyltriphenylphosphonium chloride and 2-furancarboxaldehyde or 2-thiophenecarboxaldehyde in the presence of sodium ethoxide in ethanol, as already described (1,3). The structure of diarylethylenes II was confirmed by their uv and ir spectra.

Spectra.

The uv spectra were recorded on a Hitachi Perkin-Elmer Model EPS-3T spectrophotometer in ca. 1.10^{-5} M ethanol solutions. The ir spectra were obtained in carbon tetrachloride using a Perkin-Elmer Model 237 spectrophotometer.

Kinetic Procedure.

All the isomerization kinetics were carried out in the presence of selenium as the catalyst at 170°, 180° and 190°. To a stirred solution of 0.5 g. of the *cis* isomer in 25 ml. of decahydronaphthalene were added, at constant temperature, calculated quantities

(0.5%, 1% and 3% with respect to olefin) of catalyst. In these experimental conditions selenium is completely soluble and the reaction medium is homogeneous. On cooling the solution, the selenium precipitates in the form of red selenium. At appropriate intervals, aliquots were taken with a Hamilton microsyringe and analyzed by glc to calculate the percentages of the *cis* and *trans* compounds present. For the investigated compounds the rate determinations were run in duplicate to at least 75-80% isomerization with less than 3% deviation between two rate constants. In all cases the isomerization reactions of *cis* isomers follow pseudo first order kinetics, according to equation

$$\ln(a\text{-}x) = \text{-}kt + \ln a$$

where t is the time (minutes), a is the initial concentration of the *cis* compound and k is the pseudo first order rate constant (min^{-1}). The rate constants were calculated by a least-squares program with a Hewlett-Packard 9100 B computer. Arrhenius activation parameters ($\Delta E^{\ddagger}$ and A) were calculated by plotting lg K against T^{-1}.

Gas Chromatographic Analyses.

Glc was performed on a C. Erba Fractovap C gas chromatograph using a stainless steel column (0.80m x 4mm) containing 25% methylsilicone polymer SE 30 on a Chromosorb P at 220°, and helium as a carrier (61/h).

REFERENCES

(1) A. Arcoria, S. Fisichella, G. Scarlata and M. Torre, *J. Heterocyclic Chem.*, 10, 643 (1973).

(2) S. Fisichella, G. Scarlata and D. Sciotto, *Ann. Chim.*, 63, 55 (1973).

(3) S. Fisichella, G. Scarlata, D. Sciotto and M. Torre, *Boll. Sedute Accad. Gioenia Sci. Nat. Catania*, IV, 12, 323 (1973).

(4) S. Fisichella, G. Mineri, G. Scarlata and D. Sciotto, *Ann. Chim.*, 63, 779 (1973).

(5) S. Fisichella, G. Scarlata and M. Torre, *Gazz. Chim. Ital.*, 104, 1237 (1974).

(6) S. Gruttadauria, G. C. Pappalardo, G. Scarlata and M. Torre, *J. Chem. Soc. Perkin Trans.* II, 1580 (1974).

(7) G. Scarlata, D. Sciotto and M. Torre, *Boll. Sedute Accad. Gioenia Sci. Nat. Catania*, IV, 12, 471 (1974).

(8) S. Gruttadauria, G. C. Pappalardo, G. Scarlata and M. Torre,

Bull. Chem. Soc. Japan, **48**, 1681 (1975).

(9) J. D. Fitzpatrick and M. Orchin, *J. Am. Chem. Soc.,* **79**, 4765 (1957).

(10) Idem, *J. Org. Chem.,* **22**, 1177 (1957).

(11) Gmelin, *Handbuch Anorg. Chem.,* **10**, 150 (1953).

(12) G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.,* **56**, 638 (1934).

(13) T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.,* 2078 (1938).

(14) S. Yamashita, *Bull. Chem. Soc. Japan,* **34**, 487 (1961).

(15) J. L. Magee, W. Shand and H. Eyring, *J. Am. Chem. Soc.,* **63**, 677 (1941).

(16) M. Calvin and H. W. Alter, *J. Chem. Phys.,* **19**, 768 (1951).