

On the other hand, an enolate-like transition state might be destabilized by an α -methyl group.²⁴ Further work is needed to establish firmly the existence of polar effects of alkyl groups in enolization. It is to be expected that the importance of such effects will depend on such factors as the strength of the catalyzing base, the acidity of the ketone (*i.e.*, other substituents), and the solvent.

We return now to discussion of the over-all effects, to which steric factors contribute strongly.¹³ Table II holds the rates and rate relationships pertaining to β substitution. Considering first the methyl reactivities, we see that three β -methyl groups reduce α -methyl reactivity by a factor of 2.4 only (column 4), a 2.6-fold smaller effect than that from similar α substitution (Table I). This is not unexpected, for the β substituents can get far away from the α -methyl group, at least in some conformations. Thus $k_{\text{CH}_3^{\text{H}}}$ ($\text{R} = \text{CH}_2\text{C}(\text{CH}_3)_3$) $>$ $k_{\text{CH}_3^{\text{H}}}$ ($\text{R} = \text{C}(\text{CH}_3)_3$) is not surprising.

At the methylene positions (Table II) the effects are larger, with a total 40-fold drop from 2-butanone to methyl neopentyl ketone. These effects are far from

(24) Although *m*- or *p*-methyl in benzoic acid and in phenol is acid weakening, those equilibria are not perfect models for the enolization reaction, which involves rehybridization at the seat of substitution. For data which suggest that the methyl group, relative to hydrogen, is electron donating toward sp^2 carbon and electron withdrawing from sp^3 carbon, in uncharged systems, see (a) H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **87**, 2404 (1965) and (b) V. W. Laurie and J. S. Muenster, *ibid.*, **88**, 2884 (1966), as well as references cited therein.

linear in the number of substituents, for they vary from a factor near 2 for the first methyl to a factor of 10 between the second and the third. Such behavior is well known in ester hydrolysis, where the steric substituent parameters (E_s) show a similar trend.²⁵

Finally, we come briefly to the relative reactivities of two sites in the same molecule. These are in the last columns of Tables I and II and express the relative chances of reaction of a given hydrogen at each site. The maximum effect per substituent methyl group is, by a small margin, in the α series where the value is 6.4 (*i.e.*, 12.8/2) compared to the β series where it is 5.5 (*i.e.*, 19.2/1.16 \times 3). To get from the inherent relative reactivities in the tables to numbers which predict the relative rates of reaction at the two sites, statistical factors must be included. For example, if halogenation is analogous to exchange,²⁶ then the relative amounts of monobromides, from monobromination of 2-butanone under comparable conditions, should be about: $\text{CH}_2\text{BrCOCH}_2\text{CH}_3/\text{CH}_3\text{COCHBrCH}_3 = 1.16 \times 3/2 = 1.74$.

Acknowledgment. We are grateful to the National Research Council of Canada for financial assistance, including a Postdoctoral Fellowship to C. B.

(25) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 601.

(26) Recent work by Rappe has been taken to indicate that there are halogenation mechanisms which do not have analogs in exchange processes. See ref 14d and also C. Rappe, *Acta Chem. Scand.*, **21**, 857 (1967).

The Kinetics and Mechanism of the Acid-Catalyzed Isomerization of *cis*-Stilbene^{1,2}

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Abstract: The isomerization of *cis*-stilbene to *trans*-stilbene as catalyzed by sulfuric acid involves the rate-limiting transfer of a proton to the double bond. The isomerization rate correlates well with the acidity of the medium, a plot of $\log k$ vs. H_0 being linear with a slope of -1.25 . In deuteriosulfuric acid the rate of isomerization is diminished at the same acidity. The rates of isomerization of 11 substituted *cis*-stilbenes correlated well with Hammett's equation: $\log k_{x,y} = -4.46 - 3.30(\sigma_x^+ + 0.29\sigma_y)$. Examination of the rates of isomerization of *cis*-4,4'-dimethoxystilbene, *cis*-stilbene, and *cis*-3,3'-dichlorostilbene do not provide any indication for the intervention of an olefin π complex during the isomerization reaction.

The isomerization of *cis*-stilbene to *trans*-stilbene may be catalyzed by a wide variety of reagents, including radical sources,^{5,6} light,^{7,8} and mineral acids⁹ and Lewis acids.¹⁰

(1) Supported in part by grants from the National Science Foundation (NSF G 13125 and NSF GP 1572) and by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of these funds.

(2) A portion of this work has been reported in a preliminary communication: D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Amer. Chem. Soc.*, **86**, 3584 (1964).

(3) Shell Fellow in Chemistry, 1963–1964.

(4) National Science Foundation Cooperative Fellow, 1962–1964.

(5) M. S. Kharasch, J. V. Mansfield, and F. R. Mayo, *J. Amer. Chem. Soc.*, **59**, 1155 (1937).

(6) W. Schlenk and E. Bergman, *Ann.*, **463**, 98 (1928).

We have undertaken a study of the acid-catalyzed isomerization in aqueous acids in order to gain more information regarding mechanisms of proton transfer. The hydration of isobutylene¹¹ and of styrene^{12,13}

(7) J. Saltiel and G. S. Hammond, *J. Amer. Chem. Soc.*, **85**, 2515 (1963).

(8) G. S. Hammond and J. Saltiel, *ibid.*, **85**, 2516 (1963).

(9) R. Stoermer and G. Voht, *Ann.*, **409**, 26 (1915).

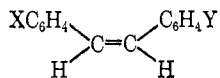
(10) C. C. Price and M. Meister, *J. Amer. Chem. Soc.*, **61**, 1595 (1939).

(11) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *ibid.*, **82**, 4729 (1960); V. Goid and M. A. Kessick, *J. Chem. Soc.*, 6718 (1965).

(12) W. M. Schubert and B. Lamm, *J. Amer. Chem. Soc.*, **88**, 120 (1966); N. C. Deno, F. A. Kish, and H. J. Peterson, *ibid.*, **87**, 2157 (1965).

has been studied thoroughly, and the initial proton transfer to generate the appropriate carbonium ion has been shown to be rate limiting. Similar conclusions were reached as the result of earlier studies in these laboratories¹⁴ on the acid-catalyzed isomerization of *cis*-cinnamic acid.

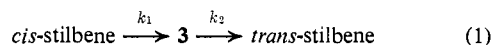
A study of the acid-catalyzed isomerization of *cis*-stilbene is a natural extension of the previous studies of *cis*-cinnamic acid. With the stilbene system it is possible to vary the substituents over relatively wide ranges at both termini of the double bond. We have examined the rate of isomerization of *cis*-stilbene (1)



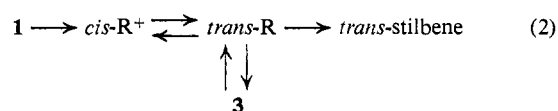
and of ten substituted stilbenes in order to assess the factor influencing the reactivity of these systems.

Results and Discussion

Isomerization of *cis*-Stilbene. The isomerization of *cis*-stilbene (1) to *trans*-stilbene (2) proceeds conveniently in 50–60% sulfuric acid. The very limited solubility of *trans*-stilbene in aqueous media dictates the use of a mixed solvent, and we have added 5% ethanol for this purpose. Measurement of the rate of appearance of *trans*-stilbene shows that there is an “induction period” for its formation. That this induction period arises due to the formation of a steady-state concentration of 1,2-diphenylethanol (3) is verified by a consideration of the detailed rate–acidity profile for the dehydration of 1,2-diphenylethanol.¹⁵ Calculation of the rate of appearance of 2 on the basis of eq 1 pro-



vides an exact replication of the observed data. This does not necessarily mean, however, that 3 is a mandatory intermediate in the isomerization of 1 to *trans*-stilbene. An alternative scheme fits equally well with these observations. Expansion of the mechanistic scheme to eq 2 fits the observations well, if the car-



bonium ion is rapidly trapped and “stored” as 1,2-diphenylethanol. Diphenylethanol is then required to be in equilibrium with the carbonium ion, a requisite which is shown to be satisfied by the rapid racemization of active diphenylethanol.¹⁵

Given the observed rates of dehydration it is easy to show that the rate of formation of *trans*-stilbene represents in fact the rate of initial reaction of 1 (once the steady-state concentration of 2 is reached).

The results of measurements at several acidities are given in Table I. It is to be noted that the isomerization reaction is very sharply acid catalyzed; moreover, a plot of $\log k_{\text{obsd}}$ vs. $-H_0$ is linear with a $\log k_{\text{obsd}}$ vs. $-H_0$ slope of 1.25 at 25°. More limited rate data

(13) J. P. Durand, M. Davidson, M. Hellin, and F. Coussmant, *Bull. Soc. Chim. Fr.*, **43**, 52 (1966).

(14) D. S. Noyce, H. S. Avarbock, and W. L. Reed, *J. Amer. Chem. Soc.*, **84**, 1647 (1962).

(15) D. S. Noyce, D. R. Hartter, and R. M. Pollack, *ibid.*, **90**, 3791 (1968).

Table I. Rates of Isomerization of *cis*-Stilbene in Ethanol–Aqueous Sulfuric Acid (5:95)

H_2SO_4 , %	10^6k , sec^{-1}	$-H_0(\text{alcohol})$	$\log k + H_0$
$T = 25.00 \pm 0.01^\circ$			
49.92	1.28	3.40	-8.29
52.00	2.36	3.63	-8.26
52.05	2.42	3.64	-8.26
53.05	3.33	3.75	-8.23
55.50	7.35	4.02	-8.15
57.62	14.3	4.28	-8.12
59.66	33.7	4.53	-8.00
59.77	33.8	4.54	-8.01
60.92	51.2	4.69	-7.98
63.17	110.0	4.95	-7.91
64.12	173.0	5.08	-7.84
66.06	384.0	5.40	-7.82
$T = 45.00 \pm 0.01^\circ$			
47.51	6.58	3.13 ^a	-7.31
51.37	19.4	3.54	-7.25
55.06	58.6	3.94	-7.17
56.32	82.2	4.07	-7.15
57.83	129.0	4.25	-7.14

^a The temperature coefficients of Gelbstein, *et al.* [A. I. Gelbstein, G. G. Shcheglova, and M. I. Temkin, *Zh. Neorg. Khim.*, **1**, 282, 506 (1956); A. I. Gelbstein, G. G. Shcheglova, and M. I. Temkin, *Dokl. Akad. Nauk SSR*, **107**, 108 (1956)], have been applied to the $H_0(\text{alcohol})$ values at 25° to obtain corrected values at 45°. These corrections were made at corresponding H_0 values rather than at the same weight percentage of acid; all the H_0 values for rates at 45° have been corrected unless otherwise stated.

at 45° show a somewhat reduced slope in the plot of $\log k_{\text{obsd}}$ vs. $-H_0$; the slope is 1.1.6.

Measurement of the rate of isomerization at 45° allows calculation of the energy of activation, $E_a = 21.7$ kcal/mol and the entropy of activation, $\Delta S^\ddagger = -25.7$ eu (extrapolated to $H_0 = 0$).

When the isomerization of *cis*-stilbene is carried out in deuteriosulfuric acid medium the rate is reduced. Data at several acidities are given in Table II.

Table II. Rates of Isomerization of *cis*-Stilbene in 5% Ethanol–95% D_2O – D_2SO_4 at 25.00°

D_2SO_4 , % ^a	Mole fraction sulfate	Equiv ^b H_2SO_4 , %	$-H_0$ (alcohol)	$10^6 k_{\text{D}_2\text{O}}$, sec^{-1}	$10^6 \times k_{\text{H}_2\text{O}}$, sec^{-1}	$k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$
52.58	0.1815	54.65	3.92	1.99	5.15	2.59
57.98	0.2163	60.05	4.57	13.5	36.2	2.68
58.10	0.2171	60.15	4.59	14.3	38.0	2.66
62.77	0.2522	64.72	5.17	69.4	204.0	2.94
65.45	0.2748	67.35	5.62	237.0	758.0	3.20

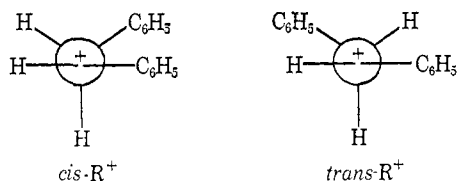
^a Weight per cent D_2SO_4 determined by direct titration of kinetic solution. ^b The weight per cent of a sulfuric acid solution with a mole fraction of D_2SO_4 . ^c Interpolated from the data in Table I.

The markedly decreased rate of reaction in the deuterated media is in accord with a rate-limiting proton transfer from the medium to carbon. The magnitude of the solvent isotope effect $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ gradually increases at higher sulfuric acid concentrations. It is to be noted that the solvent isotope effect is similar to that observed in the isomerization of *cis*-cinnamic acid.¹⁴

Finally, the product *trans*-stilbene formed in deuterated medium contains 0.8 atom of *d* per molecule, a value nearly identical with that obtained¹⁵ on dehydration of 1,2-diphenylethanol-2-*d*, showing that the product composition in the isomerization is controlled

by a step like that which controls the product composition in the case of the dehydration of 1,2-diphenylethanol.

Combination of all of these facts with the known¹⁶ difference in energy of **1** and *trans*-stilbene allows construction of a relatively complete energy diagram as given in Figure 1. The difference in energy between the two conformers of the carbonium ion, *cis*-R⁺ and *trans*-R⁺, is estimated to be 4 kcal.¹⁷



Additionally, the stability of the carbonium ion, *trans*-R⁺, can be roughly estimated from the data on the stability of a variety of carbonium ions determined by Deno and coworkers.¹⁸

The Effect of Substituents on the Rate of Isomerization. Introduction of electron-donating substituents causes a sharp increase in the rate of isomerization. Two series can be considered, a group of compounds in which X is methyl or methoxy, and Y is H; or alternatively a group of compounds in which S is varied and Y is NO₂. *cis*-4-Methoxystilbene (**4**) and *cis*-4-methylstilbene (**5**) are isomerized much more rapidly than **1** in media of the same acidity. This same phenomenon is shown in the rates of isomerization of *cis*-4-methoxy-4'-nitrostilbene (**6**), *cis*-4-methylthio-4'-nitrostilbene (**7**), *cis*-4-methyl-4'-nitrostilbene (**8**), and *cis*-4-nitrostilbene (**9**). The results of rate measurements are given in Table III.

The rates of isomerization have been extrapolated to common conditions for comparison. The most convenient comparison is at an H_0 value of -4.00 (55% sulfuric acid); this involves a minimum of extrapolation. Though the slopes of the $\log k$ vs. $-H_0$ plots are reasonably linear, the slopes of such plots vary from compound to compound. Generally somewhat greater than unity, the slopes range from 1.03 to 1.27 (for compound **7**, the slope is 0.88). This means of course that relative rates will be somewhat dependent upon the acidity at which comparisons are made.

From comparisons made at $H_0 = -4.00$, the following conclusions emerge. From the group of compounds **4**, **5**, and **1**, a correlation with Brown's σ^+ constants¹⁹ is manifest with ρ about -3.5 . A similar correlation results taking the set of compounds **6**, **7**, **8**, and **9**. The set of compounds *cis*-4,4'-dimethoxystilbene (**10**), *cis*-4-methoxy-4'-methylstilbene (**21**), **4**, *cis*-4-methoxy-3'-nitrostilbene (**12**), and **6** shows that decreasing the electron-donating ability of the aromatic moiety at one end of the olefinic system results in a relatively modest decrease in rate. The rates of isomer-

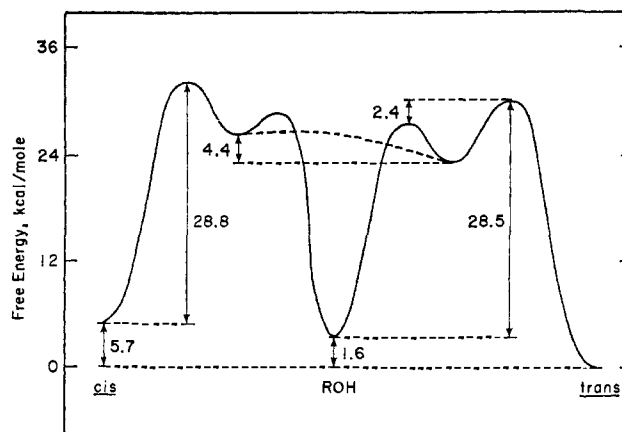


Figure 1. Reaction coordinate diagram for isomerization of *cis*-stilbene.

ization for these five compounds may be correlated with σ values with a ρ of -1 .

All of the above correlations may be combined in a single correlation expressed as eq 3, with a correlation

$$\log k_{X,Y} = -4.46 - 3.30(\sigma_X^+ + 0.29\sigma_Y) \quad (3)$$

coefficient of 0.998, if the following considerations are also taken into account. The rate of isomerization of **10** needs to be statistically corrected as there are two identical sites of protonation. Like corrections should be made for **1** and for *cis*-3,3'-dichlorostilbene (**14**).

This correlation then further has implications regarding the possible role of proton- π complexes¹¹ in the isomerization sequence. The three symmetrical compounds which we have investigated (**10**, **1**, and **14**) would be expected to show abnormal behavior (unexpectedly rapid isomerization rates) if a symmetrical proton- π complex were critically involved in the isomerization process. The lack of any such acceleration in the rates means that the concept of a proton- π complex is not needed to interpret the isomerization rates in this set of compounds. This conclusion is particularly pertinent in the case of compound **14**, as here the simple carbonium ion intermediate has only modest stability, and a proton- π complex might have provided a more favorable pathway for isomerization.

Thus, the reaction scheme in eq 2 is adequate to correlate all of the observed results.

Experimental Section²⁰

Preparation of Materials. Most of the *cis*-stilbenes were prepared by decarboxylation of the appropriately substituted α -phenyl-*trans*-cinnamic acid²¹ using copper chromite in quinoline.²² The properties of the substituted cinnamic acids were concordant with literature values.²³ Some of the cinnamic acids do not appear to have been reported previously. α -(*p*-Methoxyphenyl)-*p*-methyl-*trans*-cinnamic acid, mp 212–216°, was prepared from *p*-tolualdehyde and *p*-methoxyphenylacetic acid.

Anal. Calcd for C₁₇H₁₆O₃: C, 76.10; H, 6.01. Found: C, 76.18; H, 5.96.

(20) Melting points and boiling points are uncorrected. Analyses are by the Microanalytical Laboratory, University of California at Berkeley. Ultraviolet spectra were determined using a Cary Model 14 spectrophotometer.

(21) Prepared by the procedure of R. E. Buckles and K. Bremer, *Org. Syn.*, **33**, 70 (1953).

(22) R. E. Buckles and N. G. Wheeler, *ibid.*, **33**, 88 (1953).

(23) Cf. J. I. G. Cadogan, E. G. Duell, and P. W. Inward, *J. Chem. Soc.*, 4164 (1962); R. Ketcham and D. Jambotkar, *J. Org. Chem.*, **28**, 1034 (1963).

(16) R. B. Williams, *J. Amer. Chem. Soc.*, **64**, 1395 (1942).

(17) The method of estimation involved the use of Adrian's method (F. J. Adrian, *J. Chem. Phys.*, **28**, 608 (1958)) for estimation of energy differences between *cis* and *trans* isomers adapted for charged molecules.

(18) N. C. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugasch, *J. Amer. Chem. Soc.*, **82**, 4719 (1960). It may be estimated that C₆H₅-C⁺HCH₂C₆H₅ would be one-half formed from 1,2-diphenylethanol in 82–85% sulfuric acid.

(19) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

Table III. Rates of Isomerization of Substituted *cis*-Stilbenes in Ethanol-Aqueous Sulfuric Acid (5:95), $\text{XC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{Y}$

Compd	X	Y	Temp, °C	H ₂ SO ₄ , wt %	10 ⁵ k, sec ⁻¹	-H ₀ , (alcohol)	Compd	X	Y	Temp, °C	H ₂ SO ₄ , wt %	10 ⁵ k, sec ⁻¹	-H ₀ , (alcohol)
4	4-OCH ₃	H	25.00	31.09	3.52	1.71	9	H	4'-NO ₂	25.00	59.96	32.0	4.56
				35.96	11.9	2.05					63.90	146.0	5.05
				36.06	12.2	2.06					64.77	186.0	5.18
				40.12	26.6	2.37					45.71	5.63	2.95 ^a
				43.89	62.0	2.73					48.25	10.9	3.23
				46.25	109.0	2.99					50.48	16.4	3.47
			47.85	164.0	3.17	50.53				16.4	3.47		
			50.43	318.0	3.45	52.39				28.8	3.65		
			52.64	670.0	3.70	54.81				57.1	3.91		
			45.00	30.17	21.2	64.37				10.7	5.12		
			34.61	53.7	1.98	66.92				29.2	5.55		
			39.29	134.0	2.33	70.35				134.0	6.13		
41.07	213.0	2.48	72.43	339.0	6.48								
5	4-CH ₃	H	25.00	47.75	5.56	3.16	10	4-CH ₃ O	4'-CH ₃ O	25.00	28.76	5.65	1.54
				52.10	21.6	3.64					31.33	9.62	1.72
				53.41	31.2	3.78					31.36	10.4	1.73
				57.76	117.0	4.29					36.24	24.0	2.08
				59.96	253.0	4.56					38.13	33.9	2.21
				61.10	458.0	4.70					38.14	36.6	2.21
			61.44	501.0	4.74	41.00				71.2	2.44		
			45.00	44.83	23.8	45.00				18.75	7.35	0.86 ^a	
			48.69	63.7	3.28	23.76				15.8	1.21		
			50.46	102.0	3.47	26.37				26.5	1.40		
			52.03	173.0	3.63	28.89				59.1	1.58		
			54.15	299.0	3.84	21.59				15.8	1.07 ^a		
6	4-CH ₃ O	4'-NO ₂	25.00	40.78	8.06	2.42	11	4-CH ₃ O	4'-CH ₃	25.00	35.98	14.8	2.06
				42.95	11.7	2.62					40.78	33.4	2.42
				42.91	13.7	2.62					42.80	48.0	2.60
				48.19	38.7	3.21					45.78	120.0	2.96
				51.96	108.0	3.63					48.20	206.0	3.21
				52.35	104.0	3.67					48.23	185.0	3.21
			52.34	113.0	3.67	48.20				206.0	3.21		
			45.00	21.52	1.50	41.02				9.38	2.48		
			33.43	12.3	1.88	45.82				27.5	2.96		
			35.98	20.2	2.06	48.41				47.1	3.23		
			38.19	30.6	2.21	51.82				113.0	3.61		
			42.80	91.1	2.60	50.00				31.51	15.0	1.76 ^a	
45.71	182.0	2.95	33.51	20.2	1.90								
7	4-CH ₃ S	4'-NO ₂	25.00	48.75	13.4	2.28	13	H	3'-CH ₃ O	25.00	38.34	51.3	2.25
				48.84	13.0	3.29					40.46	82.5	2.43
				51.75	28.5	3.60					57.77	8.87	4.30
				54.72	48.0	3.93					57.93	10.3	4.31
				56.76	77.0	4.17					59.88	18.9	4.55
				56.78	85.5	4.17					62.18	44.4	4.82
			57.27	64.1	4.23	64.45				114.0	5.13		
			60.60	218.0	4.64	64.55				108.0	5.15		
			45.00	39.46	8.89	50.53				9.09	3.47 ^a		
			39.48	10.6	2.35	51.68				13.4	3.59		
			41.32	18.6	2.50	54.26				25.9	3.85		
			41.46	18.3	2.52	54.84				32.0	3.91		
42.70	17.5	2.63	56.37	56.4	4.08								
44.90	36.0	2.86	56.61	56.4	4.11								
46.52	40.5	3.04	58.06	80.2	4.28								
46.60	36.6	3.06	58.08	96.1	4.28								
48.72	51.3	3.28	59.19	18.5	5.93								
50.38	86.1	3.46	72.11	90.2	6.42								
52.16	134.0	3.64	74.95	425.0	6.90								
52.21	136.0	3.64											
8	4-CH ₃	4'-NO ₂	25.00	54.81	6.30	3.94	14	3-Cl	3'-Cl	25.00			
				58.11	18.9	4.33							

^a See footnote a, Table I.

α -(*p*-Methoxyphenyl)-*m*-nitro-*trans*-cinnamic acid, mp 195–197°, was prepared from *m*-nitrobenzaldehyde and *p*-methoxyphenylacetic acid.

Anal. Calcd for C₁₆H₁₃NO₅: C, 64.21; H, 4.38; N, 4.68. Found: C, 64.07; H, 4.61; N, 4.86.

α -(*p*-Nitrophenyl)-*p*-methyl-*trans*-cinnamic acid, mp 256–261°, was prepared from *p*-tolualdehyde and *p*-nitrophenylacetic acid.

Anal. Calcd for C₁₈H₁₃NO₄: C, 67.84; H, 4.63; N, 4.95. Found: C, 67.63; H, 4.64; N, 5.08.

α -(*p*-Methylthiophenyl)-*p*-nitro-*trans*-cinnamic acid, mp 211–215°, was prepared from *p*-nitrobenzaldehyde and *p*-methylthiophenylacetic acid.²⁴

Anal. Calcd for C₁₆H₁₃NO₄S: C, 60.94; H, 4.15; N, 4.44; S, 10.00. Found: C, 61.25; H, 4.21; N, 4.61; S, 10.17.

α -(*m*-Chlorophenyl)-*m*-chloro-*trans*-cinnamic acid, mp 166–167°, was prepared from *m*-chlorobenzaldehyde and *m*-chlorophenylacetic acid.

Anal. Calcd for C₁₅H₁₀Cl₂O₂: C, 61.46; H, 3.44; Cl, 24.19. Found: C, 61.24; H, 3.51; Cl, 24.08.

The copper chromite catalyzed decarboxylation of the *trans*-cinnamic acids gave the *cis*-stilbene. It was usually possible to

(24) J. W. Corse, R. G. Jones, Q. F. Soper, C. W. Whitehead, and O. K. Behrens, *J. Amer. Chem. Soc.*, 70, 2837 (1948).

isolate small amounts (5–10%) of the substituted *trans*-stilbene from the reaction mixture. The *cis* and *trans* isomers were separated conveniently by chromatography over neutral Woelm alumina of activity 1. The *cis* isomer was eluted first (hexane or benzene) and the *trans* isomer later (benzene or benzene-ether).

In four instances the product of decarboxylation was not primarily the *cis* isomer. Decarboxylation of α -phenyl-*p*-nitro-*trans*-cinnamic acid gave a mixture of *cis*- and *trans*-4-nitrostilbenes, which was separated by chromatography on neutral alumina to give 42% *cis*-4-nitrostilbene, mp 60–61°, and 35% *trans*-4-nitrostilbene, mp 156–157°. Decarboxylation of α -(*p*-nitrophenyl)-*p*-methoxycinnamic acid afforded *trans*-4-methoxy-4-nitrostilbene, mp 131–134°. Decarboxylation of α -(*p*-methylthiophenyl)-*p*-nitrocinnamic acid gave *trans*-4-methylthio-4-nitrostilbene, mp 171–173°. Decarboxylation of α -(*m*-chlorophenyl)-*m*-chloro-*trans*-cinnamic acid gave primarily *trans*-3,3'-dichlorostilbene and lesser amounts of *cis*-3,3'-dichlorostilbene (14). It appears that isomerization may well be occurring subsequent to decarboxylation and that a nucleophilic addition mechanism is responsible, promoted by electron-withdrawing groups. Alternatively, irradiation with a 450-W Hanovia mercury lamp with Pyrex filter allowed conversion of the appropriate *trans*-stilbene to a mixture rich in the corresponding *cis*-stilbene.

The properties of the stilbenes prepared (both *cis* and *trans* isomers) were in accord with literature values with the following reservations. *cis*-4-Methoxy-4'-methylstilbene (11) showed mp 43.5–45° and λ_{\max} 287 m μ (ϵ 13,000). Curtin, *et al.*,²⁵ reported 11 to be liquid, λ_{\max} (95% EtOH) 280 m μ (ϵ 13,000). *cis*-3-Methoxystilbene (13) is a liquid as reported by Kon and Spickett.²⁶ It showed λ_{\max} (95% EtOH) 274 m μ (ϵ 10,000). *cis*-4-Methoxy-3'-nitrostilbene (12) showed λ_{\max} (95% EtOH) 276 m μ (ϵ 16,400). *trans*-4-Methoxy-3'-nitrostilbene, mp 91.5–93.5° (lit.²⁷ 91°), showed λ_{\max} (95% EtOH) 315 m μ (ϵ 35,400).

Decarboxylation of α -(*p*-methylthiophenyl)-*p*-nitrocinnamic acid afforded *trans*-4-methylthio-4'-nitrostilbene, mp 171–173°; λ_{\max} (95% EtOH) 378 (ϵ 30,000) and 282 m μ (ϵ 11,200).

Anal. Calcd for C₁₅H₁₃NO₂S: C, 66.40; H, 4.83; N, 5.16; S, 11.82. Found: C, 66.68; H, 4.63; N, 5.05; S, 11.70.

Irradiation in benzene afforded *cis*-4-methylthio-4'-nitrostilbene (7) purified by chromatography on neutral alumina (eluted with hexane); mp 66–67°, λ_{\max} (95% EtOH) 365 (ϵ 11,000) and 281 m μ (ϵ 16,100).

Anal. Found: C, 66.38; H, 4.88; N, 5.40; S, 11.55.

Likewise, *trans*-3,3'-dichlorostilbene, mp 94–95° (lit.²⁸ 93.8–94.6°), λ_{\max} (95% EtOH) 300 m μ (ϵ 26,400), was irradiated to give a mixture containing 90% 14 which was purified by chromatography and short-path distillation to give *cis*-3,3'-dichlorostilbene (14) as a colorless liquid, λ_{\max} (95% EtOH) 280 m μ (ϵ 9300).

Anal. Calcd for C₁₄H₁₀Cl₂: C, 67.49; H, 4.05; Cl, 28.46. Found: C, 67.21; H, 3.95; Cl, 28.29.

Kinetic Procedures. The rate of isomerization was measured by observing the increase in absorption at the long-wavelength maximum for the *trans*-stilbene. The absorbance data were plotted as $\log [(A_{\infty} - A_t)/(A_{\infty} - A_0)]$ vs. time, and the best straight line was determined from the linear portion of the plot (excluding initial rate data, where the accumulation of the steady-state concentration of the diarylethanol makes the data aberrant).

Kinetic solutions were prepared by preparing a solution of the *cis*-stilbene in 95% ethanol of the appropriate concentration and diluting a 5-ml aliquot to 100 ml with sulfuric acid of the requisite concentration. The final substrate concentration was approximately 2×10^{-6} M. Samples were placed in 10-cm quartz cells in the thermostated compartment of a Beckman DU spectrophotometer.

The very limited solubility of several of the *trans*-stilbenes requires further comment. On occasion, 10^{-6} M exceeds the solubility limit of the *trans*-stilbene. This difficulty can be circumvented by working with somewhat more dilute solutions of substrate (at the expense of a large change in absorbance), or by scrupulous care to detail, so that a metastable, supersaturated solution results. These difficulties were somewhat more troublesome in more dilute sulfuric acid solutions.

Sulfuric acid concentrations were determined on the final actual kinetic solutions by titration in duplicate. These are the sulfuric acid concentrations reported in Tables I and III. H_0 values are from a previous paper from these laboratories.¹⁵ For H_0 values at higher temperatures, corrections from the reports of Gelbstein, *et al.*,²⁹ were applied. The correction never exceeded 0.05 units.

The photochemical sensitivity of stilbenes is well known. Care must be taken with the very dilute solutions used in these studies to protect them from intense fluorescent light. However, by appropriate control experiments, it was shown that no isomerization was occurring under the conditions of the Beckman DU spectrophotometric measurements.

(25) D. Y. Curtin, A. Bradley, and Y. G. Hendrickson, *J. Amer. Chem. Soc.*, **78**, 4064 (1956).

(26) G. A. R. Kon and R. G. W. Spickett, *J. Chem. Soc.*, 2724 (1949).

(27) P. L'Ecuyer, F. Turcutte, J. Giguere, C. A. Olivier, and P. Roberge, *Can. J. Chem.*, **26B**, 70 (1948).

(28) J. A. Stanfield and L. B. Reynolds, *J. Amer. Chem. Soc.*, **74**, 2878 (1952).

(29) See Gelbstein, *et al.*, Table I, footnote a.