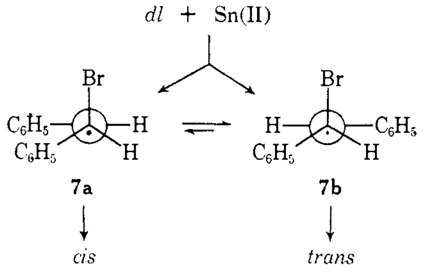
of *dl* (**2**), these factors are opposed. Energetically, we have seen that this opposition amounts to a free energy difference of *ca.* 4.4 kcal/mol in **1** and **2** (Table IV). Now, the major product (*ca.* 95%) in the case of *dl* is the result of a net *syn* elimination. To avoid the unfavorable *anti* conformation in **2**, the *dl* takes another path. Therefore, we must consider several possible transition states or intermediates on this path in detail.

Species **3** and **4** are transition states for concerted *syn* processes; compound **5** is an *erythro* intermediate formed by nucleophilic attack of tin(II) on the *dl*-dibromide; the radical pair **7** and the ion pair **6** are formed by one- and two-electron redox steps, respectively. In the appropriate conformation(s), **5**–**7** could then react to give the final products. Since dehalogenation mechanisms corresponding to **1**–**7** have been discussed,[4–8] we need only point out here that the structure and reactions implicit in **3**–**7** all could be consistent with the known chemistry of tin(II), tin(III), and tin(IV).[11–13,19,20]

The data of this paper do not allow one to favor strongly a particular mechanism or mechanisms. In part, this uncertainty stems from the fact that any route to *trans*-stilbene could be under equilibrium rather than kinetic control. For the *dl* reaction, however, two points may be made. The near-constancy of the *dl* product ratio in the range 60–100° is suggestive of partitioning of one or more unstable intermediates on one reaction path, rather than a competition along parallel paths, *e.g.*, **2** *vs.* **4**, or **2** *vs.* **5**, etc. Second, it has been found that known one-electron reductants, *e.g.*, Cu(I), Fe(II), Cr(II), Ti(III), convert the *dl*-dibromide chiefly into *trans*-stilbene, with only small amounts of *cis*-stilbene (0–5%) being formed.[4] Two-electron reagents, *e.g.*, lithium aluminum hydride, sodium iodide, platinum(II), give much higher yields of *cis*-stilbene (*ca.* 50%).[4] On this basis, we believe that a one-electron transfer by tin(II) to *dl*, as in eq 6, is an interesting possibility; while **7a** or **7b** "wait" for a second molecule of tin(II) to complete the reduction, they can isomerize by internal rotation. A mechanistic probe for tin(III) has been devised,[13] and eq 6, which is tentative, can perhaps be tested.



$$\mathrm{Sn(III)} + (\mathrm{C_6H_5CHBr})_2 \longrightarrow \mathrm{Sn(IV)} + \mathbf{7} \qquad (6)$$

$$2\mathrm{Sn(III)} \xrightarrow{?} \mathrm{Sn(II)} + \mathrm{Sn(IV)}$$

Stereoselectivity and Dehalogenation Mechanisms. The Elimination Reactions of *meso*- and *dl*-Stilbene Dibromides with Iodide in Methanol[1a]

C. S. Tsai Lee, I. M. Mathai, and Sidney I. Miller[1b]

Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616.

Received August 7, 1969

Abstract: The reaction between *meso*-stilbene dibromide (**1**) and sodium iodide in methanol is first order in *meso*-**1**, first order in iodide, and yields *trans*-stilbene (**2**); the rate data at 59.5° are $k = 1.56 \times 10^{-3}\ M^{-1}\,\mathrm{sec}^{-1}$, $\Delta H^{\ddagger} = 19.6$ kcal/mol, and $\Delta S^{\ddagger} = -13$ eu. The reaction between *dl*-**1** and sodium iodide in methanol yields *ca.* 15% *trans*-**2**, 30% *cis*-**2**, 30% *meso*-α,α′-dimethoxybibenzyl (**4**), as well as a mixture of methoxybenzoin and related hydrolysis products. Separate kinetic studies on the methanolysis of *dl*-**1** and *erythro*-α-bromo-α′-methoxybibenzyl indicate that solvolysis of *dl*-**1** accompanies the second-order elimination reaction of *dl*-**1** and iodide ion. At 59.5°, $k_{meso}/k_{dl} \simeq 65$; for the debromination of *dl*-**1**, $k = 2.37 \times 10^{-5}\ M^{-1}\,\mathrm{sec}^{-1}$, $\Delta H^{\ddagger} = 22.5$ kcal/mol, and $\Delta S^{\ddagger} = -12$ eu. Based on the products, kinetic data, substituent effects, bromine addition mechanisms in these and related systems, stepwise mechanisms are proposed for iodide promoted 1,2-debrominations. One or more onium species, *i.e.*, bromonium, carbonium ion pair, isolated carbonium ion, are presumed to lie on the reaction path. When conformational and orbital symmetry factors are aligned, as in *meso*-**1**, the reaction is *anti*-stereospecific and evidence for any short-lived transient is tenuous. In *dl*-**1**, where *anti* elimination would lead to *cis*-**2**, these two factors are opposed, and a mechanism without onium intermediates becomes implausible. In fact, the convergence of addition (Ad), elimination (E), substitution (S), and rearrangement in common onium intermediates makes for a high degree of mechanistic simplification among these diverse processes. Finally, a conformational analysis of our debromination system indicates that the difference in transition state free energies, $(G_{dl}^{\ddagger} - G_{meso}^{\ddagger}) \simeq 3.4$, a figure very similar to that for the products (**2**), $(G_{cis} - G_{trans}) = 3.7$ kcal/mol.

This work was undertaken to provide a quantitative comparison of the energetics, *i.e.*, a conformational analysis, of the elimination reactions of *meso*- and *dl*-stilbene dibromides (**1**) with iodide in methanol. Stil-

---

(1) (a) Acknowledgment is made to the Research Corporation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. This paper is abstracted in part from the M.S. thesis (1964) of C. S. T. L. (b) Author to whom inquiries should be addressed.

bene-related compounds have frequently been used as

$$(C_6H_5CHBr)_2 + 3I^- \xrightarrow{CH_3OH} C_6H_5CH{=}CHC_6H_5 + I_3^- + 2Br^- \quad (1)$$

meso- or *dl*-**1** → *trans*- or *cis*-**2**

models in stereochemical or mechanism studies, and we have used the same system to examine debromination in an aprotic solvent, halide basicity and nucleophilicity, other reductants or dehalogenation agents, and stereoselective eliminations.[2] Although the mechanistic alternatives for eq 1 seemed to be well understood, it appears that the view was too limited. Our observations now permit one to link three important processes, solvolysis–substitution, halogen addition, and halogen elimination.

Over 50 different reagents, *e.g.*, metals and one- and two-electron reductants, have been used to debrominate *meso*-**1** stereospecifically to give *trans*-**2**.[2] Some 30 reagents have been used to convert *dl*-**1** into *cis*- and *trans*-**2** with selectivities ranging from 0 to 96% *cis*-**2**; apart from a few two-electron reductants, eliminating agents give mostly *trans*-**2**.[2] In fact, there is only one old claim of a clean-cut *trans* debromination of *dl* by thiophenolate[3] and this reaction has been shown to be stereoselective rather than stereospecific.[2] Some nucleophiles, *e.g.*, quinoline,[4] chloride ion, dimethylformamide, etc., dehydrobrominate *dl*-**1** to give a bromostilbene.[2] These "problems" with the conventional *anti*-debromination of *dl*-**1** seem to depend on the fact that if the production of the high energy *cis*-**2**

$$cis\text{-}C_6H_5CH{=}CHC_6H_5 \rightleftharpoons trans\text{-}C_6H_5CH{=}CHC_6H_5 \quad (2)$$

$$\Delta H^\circ = -2.3\ \text{kcal/mol}^5$$

can be avoided, it will be. Analogous difficulties in the present system have been both interesting and instructive.

Few kinetic data have as yet been reported on our system. Although kinetic data for several 1,2-dibromides and iodide were listed for the solvent methanol, the rate ratio $k(meso\text{-}\mathbf{1})/k(dl\text{-}\mathbf{1}) \simeq 100$ was given without experimental details for the solvent acetone.[6] Difficulties, which we have uncovered, may account for the brevity of the report on the stilbene dibromide–iodide reaction in methanol.[6] A Belgian group has since published these kinetic data for acetone,[7] and Italian workers have obtained data for the reaction of *meso*-**1** with several halides in the solvents methanol, DMF, and acetone.[8] Although both groups believe that process 1 is essentially concerted (E2), this is something we shall question.

Experimental Section

The infrared spectra (ir) of all of the compounds of this study and of reaction products were routinely determined on Perkin-Elmer Model 137 and Beckman Model IR-8 spectrophotometers. Ultraviolet (uv) and visible spectra were determined on Beckman DK 12 and Cary Model 14 spectrophotometers. Melting points were determined on a Mel-Temp or Fisher-Johns melting point apparatus and are uncorrected.

Materials. Fisher absolute methanol was the solvent. For the kinetic work, some of the methanol was further treated with magnesium and distilled, but there was no apparent advantage in this. Reagent grade sodium iodide was dried at 150° for at least 3 hr and stored in a desiccator. *trans*-Stilbene (**2**), mp 124–125° (lit.[9] mp 124–125°), from ethanol, was commercially available. The following compounds were prepared by standard methods: *cis*-stilbene (**2**),[10] free of *trans*-**2** as determined by ir and uv spectra,[2,11] n^{25}D 1.6175 (lit.[10] n^{25}D 1.6188); *meso*-stilbene dibromide (**1**), mp 236–237.5° (lit.[9] mp 237–239°), from ethanol; *dl*-stilbene dibromide (**1**), mp 113–114° (lit.[9] mp 114°), from ethanol; *erythro*-1-bromo-2-methoxy-1,2-diphenylethane (**3**),[12] mp 115–116° (lit.[13] mp 115.5–116.5°), by column chromatography over alumina; *meso*-1,2-dimethoxy-1,2-diphenylethane (**4**),[12] mp 139.5–141° (lit.[14] mp 139–141°), from methanol, and λ_{max}^{MeOH} ($\epsilon \times 10^{-2}$), 268 (1.9), 264 (3.6), 258 (4.5), 252.5 (3.4), 248 (2.3) mμ.

It should be noted that *erythro*-**3** (3.5 g), which was obtained by bromine addition to *trans*-**2** (10 g) in methanol,[12,15] has *meso*-**1** and *meso*-**4** as coproducts. It seems probable that Jackson's sample of *erythro*-**3** contained some *meso*-**4**.[12] To purify it, we found it necessary to chromatograph it twice and recrystallize it from ethanol–benzene (1:1).[13,14] In the light of our present information on their solvolysis, it is recommended that bromo compounds **1** and **3** should not be "overexposed" to hydroxylic solvents, be it in preparation, purification or storage.

Analysis. Iodine was determined with standard sodium thiosulfate in the "dead-stop" titration.[16] Iodide and bromide were determined amperometrically, with standard silver nitrate. Acid was determined with standard base. Analyses of *cis*- and *trans*-**2** were based on a spectrophotometric method of simultaneous equations;[17] for *cis*-**2** λ_{max}^{MeOH} (ϵ) 320 (1695), 307 (4630) mμ; for *trans*-**2**, λ^{MeOH} (ϵ) 320 (17,840), 307 (28,400) mμ. Any iodine color was first removed, of course, with sodium sulfite. Since *dl*-**2**, *erythro*-**3**, and *meso*-**4** could interfere in these analyses at wavelengths below 300 mμ, we used the higher wavelengths. If one assumes the *cis*/*trans* product ratio in the reaction of iodide with *dl*-**1** should not change with time, the observed mean ratio is 1.9 ± 0.1, disregarding the first and last ("infinite" time) values (Table I).

Table I. Stoichiometry of the Reaction of *dl*-Stilbene Dibromide (0.0107 *M*) and Sodium Iodide (0.058 *M*) in Methanol at 101°

Time, min	I_3^-, *M* × 10^3	Stilbene, *M* × 10^3			Per cent reaction	*cis*-**2**/*trans*-**2**[a]
		cis-**2**	*trans*-**2**	Total		
40.5	1.74	0.99	0.72	1.71	16	1.37
66	2.43	1.68	0.90	2.57	23	1.82
99	3.07	2.11	1.11	3.23	29	2.11
149	3.61	2.49	1.25	3.74	34	1.99
263	4.14	2.79	1.64	4.43	39	1.70
1113	4.89	1.7	2.7	4.4	46	0.63

[a] The kinetically controlled product ratio is taken as 1.9.

---

(2) W. K. Kwok and S. I. Miller, *J. Amer. Chem. Soc.*, **92**, 4599 (1970); I. M. Mathai, K. Schug, and S. I. Miller, *J. Org. Chem.*, **35**, 1733 (1970); I. M. Mathai and S. I. Miller, *ibid.*, in press; W. K. Kwok, I. M. Mathai, and S. I. Miller, *ibid.*, in press.

(3) R. Otto, *J. Prakt. Chem.*, **53**, 1 (1896); R. Otto and F. Stoffel, *Chem. Ber.*, **30**, 1799 (1897).

(4) P. Pfeiffer, *ibid.*, **45**, 1810 (1912); P. Pffeiffer and K. v. Swidzinski, *ibid.*, **48**, 1048 (1915).

(5) G. Fischer, K. A. Muszkat, and E. Fischer, *J. Chem. Soc., B*, 1156 (1968).

(6) (a) W. G. Young, D. Pressman, and C. D. Coryell, *J. Amer. Chem. Soc.*, **61**, 1640 (1939); (b) S. Winstein, D. Pressman, and W. G. Young, *ibid.*, **61**, 1645 (1939).

(7) J. Mulders and J. Nasielski, *Bull. Soc. Chim. Belg.*, **72**, 322 (1963).

(8) E. Baciocchi and P. L. Bocca, *Ricera Sci.*, **37**, 1182 (1967); E. Baciocchi and A. Schiroli, *J. Chem. Soc., B*, 554 (1969).

(9) (a) R. E. Buckles, J. L. Miller, and R. J. Thurmaier, *J. Org. Chem.*, **32**, 888 (1967); (b) R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *ibid.*, **27**, 4523 (1962).

(10) R. E. Buckles and N. G. Wheeler, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 857.

(11) W. K. Kwok, Ph.D. Thesis, Illinois Institute of Technology, 1967.

(12) E. L. Jackson, *J. Amer. Chem. Soc.*, **48**, 2166 (1926).

(13) H. O. House and R. S. Ro, *ibid.*, **80**, 182 (1958).

(14) T. Inoue, K. Koyama, T. Matsuoka, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **40**, 162 (1967).

(15) P. D. Bartlett and D. S. Tarbell, *J. Amer. Chem. Soc.*, **58**, 466 (1936).

(16) C. W. Foulk and A. T. Bawden, *ibid.*, **48**, 2045 (1926).

(17) M. Ish-Shalom, J. D. Fitzpatrick, and M. Orchin, *J. Chem. Educ.*, **34**, 496 (1957).

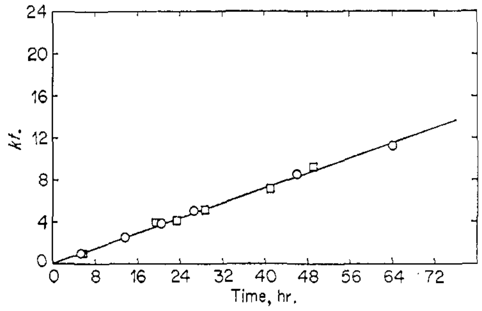


Figure 1. The reaction of *dl*-stilbene dibromide with iodide in methanol at 60.3° (two runs out of three in Table II).

Stoichiometry and Related Problems. *meso*-**1** dissolves slowly and sparingly in methanol. On long standing, these solutions develop color and contain bromide ion. Attempts to determine the solubility of *meso*-**1** in methanol were not wholly satisfactory. Dehydrobrominations with sodium hydroxide of aliquots of a saturated solution appeared to slow down after 1 equiv of bromide was produced (*ca.* 58%). The saturated solution was refluxed with zinc (30 mesh) for 2 days, and the bromide was estimated with silver nitrate: the average of three solubility determinations was $(9.5 \pm 0.1) \times 10^{-4}$ *M* at 25° and $(1.38 \pm 0.05) \times 10^{-3}$ *M* at 46°. Saturated solutions of *meso-1* with excess iodide were kept at 100° or 72° for *ca.* 15 and 50 hr, respectively, but the iodine titer was *ca.* 70% of the zinc figure; in our kinetic studies our infinity estimates of iodine were also low at 65–75%. Presumably, this must be ascribed to absorption of iodine by the solvent.

It has been reported that the reaction of *meso*-**1** with iodide in 95% ethanol yields *ca.* 100% *trans*-**2**.[9] Our preparative scale experiment with *meso*-**1** (1.0 g) gave 90–95% *trans*-**2** (mp 125–126°).

Unlike *meso*-**1**, the *dl*-**1** was reasonably soluble in methanol. In the kinetic runs, however, only 45–65% of the iodine expected on the basis of eq 1 was produced. The data given in Table I illustrate this quite well: paired ampoules were removed from a constant-temperature bath, chilled, and analyzed in two different ways, titrimetrically and spectrophotometrically.

Further information on the products came from the reaction of *dl*-**1** (1.0 g) with sodium iodide (7.4 g) in methanol at reflux for 6 days or at 101° for 49 hr. Work-up of the product gave a residue of which all but a trace of yellow solid, mp 350° dec, was soluble in carbon tetrachloride. Chromatography of the product over alumina gave in order of elution, *cis*-**2** (*ca.* 30%), from petroleum ether, impure *trans*-**2**, mp 117.5–121.5° (*ca.* 15%), from petroleum ether, *meso*-**4**, mp 141.5–143° (*ca.* 30%), from benzene:petroleum ether (2:3), and a yellow oil (*ca.* 20%) from ether:benzene (1:1). Similar products were obtained from *erythro*-**3** and iodide under comparable reaction conditions. From their ir and uv spectra, it appears that the last eluate fractions contained benzoin, its methyl ether, hydrobenzoin, and the corresponding monomethyl ether.

In the absence of iodide, solvolysis of *meso*-**1**, *dl*-**1**, and *erythro*-**3** gave similar product mixtures. For example, the *dl*-dibromide (1 g) was kept in methanol (100 ml) at 100° for 158 hr. Impure *erythro*-**3** (20 mg), mp 100–114°, *meso*-**4** (0.4 g), mp 141–142°, and an impure solid (20 mg), having carbonyl and methoxy bands in its infrared spectrum, were obtained.

In the solvolysis of *meso*-**1** and in all of the reactions of *dl*-**1** and *erythro*-**3** in methanol, some 10–20% of the products were not identified unequivocally. Based on their ir and uv spectra, plausible products are the diastereoisomeric monomethyl ethers of hydrobenzoin, *dl*-**4**, as well as products of oxidation, such as benzoin and its methyl ether; benzil, diphenylacetaldehyde or its acetal, which can be formed by acid-catalyzed rearrangement,[18] appeared to be absent.

The isomerization of *cis*-**2** under out most extreme conditions was checked. *cis*-**2** (*ca.* 0.1 ml) and 25 ml of sodium triiodide (0.01 *M*) in methanol were left at 100° for 11 hr. An uv analysis of the solution indicated *ca.* 15% *trans*-**2**. The results in Table I indicate that isomerization of *cis*-**2** does occur essentially after the production of triiodide has leveled off. In the kinetic runs, isomerization would be less since concentrations would generally be lower. In fact, reports indicate little or no isomerization under similar conditions.[2,9a]

Rate Studies. The general procedure for studying process 1 is well known.[19] We used several constant temperature water and oil baths which could be maintained at ±0.1°. For the lower temperatures, stock solutions of stilbene dibromide and sodium iodide were brought to thermostat temperature separately, then mixed thoroughly. Otherwise, the ampoule technique was used. As has become customary, an excess of sodium iodide was used to repress the dissociation of triiodide ion.[19]

Two possible side or "blank" reactions specific to the *meso*-**1** runs, which were carried out in the stoppered flasks, had to be checked. It was found that triiodide appeared in solutions of sodium iodide and methanol, and that triiodide disappeared from solutions containing stock triiodide. For the period of the reaction, these two effects compensate approximately, and no correction was applied: a run at 35.56° in which the reaction had proceeded about half-way required 36.0 ml of standard thiosulfate (9.7×10^{-4} *M*); at this time, the blank for triiodide consumption was also 0.4 ml of standard thiosulfate.

Because of the low solubility of *meso*-**1**, only pseudo-first-order runs were feasible. The treatment of the data by Guggenheims's method obviates the necessity of knowing the initial concentration of *meso*-**1**. The second-order rate constants are summarized in Table II. The activation energy was obtained by a least-squares calculation and the other parameters were calculated from the usual expressions 3 and 4 (Table III).

Table II. Rate Data for the Reaction of *meso*-Stilbene Dibromide with Sodium Iodide in Methanol[a,b]

Temp, ± 0.05°	*meso*-$(C_6H_5CHBr)_2$ $M \times 10^3$	NaI, *M*	k, M^{-1} hr^{-1} [a]
35.56	0.574	0.100	0.504 ± 0.012
	0.646	0.0501	0.552
	0.431	0.200	0.484 ± 0.023
		Mean	0.510 ± 0.025 (11)
45.20	1.23	0.050	1.47 ± 0.01
	0.821	0.200	1.57
	1.094	0.100	1.42
		Mean	1.48 ± 0.05 (7)
54.63	1.904	0.100	3.46
	1.250	0.100	3.62
	1.590	0.200	3.68 ± 0.06
	2.254	0.050	3.22 ± 0.03
			3.48 ± 0.18 (6)

[a] The data of 24 runs are summarized: average deviations and the number of runs (in parentheses) are listed. No correction for solvent expansion was necessary, since the concentrations apply to the indicated temperatures. [b] Reference 8 gives 2.52×10^{-4} and 4.7×10^{-5} M^{-1} sec^{-1} for potassium iodide in methanol at 40 and 25°, respectively; our calculated values would be 2.43×10^{-4} and 3.13×10^{-5} M^{-1} sec^{-1} at the same temperatures.

Table III. Activation Parameters for the Reactions of the Stilbene Dibromides with Iodide in Methanol

	E_{act}, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu (59.5°)
meso	20.3 ± 0.3	19.6 ± 0.3	−13
dl (elim)[a]	23.1 ± 0.5	22.5 ± 0.5	−12
dl (obsd)[b]	23.6 ± 0.5	23.0 ± 0.5	−13

[a] Preferred values from k_{elim}. [b] From k_{obsd}.

$$E_{act} = \Delta H^{\ddagger} + \mathbf{R}T \qquad (3)$$

$$k\mathbf{h} = \mathbf{k}T \exp\{\Delta S^{\ddagger}/\mathbf{R}\} \exp\{-\Delta H^{\ddagger}/\mathbf{R}T\} \qquad (4)$$

The *dl*-**1** iodide system was studied by the ampoule method. Equation 5 is the appropriate rate expression for process 1, where $a = [\mathbf{1}]_0$, $b = [\mathrm{NaI}]_0$, and $x = [I_3^-]$ in moles per liter.[19] As will be pointed out below, "infinity" values of triiodide yielded the factor

---

(18) D. A. Shearer and G. F. Wright, *Can. J. Chem.*, **33**, 1002 (1955); J. W. Huffman and R. P. Elliott, *J. Org. Chem.*, **30**, 365 (1965).

(19) (a) W. G. Lee and S. I. Miller, *J. Phys. Chem.*, **66**, 655 (1962); (b) S. I. Miller and R. M. Noyes, *J. Amer. Chem. Soc.*, **74**, 3403 (1952).

Table IV. Rate Data for the Reaction of *dl*-Stilbene Dibromide with Iodide in Methanol

Temp, ±0.1°	*dl*-$(C_6H_5CHBr)_2$, a[a]	$M \times 10^3$, af[b]	NaI, M	k_{obsd}, M^{-1} hr^{-1}[c]	$k_{elim} \times 10^5$,[d] M^{-1} sec^{-1}
60.25	8.085	4.040	0.0749	0.180	
60.20	6.064	2.756	0.0535	0.199	
60.20	4.042	2.248	0.0570	0.180	
				k_{corr} 0.194 ± 0.1	2.59 ± 0.1
72.13	8.085	4.040	0.0749	0.630	
72.15	6.064	2.756	0.0535	0.630	
72.13	4.042	2.085	0.0570	0.674	
				k_{corr} 0.681 ± 0.2	8.78 ± 0.5
100.5	8.085	4.040	0.0749	8.44	
100.75	6.064	2.756	0.0535	8.53	
100.75	4.042	2.085	0.0570	8.25	
				k_{corr} 9.31 ± 0.12	114 ± 6

[a] The initial concentration of *dl* by weight. [b] The concentration of *dl* indicated by the infinity titer of triiodide. [c] k_{corr} is the mean k_{obsd} of eq 11 corrected for solvent expansion. [d] k_{elim} is obtained from eq 13.

$$k_{obsd}t = \frac{2.303}{(b - 3a)} \log \frac{a(b - 3x)}{b(a - x)} \qquad (5)$$

by which $a = [1]_0$ had to be decreased, as in $[I_3^-]_\infty = af$; af was then used for a in the standard rate expression eq 5. Now, the usual right-hand side of eq 5 or "kt" *vs.* t plots were linear, and k could be obtained (Figure 1). The rate constants are given in Table IV and the activation parameters in Table III.

The following check experiments were carried out in connection with the *dl* runs. When the iodide and *dl* solutions were mixed at room temperature, some iodine color developed. The aliquots were distributed among several ampoules, preflushed with nitrogen. Two sealed ampoules, provided the "cold" blank of *ca.* 1-2 ml out of a possible 40 ml of sodium thiosulfate (9.72×10^{-4} M). Under conditions of the kinetic runs, methanol and iodide produced essentially no iodine, and methanol and triiodide showed almost constant titer. The consumption of iodine by the other compounds present was checked: a solution of *trans*-**2** (5.07×10^{-4} M), iodine (5×10^{-4} M), sodium iodide (10^{-3} M) and sodium bromide (1.08×10^{-3} M) was distributed among 8 ampoules. Within the period of a kinetic run, say 6 hr, there was no decrease in triiodide concentration, although 6% was consumed after 20 hr. Ampoules containing *dl*-**1** (9.5×10^{-3} M) and a known excess of iodine in methanol were kept 100° for 4 and 18 hr. Loss of iodine was negligible in the period comparable to the kinetic runs, but became appreciable (35%) in the long period. *dl*-**1** (4×10^{-4} M) and sodium iodide 0.05 M) were allowed to react to completion: dilution of the solution and measurement of the pH indicated only a slight increase in the acidity over the initial solution, certainly far less than that expected on basis of complete solvolysis; this indicated the loss of hydrogen bromide (or iodide) or its consumption by methanol.

It was hoped that the solvolysis and elimination could be followed in the *dl*-**1** iodide runs; however, we were unable to estimate the bromide ion in the product mixture when attempts to remove iodide and iodine, *e.g.*, with copper wire and cupric ion, as cuprous iodide, were made.

The possibility of affecting the reactivity of *dl*-**1** was examined. To a typical reaction mixture of *dl*-**1** (5×10^{-3} M) and excess iodide, *trans*-**2** (3.5×10^{-4} M) was added. After *ca.* 16 hr at 100°, the solution showed 74% reaction as triiodide. Thus, *trans*-**2** did not reverse or inhibit the elimination.

The reaction of iodide with *threo*-**3** in methanol was studied briefly by the ampoule method. After 4 days at 101°, a solution of *threo*-**3** (0.0343 M) and sodium iodide (1.26 M) showed an "infinity" titer of only 26% of the expected triiodide ion: solvolysis was more important than elimination. As with *dl*-**1**, the use of a in eq 5 gave rate constants which decreased by a factor of *ca.* 2 over the whole run. If $0.26a$ was used for a, the rate constants dropped by a lower factor (*ca.* 1.4); extrapolation to zero time now gave a crude rate constant (Table V) for the E2 contribution.

The methanolysis rates of the bromides, *meso*-**1**, *dl*-**1**, and *erythro*-**3** were studied briefly. The progress of the reactions was followed by titration of the hydrogen bromide with silver nitrate or with sodium hydroxide. In all three cases, the rate constants dropped steadily with time. A rough initial rate constant was obtained by extrapolating back to zero time. These rate constants are given in Table V.

Table V. Solvolysis and Elimination Rate Constants in Methanol[a]

	Temp, °C	k(E2), M^{-1} sec^{-1}	k(SN1), sec^{-1}
meso-$(C_6H_5CHBr)_2$	59.5	1.56×10^{-3}	7×10^{-6}
	100	4.34×10^{-2}	
dl-$(C_6H_5CHBr)_2$	59.5	2.37×10^{-5}	
	100	1.1×10^{-3}	1×10^{-4}
$C_6H_5CHBrCHOCH_3C_6H_5$	60.2		1×10^{-5}
	101	7×10^{-6}	4×10^{-4}

[a] The rate constants given to one significant figure were obtained by extrapolation to zero reaction, as explained in the text.

Results and Discussion

***meso*-Stilbene Dibromide (1).** The stoichiometry of the reaction of *meso*-**1** with iodide in methanol is well represented by eq 1: the yield of stilbene exceeds 95%. The reaction was first order in *meso*-**1** and first order in iodide.

Methanolysis of *meso*-**1** can only compete with elimination at high temperatures or at low iodide concentrations.

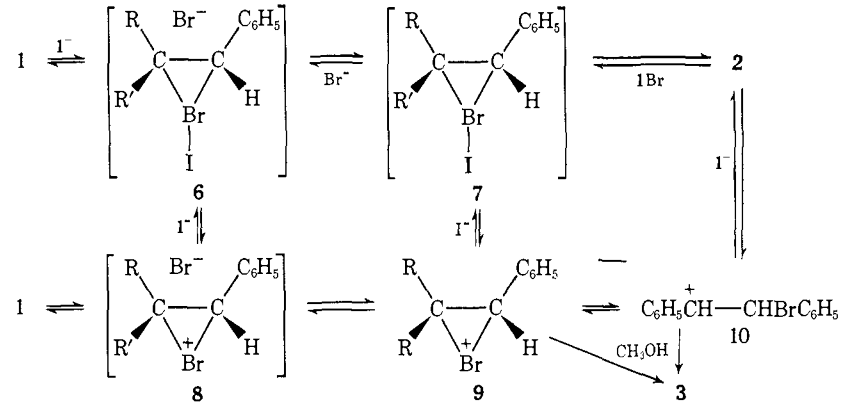
$$\mathbf{1} \longrightarrow \underset{\mathbf{3}}{C_6H_5CHBrCH(OCH_3)C_6H_5} \xrightarrow{CH_3OH} \underset{meso\text{-}\mathbf{4}}{(C_6H_5CHOCH_3)_2} \qquad (6)$$

Both bromine atoms were eventually replaced from *meso*-**1**, the major product being *meso*-**4**. The solvolytic rate constants for **1** fell rapidly as the reaction progressed. Under these conditions the entry of the second methoxy group *appears* to be slower than the first, in contrast to what one might predict from initial rates (Table V). Therefore, the formation of *trans*-**2** according to eq 1 and to a second-order rate law shows that process 6 cannot be important. More will be said about solvolysis presently.

Concerning the debromination process itself there is no reason to suppose that it is other than a bimolecular process proceeding through an *anti*-transition state **5** from *meso*-**1**. A four-center *anti*-transition state would be favored by coplanarity of the reacting centers, orbital symmetry, and conformational considerations.[20] But does *trans*-**2** form directly or after one or more intermediates? A concerted 1,2-elimination would require that the reverse reaction be trimolecular. On the other hand, a stepwise elimination would be consistent either with second- or third-order kinetics of

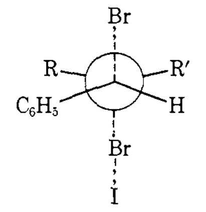
---

(20) S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968).

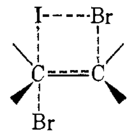


(7)

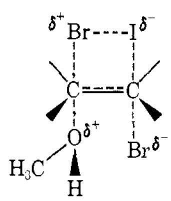
meso (*erythro*) series, R = H; R′ = C$_6$H$_5$ *dl* (*threo*) series, R = C$_6$H$_5$; R′ = H



meso-**5**, R = H; R′ = C$_6$H$_5$
dl-**5**, R = C$_6$H$_5$; R′ = H



11



12

bromine addition to *trans*-**2**. In the absence of iodide, such addition, which is second order in hydroxylic solvents, *anti*-stereospecific, and multistep,[9,15,21] should be a faithful model of our elimination process. Therefore, we favor a stepwise mechanism: either the rate-determining attack of iodide on **1** or on **8** to form **6** in eq 7 would suffice. The proposed transition state would be similar to species **6**. Further elaboration of this scheme will be given in the following sections.

Previous opinion has favored the one-step elimination of *meso*-**1**.[7,8] The absence of rate retardation by bromide ion in acetone has been used as evidence against a multistep process.[7] In a study of iodide debromination of *erythro*-stilbene bromochloride and substituted *meso*-stilbene dibromides, there was a strong leaving group effect ($k_{\mathrm{Br}}/k_{\mathrm{Cl}}$ = 87 at 50°), but only small rate enhancements in the *para*-nitro or methoxydibromides.[8] Although a concerted E2 process was suggested, these data are not inconsistent with scheme 7.

***dl*-Stilbene Dibromide.** The reaction of *dl*-**1** with iodide in methanol appears to be complex. Based on the yield of triiodide, only 45–60% of *dl*-**1** took an elimination route. Separate experiments indicated that the major products were *trans*-**2** (*ca.* 15%), *cis*-**2** (*ca.* 30%), and *meso*-**4** (*ca.* 30%). However, the ratio *cis*-**2**/*trans*-**2** ≃ 1.9 under kinetic conditions. Under the conditions of debromination kinetics, the triiodide does not catalyze significant isomerization of *cis*- to *trans*-**2**; furthermore, iodine does not appear to affect *dl*-**1** or promote methoxylation of the stilbenes under the same conditions. Clearly, elimination and solvolytic paths are competitive. Although *erythro*-**3** has not been isolated under elimination conditions (60–100°), we have found it as well as *meso*-**1** and *meso*-**4**, when bromine was added to stilbene in methanol (*ca.* 25 and 64°). Further, when *erythro*-**3** was treated with iodide ion in methanol at 101°, only *ca.* 0.26 equiv of triiodide was produced; the balance of reaction went chiefly to *meso*-**4**. The elimination product was mostly *trans*-**2**,

$$\textit{erythro}\text{-}\mathbf{3} + \mathrm{CH_3OH} + \mathrm{I^-} \longrightarrow \underset{\sim 25\%}{\mathbf{2} + \mathrm{I_3^-}} + \underset{\sim 75\%}{\textit{meso}\text{-}\mathbf{4}} \qquad (8)$$

but curiously enough it did contain a trace of *cis*-**2**. (At present, the possible role of *threo*-**3** is unknown.)

A brief study of the reaction of iodide with *erythro*-**3** was carried out at 101°. Because only *ca.* 25% of the theoretical amount of triiodide was produced, the second-order rate constants fell with time, even though allowance was made for diversion to other products. Nevertheless, extrapolation to zero time gave an approximate value of the elimination rate constant (Table V). This was substantially lower than the elimination rate constants for the *meso* and *dl*-**1**. Clearly, the E2 component of process 8 cannot be significant during the reaction of *dl*-**1** and iodide ion, even if *erythro*-**3** is formed.

As with *meso*-**1**, the solvolysis (first order) rate constants of *dl*-**1** and *erythro*-**3** fell with time. Falling rate constants have been noted previously in the solvolysis of other bromides and have been attributed to a mass law effect[22a] or to the disappearance of hydrogen bromide, whose formation is normally followed.[23] Our rate constants were determined by extrapolation to zero reaction time; therefore, they are crude estimates, and should be even more uncertain under the elimination conditions (Table V). It is clear, however, that solvolysis can compete with elimination, not only because of the product distribution, but also because

---

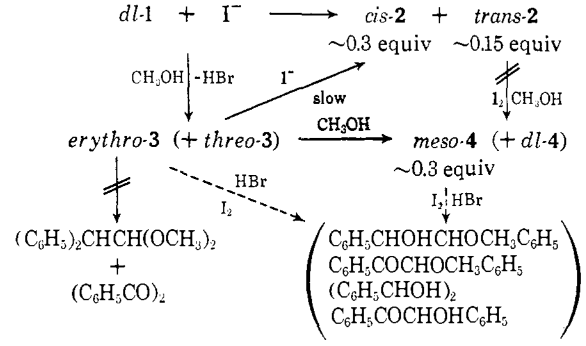
(21) (a) J. E. DuBois and G. Barbier, *Tetrahedron Lett.*, 1217 (1965); (b) J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 3260 (1963); (c) N. P. Kanyaev, *Zh. Obshch. Khim.*, **29**, 841 (1959); *Chem. Abstr.*, **54**, 1249 (1960).

(22) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., Amsterdam, 1963: (a) Chapter 5; (b) Chapter 1; (c) Chapter 2.

(23) S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, **70**, 828 (1948); **69**, 2951 (1947); H. L. Goering and H. H. Espy, *ibid.*, **78**, 1454 (1956).

the half-lives for *dl*-**1** at 100° in the presence or absence of added sodium iodide (conditions of Table IV) are comparable.

We can now describe the disappearance of *dl*-**1** under our elimination conditions. Any gaps in product identification and in the routes favored, of eq 9 are chiefly in the later stages of the reaction. We have no proof, for example that *erythro*-**3** actually is an intermediate on the path from *dl*-**1** to *meso*-**4**, but we believe this is highly probable. The possibility of initial displacement of bromide from **1** by iodide will be examined below. It does appear, however, that neither the stilbene iodobromides nor their solvolysis products arise from reaction between the stilbenes and triiodide in methanol.



(9)

There is now the problem of matching the elimination process, which produces triiodide, with the observed rate data. For *dl*-**1**, recall that the initial concentration a of *dl*-**1** is adjusted in eq 10. If product partitioning

$$f = [I_3^-]_\infty/a = x_\infty/a \qquad (10)$$

by elimination and solvolysis occurred *after* the rate-determining step, eq 11 holds

$$dx/dt = k_{obsd}(b - 3x)(af - x) \qquad (11)$$

If, however, parallel second-order elimination and first-order solvolysis prevailed, eq 12 would hold

$$f = k_{elim}[I^-]/(k_{elim}[I^-] + k_{solv}) \qquad (12)$$

For the condition $b \gg 3a$, we would again use eq 11, but the appropriate rate constant would be given by eq 13

$$k_{obsd} = fk_{elim} \qquad (13)$$

Only a few of the possible mechanisms consistent with this kinetic behavior can be considered.

According to Csapilla, transition states **11** and/or **12** could lie on routes to **2**, **3**, **10** or stilbene iodobromide.[24] The relevance of such merged transition states to real situations is still controversial.[25] In **11**, for example, the reaction coordinate must encompass normal vibrations which simultaneously (a) make or break a C–I bond, (b) make or break two C–Br bonds, (c) make or break a Br–I bond, (d) make or break a C–C bond. Since multiple bond making and bond breaking are usually associated with different normal vibrational modes, it would appear that several of these would have to be excited in the transition state. According to Herzberg, such multiple excitation is energetically costly.[26]

The formation from *dl*-**1** either of stilbene iodobromide or **3** followed by their rapid disappearance along elimination or solvolytic paths is formally consistent with the observed rate law. Judging from the *meso*-**1** iodide system, it appears likely that any SN2–E2 sequence *via* stilbene dibromide would give *trans*-**2** with high stereoselectivity; this was not found. Our rate and product studies indicate that *erythro*-**3** would not contribute significantly to the formation of triiodide; we also suppose that *threo*-**3** should be an even less reactive substrate in elimination, for conformational reasons.

The mechanisms which we favor all involve portions of eq 7. If *threo*-**6** is generated from *dl*-**1** and iodide in a slow step, and rapid conversion to and partitioning of **7**–**10** follow, eq 11 applies: the elimination rate constant is identified with k_{obsd}. If *dl*-**1** and ion pair **8** are in equilibrium, and **8** is partitioned between iodide (elimination) and methanol (solvolysis), eq 12 and 13 apply; now an equilibrium constant is contained in k_{elim}. If there was only the simple competition between the "pure" EN2 and SN1 components of (7),[27] eq 12 and 13 would again hold.

It would be desirable, of course, to know how much of eq 7 to retain in any given case. Since *dl*-**1** solvolyzes both in the presence and absence of iodide ion, it seems that the lower part of eq 7 is essential. Obviously, some of the upper portion must be retained too, but the data do not permit a more detailed decision. An implicit feature of all of these variations is that the paths from *dl*-**1** and related onium species are *directed* through the open carbonium ions (**10**). These provide a switching point for the conversion of *dl to meso* forms, **6**–**9**, and for the formation of both *cis*- and *trans*-**2**. The fact that the leakage is chiefly one way, that is from *dl*- to *meso*-related forms, is presumably of conformational origin.

1,2-Halogenation and 1,2-Dehalogenation Mechanisms. Equation 7 is probably the most general ever given in the context of iodide debromination. That several reaction routes, substitution, (SN, SE), eliminations (E), addition (AdE, AdN), and rearrangement may intersect at ion pair or carbonium ion intermediates is well known,[22b,28] but the reciprocal relation between addition and elimination has rarely been exploited. Too often one speaks of "addition" and "elimination" as though they were different, despite the fact both terms may apply to a single process and are merely labels indicating on what side one must stand to get a particular view. A detailed discussion of a reversible system has been given by Miller and Noyes,[19b] and common intermediates similar to **6**–**8** have been considered by Hine.[29]

In hydroxylic solvents, the rate of bromine addition to an alkene (A) often takes the form of eq 14.[28–31]

---

(24) J. Csapilla, *Chimia*, 18, 37 (1964).

(25) D. Eck and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 3099 (1969).

(26) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1945, pp 125 ff.

(27) This is analogous to the "united" SN mechanism: R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, 91, 6031 (1969).

(28) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., Amsterdam, 1966, Chapters 1, 7.

(29) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 209–220.

(30) J. E. Dubois and E. Bienvenue-Goetz, *Bull. Soc. Chim. Fr.*, 2086 (1968).

(31) R. P. Bell and M. Pring, *J. Chem. Soc.*, *B*, 1119 (1966).

The first term may correspond to AdE2 or AdEN3 mechanisms.[32] Although such terms allow for either

$$-\mathrm{d}[\mathrm{Br_2}]/\mathrm{d}t = (k_1 + k_2[\mathrm{Br^-}])[\mathrm{A}][\mathrm{Br_2}] \qquad (14)$$

concerted or stepwise processes, it is generally accepted that the preference for *anti* addition and the formation of mixed products (BrAX), when another nucleophile (X^-) is present, are indicative of the stepwise mechanism.[28,29] Kinetically, the reverse of either term of eq 14 may be E1 or EN2. If iodide is now allowed to stand in for bromide ion, then appropriate portions of eq 7 are consistent with the kinetics in either direction.

Armed with hindsight, we can pull together a number of disparate observations on stilbene and related systems which provide analogies and/or support for eq 7. In general, 1,2-dihalides react with hydroxylic solvents, presumably *via* onium species.[23,33] Anodic bisdecarboxylation of *meso*- and *dl*-1,2-diphenylsuccinic acids yields *trans*-**2**, presumably *via* a cationic intermediate.[34] In carbon disulfide, bromine addition to *cis*-**2** gives *dl*-**1** in an *anti* selective process; in polar solvents such as nitrobenzene or ethanol, more *meso*-**1** is produced; in the presence of added bromide ion, *anti* addition to *dl*-**1** becomes predominant, even in polar solvents: the interpretation[9,35] is that a polar solvent stabilizes onium species and allows both for partial or complete equilibration before their capture by bromide ion, by a hydroxylic solvent,[15,36] etc. Starting with *dl*-**1** in acetic acid, Heublein showed qualitatively that exchange with labeled bromide ion, isomerization to *meso*-**1**, solvolysis, and elimination are competitive: onium species are presumably involved.[37] Using a high-frequency titration technique as a probe during bromine addition to stilbene, Heublein and Umbreit believe they found evidence for at least two of the *intermediates* of eq 7.[38] These miscellaneous observations are consistent both with the presence of onium intermediates in eq 7 and their directed leakage to more stable forms.

Now there are also a number of apparently unrelated observations specific to elimination studies, which appear to fit a pattern. Van Duin noted that solvolysis accompanied elimination in the dibromides of maleic acid or of the *p*-sulfonate of *cis*-cinnamic acid in aqueous ethanol; the corresponding eliminations of the *trans*-alkene dibromides went cleanly.[39] Recent work on the cinnamic acid dibromides on aqueous methanol is similar: the *erythro*-dibromide with iodine gave *anti* elimination and clean second-order kinetics; the *threo* compound gave products which were not identified and displayed a rate behavior which was not defined.[40] Two stereoconvergent eliminations are appropos: *erythro*- and *threo*-benzalacetone dibromides with sodium iodide gave the more stable *trans*-benzalacetone exclusively;[41] Buckles, *et al.*, reported, without comment, that when *dl*-**1** was heated with sodium iodide in 95% ethanol, a 45% yield of **2** (*trans*/*cis* = 2/1) was obtained, whereas with *meso*-**1**, 100% *trans*-**2** was obtained.[9b] Assisted by silver acetate, both 1,2-stilbene dichlorides solvolyze, probably *via* a *meso* chloronium intermediate, and form *erythro*-α-acetoxy-α′-chlorobibenzyl.[33] As in our system, complexity in the kinetics of elimination and multiplicity of products seem to be associated with the reluctance of certain *dl* or *threo* species to undergo normal *anti* elimination. Here, the *anti* process would lead to a relatively unstable alkene. The equilibrium constants favoring the *trans* isomers in the stilbenes, cinnamic acids, and maleic–fumaric pair are at least 100/1.[5,42] With a "*cis*" effect operating, it seems plausible to postulate one or more of the onium species as intermediates, which may react with bromide ion or solvent, isomerize, shed a second bromide ion, etc. Two major energy factors, electronic and steric, which are normally aligned in the *meso* (or *erythro*) reaction, are opposed in the *dl* (or *threo*) reaction.[20] It is not unreasonable that, if different reaction paths are available to *dl*, one or more may become more favorable than *anti* elimination.

Structure–Reactivity and Mechanism in Debromination. A general order of reactivity can be constructed for iodide promoted debrominations from available data.[24,43–45] The present reactivity scale is limited to certain data for methanol at 59.6°.[6a,19a,43,46] For *meso*- and *erythro*-1,2-dibromides and others, the 1- and 2-substituents followed by a relative reactivity are: $(CH_3)_2$, $(CH_3)_2$ (23); C_6H_5, C_6H_5 (19); COOH, COOH (4); $(CH_3)_2$, CH_3 (2.3); COOH, H (1.4); C_6H_5, H (1.3); H, H (1.00); *n*-C_3H_7, CH_3 (0.1); *n*-C_3H_7, *n*-C_3H_7 (0.09); $HOCH_2$, H (0.06); *n*-C_3H_7, H (0.06); $C_6H_5CH_2$, H (0.06); C_2H_5, CH_3 (0.06); C_2H_5, H (0.05); CH_3, H (0.04); CH_3, CH_3 (0.03); **Br**, **Br** (0.0011). For the *dl* and *threo* isomers, the order is H, H (1.00); C_6H_5, C_6H_5 (0.3); COOH, COOH (0.08); *n*-C_3H_7, *n*-C_3H_7 (0.07); C_2H_5, CH_3 (0.03); *n*-C_3H_7, CH_3 (0.03). We emphasize that this order is probably of more practical than theoretical interest. The compounds of these series do not form a homogeneous group. There are wide variations in the activation parameters, in the relative stabilities of the product alkenes, and possibly in the debromination mechanisms. Nevertheless, it is of interest to see whether any clues on probable mechanisms or transition states are in evidence.

We omit from consideration terminal bromides, which may undergo the SN2–E2 sequence, as is the case with ethylene bromide.[29] Beginning with the

---

(32) AdEN3 means a third-order addition process; depending on whether the electrophile leads or follows the initial attack, we write E,N or N,E; in a trimolecular concerted addition the subscript would be EN.

(33) S. Winstein and D. Seymour, *J. Amer. Chem. Soc.*, **68**, 119 (1946).

(34) E. J. Corey and J. Casanova, Jr., *ibid.*, 85, 165 (1963).

(35) G. Heublein, *J. Prakt. Chem.*, 31, 84 (1966).

(36) D. R. Dalton, V. P. Dutta, and D. C. Jones, *J. Amer. Chem. Soc.*, **90**, 5498 (1968).

(37) G. Heublein, *Z. Chem*, **6**, 221 (1966).

(38) G. Heublein and P. Umbreit, *Tetrahedron*, 24, 4733 (1968).

(39) C. F. Van Duin, *Rec. Trav. Chim.*, **43**, 341 (1924); **45**, 345 (1926).

(40) E. R. Trumbull and K. M. Ibne-Rasa, *J. Org. Chem.*, 28, 1907 (1963).

(41) P. L. Southwick and R. J. Shozda, *J. Amer. Chem. Soc.*, 81, 3298 (1959).

(42) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 338–340.

(43) W. Hückel and H. Waiblinger, *Ann.*, **666**, 17 (1963).

(44) (a) J. Weinstock, S. N. Lewis, and F. G. Bordwell, *J. Amer. Chem. Soc.*, 78, 6072 (1956); (b) L. H. Schwartzman and B. B. Corson, *ibid.*, 78, 322 (1956). The order for substituted styrene dibromides at 39.6° in methanol is given as: H (0.058), 2-CH_3 (1.74), 3-CH_3 (0.087), 4-CH_3 (0.30), 2,6-$(CH_3)_2$ (1.5), 2.5-$(CH_3)_2$ (2.4), 2,4-$(CH_3)_2$ (7.6), 3,5-$(CH_3)_2$ (0.12). Although these workers favor the SN2-E2 mechanism, their data are also consistent with the formation of an onium species.

(45) J. A. Berson and R. Swidler, *J. Amer. Chem. Soc.*, **76**, 4057 (1954).

(46) R. T. Dillon, W. G. Young, and H. J. Lucas, *ibid.*, **52**, 1953 (1930); R. T. Dillon, *ibid.*, **54**, 952 (1932); D. Pressman and W. G. Young, *ibid.*, **66**, 705 (1944).

2-butene dibromides, the rate increases roughly with the bulk and branching in the alkyl substituents. In fact, a rate increase in the order; $1:10^2:10^4$ for (secondary–secondary) > (secondary–tertiary) > tertiary–tertiary), have been demonstrated, where secondary and tertiary characterize alkyl-substituted 2-butene or cyclohexene dibromides.[43] As is well known, SN2 rate constants decrease in this same series.[22c] Excluding the electron-withdrawing groups, these series seem to follow an SN1 order, and in this sense are consistent with the iodide-assisted formation of onium species. (It is interesting that many of the AdE2 and AdE,N3 rate constants for bromide addition to the corresponding alkenes are affected by substituents in the same way as the elimination rates are.[30]) We believe that the SN1 rather than SN2 order of reactivity also amounts to compelling evidence against merged displacement–elimination transition states **11** and **12**.

Now consider the other substituents. Normally an α-carboxyl reduces the SN2 rate. Relative to ethylene dibromide as the SN2 standard, there is no rate reduction in acrylic acid dibromide. Judged by suitable model compounds,[22b,47] *meso*-**1** and *meso*-dibromosuccinic acid react *faster* with iodide ion than one would expect on an SN2–E2 path; on the other hand, their *dl* isomers have rate constants which may fall in the SN2 range. In this context, the relative reactivity by itself is inconclusive as a criterion of mechanism.

Conformational Analysis. It is now possible to make a conformational comparison for the *anti*-eliminations of *meso*-**1** and *dl*-**1** in process 1. In terms of eq 7, this could amount to a comparison of transition states resembling *erythro*- and *threo*-**6**. The required relation is given by eq 15, in which the terms G, $G^{\ddagger}$, and $\Delta G^{\ddagger}$

$$(G_{dl}^{\ddagger} - G_{meso}^{\ddagger}) = (\Delta G_{dl}^{\ddagger} - \Delta G_{meso}^{\ddagger}) + (G_{dl} - G_{meso}) \quad (15)$$

relate to the ground state, transition state, and activation free energies, respectively.[2,20,48] Since the value of $(G_{dl} - G_{meso}) = 0.78$ kcal/mol was found for the solvent benzene at 80°,[2,11] there is an uncertainty, albeit a small one, in doing the analysis for the solvent methanol. From our data we find $(\Delta G_{dl}^{\ddagger} - \Delta G_{meso}^{\ddagger}) \simeq 2.6$ and compute $(G_{dl}^{\ddagger} - G_{meso}^{\ddagger}) \simeq 3.4$ at 80° in kilocalories per mole. For the product stilbenes, we have $(G_{cis} - G_{trans}) = 3.7$ kcal.[5] The whole analysis is presented graphically in Figure 2. Taking all of the uncertainties into account, the uncertainity in the computed free energies can be taken as <0.5 kcal/mol. The conclusion from this analysis is that the transition states for iodide promoted debromination from **1** is "product-like."

If conformational analysis is applied generally to several addition reactions of the stilbenes, a pattern emerges. The relative rates of addition to *cis*- and *trans*-stilbenes, $k(cis)/k(trans)$, are 1.3 for bromine addition in methanol at 25°,[21a] *ca.* 0.7 for the addition of 2,4-dinitrosulfenyl chloride in acetic acid at 55°,[49] *ca.* 0.5 for peroxidation with phthaloyl peroxide in carbon tetrachloride at 80°,[50] *ca.* 1–2 for nitrosyl chloride and bromide additions in aprotic solvents,[51] *ca.* 1–2 for epoxidation, *e.g.*, with perbenzoic acid in benzene.[52] In all of these cases, the term $(\Delta G_{cis}^{\ddagger} - \Delta G_{trans}^{\ddagger})$ is relatively small, $(G_{cis}^{\ddagger} - G_{trans}^{\ddagger}) \simeq (G_{cis} - G_{trans})$, and the transition states are energetically "like" the reactant stilbenes. The energy scheme of Figure 2 would seem to be appropriate for other systems in which the energy difference was relatively large in the alkenes, *e.g.*, maleic and fumaric acids, and small in the saturated diastereoisomers.

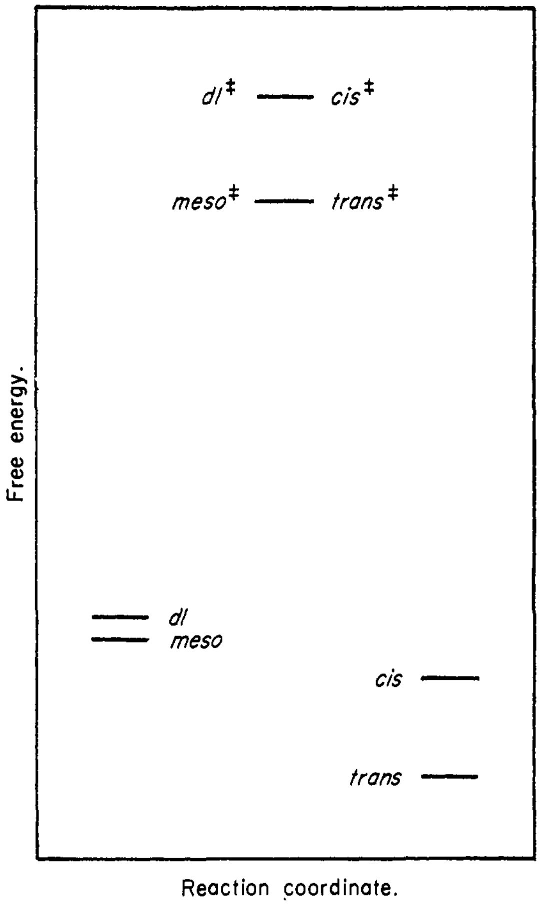


Figure 2. Conformational energy diagram for debromination of *meso*- and *dl*-stilbene dibromide to give *trans*- or *cis*-stilbenes. Apart from the reactant and product free energies whose positions may change slightly, this scheme applies to several interconversions between the stilbenes and various 1,2-diphenylethanes.

Acknowledgment. We wish to thank Dr. R. A. More O'Ferrall for some helpful discussion.

---

(47) A. Streitwieser, Jr., *Chem. Rev.*, 56, 571 (1956).

(48) W. K. Kwok and S. I. Miller, *Can. J. Chem.*, 45, 1161 (1967); W. G. Lee and S. I. Miller, *J. Amer. Chem. Soc.*, 82, 2463 (1960).

(49) N. R. Slobodkin and N. Kharasch, *ibid.*, 82, 5837 (1960).

(50) F. D. Greene, *ibid.*, 78, 2250 (1956).

(51) G. Heublein and G. Hübner, *Z. Chem.*, 7, 304 (1967).

(52) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955); W. Stumpf and K. Rombusch, *Ann.*, 687, 136 (1965).