

Debromination of *meso*- and *DL*-Stilbene Dibromides by Lithium Bromide in Dimethylformamide^{1a,b}

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In the title system, *meso*-stilbene dibromide gave *trans*-stilbene, while *dl*-stilbene dibromide gave both stilbenes, [*trans*]/[*cis*] \simeq (83 \pm 2)/(17 \pm 2). The rate data at 59.4° were, for *meso*, $\Delta H^\ddagger = 20.6$ kcal/mol and $\Delta S^\ddagger = -9$ eu; for *dl*, $\Delta H^\ddagger = 28.9$ kcal/mol and $\Delta S^\ddagger = 8$ eu; $k(\textit{meso})/k(\textit{dl}) = 50$. Stannous chloride proved to be an efficient scavenger in the *dl* reaction, for which rate data could not otherwise have been obtained. In methanol, lithium bromide is inert; in the aprotic solvent (DMF), it is an effective debrominating agent. A complete conformational analysis has been performed: the reactant free-energy difference in benzene at 80° has been measured, ($G_{dl} - G_{meso}$) = 0.78 kcal/mol; the transition state free-energy difference in DMF at 80° has been estimated, ($G^\ddagger_{dl} - G^\ddagger_{meso}$) \simeq 4.6 kcal/mol. Our rates show the trend, *anti* debromination of *meso* \gg *syn* debromination of *dl* \simeq *anti* debromination of *dl* $\gg \gg \gg$ *syn* debromination of *meso*, in accordance with the idea that "discrete" stereoelectronic and steric factors may make aligned or opposed contributions to the rates.

This study is concerned with the mechanism and stereoselectivity of the debromination of *meso*- and *dl*-stilbene dibromides (1) by bromide ion in dimethylformamide (DMF). In related work, we have investi-



gated several facets of dehalogenation, namely, kinetics, stereoselectivity, mechanism, nature of reductant and dihalide, medium effects, etc.²⁻⁴ At first glance, bromide ion might appear to be an impractical choice as a nucleophile: after all, bromine additions in the presence of bromide ion or the reverse of process 1 are commonplace. Nevertheless, the kinetics of dehalogenation by bromide ion of *meso* and *erythro* forms in aprotic solvents have been published recently.^{5,6} The scope of the reaction, as well as the difficulties likely to be encountered for *dl* forms, have also been surveyed.⁵ However, we were able to solve the problem of reversibility and associated problems for *dl*-1. Then, we could investigate DMF as a medium for eq 1, the nucleophilicity of bromide ion toward 1, and stereoselection in bromide-promoted debromination in an aprotic solvent.

Experimental Section^{1b}

Our DMF, lithium bromide, stannous chloride (95.5%), 1, and 2 have been described.^{2a,4a} Bromide ion was estimated with standard silver nitrate, either potentiometrically or by the eosin indicator method. Stannous chloride (~ 0.1 – 0.05 M) in DMF was diluted with water, acidified with concentrated sulfuric acid, and titrated with standard iodine to the starch end point.

Kinetic studies and some product identifications were made spectrophotometrically in Beckman DK-2 or Cary-11 spectro-

photometers. Since the extinction coefficients, ϵ , for *cis*- and *trans*-2 are much greater than those of the reactants, it was possible to monitor them in process 1.^{2c} When both stilbenes were produced, the ratio of [*cis*-2]/[*trans*-2] could be obtained by a method of simultaneous equations,⁷ or preferably as described below.

Kinetic Procedures.—For process 1, we used lithium bromide and 1 in DMF; the *dl*-1 runs also contained stannous chloride. This removes bromine on mixing in DMF, and does not interfere with product analysis. Incidentally, β -naphthol also appeared to be an excellent trap for bromine, but its ϵ (310 m μ) 750 and ϵ (297 m μ) 428 were high, and it reacted slowly with *dl*-1 at $\sim 25^\circ$ to produce *trans*-2. Acetone reacted too slowly with bromine to be useful.

In some of our first runs, the eliminations were carried out in a specially designed flask (Figure 1). The thermostated flask, containing lithium bromide in DMF was flushed with nitrogen; in the case of *dl*-1, stannous chloride solution was added at this time. With the stirrer going, an aliquot of 1 in DMF at thermostat temperature was added to the flask against a stream of nitrogen, and the port was then closed. Under these conditions, essentially no air oxidation of the stannous ion was observed. Aliquots were taken at intervals and analyzed as described below.

The ampule technique was used for most of the runs, particularly at the higher temperatures. Typically, solutions were made up at room temperature and distributed among nitrogen-flushed ampules, which were then capped and later sealed. The ampules were immersed in thermostated baths, removed after known periods, then cooled quickly in Dry Ice-acetone slush; later, the contents of the ampules were diluted with DMF and analyzed spectrophotometrically.

The eliminations were carried out under pseudo first order conditions with an excess of lithium bromide over stannous chloride and 1. The pseudo first order rate constants, k_ψ , were obtained from the slope of a plot of $\log(A_\infty - A)$ against t , where A_∞ and A are the optical densities at times, t_∞ and t , respectively. The second-order rate constants were obtained from $k = k_\psi/[\text{Br}^-]$ and were corrected for solvent expansion.⁸

Activation parameters were determined from Arrhenius plots and the standard relations (eq 4, ref 2a). All of the rate data are given in Tables I–III.

In the case of *dl*-1, both 2's were produced. Under pseudo first order conditions, it is possible to "follow" both products at 310 m μ and yet have a simple rate law. We take [*dl*-1] = a , L as the cell length, and C and T as labels for *cis*- and *trans*-2. If *dl*-1 disappears along one path, (2) applies; for $\epsilon_a \simeq 0$, we derive (3)

$$\ln a/a_0 = -k_\psi t \quad (2)$$

$$\ln(A_\infty - A) = -k_\psi t + \ln La_0(\epsilon_C F + \epsilon_T)/(1 + F) \quad (3)$$

in which $A_\infty = A_C + A_T$ and $F \equiv [\textit{cis}\text{-}2]/[\textit{trans}\text{-}2]$. On the other hand, if *dl*-1 decomposes along competitive paths to give both 2's, then we would have $k = k_T + k_C$ and $F = k_C/k_T$. The plots of

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

(8) "A Review of Catalytic and Synthetic Applications for DMF/DMAC," and Supplement; and "DMF", a product information bulletin, prepared and published by E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.

(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. This paper was presented in part at the 151st National Meeting, American Chemical Society, Pittsburgh, Pa., March 1966, Abstract 68 N. (b) Taken largely from the Ph.D. Thesis of W. K. Kwok, Illinois Institute of Technology, 1967. (c) Author to whom inquiries should be addressed.

(2) (a) I. M. Mathai and S. I. Miller, *J. Org. Chem.*, **35**, 3416 (1970); (b) I. M. Mathai, K. Schug, and S. I. Miller, *ibid.*, **35**, 1733 (1970); (c) C. S. T. Lee, I. M. Mathai, and S. I. Miller, *J. Amer. Chem. Soc.*, **92**, 4602 (1970); (d) W. K. Kwok and S. I. Miller, *ibid.*, **92**, 4599 (1970); (e) W. K. Kwok and S. I. Miller, *J. Org. Chem.*, in press.

(3) (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).

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

(5) (a) F. Badea, T. Constantinescu, A. Juvara, and C. D. Nenitzescu, *Justus Liebig's Ann. Chem.*, **706**, 20 (1967). (b) F. Badea, S. Rosca, I. G. Dinulescu, M. Avram, and C. D. Nenitzescu, *Rev. Roumaine Chem.*, **10**, 1201 (1965).

(6) (a) E. Baciocchi and P. L. Bocca, *Ric. Sci.*, **37**, 1182 (1967); (b) E. Baciocchi and A. Schirolli, *J. Chem. Soc. B*, 554 (1969).

TABLE I
DEBROMINATION OF meso-STILBENE DIBROMIDE BY BROMIDE IN DIMETHYLFORMAMIDE

Temp, ±0.05°	meso-Dibromide, M × 10 ³	LiBr, M × 10 ³	k, ^a M ⁻¹ sec ⁻¹ × 10 ³
59.40	11.27	9.31	2.36
	2.88	4.65	2.43 ^b
	2.31	8.79	2.27
	2.40	4.81	2.37
	0.51	4.86	2.38
	0.52	1.44	2.40
			k _{av} 2.36 ± 0.03
39.51	2.47	9.95	0.304
	11.74	9.96	0.301
	2.41	5.13	0.310
		k _{av} 0.305 ± 0.003	
49.50	2.39	9.35	0.864
	11.55	10.83	0.873
		k _{av} 0.869 ± 0.005	
50.20	0.52	5.15	0.892
	2.47	9.79	0.903
	0.52	9.28	0.916
	2.49	4.86	0.939
	0.52	1.44	0.945
		k _{av} 0.919 ± 0.018	

^a Reference 6 gives *k* values of 0.827 × 10⁻³ at 50.0° for sodium bromide and 7.35 × 10⁻³ at 25.0° for tetrabutylammonium bromide. ^b Run contains stannous chloride (5.84 × 10⁻³ M); *k* was not included in the average.

TABLE II
DEBROMINATION OF dl-STILBENE DIBROMIDE BY BROMIDE IN DIMETHYLFORMAMIDE

Temp, ±0.05°	dl-1, M × 10 ²	LiBr, M × 10 ²	SnCl ₂ , M × 10 ³	k, M ⁻¹ sec ⁻¹ × 10 ³ (1 + F) ^{-1a}
59.48	0.62	38.97	1.51	0.049
	2.97	46.85	7.75	0.047
	0.62	55.25	1.44	0.046
			k _{av} 0.047 ± 0.001	0.844
74.90	0.62	21.04	1.53	0.338
	2.92	20.30	5.52	0.306
	0.68	21.38	2.24	0.355
	2.86	15.75	5.94	0.367
				k _{av} 0.342 ± 0.019
83.90	0.64	8.82	1.94	1.17
	2.92	12.56	7.31	1.10
	0.65	8.91	7.37	1.11
	0.65	6.57	2.11	1.13
	0.13	3.74	0.53	1.15
			k _{av} 1.13 ± 0.02	0.837
85.44	0.32	4.63	1.09	1.25
	0.65	9.06	2.26	1.20 ^b
			k _{av} 1.23 ± 0.03	0.81
100.22	0.63	2.81	2.05	6.18
	0.67	3.52	1.98	6.03
	0.33	3.97	1.09	6.14
			k _{av} 6.12 ± 0.06	0.79

^a Fraction of *trans* in the stilbene product; *F* = [*cis-2*]/[*trans-2*]. ^b Water (0.1%) was added in this run.

the left-hand side of eq 3 against *t*, including 15–25 points, were, in fact, linear and gave the *k* values of Table II. Note that, if eq 3 is to apply, the partitioning factor *F* must remain constant and kinetic control of product formation must prevail. We evaluated *F* (Table II) from the intercept of plots of eq 3; this was far more convenient and reliable than a direct determination of *F* based on the optical density of the solution at two wavelengths.^{2,7}

A number of ancillary experiments are of interest. Rate constants for the reaction of *meso-1* with lithium bromide (39–60°) are the same in the presence or absence of stannous chloride. At higher temperatures, the debromination of *meso-1* by stannous

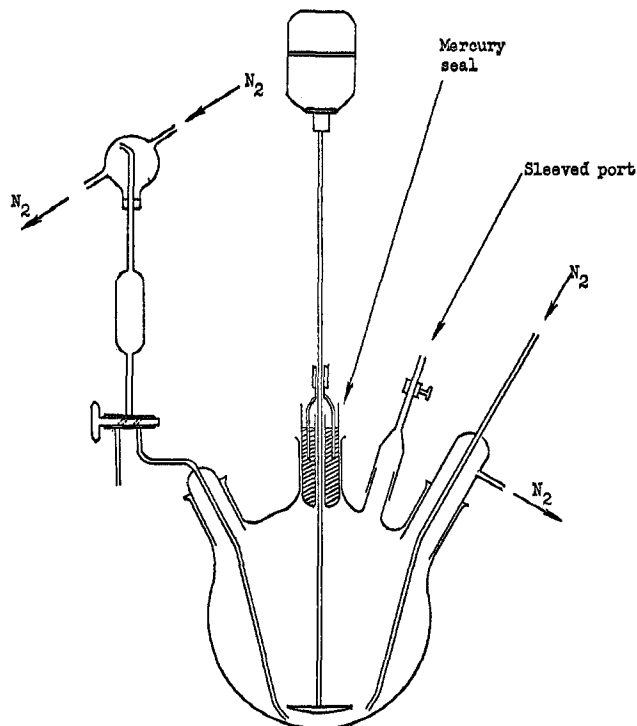


Figure 1.—Reaction vessel.

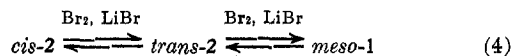
TABLE III
ACTIVATION PARAMETERS AND RATE CONSTANTS AT 59.4° FOR THE REACTION OF THE STILBENE DIBROMIDES WITH BROMIDE OR IODIDE IONS IN DIMETHYLFORMAMIDE

(C ₆ H ₅ -CHBr) ₂	X ⁻	ΔH [‡] , ^a kcal/mol	ΔS [‡] , ^b eu	k, M ⁻¹ sec ⁻¹ × 10 ³	k(<i>meso</i>)/k(<i>dl</i>)
<i>meso</i>	Li ⁺ Br ⁻	20.6	-9.0	2.36	50
<i>dl</i>	Li ⁺ Br ⁻	28.9	8.4	0.047	
<i>meso</i> ^c	Na ⁺ I ⁻	16.3	-15.1	74.2	154
<i>dl</i> ^c	Na ⁺ I ⁻	22.3	-6.9	0.481	

^a ±1.0 kcal/mol. ^b ±3 eu. ^c Reference 2a.

ion (50–75°) and by DMF (75°) does occur.^{2d} Although DMF dehydrobrominates *dl-1* in our temperature range,^{2b,c} this reaction is inhibited (fortunately) by stannous chloride. As for debromination of *dl-1*, adjustment of the ratio, [LiBr]/[SnCl₂], makes a kinetic study of either reductant feasible.^{2d}

In the absence of stannous chloride, the processes of elimination, addition, isomerization, and bromine consumption, all temperature dependent, may compete in our system



A fresh solution of *meso-1* (0.01 M) in DMF or lithium bromide (0.35 M) in DMF gave no color, but a solution of all three produced an immediate color similar to that obtained from solutions of bromine in DMF; after 19 hr at 36°, sodium iodide was added and titration with thiosulfate indicated ~82% reaction. *meso*- or *dl-1* (0.5 g) and lithium or ammonium bromide (5 g) in DMF (30 ml) at 70° for 48 hr gave *trans-2* (0.2 g) in ~80% yield.

trans-2 (1 g), lithium bromide (5 g), and bromine (1 ml) were left in DMF (50 ml) at room temperature for 2 days. Work-up of the products gave *meso-1* (0.6 g), mp 233–236°, from benzene; without lithium bromide, bromine addition appeared to proceed more slowly. Infrared examination of the residues established that *cis-2* and *dl-1* were absent. When similar experiments were carried out at 70° with or without lithium bromide, *trans-2* and little or no *meso* could be isolated.

It was shown that the oxidizing power of DMF solutions of bromine (0.33 M) fell rapidly, ~37% in 14 hr at 60°. Added bromide ion appears to retard the consumption of bromine. In the presence of bromine, the isomerization (eq 4) of *cis-2* to *trans-2* in DMF was found to proceed readily at 70–100°. In

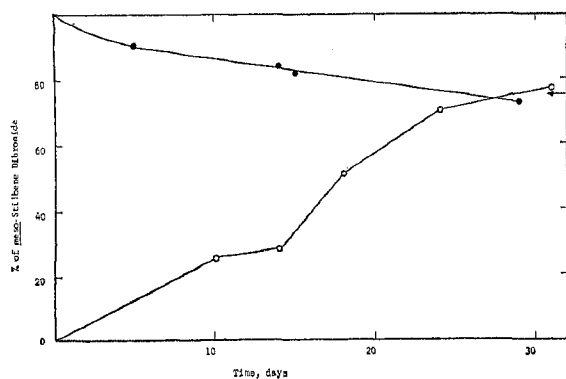


Figure 2.—Progress of the isomerization of *meso*- and *dl*-stilbene dibromide (1) in benzene at 80°. Starting compound (and a trace of I₂): ● *meso*-1; ○ *dl*-1. The arrow indicates 75% *meso*.

DMF alone, or with lithium bromide and/or stannous chloride, no isomerization of *cis*-2 occurred in 140 hr at 60–100°.

Isomerization of the Stilbene Dibromides (1).—Preliminary experiments indicated that a solution of *dl*-1 (0.5 g, 1.5 × 10⁻³ mol) and iodine (0.01 g, 4 × 10⁻⁵ mol) in benzene (10 ml) deposited *meso*-1 after 20 hr at 100° or 20 days at 25°. Equilibration studies were actually made on solutions which did not deposit *meso*-1, *i.e.*, *meso*-1 or *dl*-1 (0.35 g, 1.03 × 10⁻³ mol) and iodine (6 × 10⁻³ g) in benzene (40 ml) at reflux temperature (80°). After a fixed period, the solution was cooled, evaporated under reduced pressure, and the residue taken up in DMF (100 ml) containing sodium iodide (1.5 g, 0.01 mol). After 20 hr at ~25°, an aliquot (10 ml) of the DMF solution was titrated with standard sodium thiosulfate to the starch end point.^{2a} This gave the quantity of *meso*-1 in the mixture. Another portion of the solution was kept at 60° for 24 hr, then analyzed in the same way to give both [1]'s. In order to test the precision of the analysis, a blank was run with a mixture of *meso*-1 (0.1925 g) and *dl*-1 (0.1560 g) or [*meso*-1]/[*dl*-1] = 1.30. Our method gave the ratio 1.36: the accuracy was ~5%. Some results are given in Figure 2.

Results and Discussion

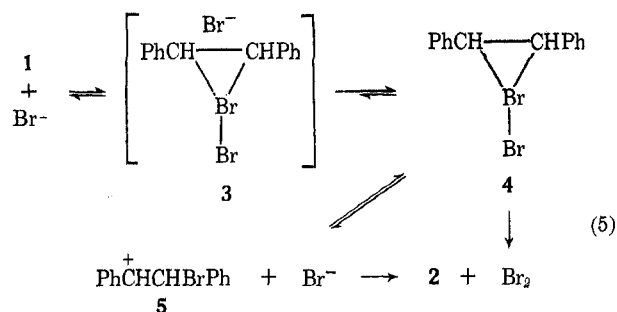
In DMF, process 1 was kinetically second order, first order in 1 and first order in lithium bromide. The stoichiometry of eq 1 was established, since high conversions (>98%) were observed spectrophotometrically. Although DMF debrominates *meso*-1 at 152°, and dehydrobrominates *dl*-1 at ~75°, these reactions did not complicate our kinetic studies.^{2b} With *meso*-1 and excess lithium bromide, process 1 is much faster than the solvent reaction and also appears to be irreversible. As for *dl*-1, we could not follow its kinetics according to eq 1, unless we added a scavenger to destroy the bromine produced. Stannous chloride proved to be efficient both for removing bromine quickly and for rendering the DMF ineffective as a dehydrobrominating agent; although stannous ion also reduces *dl*-1, the rate was relatively low under our conditions.^{2d}

A few general remarks about our system can be made. At 59.4°, *meso*-1 reacts ~50 times as fast with bromide ion as does *dl*-1. By taking into account product compositions, we can alter the comparison: $k(\textit{meso-1})/k(\textit{dl-1}) \approx 60$ for the production of *trans*-2 but ≈ 310 for the *anti* eliminations. Unlike iodide, bromide does not debrominate 1 in methanol;^{2c,3} yet their elimination rates are similar in DMF. This striking rate enhancement is presumably due to the large and favorable transfer energy (destabilization) of bromide ion between the two solvents.⁹

(9) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

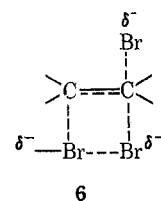
Lithium bromide may be associated. Assuming $K_a \approx 0.3$, Nenitzescu, *et al.*, were able to remove a trend in the rate constants in the debromination of *meso*-methyl dibromosuccinate by lithium bromide.^{5a} We found no such trend, perhaps because our salt concentrations were low. The possibility that both associated and free bromide ion are reacting adds to the complexity of the system.

The debromination by bromide ion converts *meso*-1 into *trans*-2 and *dl*-1 into 83 ± 2% *trans*-2 and 17 ± 2% *cis*-2. In the absence of a scavenger, *dl*-1 gives only *trans*-2. In the other papers of this series,² we have argued that a slow halide-promoted ionization, such as the formation of 3 in eq 5, provides a useful mechanistic



framework for such dehalogenations. The virtues of this scheme are that the steps can be telescoped to accommodate a concerted process, that the incursion of onium rearrangements or solvolysis in hydroxylic solvents is possible, that the intermediates 3–5 can linger if the energetic barrier they face is unfavorable, and, most important, that polar debromination and bromine addition mechanisms in protic and aprotic solvents are unified.² Here we assume that the *dl*-1 reaction is diverted, at least in part, through the open onium ion 5 which can be partitioned to give both 2.²

Although other mechanistic possibilities cannot be ruled out in specific cases,^{10–12} we believe the weight of the evidence favors eq 5.² Some of these are recalled. A concerted *anti* elimination from *meso*-1 could account for the stereospecific production of *trans*-2, and various combinations of the following *discrete* processes could conceivably account for the *dl* product, namely *anti* elimination, *syn* elimination, and displacement followed by elimination. Alternatively, the merged transition state 6 could lead either to *anti* elimination or



isomerization of *dl*-1 to *meso*-1. Note that in general each one of the many recognized halogen addition mechanisms, *e.g.*, attacks led by halogen or halide in second, third, and complex rate laws, is necessarily the reverse of a dehalogenation. While eq 5 includes a number of these, which involve 1 and halide ion in a rate-determining step, there must, of course, be other

(10) D. V. Banthorpe, "Elimination Reactions," Elsevier, New York, N. Y., 1963, Chapters 1, 6.

(11) J. Csapilla, *Chimica*, **18**, 37 (1964).

(12) J. Mulders and J. Nasielski, *Bull. Soc. Chem. Belg.*, **72**, 322 (1963).

dehalogenation paths for some 1,2-dihalides and for other reaction conditions.

In addition to previous rationalizations of eq 5, we now find that the product ratio from *dl*-1 is essentially constant over the temperature range (Table II). Our interpretation is that there is one rate-determining step and rapid partitioning of unstable intermediates (*e.g.*, 4, 5),^{2b} rather than two or more competitive slow steps to 2. Secondly, we find that in the debromination of *dl*-1 in DMF $k(\text{Br}^-)/k(\text{I}^-) \simeq 0.1$ (Table III). Since bromide ion is a more powerful nucleophile than iodide toward carbon in S_N2 processes in DMF,⁹ we believe that observed rate ratio is a strong indication that rate-determining displacement¹⁰ or a merged transition state (6)¹¹ are *not* involved in process 1.¹³

Conformational Analysis.—In systems such as ours, conclusions about conformational effects are best made when all of the necessary energy terms are at hand.¹⁴ The determination of the equilibrium constant for the isomerization of 1 had never been done satisfactorily. Eliel cites the figure $K \simeq 4$, on the basis of work by Buckles.¹⁵ Because their spectra lack strong character-



istic absorptions in the wavelength region accessible to us, ir and uv analysis of 1 could not be used. (During the period of our work, however, Heublein devised a convenient method of analysis for mixtures of 1 based on their ir absorption spectra below 600 cm⁻¹.¹⁶) We found that the low solubility of *meso*-1 in several solvents, *e.g.*, carbon tetrachloride, DMF, benzene, acetonitrile, methanol, precluded accurate nmr analysis. Buckles promoted the isomerization of 1 by bromine vapor on the solid, and estimated the product composition, after recrystallization, from its melting point.

Although our analytical procedure for mixtures of 1 was not elegant, it did work (Experimental Section). It is based on selective debromination rates with iodide in DMF: the relative rate of reaction of *meso*-1 and

dl-1 is ~ 320 at 36°. ^{2a} DMF cannot be used as the solvent for the isomerization (eq 6) because it debrominates *meso*-1 and dehydrobrominates *dl*-1.^{2e} Benzene was suitable for the equilibrium measurements; both 1's, at concentrations below the saturation value of *meso*-1, could be equilibrated at 80°. As shown in Figure 2, the approach to equilibrium is slow. At 80°, the value $K = [\textit{meso-1}]/[\textit{dl-1}] = 3.0 \pm 0.3$ or ($G_{dl} - G_{meso}$) = 0.78 \pm 0.1 kcal/mol.

It is now possible to look at the conformational terms that contribute to the *dl*-1 vs. *meso*-1 rates at 80° (eq 8, ref 2a).^{2,4,14} A minor assumption is that the ground state free energy difference determined in benzene can be used for DMF.¹⁷ Since ($\Delta G_{\ddagger dl} - \Delta G_{\ddagger meso}$) = 3.8 for the *anti* eliminations, ($G_{\ddagger dl} - G_{\ddagger meso}$) = 4.6 \pm 0.2 kcal/mol. Since the products have ($G_{cis} - G_{trans}$) = 3.7 \pm 0.1 kcal/mol, one might be inclined to say that the transition states in eq 1 are "product like." Because the transition state difference is *not* bracketed, or ($G_{dl} - G_{meso}$) < ($G_{\ddagger dl} - G_{\ddagger meso}$) < ($G_{cis} - G_{trans}$), it is clear that conventional analogies of the type contained in the Hammond postulate, the Brønsted α , etc. are inadequate.⁴ Judging from the activation parameters in Table III, the mix of enthalpy and entropy contributions in the transition states of *meso*- and *dl*-1 are substantially different. If the transition states of the rate determining step of eq 1 do, in fact, resemble 3, then there are obvious reasons, such as shape, charge distribution, etc., for their properties not to lie between those of reactants and products.

The preceding analysis is consistent with a rather general approach to stereoselection. *anti* elimination is favored *stereoelectronically* or by favorable orbital symmetry and energies of the reacting centers.¹⁴ The total structure, however, is subject to geometric or bulk limitations which we label as the *steric* factor (for lack of a more elegant term).¹⁴ For the *anti* eliminations, both factors are favorable for *meso*-1 and opposed for *dl*-1; for hypothetical *syn* eliminations, both factors are unfavorable for *meso*-1 and opposed for *dl*-1. We can expect, therefore, the kind of rate sequence implicit in Table III: *anti* debromination of *meso* >> *syn* debromination of *dl* \sim *anti* debromination of *dl* >>> *syn* debromination of *meso*.

Registry No.—*meso*-1, 13440-24-9; *dl*-1, 13027-48-0; lithium bromide, 7550-35-8.

(17) (a) R. J. Abraham, L. Cavalli, and K. G. R. Pachler, *Mol. Phys.*, **11**, 471 (1966); (b) L. I. Peterson, *J. Amer. Chem. Soc.*, **89**, 2677 (1967).

(13) According to our mechanism, the higher proportion of *trans*-2 formed from *dl*-1 with bromide ion as compared with iodide ion would depend on the fate of 4 as compared with its iodo analog (Table III). We find it difficult to rationalize these results convincingly.

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

(15) (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 25; (b) R. E. Buckles, W. E. Steinmetz, and N. G. Wheeler, *J. Amer. Chem. Soc.*, **72**, 2496 (1950).

(16) (a) G. Heublein, *J. Prakt. Chem.*, **31**, 84 (1966); (b) G. Drefahl and G. Heublein, *ibid.*, **21**, 18 (1963).