Stereoselectivity in the Debromination of the Stilbene Dibromides with Stannous Chloride in Dimethylformamide[1a,b]

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Abstract: The debromination of *meso-* or *dl*-stilbene dibromide by stannous chloride in dimethylformamide is a second-order reaction. The rate data at 59.4° are as follows: for *meso*, $k = 3.73 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$, $\Delta H^{\ddagger} = 15.5$ kcal/mol, $\Delta S^{\ddagger} = -28$ eu; for *dl*, $k = 3.36 \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$, $\Delta H^{\ddagger} = 19.3$ kcal/mol, $\Delta S^{\ddagger} = -21$ eu. The *meso* gives only *trans*-stilbene, while the *dl* gives *ca.* 95% *trans-* and 5% *cis*-stilbene over the range 60–100°. A concerted E2 process seems appropriate for *meso*, but this is difficult to verify. The formation of a tin(III) species in a bromine atom (one electron) transfer is proposed as the slow step for *dl*; this reaction is completed by another one-electron step involving the radical intermediates (7). A conformational analysis and product patterns of this system are consistent with the proposed mechanisms.

To what extent can the stereoselectivity of a given debromination be affected by the reductant? We have explored this problem both qualitatively and quantitatively, first for *sym*-tetrabromoethane[2,3] and, in this series of papers, for the stilbene dibromides. Numerous dehalogenating agents have now been examined, among them tin(II);[4] kinetic data for the reductants, iodide,[5,6] bromide,[7] chloride,[8] thiosulfate,[9] and dimethylformamide,[8] have been obtained. Here we show that debromination by stannous ion, a redox elimination, can be studied kinetically.

$$\underset{meso\text{ or }dl}{C_6H_5CHBrCHBrC_6H_5} + SnCl_2 \xrightarrow{\text{DMF}} \underset{trans\text{ or }cis}{C_6H_5CH{=}CHC_6H_5} + SnCl_2Br_2 \quad (1)$$

Reductive eliminations by chromium(II) of *erythro-* and *threo*-2-bromo-3-butyl derivatives and by pentacyanocobaltate(II) of *meso-* and *dl*-dibromosuccinate dianion have been reported.[10] Otherwise, such quantitative studies have usually been limited to iodide attacks on 1,2-dibromides.[5,6] In this respect, we believe the use of tin(II) is new: we are not aware of any quantitative studies involving tin(II) and organic oxidants. In fact, the number of kinetic studies of tin(II) with inorganic species is small,[11–14] surprisingly so, because it is such a widely used reductant.

Experimental Section[1b]

Since the instruments, materials, analyses, blanks, kinetic methods, competing processes, etc., have been described in companion papers,[5–8] we can be brief.

Although some of the kinetic runs at the lower temperatures were made in batches in a special flask,[7] the ampoule technique was used for most of the work. In either case, the formation of the stilbenes was followed spectrophotometrically (310 mμ). We found it essential to work under pseudo-first-order conditions, that is, with a 15–20-fold excess of stannous chloride over the stilbene dibromides. Typically, our pseudo-first-order plots of $\log(A_\infty - A)$ *vs.* time (A = optical density) were satisfactorily linear for three half-lives. The slopes of these plots gave $k(\psi)$. The second-order rate constants, k, were obtained from the quotient, $k(\psi)/[SnCl_2] = k$. (The concentration of the stannous chloride had been corrected for solvent expansion.) Judging from A_∞, the reaction went to 97% completion. The composition of the product was also determined spectroscopically.[7] All of the data are collected in Tables I–III.

Table I. Debromination of *meso*-Stilbene Dibromide by Stannous Chloride in Dimethylformamide

Temp, ±0.05°	*meso*, $M \times 10^3$	$SnCl_2$, $M \times 10^3$	k_2, M^{-1} sec^{-1} $\times 10^{3\,a}$	$k(meso)/k(dl)$
50.10	4.62	71.44	0.170	
	15.71	254.7	0.207	
	7.60	118.7	0.188	
	11.65	180.6	0.203	
	2.17	40.1	0.167	
		k_{av}	0.187 ± 0.015	
		k^0	0.160 ± 0.005	
59.41	2.12	27.65	0.362	
	4.65	68.5	0.390	
	4.26	74.98	0.377	
	7.50	118.77	0.383	
	2.87	40.45	0.352	
		k_{av}	0.373 ± 0.013	11.2
		k^0	0.352 ± 0.013	
74.8	2.81	38.91	1.11	
	4.43	75.86	1.12	
	2.11	29.90	1.07	
	7.07	111.39	1.15	
		k_{av}	1.11 ± 0.02	9.1
		k^0	1.06 ± 0.018	
59.4^b	14.9	148.5	0.765	
	13.1	149.2	0.745	
	10.8	148.6	0.773	
	9.0	148.7	0.762	
		k_{av}	0.761 ± 0.008^b	

[a] k_{av} is the mean value for the runs with an average deviation indicated. k^0 is the value obtained by a least-squares extrapolation to zero stannous chloride concentration; the standard deviation is indicated. Occasionally a "bad" point is not included in these k values. [b] These runs were made with the dihydrate, $SnCl_2 \cdot 2H_2O$.

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Table II. Debromination of *dl*-Stilbene Dibromide by Stannous Chloride in Dimethylformamide

Temp, ±0.05°	*dl*, $M \times 10^3$	$SnCl_2$, $M \times 10^2$	k_2, M^{-1} sec^{-1}, $\times 10^4$ [a]	F[b]
59.4	4.60	7.50	0.347	0.94
	7.38	11.12	0.317	0.96
	11.78	19.88	0.343	0.95
			k_{av} 0.336 ± 0.032	
74.83	4.55	7.40	1.29	0.96
	2.52	3.77	1.11	0.98
	7.11	11.00	1.20	0.98
	11.54	19.34	1.26	0.94
			k_{av} 1.22 ± 0.06	
			k^0 1.15 ± 0.08	
82.60	4.44	7.36	2.22	0.98
	2.33	3.71	1.98	0.94
	6.96	10.96	2.28	0.98
	11.45	19.72	2.22	0.97
	22.92	39.24	2.48	0.91
	38.26	65.97	2.73	0.90
			k_{av} 2.32 ± 0.19	
			k^0 2.07 ± 0.06	
101.76	4.44	7.24	10.17	0.92
	2.28	3.63	9.67	0.93
	6.88	10.84	10.28	0.94
	12.55	21.67	10.42	0.90
	11.21	19.21	10.38	0.93
			k_{av} 10.18 ± 0.21	
			k^0 10.08 ± 0.04	

[a] See Table I. [b] F = fraction of *trans* in the stilbene product. See ref 7 for the uv method of analysis.

Since k increased slightly with increasing stannous chloride concentration, we treated the results in two ways. The results for the different runs were simply averaged to give k_{av}. Alternatively, k was extrapolated to k^0 at zero stannous chloride concentration. These rate constants were used to compute the activation parameters of Table III. For consistency, we shall use k_{av} and activation parameters derived from k_{av} for our discussion. No serious error would be involved, however, if the extrapolated value of k were in fact correct.

Since bromide ion is a competing reductant in this system,[7] it was instructive to define its role. Our first experiments were carried out with *meso*-dibromide and stannous chloride hydrate at comparable concentrations. The disappearance of stannous ion was followed titrimetrically.[7] The rate constants, which were calculated by the standard second-order rate expression, increased as the time or bromide ion concentration increased (Figure 1). This behavior suggested autocatalysis, that is, the product bromide may be reacting with the *meso*-dibromide. By extrapolating the rate constants to zero bromide ion concentration, we obtained a value of 7.0 × 10^{-4} in reasonable agreement with the value of 7.61 M^{-1} sec^{-1} obtained under pseudo-first-order conditions (Table I).

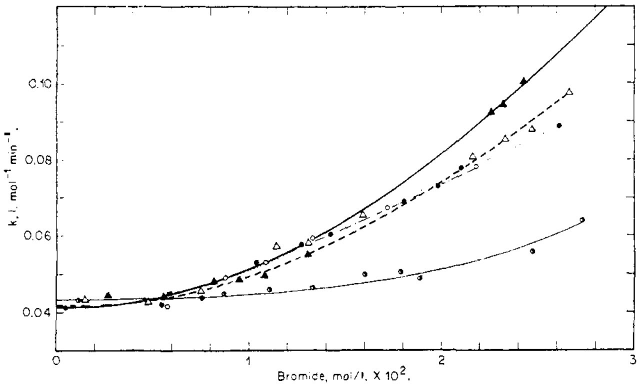


Figure 1. Reaction between *meso*-stilbene dibromide with stannous chloride hydrate at 59.4° under second-order conditions (five runs included).

The competition for *meso*-dibromide by bromide and stannous chloride was examined in another way. Two kinetic runs were made up to 0.05155 and 0.02758 M lithium bromide, respectively; each run had 0.1488 M stannous chloride hydrate and 0.010865 M *meso*-dibromide. By plotting A of *trans*-stilbene *vs.* time, we could then estimate the initial slopes (v^0) of these curves graphically.[1b] This in turn led us to estimate $k \simeq 0.0021$ M^{-1} sec^{-1} (eq 2, 3) for the reaction of lithium bromide with *meso* at 59.4°, which approaches the precise value 0.00236 M^{-1} sec^{-1}.[7]

Table III. Rate Data for Debromination of the Stilbene Dibromides in DMF at 59.4°

		NaI[a]	LiBr[b]	LiCl[c]	$SnCl_2$
meso	$\Delta H^{\ddagger}$, kcal/mol	16.3	20.6	21.6	15.5[d]
	$-\Delta S^{\ddagger}$, eu	15	9.0	9.1	28
dl	$\Delta H^{\ddagger}$, kcal/mol	22.3	28.9		19.3[d]
	$-\Delta S^{\ddagger}$, eu	7	−8.4		21

[a] Reference 6. [b] Reference 7. [c] Reference 8; the *dl* is dehydrobrominated. [d] Values computed by least squares from k_{av} of this study. From k^0, we find $\Delta H_{meso}^{\ddagger} = 16.4$ and $\Delta H_{dl}^{\ddagger} = 19.2$ kcal/mol. The uncertainty in $\Delta H^{\ddagger}$ is set at *ca.* 1 kcal/mol and in $\Delta S^{\ddagger}$ *ca.* 3 eu.

The basis of this method follows. The rate of formation of stilbene (S) from stilbene dibromide (SBr_2) is given by expression 2.

$$d[S]/dt = v = (k_b[Br^-] + k_s[SnCl_2])[SBr_2] \quad (2)$$

If only the bromide ion concentration is varied between two runs, we can write eq 3

$$v_1 - v_2 = k_b[SBr_2]([Br^-]_1 - [Br^-]_2)$$

or

$$k_b = [SBr_2]([Br^-]_1 - [Br^-]_2)/(v_1 - v_2) \quad (3)$$

At time zero, the bromide ion concentration is known, and v can be estimated.

Results and Discussion

Provided that their reaction with bromide ion is minimized, the stilbene dibromides react with stannous chloride according to the stoichiometry of eq 1. The process is first order in organic dibromide and first order in stannous chloride (anhydrous or dihydrate). The reaction of *meso* is stereospecific and leads to *trans*-stilbene; the reaction of *dl* is stereoselective and leads to both stilbenes, *ca.* 92–96% *trans* and *ca.* 4–8% *cis*.

Several rate comparisons for process 1 at 59.4° are possible. Overall, $k(meso)/k(dl) = 11.1$. For the production of *trans*-stilbene, $k(meso)/k(dl) = 11.6$. For *anti* processes only, $k(meso)/k(dl) \simeq 220$.

In Table III, we compare the activation parameters for debrominations of the stilbene dibromides in DMF. Although the *meso* rate constants for the nucleophiles, bromide, chloride, and stannous chloride, fall within a factor of 6 at 59.4°, the activation quantities differ widely. A similar effect is found with *dl*. The extreme values for stannous chloride are probably significant. Judging from a table of solvation enthalpies,[15] we would expect that, among those oxidized species relevant to Table III, tin(IV) would have by far the highest value. This could account for the lowered $\Delta H^{\ddagger}$ for tin(II). At the same time, the reorientation of solvent to coordinate with the tin could lead to the relative decrease in $\Delta S^{\ddagger}$. Although we have provided a rationale for the large observed energy–enthalpy compensation, the details of this balance are not at all clear.

Conformational Analysis. To characterize the transition states, we examine the free energy pattern of the reaction.[2,6,7,16] The basic relation, eq 4, has been used to obtain the left-hand term

$$(G_2^{\ddagger} - G_1^{\ddagger}) = (\Delta G_2^{\ddagger} - \Delta G_1^{\ddagger}) + (G_2 - G_1) \quad (4)$$

and this has been listed in Table IV. Although eq 4 is independent of the paths taken by *dl* and *meso*, any comparison should take these into account explicitly. Since we shall argue (below) that the mechanistic routes to *trans*-stilbene from *meso* and *dl* are probably different, we do not consider it useful to attempt to compare the transition states. On the other hand, the *anti* processes from *meso* and *dl may be* bimolecular, single-step, eliminations.

Table IV. Conformational Analysis at 59.4° for the Reactions of Stilbene Dibromides with Stannous Chloride in Dimethylformamide[c]

	$(G_{dl} - G_{meso})^a$	$(\Delta G_{dl}^{\ddagger} - \Delta G_{meso}^{\ddagger})$	$(G_{dl}^{\ddagger} - G_{meso}^{\ddagger})$	$(G_{cis} - G_{trans})^b$
anti process	0.78	3.6	4.4	3.8
anti products	0.78	1.6	2.4	3.8

[a] These figures actually apply to the reactants in benzene at 80°. [b] Data for the stilbenes are from ref 17. [c] Units are kilocalories per mole.

The free-energy difference in the two transition states, 4.38 kcal/mol at 60°, appears to be closer to that of the product stilbenes than that of the reactants, but is not bracketed. Fortunately, the *cis–trans* free energy

$$(G_{dl}^{\ddagger} - G_{meso}^{\ddagger}) > (G_{cis} - G_{trans}) > (G_{dl} - G_{meso}) \quad (5)$$

of isomerization is now known accurately, and we do have a reasonable estimate of $(G_{cis} - G_{trans}) = 3.8$ kcal/mol at 60°.[17]

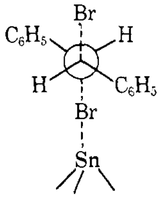
The situation in eq 5 in analogous to a Brønsted α which lies outside the range 0–1.0; clearly, Hammond's postulate is also inapplicable.[18] Possibly the simplest interpretation of eq 5 is that one *cannot* assume that the two *anti* processes are similar.

Mechanism. First, some comments on the tin species may be useful. Reports indicate that the favored coordination numbers are three for tin(II)[11,19] and four to six for tin(IV).[20] The tin(II) is probably coordinated to the oxygen,[11] since we find that the ir carbonyl frequency shifts from 1665 in pure DMF to 1650 cm^{-1} in DMF solutions saturated with stannous chloride.

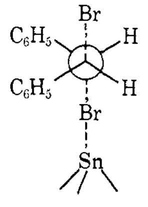
Free chloride ion also reacts with the stilbene dibromides: the debromination of *meso* with stannous chloride is somewhat slower than with chloride; the debromination of *dl* by stannous chloride to yield stilbene is *ca.* four to five times slower than the dehydrobromination of *dl* by chloride to yield bromostilbene.[8] Since no dehydrobromination of *dl* was observed here, we believe that there was little, if any, dissociation of the stannous chloride. Moreover, the stannous chloride concentration was varied widely in this study, yet the stoichiometric concentrations gave satisfactory rate constants. For these reasons, we consider $Cl_2(DMF)$-Sn: to be the important reacting tin species; electron transfer presumably takes place from tin(II) to the bromine of the organic bromide as in **1** and **2**.

Process 1 involves the ionization of a neutral species and should be facilitated by solvents of high polarity.[21] We do, in fact, find that the stannous chloride is "faster" in high concentrations than when it is dilute and/or anhydrous (Tables I, II). A similar effect of water was observed in 1,2-dehalogenations with lithium aluminum hydride in tetrahydrofuran.[22]

Superficially, the *anti* debrominations, *e.g.*, *meso* → *trans* and *dl* → *cis*, might seem straightforward, that is, concerted E2.[6–8] The *anti* alignment in **1** and **2** would, of course, be favored by the orbital symmetry rules.[16,23] In the case of *meso* (**1**), the favored orbital configuration is aligned with a conformational preference; in the case



1 *meso*



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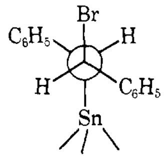
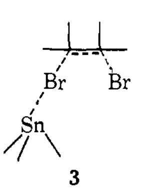


5 *erythro*



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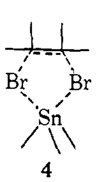

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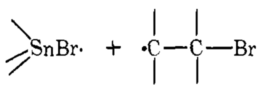

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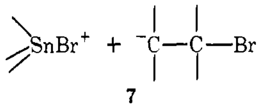

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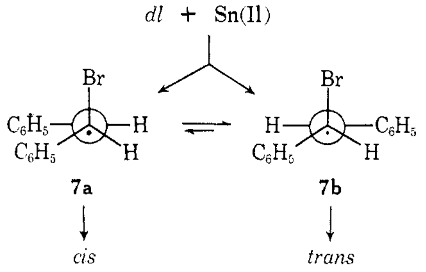
of *dl* (**2**), these factors are opposed. Energetically, we have seen that this opposition amounts to a free energy difference of *ca.* 4.4 kcal/mol in **1** and **2** (Table IV). Now, the major product (*ca.* 95%) in the case of *dl* is the result of a net *syn* elimination. To avoid the unfavorable *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]

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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-

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