mixture of inseparable isomers as determined by nmr and mass spectroscopy.

Phenyl 2-Chloro-1-phenylethene Disulfide (XIII).—A solution of 0.268 g (2.44 mmol) of thiophenol in 5 ml of dry ether was added to a stirred solution of 0.50 g (2.44 mmol) of XII in 20 ml of dry ether at room temperature. After 15 min the ether was evaporated *in vacuo* to leave 0.68 g (100%) of viscous, rather unstable yellow liquid (XIII): nmr (CCl_4) 6.49 (s, 1, vinyl H) and 7.19 (m, 10, ArH). The mass spectrum showed no parent ion but proved the incorporation of thiophenol by the spectrum's base peak at 109 (PhS).

Addition of diethylamine to XII in the same fashion afforded the unstable N,N-diethylsulfenamide derivative (XIV): nmr (CCl_4) 1.06 (t, 6, methyl H), 2.80 (q, 4, methylene H), 6.30 (s, 1, olefinic H), and 7.31 (complex m, 5, ArH).

General Procedure for Competition Reactions.—A solution of 0.5 equiv of sulfur dichloride in 10 ml of dry ether was added over 15 min to a stirred solution containing 1 equiv each of alkene and alkyne in 20 ml of dry ether at 30° (molar ratio, SCl_2 to alkene to alkyne of 0.5:1:1). Stirring was continued for 0.5 hr and the solvents were evaporated. Products were immediately examined by nmr and areas were correlated to the relative amounts of the various products.

Registry No.—Sulfur dichloride, 10545-99-0; III, 23852-88-2; IV, 2326-63-8; Va, 23852-90-6; Vb, 23852-91-7; Vc, 23852-92-8; VIII, 23852-93-9; IX, 23852-94-0; XII, 23852-95-1.

Acknowledgments.—The authors are indebted to both the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health, Public Health Service (Grant GM 16689-01), for support of this work.

Stereoselectivity in the Debromination of the Stilbene Dibromides by Several Metals and Inorganic Reductants in Several Solvents[1a]

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If *meso*-stilbene dibromide is debrominated by any reductant in any solvent, the product is always 100% *trans*-stilbene. With *dl*-stilbene dibromide, the debromination results are variable: two-electron reductants such as iodide, platinum(II), benzenesulfinate, thiophenolate, and hydride yield *ca.* 75–90% *cis;* one-electron reductants, such as β-naphthol, copper(I), iron(II), chromium(II), titanium(III), etc., yield *ca.* 0–4% *cis;* metals such as zinc, cadmium, tin, etc., in a variety of solvents, yield variable quantities of *cis* (<25%). We have tentatively suggested a carbonium ion process (eq 4) for the two-electron reductants, a radical process for the one-electron reductants, and a surface radical process for the metals. Three factors appear to determine the stereochemical course of these redox reactions, namely, the electronic (orbital) and conformational preference for *anti* over *syn* elimination and the nature of the reductant (mechanism).

Normally, 1,2 dehalogenation in solution occurs in the *anti* sense[2,3] as is shown in the following equation.

$$\underset{meso\ \text{or}\ dl}{(C_6H_5CHBr)_2} + M \longrightarrow \underset{trans\ \text{or}\ cis}{C_6H_5CH{=}CHC_6H_5} + MBr_2 \qquad (1)$$

There are enough interesting cases of *syn* dehalogenation, however, to make decisions about the mechanism(s) equivocal.[3-7] In this survey of reductants, we posed two questions: could we find conditions under which the debrominations of the stilbene dibromides were clearly *anti*, and equally could we find conditions under which these debrominations were wholly *syn?*

As a reaction type, dehalogenation goes back a long time; iodide-promoted elimination was used on coumarin dibromide by Perkin[8] and has since been used in series as simple as the 1,2-diiodoethylenes[3] or as complex as steroid dibromides.[9] Variants on the dihalide may include substitution of hydroxy, alkoxy, acetoxy, tosylate, etc., for one or both of the halogen atoms.[2,10] Among the many possible dehalogenating agents are sodium in tetrahydrofuran[11] or liquid ammonia,[12] iron(II),[13] vanadium(II),[14] titanium(III),[14] cadmium,[15] lithium,[16] phosphines,[17] phosphites,[18] thiolates,[19] selenide,[20] acetate,[17] carbonate,[17] hydroxide,[19] triethyltin hydride,[21] cobalt(II),[22] etc.[9b] (see also below and Tables I and II). It is useful to look at the overall process (eq 1) either as a nucleophilic attack on positive halogen or as a redox process involving a two-electron reduction of the dihalide (oxidant).[10]

meso-Stilbene dibromide has frequently been chosen as a model compound. However, the results of debromination are always the same: under a wide variety of conditions, *trans*-stilbene is the exclusive product. Some results have been tabulated;[9b] we shall indicate several reductants here: ethanol,[23] phenyl-

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[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Presented: Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, 36P. (b) To whom inquiries should be addressed.

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TABLE I

REDUCTIVE ELIMINATION REACTIONS OF *dl*-STILBENE DIBROMIDE[a]

Reductant	Conditions	*cis*-Stilbene, %[b]
NaI	Acetone	96
	DMF	90
	Acetonitrile	88
	1-Propanol	88
	MEK	95
	Ethanol[c]	93
	Glycol ether	92
	DMSO	89
	Methanol[d]	65
LiBr[e]	DMF 50–100°	16
K_2PtCl_4	DMSO	85
$C_6H_5SO_2Na$[f]	DMSO	88
	DMF	89
	Ethanol	...[g]
p-$CH_3C_6H_4SNa$[f]	Ethanol	>75[h]
	DMF	>75[h]
	DMSO	>75[h]
$LiAlH_4$[i]	THF, −10° (and 25°)	95 (and 50–65)
$NaBH(OCH_3)_2$[i]	Diglyme, 1 hr, 25°	0
$NaBH_4$[i]	Diglyme, 0.5 hr, 25°	25
NaH[j]	HMPA, 35°	27
$SnCl_2/HgCl_2$[e]	DMF, 25°	0
$SnCl_2$[k]	DMF, 50–75°	6 ± 3
$SnCl_2$	Ethanol	33–40[h]
	DMSO	26[h]
C_6H_5MgBr	Ether, 6 hr, *ca.* 25°	0
$Na_2S_2O_3$[l]	$CH_3OH-(CH_3)_2CO$ (3:1), 70–100°	Trace
β-Naphthol[l]	DMF, 25°	0
$(C_6H_5)_3P$	Toluene	0[g]
Di-*p*-tolylmercury[m]	$C_6H_5CH_3$, 25°, 4*d*	0
CuCl	Ethanol	...[g]
	DMF	0–5
	Ethanol, Dipy	0–5
	Ethanol, Py	0
	Ethanol, Pda	0
	Ethanol, Pyo	<15[h]
	Ethanol, Dma	...[h]
	DMSO	0–2
$FeCl_2$	Ethanol	...[g]
	Ethanol, Dipy	0–5
	Ethanol, PyO	2
	DMF	0
	DMSO	0
$CrCl_2$	Ethanol	0–4
	Ethanol, Dipy	0–1
	DMF	0–2
	DMSO	0–3
$TiCl_3$[n]	Ethanol	4
	DMF	12[h]
$CoCl_2$	Ethanol, NaCN	<32[h]

[a] The reactions were usually run for *ca.* 48 hr at the boiling point of the solvent or at 60–70° in the case of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), unless otherwise specified. Other reagents are tetrahydrofuran (THF), methyl ethyl ketone (MEK), dipyridyl (Dipy), pyridine (Py), *o*-phenylenediamine (Pda), pyridine N-oxide (Pyo), and dimethylaniline (Dma). The reactions were complete, unless otherwise indicated. [b] This is the fraction of *cis*-stilbene in the *cis–trans* mixture. The actual yield may be lower. [c] Reference 34 reports 45 ± 10% reaction after 22 hr at reflux in 95% ethanol. The product contains 69 ± 5% *cis* isomer. [d] Reference 4 reports *ca.* 50% solvolysis products, *ca.* 30% *trans*-stilbene, and *ca.* 20% *cis*-stilbene. [e] Reference 6. The reaction mixture contains stannous chloride to reduce the bromine. In the absence of stannous chloride the product is 100% *trans*-stilbene. [f] R. Otto [*J. Prakt. Chem.*, **53**, 1 (1896)] and R. Otto and F. Stoffel [*Chem. Ber.*, **30**, 1799 (1897)] report 100% *cis* isomer with thiophenoxide in ethanol. [g] The reaction was incomplete after 48 hr at reflux temperature. [h] The per cent *cis* isomer is uncertain because of the presence of reagents which interfered with the analysis. [i] Reference 9. Lithium aluminum hydride promotes *cis–trans* isomerization. [j] P. Caubere and J. Moreau, *Tetrahedron*, **25**, 2469 (1969). Bibenzyl is also formed and sodium hydride promotes *cis–trans* isomerization. [k] Reference 7. [l] Reference 28. [m] Reference 32. [n] Titanium(III) reacts with DMSO.

hydrazine,[24] dimethylformamide,[5,7] potassium hydrosulfite,[25] sodium benzenesulfinate,[26] silver oxalate,[27] sodium thiosulfate,[28] lithium aluminum hydride,[9b,29] sodium methoxyborohydrides,[9a] copper(I),[30] pyridine,[31] di-*p*-tolymercury,[32] chromium(II),[33] tin(II),[7] magnesium,[12] copper,[34] zinc,[11,12,34] chloride,[6,35] bromide,[6,35] and iodide,[4,5,34,35] as well as the reductants in Tables I and II.

The debrominations of the *dl* dibromide display variable stereoselectivity (Tables I and II). This

TABLE II

METAL-PROMOTED ELIMINATION FROM *dl*-STILBENE DIBROMIDE[a–c]

Solvent[b]	*cis*-Stilbene in product, %		
	Zn	Zn–Hg	Cd
Acetonitrile	3	...	26
Methanol	18	21	25
THF	11	...	28
$CH_3OCH_2CH_2OH$	11	...	24
Acetone	5	25	16
MEK	11	...	...
1-Propanol	15	...	21
Ethanol	14	14	12
Ethyl acetate	8	...	...
DMSO	25	...	25

[a] Reactions were normally carried out at the boiling point of the solvent for 4–5 hr. In DMF and DMSO the reaction temperature was 60–70°. [b] A few other reactions were carried out. The reductant, solvent, and per cent *cis*-stilbene were Cd–Hg, ethanol, 4%; Mg, DMSO, 45%; Al, DMSO, 53%; Pb, DMSO, 7%. Related work in the literature is as follows: Mg, THF, 10%;[12] Mg, THF, 65%; Cu, 95% C_2H_5OH, 18%;[34] and Zn, 95% C_2H_5OH, 13% [R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962)]; Zn, H_2O, 12%;[11,12] Zn, HCl (aqueous), 0% (Table I, footnote *f*). [c] Debrominations with several reductants (Zn, Zn–Hg, Cd, Cd–Hg, Mg, Al, Cu, Pb, and Sn) in DMF gave stilbene(s) apparently contaminated with bromostilbene (eq 2).

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dibromide is obviously more sensitive to the reductant and is also the one on which far less work had been done. Accordingly, we were most interested in it and surveyed its reactions with 17 reductants in one or more of 11 solvents. It is interesting that the most extensive and recent studies on reductive elimination deal with the reductant, chromium(II),[10] or several hydrides,[9] and a variety of disubstituted organic oxidants. We have varied the reductant widely and used only the stilbene dibromides as oxidants.

Experimental Section

The stilbene dibromides were prepared by standard methods: the *meso* form, mp 237–238°, from xylene; the *dl* form, mp 112–113°, from ethanol.[4,5] All of the other substances were reagent grade where possible. The zinc or cadmium amalgams were prepared from a mixture of the metal and mercuric chloride in aqueous hydrochloric acid. The amalgam was washed with water, filtered, and stored. Copper(I) chloride was a freshly prepared sample.

The composition of *cis–trans*-stilbene mixtures was determined by the absorbance ratio method on a Cary Model 14 spectrophotometer at 280, 290, 300, and 310 mμ.[4,36] Normally, the product mixture was treated with water and ether; after the ether extract was dried with calcium chloride, the solvent was evaporated and the residue was taken up in absolute ethanol to be analyzed. Under conditions of the debromination reaction, there was little or no isomerization of the *cis*-stilbene (Table III). The accuracy and precision of the stilbene analyses are suggested by the values in Table III—*i.e.*, *ca.* ±4%, absolute. Products of competing reactions can complicate matters, as we shall see.

TABLE III

ATTEMPTED ISOMERIZATION OF *cis*-STILBENE[a]

Reagent	Solvent	*cis*-Stilbene, %[b]
Zn, ZnBr$_2$	THF	97
	Ethanol[c,d]	96
	Acetone	98
	DMF	97
Cd, CdBr$_2$	DMF	98
	Acetone	97
	Ethanol	99
Fe^{2+}, Fe^{3+}	DMF	100
	Ethanol	100
	DMSO	96
Cr^{2+}, Cr^{3+}	DMF	99
	DMSO	100
Cu^{+}, Cu^{2+}	DMF	99
	DMSO	98
	Ethanol[d]	97
Sn^{2+}, Sn^{4+}	DMF	98
	DMSO	99
I^{-}, I$_2$	Acetone	100
	DMF	98
	DMSO	96
	Methanol	85[e]

[a] For reaction conditions see Table I, footnote *a*. [b] The uncertainty in the figure is probably <4%. [c] Reference 11 reports essentially no (<2%) isomerization under similar conditions. [d] Reference 34 reports essentially no isomerization under similar conditions. [e] At 100° in a sealed tube for *ca.* 11 hr.

Typically, the reactions were carried out with the stilbene dibromide (*ca.* 0.05 g) and an excess of reductant (*ca.* 1–2 g) in *ca.* 30 ml of solvent. Except for the solvents DMF and DMSO, reactions with the metals were carried out at reflux for *ca.* 4–8 hr. This "standard" period was insufficient for the metals copper, cadmium, lead, iron, and chromium in ethanol and acetone. Because DMF reacts with the stilbene dibromides at its boiling point,[6] reactions in it were carried out at 60–70°; these conditions were also used for DMSO. In these solvents, the reaction period was extended to 2 days for zinc, cadmium, zinc-cadmium amalgam, aluminum, and magnesium. Where the reaction was incomplete, the data are not usually given in Tables I and II. Besides isomerization of the product stilbenes, a possible complication in these reactions was dehydrobromination as in eq 2. The presence of either bromostilbene or tolan would,

$$(C_6H_5CHBr)_2 \xrightarrow{\text{base}} C_6H_5CH{=}CBrC_6H_5 \xrightarrow{\text{base}} C_6H_5C{\equiv}CC_6H_5 \quad (2)$$

of course, interfere with our analyses. *dl* dibromide with copper and cyanide ion in ethanol led to tolane. The diversion from eq 1 to eq 2 is also noted in Table II with some reagents.

Results and Discussion

In any attempt to account for stereoselectivity, we must remember that *trans*-stilbene is more stable than *cis*-stilbene in the range 25–150°: the *trans* to *cis* ratio is 500 at 25°.[37] By actual test, isomerization of the product stilbenes was usually small or negligible under typical reaction conditions (Table III). Although this establishes that we obtained products under kinetic control, there is no assurance that possible intermediates along the reaction path also retained their configurations.

Treated with diverse reductants, metals, anions, and cations, in several solvents, *meso*-stilbene dibromide gave *trans*-stilbene exclusively. For the most part, these reductants are the same as those given for the *dl* dibromide in Tables I and II and will not be listed separately. Clearly, our survey has not uncovered any reductant which could convert the *meso* dibromide by an overall *syn* process into *cis*-stilbene.

Since *all* reductants debrominate the *meso* dibromide stereospecifically in the *anti* sense to give the more stable *trans*-stilbene, little can be said about the elimination mechanism. For the two-electron reductants, orbital symmetry and orbital overlap as well as conformational factors favor the conventional E2 process.[2–7] For any reductants which may initiate a multistep process, the intermediates formed, *e.g.*, ionic, radical, or organometallic, are likely to be "set up" for subsequent conversion into *trans*-stilbene (eq 3 and 4).

Treated with diverse reductants, *dl*-stilbene dibromide gave a wide range of product compositions containing 0–96% *cis*-stilbene (Tables I and II). Judging from the products obtained it would appear that the mechanisms of elimination by two-electron, one-electron, and metallic reductants are different. For the nonmetal reductants, one can perhaps make the rough generalization that one-electron reductants give mainly *syn* elimination, and two-electron reductants give chiefly *anti* elimination. Unlike the results reported for the reaction of *dl*-2,3-dibromobutane and chromium(II),[10] the product ratio was not sensitive to changing solvent. Nevertheless, despite the fact that the role of the solvent is obscure[10] and sometimes unimportant (Table II), it does appear that the course of reductive elimination of the *dl* dibromide can be preselected.

With the two-electron reductants, *e.g.* Pt(II), RS$^-$, I$^-$, or H$^-$, one might suppose that the *dl* dibromide follows the concerted *anti*-elimination path to the

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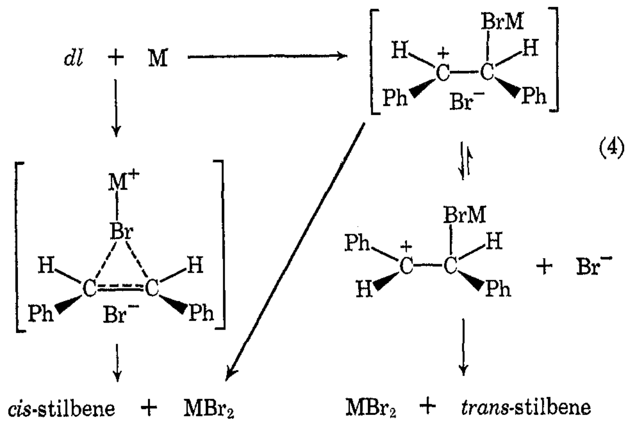
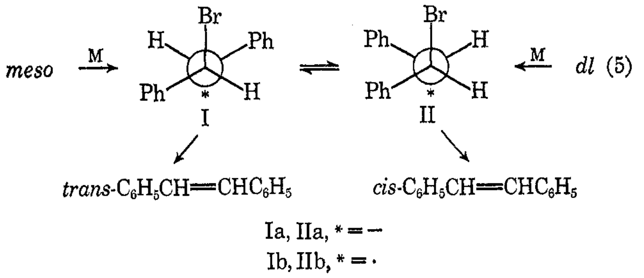
major product, *cis*-stilbene. The conformation of such a transition state necessarily involves *syn* phenyl-phenyl interactions. To alleviate this steric problem,

$$dl\text{-}(C_6H_5CHBr)_2 \xrightarrow{M} erythro\text{-}C_6H_5MCHCHBrC_6H_5 \xrightarrow{M} trans\text{-}C_6H_5CH{=}CHC_6H_5 \quad (3)$$

the *dl* dibromide may take a second path, one that is necessarily minor, since *trans*-stilbene is the minor product. Such a route could conceivably involve a concerted *syn* transition state, an SN2–E2 sequence (eq 3), a carbonium ion (eq 4), or a carbanion (eq 5) mechanism.[2,9b]





Although there is no need to insist that any one path would hold for all of the reductants, the fact that the *dl* product ratio is not changed much by changes in two-electron reductant, solvent, or reaction temperature suggests that we are dealing with one mechanism. Furthermore, this apparent similarity in the product-determining steps indicates to us that we are dealing with the partitioning of one or more reactive intermediates. Put another way, two fast processes with low activation enthalpies (or free energies) are likely to have smaller differences ($\Delta H_t^{\ddagger} - \Delta H_c^{\ddagger}$) than two slow processes with high activation enthalpies. Finally, the intermediate or intermediates must be sufficiently short lived so as to preclude equilibrations, for this can only lead to the more stable *trans*-stilbene.

For these reasons, we believe that the *dl* dibromide is debrominated on one of those paths (eq 4) analogous to those proposed for bromine additions to alkenes.[38,39] It is known that bromine additions to *cis*-stilbene can be *anti* stereoselective; in nonpolar solvents (dielectric constant, ϵ 2–3) the amount of *dl* dibromide is *ca.* 90–100%. As ϵ increases to *ca.* 35, the amount of *meso* dibromide has become *ca.* 80–100%; the presence of bromide ion in the polar solvents decidedly increases the relative yield of *dl* dibromide.[34,40] In eq 4, the formation of a configurationally oriented positive ion, whether cyclic or acyclic, assists in the slow step. Subsequently, the formation of some unencumbered carbonium ion allows leakage into the sequence from *meso*- to *trans*-stilbene.

A two-electron carbanion process[11] (eq 5) cannot be completely discounted at this stage, although we consider it less probable. The carbanions could form from any one of the three *dl* rotomers, and there appears to be no obvious reason why the rotomer IIa pictured should be favored, either in its formation or, subsequently, by internal rotation of the other two rotomers. It would seem, in fact, that this mechanism provides for *too easy* leakage of the *dl* carbanions to Ia by inversion and rotation of the carbanion, processes which would lead to *trans*-stilbene as the major product.

We come now to the one-electron reductants of the *dl* dibromide, which appear at the bottom of Table I. These range from ferrous and chromous species to others such as hydride, tin(II), and thiosulfate, whose purported one-electron character in a given reaction would have to be established. Based on their product pattern, however, we propose the gross radical mechanism of eq 5 for all of these reductants. The radical first formed is a relatively stable benzylic species. Before it encounters another molecule of reductant, it presumably equilibrates with Ib by internal rotation. We further assume that specific reductants can at best modify the product-forming steps only in a minor way.

The reductions of *dl* dibromides by metals gave results (Table III) difficult to interpret. Curiously, all of these debrominations yielded some *cis*-stilbene; some of the yields were solvent sensitive. There have been indications in the past that certain metal debrominations may display a variable stereoselectivity.[11,12,34,41] Our results show that this is general. Concerning the mechanism(s), we believe that "free" ions or radicals can probably be excluded as intermediates, since they would have been susceptible to capture by protonation or solvolysis in at least some of our solvents. Here, it appears that a given reductant had a specific role right up to the product-determining steps. Whether this involved ion or radical pairs and possibly the metal surface is not clear in detail, but some variant of this seems necessary to account for the data.

Registry No.—*dl*-Stilbene dibromide, 13627-48-0.

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