

TABLE X
 PREDICTED MOLECULAR ROTATIONS OF (S)-RX, [M]_D

X	ΣR_D^a	<i>sec</i> - Butyl	<i>sec</i> - Pentyl	<i>sec</i> - Octyl	α -Phenethyl
-C \equiv C-H	7.17	36	54	52	-148 or 28
-C \equiv N	6.12	... ^c	48	43	... ^c
-HgR ^b	15.02	... ^c	95	125	-244
-HgCl	18.4	... ^c	113	157	... ^c
-HgBr	22.0	... ^c	132	190	-330
-CPh ₃	6.07	31.7	48	42	-134
-SiPh ₃	11.3	51.5	76	91	-199
-SiR' ₃ ^d	10.1	47.0	70	80	-184
-GePh ₃	11.93	53.9	79	97	-206
-GeR' ₃	12.2	54.9	80	99	-210
-SnPh ₃	15.5	67.4	98	130	-250
-SnR' ₃	16.6	71.5	104	140	-264
-PbPh ₃	30.9	125.6	180	273	-440
-PbR' ₃	24.0	99.5	143	209	-355

^a Bond refractions taken from ref 16. ^b One group active.
^c Known compound, see Table III. ^d R' = an alkyl group.

unusual conformational preference or significant contributions from lower wavelength absorptions.

Experimental Section

Melting points and boiling points are uncorrected. Rotations were measured with a Zeiss photoelectric polarimeter. All solvents and reagents were of the best commercial grades.

(+)-2-Methylbutyric Acid.—Using the procedure of Freudenberg and Lwowski,³¹ 40 g (0.455 mol) of 2-methylbutanol ($[\alpha]_D^{25}$ -4.04°, neat, 1 dm, K & K Laboratories) was oxidized by basic permanganate to (+)-2-methylbutyric acid. The acid exhibited bp 78–80° (16 mm), $[\alpha]_D^{25}$ +16.2° (neat); lit. bp 78° (15 mm),

(31) K. Freudenberg and W. Lwowski, *Justus Liebigs Ann. Chem.*, **594**, 76 (1955).

d_D^{25} , 0.9332. The yield was 20 g (43%). The product was diluted with racemic material for further use.

(+)-2-Methylbutyronitrile.—A mixture of 20 g (0.2 mol) of (+)-2-methylbutyric acid, $[\alpha]_D^{25}$ +4.90°, neat, and 47 g (0.4 mol) of thionyl chloride was stirred at room temperature for 5 hr. The excess thionyl chloride was removed at room temperature on a rotary-film evaporator and the remaining acid chloride added slowly to 100 ml of concentrated NH₄OH solution at -45°. The resulting amide was filtered while cold, the solid partially dissolved in chloroform and filtered to remove the insoluble ammonium chloride, and the amide precipitated by addition of petroleum ether (60–90°). The amide was filtered and dried to yield 9.3 g (40%) of (+)-2-methylbutyramide. The product was not crystallized in order to avoid optical fractionation, and was used directly in the next step.

Using the procedure of Jensen and Rickborn³² 5.9 g (0.0505 mol) of (+)-2-methylbutyramide was treated with 7 g (0.048 mol) of phosphorus pentoxide. The solids were mixed in a simple distillation flask and then placed in a vacuum distillation apparatus, in which the receiver was cooled in liquid nitrogen. A vacuum was applied and the pot immersed in a 140° oil bath. The nitrile distilled as formed and 3.7 g (88.5%) was collected: $[\alpha]_D^{25}$ +9.00° (neat); d_D^{25} 0.806, n_D^{25} 1.3955 (lit.³³ n_D^{25} 1.3900).

(+)-2-Methylbutyronitrile of +9.0 degrees rotation was prepared in two steps, not involving the asymmetric center, from (+)-2-methylbutyric acid, $[\alpha]_D^{25}$ +4.90 (neat). Freudenberg and Lwowski determined the rotation of optically pure acid to be $[\alpha]_D^{25}$ 19.8° (neat); thus the starting acid was 24.7% optically pure and an upper limit to the optical purity of the nitrile is 24.7% and a lower limit to the rotation for optically pure 2-methylbutyronitrile is 9.00/0.247 or $[\alpha]_D^{25}$ 36.3° (neat). Kenyon's³⁴ reported upper limit for the rotation of optically pure material is $[\alpha]_D^{25}$ 39.1°.

Registry No.—(+)-2-Methylbutyronitrile, 25570-03-0.

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(32) F. R. Jensen and B. Rickborn, *J. Org. Chem.*, **27**, 4608 (1962).

(33) L. Friedman and H. Shechter, *ibid.*, **25**, 877 (1960).

(34) J. Kenyon and W. A. Ross, *J. Chem. Soc.*, 3407 (1951).

Debromination of *meso*- and *DL*-Stilbene Dibromides by Sodium Iodide in Dimethylformamide^{1a}

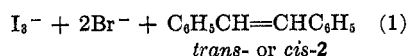
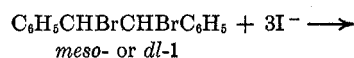
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In the sodium iodide promoted debromination of the stilbene dibromides in DMF, the *meso*-dibromide gives *trans*-stilbene while the *dl*-bromide gives both stilbenes with $[cis]/[trans] \approx 10$. The activation parameters for elimination in the temperature range of 25–60° are, for *meso*, $\Delta H^\ddagger = 16.3$ kcal/mol and $\Delta S^\ddagger = -15$ eu; for *dl*, $\Delta H^\ddagger = 22.3$ kcal/mol and $\Delta S^\ddagger = -7$ eu. At 36°, the relative rates are $k[meso]/k[dl] = 323$. A detailed estimate of the free-energy terms for solvation in DMF relative to methanol indicates that the iodide term is most important in this elimination. Sodium nitrate and lithium bromide exert a positive salt effect on the iodide reaction. As compared with methanol, the rates in DMF are larger, the spread in the *meso* and *dl* rates is greater, and the *anti* stereoselectivity of the *dl* reaction is higher: this is termed *solvent dispersion* of the rates of isomers into a *selectivity spectrum*. Our observations appear to be more consistent with stepwise ion-pair processes than with one-step dehalogenation mechanisms.

Broadly speaking, this series of papers deals with the conformational responses of a pair of diastereoisomers, the stilbene dibromides (1), subjected to a given process, elimination, under widely varying circumstances.²



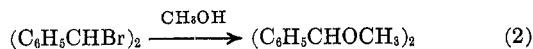
Kinetic and mechanistic information was obtained for the iodide-promoted debromination of the *dl*- and

meso-1 in the standard solvent methanol.^{2c} Here, we hoped to uncover any differential conformational medium effects that might be typical of an aprotic solvent,

(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. This paper was presented at the 148th National Meeting, American Chemical Society, Chicago, Ill., Sept 1964, Abstracts p 39V. (b) Author to whom inquiries should be addressed.

(2) (a) W. K. Kwok, I. M. Mathai, and S. I. Miller, *J. Org. Chem.*, **35**, 3420 (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**, 4802 (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.

e.g., dimethylformamide (DMF). Moreover, some 1,2-dibromides, e.g., *dl*-1, are reluctant to undergo elimination and in hydroxylic solvents may choose a solvolytic decomposition route (eq 2).^{2c} In DMF, the elimina-



tion process would, of course, not be complicated by competing hydrolysis. The advantages of DMF as a medium for 1,2 debrominations as well as for their kinetic study was realized by Roumanian workers.³

Kinetic data on the reactions of both 1 with iodide in acetone were available,^{4,5a} and more on *meso*-1 in DMF appeared recently.⁵ It turned out that our emphasis on the *dl*-1 reaction was fortunate, in that this led to an expanded view of the debromination mechanism.

Experimental Section

Materials.—Our solvent was Fisher certified dimethylformamide (DMF). *meso*-1 had mp 237–238°, from xylene; *dl*-1 had mp 112–113°, from ethanol.^{2b} All of the other substances were reagent grade; the salts, sodium nitrate, sodium iodide, and lithium bromide were dried at 150° for ~3 hr and stored in a desiccator until required.

Analysis.—Triiodide production in eq 1 was followed by titration with standard thiosulfate.^{2c} In DMF, the starch indicator is ineffective; undoubtedly the DMF-iodine complex is involved here. However, if a tenfold dilution of the DMF-iodine solution with water is made and 1 ml of acetic acid added, titration to the starch end point is feasible. Near the end point the thiosulfate should be added slowly. In some experiments, the amount of bromide ion was estimated with standard silver nitrate.

The composition of *cis*-*trans*-2 mixtures was determined by the absorbance ratio method on a Cary Model 11 spectrophotometer at 280, 290, 300, and 310 mμ.⁶ Solutions in absolute ethanol were made up to contain 28.5%, 13.6% *cis* and 71.5%, 86.4% *trans* respectively. Our method of analysis yielded 29%, 15% *cis* and 71%, 85% *trans* respectively. Of course, *cis*-*trans* mixtures recovered after reaction are not likely to be more accurately determined.

Kinetics in DMF.—Aliquots of stock solutions of 1 and sodium iodide in DMF were placed in separate compartments of a flask (125, 150, or 250 ml) containing an inner well. The flask was stoppered and placed in a constant temperature bath. After reaching bath temperature, the closed flask was inverted and shaken vigorously (~40 sec) and replaced in the bath. Aliquots (5.00 or 10.00 ml) were taken at intervals, run into ice water, and titrated with thiosulfate. Conversions ranged from 50% to 80% and were normally ~60%. Since DMF has bp 152° and our highest temperatures for the kinetic runs was 60–70°, it is unlikely that solvent evaporation from the stoppered flasks was significant.

Since organic halides react with DMF,^{2b,6,7} both 1's were checked. By bromide analysis, less than 1% decomposition of stock solutions (0.015 M) of *meso* at 46° in 24 hr and *dl* at 70° in 20 hr was observed; these conditions are more severe than those used in the kinetic runs. However, when *meso*-1 (0.2 g) in DMF was refluxed (~152°) for 10 hr, an 80% yield of *trans*-stilbene, mp 123°, was isolated. Indeed, even at ~25°, stock stilbene dibromide solutions turn yellow on long standing. For this reason, freshly prepared solutions were used in the kinetic studies.

The possibility that iodine might be consumed by DMF was

tested; a DMF solution of sodium iodide (0.26 M) and iodine (0.017 M) showed no loss in titer after 20 hr at 70°.

The stoichiometry of the iodide-stilbene dibromide reaction is substantially that given by eq 1. Weighed samples of the dibromides were treated with excess sodium iodide (6 g) in DMF; the iodine content was determined. After 23 or 48 hr at 70° a total of six trials for *meso* indicated 93.5% reaction; after 48 hr at 70° three trials for *dl* indicated 93.9% reaction. In other experiments, debrominations were carried out at 70° for 48 hr. The iodine was decolorized with aqueous sodium sulfite, the solution was extracted with ether, and the extract was dried with calcium chloride and evaporated. On the basis of their infrared and ultraviolet spectra, the residues appeared to be the stilbenes. Yields from the *meso*- and *dl*-1 (0.2 g scale) were 85 and 88% respectively. Spectrophotometric analyses indicated that the *meso*-iodide system led to *trans*-2 and the *dl*-iodide system led to 88% *cis*-2 and 12% *trans*-2. Under the same experimental conditions the conversion of *cis*- to *trans*-2 by sodium triiodide was less than 5%.^{2b}

Rate constants for process 1 were obtained from the standard expression ($a = [I]_0$, $b = [NaI]_0$) or from the slopes of plots of

$$kt = \frac{2.303}{(b-3a)} \log \frac{a(b-3x)}{b(a-x)} \quad (3)$$

the right-hand side of eq 3 vs. t . Typically, 6–10 points were taken per run for 4–7 runs and the average deviation in k was <4%. The applicability of eq 3 depends on several factors: the initially formed IBR is rapidly transformed into I_3^- ; there is sufficient iodide ion ($b > 3x$); the triiodide is stable ($K_{diss} \approx 10^{-7}$ at 25° in DMF⁸). The rate constants together with their average deviations are collected in Tables I and II. Because of solvent

TABLE I
DEBROMINATION OF meso-STILBENE DIBROMIDE BY
SODIUM IODIDE IN DIMETHYLFORMAMIDE^{a,b}

Temp, °C ± 0.05°	<i>meso</i> - Dibromide, M × 10 ³	NaI, M × 10 ²	k , M ⁻¹ sec ⁻¹ × 10 ²	
36.1	17.18	8.09	1.13	
	9.71	4.57	1.10	
	5.81	3.51	1.12	
	4.29	1.62	1.00	
	3.99	3.00	1.07	
	9.61	5.28	1.09	
	9.55	7.04	1.13	
			k_{corr} 1.10 ± 0.04	
	25.0	7.97	7.51	0.390
		5.82	3.51	0.368
4.19		2.10	0.361	
11.13		7.54	0.384	
9.59		8.12	0.381	
6.56		6.95	0.366	
			k_{corr} 0.372 ± 0.01	
45.8	8.20	8.41	2.32	
	7.56	4.95	2.48	
	4.31	2.35	2.33	
	4.31	5.88	2.25	
			k_{corr} 2.39 ± 0.07	

^a The mean rate constant was corrected for solvent expansion to k_{corr} . The average deviation is indicated. ^b Reference 5 reports rate constants of 2.68×10^{-2} M⁻¹ sec⁻¹ for KI at 50.3° and 5.2×10^{-3} M⁻¹ sec⁻¹ for (*n*-C₄H₉)₄NI at 25°. The quaternary salt was more reactive than KI by a factor of ~2.

expansion, correction factors were applied to the mean rate constants to yield mean corrected rate constants given as k_{corr} . The factors were 0.998 at 25°, 1.005 at 36°, 1.011 at 46°, and 1.019 at 60.1°. ^{7b}

Activation energies were obtained from Arrhenius plots. The other activation parameters given in Table III were calculated in eq 4. Salt effects on the rate constants are given in Table IV.

$$\Delta H^\ddagger = E_{act} - RT \quad k = (kT/h)e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad (4)$$

(8) R. Alexander, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, **89**, 3703 (1967).

(3) F. Badea, T. Constantinescu, A. Juvara, and C. D. Ninitescu, *Justus Liebig's Ann. Chem.*, **706**, 20 (1967).

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

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

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

(7) (a) R. S. Kittila, "Dimethylformamide," E. I. du Pont de Nemours and Co., Wilmington, Del., 1967, Chapter 12. (b) "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.

TABLE II
DEBROMINATION OF *dl*-STILBENE DIBROMIDE BY SODIUM
IODIDE IN DIMETHYLFORMAMIDE^a

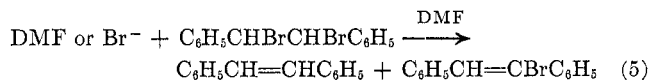
Temp, °C ± 0.05°	<i>dl</i> -Dibromide <i>M</i> × 10 ³	NaI <i>M</i> × 10 ²	<i>k</i> , <i>M</i> ⁻¹ sec ⁻¹ × 10 ⁴	
36.1	9.15	5.50	0.338	
	11.12	6.73	.341	
	13.68	13.25	.352	
	13.72	6.60	.341	
	17.79	10.77	.318	
		<i>k</i> _{corr} 0.340 ± 0.01		
45.8	13.68	13.25	1.13	
	11.12	6.73	1.04	
	21.89	9.05	1.07	
	13.72	6.60	1.13	
	7.33	6.93	1.07	
	9.15	5.50	1.09	
			<i>k</i> _{corr} 1.10 ± 0.04	
60.1	21.89	9.05	4.81	
	13.79	14.48	4.88	
	11.21	7.35	4.79	
	6.96	5.28	4.94	
	7.33	6.95	4.91	
	9.38	6.40	5.07	
			<i>k</i> _{corr} 4.99 ± 0.07	

^a The mean rate constant was corrected for solvent expansion to *k*_{corr}. The average deviation is indicated.

Did bromide ion compete with iodide to any significant degree in the kinetic runs? The rate constants for the reactions of lithium bromide with *meso*-1 was ~40 times lower at 46° and with *dl*-1 was ~10 times lower at 60° than the corresponding constants for the iodide reactions.^{2a} Given the concentrations in our runs (Tables I, II), rate acceleration due to bromide ion would be insignificant in the usual range of our kinetic observations.

Results and Discussion

The reaction of iodide with either stilbene dibromide is first order in each reactant. In the concentration range of 0.02–0.14 *M* sodium iodide, salt effects were within the experimental uncertainty. The stoichiometry is essentially that of eq 1: based on iodine production, infinite time reaction is ~93–94% for both dibromides; based on preparative scale work, the yield of stilbenes was ~90%. The products (2) were produced under conditions of kinetic control, *i.e.*, little or no isomerization. Processes 5 were not significant



under the conditions of the kinetic runs, but may interfere at higher temperatures.^{2a,b,e} All of the rate data are given in Tables I–IV.

The debromination of *meso*-1 is stereospecific—only *trans*-2 is produced.⁹ The debromination of *dl*-1 is stereoselective giving 88% *cis*- and 12% *trans*-2. Thus, the *anti* elimination predominates in both cases. Considering that $K = [\textit{trans}\text{-}2]/[\textit{cis}\text{-}2] > 300$ in the range of 25–75°, the selectivity of the *dl*-1 reaction is remarkably high.⁹

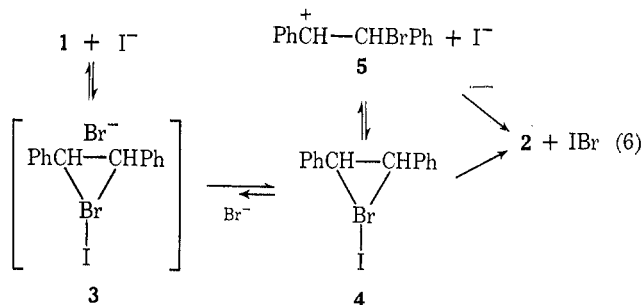
The 12% *trans*-stilbene found in the product of *dl*-1 can be rationalized in several ways.¹¹ One may suppose

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

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

(11) (a) D. V. Banthorpe, "Elimination Reactions," Elsevier, New York, N. Y., 1963, Chapters 1, 6. (b) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 116–119.

that there is an independent path from *dl*-1 to *trans*-2, *e.g.*, by *syn* debromination¹² or by an S_N2–E2 sequence via *erythro*-1-bromo-2-iodo-1,2-diphenylethane;¹³ our arguments against these alternatives are best characterized as cumulative and indicative rather than as conclusive.^{2a–c} Here and in related work, we prefer the single scheme in which both *cis*- and *trans*-2 can be formed, as in eq 6.^{2c}



In the general case (Ph = any group), if there is no great energy difference in the products, the intermediate can fall apart to yield 2, before isomerization sets in; if there are large energy factors favoring one of the products, this would probably be reflected in 5 and the relative rates from 4 to 5 vs. 4 to 2. Thus, a range of selectivity has been observed:⁹ *anti* stereospecificity for *meso*-1 under all conditions;² *anti* selectivity for *dl*-1 and sodium iodide in methanol^{2c} or DMF; *syn* selectivity for *dl*-1 and lithium bromide or stannous chloride in DMF.^{2a,d} Equation 6 also allows for a range in sensitivity of the intermediates to the medium. In eq 6, the open carbonium ion represents several rotomers which can lead to both 2's or be captured by another nucleophile, *e.g.*, methanol.^{2c} Since stable open carbonium ions are less likely to return to starting dibromide in the presence of bromide salts, aryl and highly substituted alkyl dibromides show less rate retardation with lithium bromide than simpler dibromides.⁴ Finally, eq 6 is also consistent with accepted mechanisms for bromine addition to 2¹⁴ or isomerization of 2 in the presence of halogen and halide ions. Although portions of eq 6 have been examined previously for specific systems,⁴ our position is that it is useful to regard *all* of the iodide promoted debrominations in this way.² (We exclude, of course, cases which go *via* radicals,² carbanions, or the S_N2–E2 path¹¹.)

Following the analytical approach that has been systematized by Parker,¹⁵ one can dissect the relative

$$\log k^M/k^D = \log P\gamma_1^M + \log P\gamma_{RBz}^M - \log P\gamma_2^M \quad (7)$$

(12) A concerted *syn* process would lead to IBr₂⁻ and *trans*-2. From the viewpoint of the products, this would be thermodynamically superior to the *anti* process, which gives IBr + *cis*-2 + Br⁻. A *syn* transition state would have serious steric interactions and would violate the orbital *anti* rule.⁹

(13) The displacement–elimination path has been established for terminal dibromides.¹¹ A crude S_N2 estimate follows. Consider stilbene dibromide to be derived from ethyl bromide for which the exchange rate constant with iodide in acetone at 25° is $k = 1.7 \times 10^{-8} \text{ M}^{-1} \text{ sec}^{-1}$. Data for the analogous reaction with substituted chlorides and bromides have been tabulated so that the independent effects of α - and β -phenyl groups, β -bromine, and β branching as in isobutyl bromide can be estimated [C. K. Ingold, *Quart. Rev.*, **11**, 1 (1957); A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.] If one further assumes that exchange rates in acetone and DMF are the same, $k \approx 8 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$ at 25° for iodide attack at carbon of stilbene dibromide. This figure does establish the possibility of S_N2 attack in *dl*-1 (Table III).

(14) P. S. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, Amsterdam, 1966, Chapter 6, 7.

(15) (a) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969); (b) C. F. Ko and A. J. Parker, *J. Amer. Chem. Soc.*, **90**, 6447 (1968).

TABLE III
 RATE DATA OF THE IODIDE-STILBENE DIBROMIDE REACTION

Stilbene dibromide	Solvent	ΔH^\ddagger , kcal/mol	$-\Delta S^\ddagger$, eu	Temp., °C	$k \times 10^3$, $M^{-1} \text{sec}^{-1}$	$\frac{k(\text{meso})}{k(\text{dl})}$	$\frac{k(\text{solvent})}{k(\text{CH}_3\text{OH})}$
meso	CH ₃ OH	19.8	14	36	0.14 ^a		
dl	CH ₃ OH	23.2	9	36	0.0035 ^{a,b}	40	
meso	DMF	16.3 ^c	15 ^d	36	11.0		78.5
dl	DMF	22.3 ^c	7 ^d	36	0.034	323	9.7
meso ^e	(CH ₃) ₂ CO	15.4		23	1.48		~100
dl ^e	(CH ₃) ₂ CO			23	0.066	22	~95

^a Reference 2. ^b Extrapolated value. ^c Estimated uncertainty ± 1 kcal/mol. ^d Estimated uncertainty ± 3 eu. ^e Reference 4.

 TABLE IV
 SALT EFFECTS IN THE REACTIONS OF STILBENE DIBROMIDES WITH IODIDE ION IN DIMETHYLFORMAMIDE

System	Added salt	M	$k \times 10^3$, $M^{-1} \text{sec}^{-1}$	
meso, 0.002786 M NaI, 0.03156 M Temp, 25.0°	NaNO ₃	0	3.04	
		0.1544	3.12	
		0.2566	3.39	
		0.3592	3.45	
		0.5132	3.62	
meso, 0.009961 M NaI, 0.05231 M Temp, 36.1°	LiBr	0	10.9	
		0.1187	11.7	
		0.2091	12.0	
		0.02869	0.522	
		0.05739	0.550	
	dl, 0.009403 M NaI, 0.06464 M Temp, 60.1°	LiBr	0	0.499
			0.08608	0.55
			0.1148	0.570
			0.1429	0.587
			0.2000	0.63
dl, 0.007116 M NaI, 0.04318 M Temp, 45.8°	NaNO ₃	0	0.0945	
		0.6158	0.100	

rate in two solvents. Here ${}^D\gamma_Y^M$ is a "solvent transfer" activity coefficient for Y at infinite dilution in D (e.g. DMF) and M (e.g. methanol). Taking $\log {}^D\gamma_{\text{I}^-}^M \simeq 2.6$,¹⁵ $\log {}^D\gamma_{\text{RBr}_2}^M \simeq 0.3$,¹⁵ and k values at 36° from Table III, we obtain $\log {}^D\gamma_{\text{I}^-}^M \simeq 0.4$ for the meso-1 reaction and $\log {}^D\gamma_{\text{I}^-}^M \simeq 1.3$ for the dl-1 reaction. In essence this indicates that the transfer term of iodide ion, which favors methanol over DMF, is the dominant solvation factor in these eliminations. Transition state solvation favors methanol over DMF, but this is a much larger contributor in the dl reaction as compared with the meso reaction. These results are qualitatively consistent with a somewhat larger charge dispersal in the transition state.¹⁵ One cautionary note: the terms in eq 7 do vary with concentration¹⁶ and we did have to guess at the value ${}^D\gamma_{\text{RBr}_2}^M$; therefore, this analysis is semiquantitative.

In a practical sense, the rate discrimination of the diastereoisomers in the protic and aprotic solvents is interesting (Table III). At 36°, $k[\text{meso}]/k[\text{dl}] \simeq 320$ for DMF and 40 for methanol; at 23° the same ratio is 22 for acetone. It should be obvious that relative reaction rates of any pair of compounds will change with solvent as they do with temperature, coreactant, etc. Although its origin is complex and often obscure, the device of solvent dispersion of rates into a selectivity spectrum can be applied to any pair of isomers to effect their separation.

When comparing the rate processes for two isomers, it is useful to break down the energetics. The appropriate relation is eq 8, where the terms refer to free energies of reactants and transition states, and the free energies of activation.^{2c,9} It is convenient to extrapolate our rate data to 80°, at which temperature we have the only available figure for the first term, $(G_{dl} - G_{\text{meso}}) \simeq 0.78$ kcal/mol (from benzene).^{2a} Since $k_{\text{meso}}/k_{dl} \simeq 115$ at 80°, the second term in eq 8 is 3.3 kcal/mol. Therefore, $G_{dl}^\ddagger - G_{\text{meso}}^\ddagger \simeq 4$, a figure similar to that given for the product difference, $(G_{\text{cis}} - G_{\text{trans}}) \simeq 3.7$ kcal/mol.¹⁰ Since we believe that the time scale and reaction profile of eq 6 vary from meso to dl, we should not insist that the transition states themselves are literally "productlike."

$$(G_{dl} - G_{\text{meso}}) + (\Delta G_{dl}^\ddagger - \Delta G_{\text{meso}}^\ddagger) = (G_{dl}^\ddagger - G_{\text{meso}}^\ddagger) \quad (8)$$

The Effect of Lithium Bromide.—Observations of salt effects in debrominations have often been scattered and unsystematic.^{5,17,18} The data (Table IV) for sodium nitrate on the elimination from meso-1 indicate a small positive effect of ~25% at concentrations of 0–0.6 M. These data establish the scale of "ordinary" salt effects whatever their origin.

In contrast to our observations (Table IV), lithium bromide depresses the rate of the reaction of iodide with meso-1 in acetone,⁴ and of bromide with fumaric ester dibromide in DMF.³ As the sodium iodide concentration increases, the rate constant for its reaction with sym-tetrabromoethane decreases.¹⁷ It is interesting that the rate constant for meso-2 with tetrabutylammonium iodide is appreciably larger (~2) than that for potassium iodide in methanol or DMF.⁵ We take all of this as evidence for the presence of ion pairs which are less nucleophilic than free halide.

The addition of 0.2 M lithium bromide to iodide-stilbene dibromide reactions leads to a rate enhancement of ~30%. This appears to be a larger than ordinary effect. Separate experiments without iodide established that the reaction of bromide ion with the stilbene dibromides was too slow to increase the apparent rate when iodide was present.^{2a} Our tentative explanation is that BrI₂⁻ forms in these solutions⁸ and increases the concentration of iodide ion. The rate enhancement by bromide ion also indicates that there must be little or no return to dl-1 from 4 in mechanism 6. Whether bromide ion also assists in the destruction of 3 before it returns to dl-1 is a matter of conjecture at this stage.

Registry No.—meso-1, 13440-24-9; dl-1, 13027-48-0; sodium iodide, 7681-82-5.

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