in that order. The yield was 80 mg. (80%) of a faintly yellow powder, m.p. 309–310° dec. (s. t. inserted at 300°). The infrared spectrum of this material was identical with that of V isolated in the cyclization experiments.

(b) **By Light.**—One hundred milligrams of benz[b]acridizinium bromide was placed in a covered petri dish and irradiated for 48 hours with the light from a 150 watt General Electric frosted bulb. During the course of the irradiation the color of the solid changed from red to yellow. The weight was essentially unchanged, m.p. 320–321° dec. (s. t. inserted at 300°). This product was shown to be identical with that of V isolated in the cyclization experiments by mixed melting point and infrared spectra.

2-(4-Methylbenzyl)-3-aldoximinoisoquinolinium Bromide (VIII).—The quaternization of 5.23 g. of isoquinoline-3-aldoxime by 10 g. of α-bromo-*p*-xylene in 20 ml. of dimethylformamide was carried out for 4 days at room temperature. Trituration of the reaction mixture with 60 ml. of ethyl acetate gave 9.60 g. (81%) of colorless irregular plates, m.p. 210–211° dec. (s. t.). The analytical sample was prepared from ethanol, m.p. 211–212° dec. (s. t.).

Anal. Calcd. for $C_{18}H_{17}BrN_2O$: C, 59.51; H, 4.91; N, 7.72. Found: C, 59.53; H, 4.92; N, 7.43.

2-Methylbenz[b]acridizinium Bromide (X).—A solution of 8.0 g. of the crude bromide VIII in 40 ml. of hydrobromic acid was refluxed for 4 minutes. The acid was removed *in vacuo* and the residue taken up in 50 ml. of hot methanol. On cooling, this solution deposited 5.44 g. (71%) of orange-red irregular plates, m.p. 242–243° dec. (s. t. inserted at 240°). The melting point of the analytical sample, taken in the same way, was 243–244° dec.; λ_{max} (log ε): 240 (4.12), 257 (4.06), 280 (4.28), 340 (3.59), 398 (3.43), 420 (3.81), 458 (3.16), 487 (3.55); λ_{min} 252 (4.05), 262 (4.04), 317 (3.57), 368 (2.88), 404 (3.40), 448 (3.11), 478 mμ (2.45).

Anal. Calcd. for $C_{18}H_{14}BrN \cdot H_2O$: C, 63.17; H, 4.72; N, 4.10. Found: C, 63.01; H, 4.47; N,[12] 4.24.

The picrate was prepared from ethanol as orange-red rectangular plates, m.p. 267–268° dec. (s. t. inserted at 250°).

Anal. Calcd. for $C_{24}H_{16}N_4O_7$: C, 61.01; H, 3.41; N, 11.85. Found[11,12]: C, 60.50, 61.51; H, 3.27, 3.53; N, 11.75, 11.55.

Dimerization of 2-Methylbenz[b]acridizinium Bromide (X). (a) **By the Action of Boiling Hydrobromic Acid.**—A solution of 500 mg. of X in 15 ml. of 48% hydrobromic acid was refluxed for 2 hours. The reaction mixture was cooled, diluted with water, and the product separated. After washing with water, cold ethanol, and ether, a colorless powder remained; yield 300 mg. (60%), m.p. 297–299° dec. (s. t. inserted at 250°). The melting point of a mixture of this material and that of VI isolated in the cyclization experiment was undepressed.

(b) **By Light.**—One hundred milligrams of X was irradiated for 48 hours to produce a yellow powder, m.p. 298–299° dec. (s. t. inserted at 250°). The weight was essentially unchanged. A mixture of this material and that isolated in the cyclization experiment also showed no melting point depression.

2-(2-Methylbenzyl)-3-methylisoquinolinium Bromide.—The quaternization of 3-methylisoquinoline (1.43 g.) by α-bromo-*o*-xylene (1.85 g.) in 1 ml. of dimethylformamide was carried out at room temperature for 20 hours. The reaction mixture was triturated with ethyl acetate and the product collected. The yield was quantitative, m.p. 198–202°. The analytical sample crystallized from ethanol–ether as colorless irregular plates, m.p. 203–207°.

Anal. Calcd. for $C_{18}H_{18}BrN \cdot {}^1/_2H_2O$: C, 64.10; H, 5.68; N, 4.15. Found[12]: C, 64.47; H, 5.67; N, 4.44.

DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Studies in Stereochemistry. XXXII. Mechanism of Elimination of Sulfoxides[1]

BY CHARLES A. KINGSBURY[2] AND DONALD J. CRAM

RECEIVED AUGUST 4, 1959

The preparation and properties of the four diastereomeric 1,2-diphenyl-1-propyl phenyl sulfoxides are described. When heated to 80°, these diastereomers undergo elimination reactions to give the isomeric α-methylstilbenes. These reactions are predominantly stereospecific, and the product of *cis* elimination dominates over the product of *trans* elimination by factors that vary between 3 and 16. The stereospecificity of the reaction varies little with the configurations about either of the two asymmetric carbon atoms or about asymmetric sulfur. The pyrolysis reactions display good first-order kinetics in dioxane, dimethylformamide, and 50% dioxane–50% methanol as solvents. The reaction rates and the stereospecificity of the transformations vary little as solvent is changed from dioxane to 50% dioxane–50% methanol, to pyridine, to dimethylformamide. In pure methanol, the reaction rate is dramatically depressed, but the stereospecificity is not changed. At higher temperatures (*e.g.*, 120°), the stereospecificity of the reaction is lost. The values of $\Delta H^{\ddagger}$ are not constant with temperature over a 40° range, and therefore two primary processes are operative. At lower temperatures the classical, cyclic, concerted mechanism appears to apply. At higher temperatures, a second process predominates, which may assume either a *cis* or *trans* steric course. In the preferred mechanism for this process, a radical pair is produced in a first stage, which disproportionates by a hydrogen atom transfer in a second stage. The steric direction of this latter reaction is controlled by the relative rates of hydrogen abstraction and of configurational adjustments of the radical pair within the solvent cage.

Pyrolysis of esters,[3] xanthates,[4] carbonates,[5] halides[6] and amine oxides[7] have been observed to result in *cis* elimination reactions to give olefins. Evidence has been presented that the minor product of the Hoffman elimination reaction may proceed through an *ylid* intermediate which undergoes a *cis* elimination reaction.[8] Other base-catalyzed reactions have also been observed to assume a *cis* steric course,[9] but probably mechanisms apply which are different from those observed in the pyrolytic reactions.

Sulfoxides have been postulated to have a dipolar sulfur–oxygen bond[10] analogous to the

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[1] This research was supported in part by the Office of Ordnance Research, U. S. Army.

[2] U. S. Rubber Co. Fellow, 1958–1959.

[3] (a) D. Y. Curtin and D. B. Kellom, THIS JOURNAL, **75**, 6011 (1953); (b) D. H. R. Barton, A. J. Head and R. J. Williams, *J. Chem. Soc.*, 1715 (1953); (c) W. J. Bailey and R. A. Baylouny, THIS JOURNAL, **81**, 2126 (1959).

[4] (a) D. J. Cram, *ibid.*, **71**, 3883 (1949). (b) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5828 (1952); (c) E. R. Alexander and H. Mudrak, *ibid.*, **72**, 1810 (1950); **72**, 3194 (1950); and **73**, 59 (1951).

[5] G. L. O'Connor and H. R. Nace, *ibid.*, **75**, 2118 (1953).

[6] D. H. R. Barton, A. J. Head and R. J. Williams, *J. Chem. Soc.*, 453 (1952).

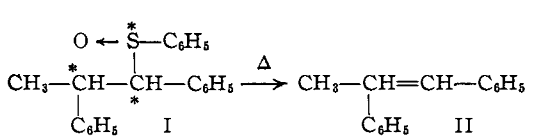
[7] D. J. Cram and J. McCarty, THIS JOURNAL, **76**, 5740 (1954).

[8] F. Weygand, H. Daniel and H. Simon, *Ber.*, **91**, 1691 (1958).

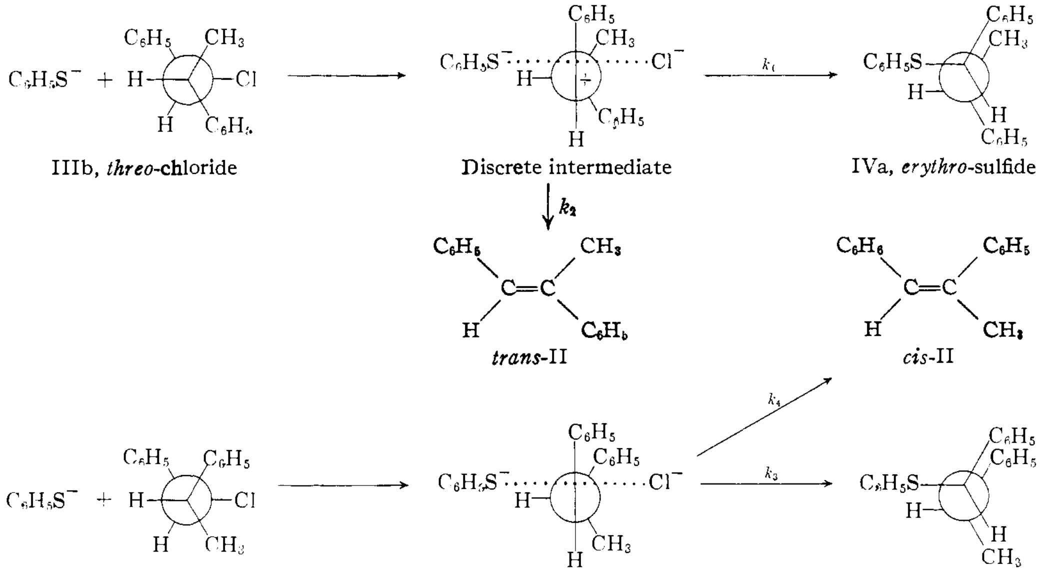
[9] F. G. Bordwell and P. S. Landis, THIS JOURNAL, **79**, 1593 (1957).

nitrogen–oxygen bond in amine oxides.[11] Accordingly, it seemed likely that sulfoxides would undergo stereospecific *cis*-pyrolytic elimination reactions as do amine oxides. The expectation was justified.

The system chosen for study was 1,2-diphenyl-1-propyl phenyl sulfoxide (I). This compound has three asymmetric centers and therefore exists as four diastereomeric racemates. This system was selected for the following reasons: (1) The four diastereomers of I are high-melting solids which could be readily separated from one another. (2) The relative configurations about the two asymmetric carbon atoms of the four diastereomers of I were established through the mode of synthesis of the four isomers. (3) The olefinic products, *cis*- and *trans*-α-methylstilbene (II) are both solids which exhibit different melting points, solubility and spectral properties.[12] (4) The system possesses only one β-hydrogen, and therefore the reaction can proceed in only one direction. (5) Unlike cyclic systems, the conformations of I can adjust themselves to the preferred stereochemical course of the reaction.



$$\underset{\textstyle\text{I}}{CH_3-\overset{*}{C}H(C_6H_5)-\overset{*}{C}H(\overset{*}{S}(\rightarrow O)C_6H_5)-C_6H_5} \xrightarrow{\Delta} \underset{\textstyle\text{II}}{CH_3-C(C_6H_5)=CH-C_6H_5}$$



IIIb, *threo*-chloride

Discrete intermediate

IVa, *erythro*-sulfide

trans-II

cis-II

IIIa, *erythro*-chloride

Discrete intermediate

IVb, *threo*-sulfide

Preparation of the Four Diastereomeric Sulfides.—The configurations of *erythro*- and *threo*-1,2-diphenyl-1-propyl chloride (IIIa and IIIb, respectively) have been established[13] previously. When the *threo*-chloride IIIb was treated with sodium thiophenoxide, an 87% yield of sulfide IVa was produced. However, when the *erythro*-chloride IIIa was submitted to the same treatment, only *cis*-α-methylstilbene (46% yield) and starting material were isolated. A substantial difference in rate of bimolecular substitution for diastereomers in this system was noted in an earlier study,[14] and halide ions were found to displace brosylate and tosylate groups from the *threo*-ester to give *erythro*-halides considerably faster than from the *erythro*-ester to give *threo*-halides. In the present study, the increased size of the nucleophile apparently accentuates the difference in rates for the two diastereomers to the point where the *erythro*-chloride underwent substitution so slowly that the side reaction to produce olefin intervened. Possibly these reactions pass through the discrete intermediates formulated, which partition between substitution and elimination products.[15] In terms of such a scheme, $k_1 > k_2$, and $k_4 > k_3$. In a classical scheme, S_N2(*threo*) > E_2(*threo*), but E_2(*erythro*) > S_N2(*erythro*). Whichever mechanisms apply, these results demonstrate that *eclipsing effects in the substitution reaction are more important than in the elimination reaction*, probably because in the product-governing transition states three sets of groups are becoming eclipsed in the substitution and only two sets in the

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[10] (a) F. Arndt and B. Eistert, *Ber.*, **74**, 423 (1941); (b) C. C. Price and R. B. Gillis, THIS JOURNAL, **75**, 4751 (1953).

[11] The character of the sulfur–oxygen bond has been the subject of considerable controversy. The majority of authors consider sulfur and oxygen to be bound by a double bond and that sulfur expands its octet. Evidence for this viewpoint is taken from dipole moment [(a) D. Barnard, J. M. Fabian and H. P. Hoch, *J. Chem. Soc.*, 2442 (1949)], spectral [(a), (b) E. D. Amstutz, I. M. Hunsberger and J. J. Chessick, THIS JOURNAL, **73**, 1220 (1951); (c) C. C. Price and R. D. Gilbert, *ibid.*, **74**, 2073 (1952); and (d) G. Leandri, A. Mangini and R. Passerini, *Gazz. chim. ital.*, **84**, 73 (1954)], and thermal [(e) G. M. Phillips, J. S. Hunter and L. E. Sutton, *J. Chem. Soc.*, 146 (1945)] properties, from dipole moments [(f) C. W. N. Cumper and L. S. Walker, *Trans. Faraday Soc.*, **52**, 193 (1956); and (g) E. N. Gur'yanova, *Zhur. Fiz. Khim.*, **24**, 497 (1950)] and from bond lengths (ref. 10). However, some of these authors[a,b] point out that bond order may vary significantly between sulfoxides and sulfones. The large differences in properties between sulfoxides and sulfones (*e.g.*, spectra, basicity and reactivity) probably to some extent reflect such a difference in bond order.

[12] D. J. Cram and F. A. Abd Elhafez, THIS JOURNAL, **74**, 5828 (1952).

[13] F. A. Abd Elhafez and D. J. Cram, *ibid.*, **74**, 5846 (1952).

[14] D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5851 (1952). See also L. D. Bergel'son and L. P. Badenkova, *Izvest. Akad. Nauk S.S.S.R., Oldel. Khim. Nauk*, 793 (1958).

[15] (a) W. Winstein, D. Darwish and N. J. Holness, THIS JOURNAL, **78**, 2915 (1956); (b) E. L. Eliel and R. S. Ro, *Chemistry and Industry*, 251 (1956).

TABLE I

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR ISOMERIC 1,2-DIPHENYL-1-PROPYL DERIVATIVES

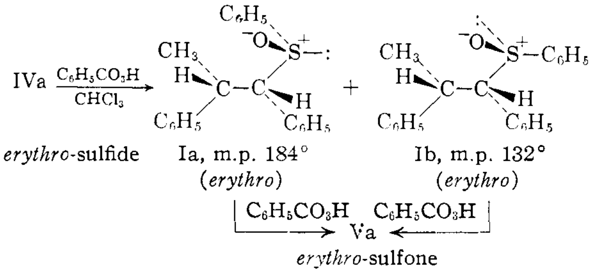
Compound	Diastereomer	M.p., °C.	Ultraviolet spectra[a] λ_{max}*	Ultraviolet spectra[a] ϵ	Mol. formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Phenyl sulfide	*erythro*(IVa)	104–105	...	...	$C_{21}H_{20}S$	82.84	82.65	6.62	6.72
Phenyl sulfide	*threo*(IVb)	43–44	...	...	$C_{21}H_{20}S$	82.84	82.62	6.62	6.60
Phenyl sulfoxide	*erythro*(Ia)	184–184.5	254	4900	$C_{21}H_{20}OS$	78.71	78.51	6.29	6.05
Phenyl sulfoxide	*erythro*(Ib)	132–133	254	4800	$C_{21}H_{20}OS$	78.71	78.79	6.29	6.05
Phenyl sulfoxide	*threo*(Ic)	155–155.5	254	6000	$C_{21}H_{20}OS$	78.71	78.47	6.29	6.17
Phenyl sulfoxide	*threo*(Id)	75.5–76	251	4600	$C_{21}H_{20}OS$	78.71	78.65	6.29	6.13
Phenyl sulfone	*erythro*(Va)	182.5–183.5	...	...	$C_{21}H_{20}O_2S$	74.97	75.15	5.99	6.00
Phenyl sulfone	*threo*(Vb)	138–139		...	$C_{21}H_{20}O_2S$	74.97	75.17	5.99	6.00

[a] Determined in 95% ethanol on a Cary recording spectrophotometer, model PMS.

elimination reaction. The production of a single sulfide from the *threo*-chloride is good evidence that the reaction occurred with inversion, and thus the product possesses the *erythro* configuration.

The *threo*-sulfide IVb was prepared by solvolyzing a diastereomeric mixture of 1,2-diphenyl-1-propanols in thiophenol in the presence of an acid catalyst. The diastereomeric sulfides produced were separated by combined chromatographic and crystallization procedures. Each of the diastereomeric sulfides was oxidized to a mixture of diastereomeric sulfoxides, which were separated to give the four racemates Ia, Ib, Ic and Id. Confirmation that Ia and Ib differed only in their configurations at sulfur was obtained by oxidizing both isomers to the same *erythro*-sulfone (Va). Similar treatment of Ic and Id gave the same *threo*-sulfone (Vb). The physical properties and analytical data that pertain to these compounds are recorded in Table I. The relative configurations assigned to the sulfur atoms of Ia, Ib, Ic and Id will be justified in a later section of the paper.

In the oxidation of the diastereomeric sulfides to the sulfoxides, asymmetric induction occurred. Thus *erythro*-sulfide IVa gave a two-to-one predominance of Ia over Ib, whereas in the oxidation of IVb a three-to-one predominance of Id over Ic was observed. Since the relative configurations about sulfur and the asymmetric carbon to which it is attached are different in Ia and Id (the dominant products), it appears that the steric direction of oxidation of IVa is controlled by one of its two asymmetric carbon atoms, and of IVb by the other.

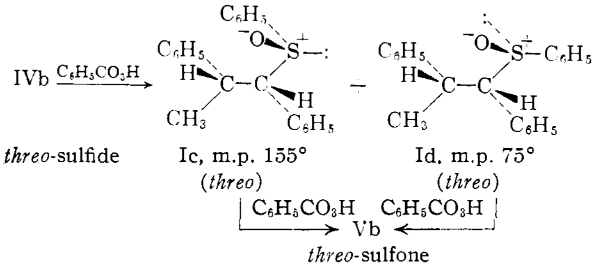


erythro-sulfide

Ia, m.p. 184° (*erythro*)

Ib, m.p. 132° (*erythro*)

erythro-sulfone



threo-sulfide

Ic, m.p. 155° (*threo*)

Id, m.p. 75° (*threo*)

threo-sulfone

Pyrolysis of the Diastereomeric Sulfoxides (I).—Pyrolyses of the four sulfoxides were carried out in sealed ampules at temperatures that ranged from 80 to 120°, and in dioxane, pyridine, dimethylformamide and methanol as solvents. The mixtures of olefins were isolated with the use of chromatography, and in most cases were analyzed spectroscopically. Use was made of the fact that *cis*-α-methylstilbene has $\lambda_{max}^{ethanol}$ 263 mμ (ϵ 11,700), and *trans*-α-methylstilbene $\lambda_{max}^{ethanol}$ 274 mμ (ϵ 20,700) in their ultraviolet spectra. Spectra of known mixtures of the two olefins were taken, and plots of λ_{max} *vs.* % composition and of ϵ *vs.* % composition were prepared. The wave length of λ_{max} of the unknown mixture was then employed to estimate the ratio of *cis* to *trans* isomers, and the extinction coefficient was employed to calculate the yield. This method allowed as little as 30 mg. of sulfoxide to be used. The probable error in product composition is ±12%, and in yield ranged from ±7 to ±12%. In a few representative cases, the olefinic products were separated and compared with authentic samples. The results were comparable to those obtained by the spectroscopic method. Table II records the results.

In runs 23, 28 and 29, starting material was recovered unchanged. However, in run 10, an 8% yield of *erythro*-sulfone was isolated. No attempt was made to isolate benzenesulfenic acid or its decomposition products from these runs.[16]

In other studies[17] it was established that the two olefins equilibrate at 75° in solutions of *p*-toluenesulfonic acid in glacial acetic acid. However, the following facts establish that little if any isomerization of olefins occurred under the conditions of these pyrolysis reactions. (1) The pattern of results in the presence and absence of pyridine are the same, and therefore no isomerization catalyzed by acidic decomposition products is evident. (2) At 120°, a 0.0304 *M* solution of *cis*-α-methylstilbene in 0.15 *M* pyridine–dioxane was found to isomerize only 5% during 12 hours. (3) A dioxane solution 0.0375 *M* in sulfoxide Ia and 0.220 *M* in *cis*-α-methylstilbene was heated to 123° for 2.25

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[16] L. Horner and O. H. Basedow, *Ann.*, **612**, 108 (1958), have demonstrated that benzenesulfinic acid forms the phenyl thioester of benzenesulfonic acid by an autoxidative process.

[17] D. J. Cram, F. D. Greene and C. H. DePuy, THIS JOURNAL, **78** 790 (1950).

TABLE II

RESULTS OF PYROLYSES OF THE DIASTEREOMERIC 1,2-DIPHENYL-1-PROPYL PHENYL SULFOXIDES (I)

						α-Methylstilbene				
Run	Isomer	Solvent	Concn., *M*	Temp., °C.	Time, hr.	Yield, %	% *cis*	% *trans*	Method analysis	Predom. steric course
1	Ia	Dioxane	0.045	80	120	79	24	76	U.v.	*cis*
2	Ib	Dioxane	.038	80	60	90	6	94	U.v.	*cis*
3	Ic	Dioxane	.038	80	60	92	84	16	U.v.	*cis*
4	Id	Dioxane	.038	80	60	100	84	16	U.v.	*cis*
5	Ib	Dioxane	.188	80	20	65	15	85	U.v.	*cis*
6	Id	Dioxane	.188	80	20	100	90	10	U.v.	*cis*
7	Ia	Dioxane	.038	95	36	100	11	89	U.v.	*cis*
8	Id	Dioxane	.038	95	36	98	69	31	U.v.	*cis*
9	Ib	Dioxane	.038	95	36	58	10	90	Isolation	*cis*
10	Ia	Dioxane	.038	100	43	57	23	77	Isolation[a]	*cis*
11	Ia	Dioxane	.038	120[b]	8	100	16	84	U.v.	*cis*
12	Id	Dioxane	.038	120[b]	8	100	27	73	U.v.	*trans*
13	Ia	Dioxane[c]	.037	80	60	71	10	90	U.v.	*cis*
14	Ia	Dioxane[c]	.030	120	2.5	73	11	89	U.v.	*cis*
15	Ib	Dioxane[c]	.037	80	60	91	6	94	U.v.	*cis*
16	Ic	Dioxane[c]	.037	80	60	93	84	16	U.v.	*cis*
17	Id	Dioxane[c]	.037	80	60	94	84	16	U.v.	*cis*
18	Id	Dioxane[c]	.037	120	2.5	93	37	63	U.v.	*cis*
19	Id	Dioxane[d]	.037	80	60	79	100[e]	0	Isolation	*cis*
20	Ia	Pyridine	.038	80	60	68	11	89	U.v.	*cis*
21	Id	Pyridine	.038	80	60	100	Predom.[f]	...	U.v.	*cis*
22	Ia	Pyridine	.038	95	36	72	2	80	U.v.	*cis*
23	Ia	Pyridine	.038	80	36	40	...	100[g]	Isolation	*cis*
24	Ia	DMF[h]	.038	80	60	65	11	89	U.v.	*cis*
25	Id	DMF[h]	.038	80	60	98	77	23	U.v.	*cis*
26	Ia	DMF[h]	.038	120[b]	8	86	24	76	U.v.	*cis*
27	Id	DMF[h]	.038	120[b]	8	72	11	89	U.v.	*trans*
28	Ia	Methanol	.038	80	96	0[i]	...	...	U.v.	...
29	Ib	Methanol	.038	80	140	0[j]	...	...	U.v.	...
30	Id	Methanol	.038	80	96	46	86	14	U.v.	*cis*
31	Ia	Water–dioxane[k]	.028	105	13	56	6	94	U.v.	*cis*
32	Ia	DEDEG[l]	.090	80	13	79	15	85	U.v.	*cis*

[a] An 8% yield of *erythro*-1,2-diphenyl-1-propyl phenyl sulfone was isolated. [b] Reaction mixture was dark. [c] Solution was 0.15 *M* in pyridine. [d] Solution was 0.07 *M* in pyridine. [e] Only *cis* material was isolated, although a small amount of the *trans* isomer was probably present. [f] Analysis was somewhat obscured by a contaminant which absorbed strongly at 245 mμ, and made other than qualitative analysis impossible. [g] Only *trans* material was isolated in a pure state, although some *cis* isomer was undoubtedly present. Starting material (40%) was recovered. [h] Dimethylformamide. [i] Starting material (60%) was recovered. [j] Starting material (40%) was recovered. [k] Solution was 0.05 *M* in HCl. [l] Diethyl ether of diethylene glycol.

TABLE III

RATE DATA FOR ELIMINATION OF 1,2-DIPHENYL-1-PROPYL PHENYL SULFOXIDE (ISOMER Ic), 0.0544 *M* AT 79.7° IN DIOXANE (RUN 40)[a]

Time, 10^{-4} sec.	$\lambda_{\max}^{\text{ethanol}}$	Absorbance[b]	Olefin, *M*	Sulfoxide, *M*	10^6 *k*, sec.$^{-1}$
0.00	...	...	0	0.0544	..
0.70	264	0.199	0.0079	.0466	2.21
2.21	263	.535	.0219	.0333	2.22
3.81	264.5	.828	.0328	.0217	2.41
6.76	264	1.090	.0427	.0118	2.26
11.77	264	1.289	.0510	.0035	2.33
					——
				Mean	2.28 ± 0.07

[a] Table V. [b] At λ 264 mμ.

TABLE IV

RATE DATA FOR ELIMINATION OF 1,2-DIPHENYL-1-PROPYL PHENYL SULFOXIDE (ISOMER Ib), 0.0234 *M* AT 80.0° in 50% DIOXANE–50% METHANOL[a] (RUN 38)[b]

Time, 10^{-4} sec.	$\lambda_{\max}^{\text{ethanol}}$	Absorbance[c]	Olefin, *M*	Sulfoxide, *M*	10^6 *k*, sec.$^{-1}$
0.00	..	...	...	0.0234	..
5.76	273	0.521	0.0068	.0165	6.07
7.97	272	.627	.0082	.0151	5.50
11.86	273	.890	.0117	.0117	5.85
14.42	272	1.004	.0132	.0101	5.83
17.38	272	1.150	.0151	.0083	5.94
25.26	273	1.304	.0171	.0062	5.26
29.24	273	1.404	.0184	.0049	5.35
					——
				Mean	5.69 ± 0.27

[a] By volume. [b] Table V. [c] At λ 273 mμ.

hours. The product (99% yield and recovery) proved to be 18% *trans*- and 82% *cis*-olefin, a composition expected if little isomerization of olefin occurred.

Kinetics of the Elimination Reaction.—The kinetics of the elimination reaction were followed through about 75% reaction, at which point a positive deviation with much scattering of points occurred. It appeared that the olefin was subject to slow destruction which became apparent after

TABLE V

FIRST-ORDER RATE CONSTANTS FOR PYROLYTIC ELIMINATION OF ISOMERS OF 1,2-DIPHENYL-1-PROPYL PHENYL SULFOXIDE AT 80.0°

Run	Isomer	Solvent	k, sec.$^{-1}$
33	Ia	Dioxane	$7.30 \pm 0.34 \times 10^{-6}$
34	Ia	50% dioxane–50% methanol[b]	$2.10 \pm .11 \times 10^{-6}$
35	Ia	Dimethylformamide	$1.96 \pm .15 \times 10^{-6}$
36	Ib	Dioxane	$2.19 \pm .13 \times 10^{-5}$
37	Ib	99.7% dioxane–0.3% methanol[b]	$2.24 \pm .15 \times 10^{-5}$
38	Ib	50% dioxane–50% methanol[b]	$5.69 \pm .27 \times 10^{-6}$
39	Ib	Methanol	$<0.002 \times 10^{-5}$
40	Ic	Dioxane[a]	$2.28 \pm .07 \times 10^{-5}$
41	Ic	50% dioxane–50% methanol[b]	$6.78 \pm .30 \times 10^{-6}$
42	Id	Dioxane	$4.24 \pm .30 \times 10^{-5}$
43	Id	50% dioxane–50% methanol[b]	$1.13 \pm .09 \times 10^{-5}$
44	Id	Dimethylformamide	$2.09 \pm .28 \times 10^{-5}$

[a] At 79.7°. [b] By volume.

TABLE VI

TEMPERATURE DEPENDENCE OF RATE AND STEREOSPECIFICITY IN PYROLYSIS OF SULFOXIDES IN DIOXANE

Run	Isomer	Temp., °C.	α-Methylstilbene % *cis*	% *trans*	k, sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
45[a]	Ib	70.15	11	89	$7.16 \pm 0.17 \times 10^{-6}$	$+26.3 \pm 1.0$	-5.8 ± 2.7
46[a]	Ib	85.2	15	85	$3.77 + .17 \times 10^{-5}$	$+30.1 \pm 0.6$	$+4.6 \pm 1.4$
47[a]	Ib	108.7	15	85	$5.42 \pm .11 \times 10^{-4}$		
48[b]	Ic	65.2	90	10	$5.35 \pm .29 \times 10^{-6}$	$+26.2 \pm 1.4$	-5.5 ± 3.8
49[b]	Ic	83.6	90	10	$4.21 \pm .21 \times 10^{-5}$	$+27.8 \pm 1.2$	-1.0 ± 3.5
50[b]	Ic	108.7	90	10	$5.94 \pm .36 \times 10^{-4}$		

[a] Solutions were 0.0233 M in sulfoxide and 0.0995 M in pyridine. [b] Solutions were 0.0262 M in sulfoxide and 0.1045 M in pyridine.

two half-lives of its formation. The reaction was followed by measuring the absorbance of the olefin produced at $\lambda_{\max}$ in the ultraviolet spectrum. Five to eight points were taken per run (ampoule technique), and good first-order kinetics were observed in each run. Data obtained in two typical runs are recorded in Tables III and IV, and Table V records the final rate constants. The probable errors ranged from 3 to 8%.

Table VI records the kinetic results of runs conducted at three different temperatures with dioxane as solvent, and with isomers Ib and Ic as starting materials. These data allow $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ to be calculated for two different temperature ranges. The values obtained are recorded in Table VI.

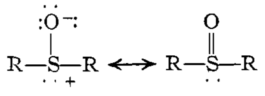
Discussion

Comparison of E_i Reaction of Sulfoxides and Other Systems.—The data of Table II demonstrate that at 80°, the *erythro* pair of sulfoxides (Ia and Ib) give predominantly *trans*-α-methylstilbene, and that the *threo* pair (Ic and Id), *cis*-α-methylstilbene. In other words, a *cis* elimination occurs, and at 80°, the ratio of *cis* to *trans* elimination ranges between factors of 3 and 16. In this respect, the pyrolysis of sulfoxides is analogous to the pyrolyses of halides, esters, xanthates and amine oxides mentioned above. Because of the relative ease of preparation of sulfoxides, and the low temperature and high yields associated with their transformation to olefin, the reaction may be useful in synthesis.

The temperature required for these pyrolyses (80°) is considerably lower than those needed for the other olefin-forming pyrolyses. Xanthates of the 1,2-diphenyl-1-propyl system go to olefin at 180°,[4b] 1-acetoxy-1,2-diphenylethane[3a] reacts at 400°, and sulfites[18] and carbonates[5] at 170 to 260°. Amine oxides pyrolyze at temperatures of from 85 to 150°,[19] but the stereospecificity of this reaction is somewhat higher (*cis/trans* elimination varies from ~20 to 400)[7] than that of the sulfoxides. On the other hand, the sulfoxide elimination is more stereospecific than those of systems other than the amine oxides.

Both *erythro*- and *threo*-1,2-diphenyl-1-propyl phenyl sulfone were completely unreactive at 120°, and at 180° decomposition occurred but α-methylstilbene was not produced.

The similarity of conditions for the amine oxide and sulfoxide elimination reactions suggests that the reactions are of the same charge type. The analogy between the two reactions can be better illustrated with structure VI than VII, and therefore for VI will be used in the subsequent discussion. The fact that sulfoxides undergo elimination and sulfones do not correlate with the generally



$$R-\underset{\cdot\cdot\,+}{\overset{:\ddot{O}:^{-}}{\overset{|}{S}}}-R \longleftrightarrow R-\underset{\cdot\cdot}{\overset{O}{\overset{\|}{S}}}-R$$

VI VII

greater reactivity[20,21] associated with the former class of compounds.

Stereochemistry and Kinetics of the Sulfoxide Elimination Reaction.—The partial stereospecificity of these elimination reactions indicates that at least two mechanisms are operative, one of which is stereospecific and *cis* in steric direction, and the other of which is either stereospecific and *trans*, or can assume either steric course.

The rate and product data demonstrate that the competing reactions have the same kinetic order. In runs 2 and 5 with isomer Ib, and runs 4 and 6 with Id (Table II), the concentrations of sulfoxide in dioxane were varied fivefold. Within experi-

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[18] (a) C. C. Price and G. Berti, THIS JOURNAL, **76**, 1207, 1211 (1954); (b) G. Berti, *ibid.*, **76**, 1213 (1954); (c) F. G. Bordwell and P. S. Landis, *ibid.*, **80**, 6379 (1958).

[19] A. C. Cope, N. A. LeBel, H. H. Lee and W. R. Moore, *ibid.*, **79**, 4720 (1957).

[20] D. C. Wimer, *Anal. Chem.*, **12**, 2060 (1958).

[21] H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

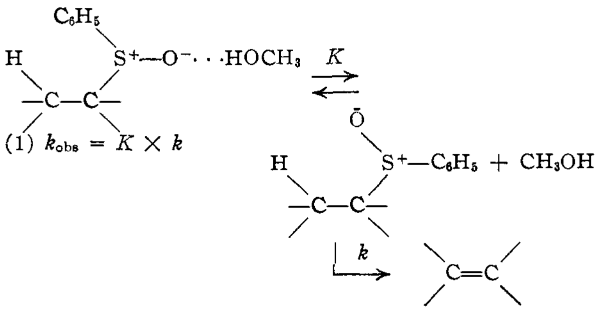
mental error, the stereospecificities of the reactions of the reactions are the same, and no trends are visible. Furthermore, the data of Tables III and IV and that of other runs show that the relative proportions of *cis-* and *trans*-olefin do not change as the reaction proceeds. These results coupled with the first-order rates indicate that none of the reactions can be bimolecular or second order in sulfoxide. Although sulfoxides are weak bases,[20] a 6% solution of dimethyl sulfoxide in dioxane at 105° (13 hours) was not a strong enough base to catalyze elimination of *erythro*-1,2-diphenyl-1-propyl chloride to give α-methylstilbene. Only starting material (60%) was recovered from the reaction mixture.

The stereospecificity of the transformation was shown to be remarkably insensitive (within experimental error) to changes in the character of the medium. Isomer Ia when pyrolyzed at 80° in dioxane (run 1), in dioxane 0.15 molar in pyridine (run 13), in pyridine (run 20), in dimethylformamide (run 24) and in diethyl ether of diethylene glycol (run 32) gave olefin in which the *trans* isomer dominated by factors that ranged in random fashion from 3 to 10. To the extent that data are available, isomer Ib (run 2 and 15) behaved similarly. Isomer Id at 80° in dioxane (run 4), in dioxane 0.15 molar in pyridine (run 17), in pyridine (run 21), in dimethylformamide (run 25) and in methanol (run 30) gave olefin in which the *cis* isomer dominated by factors that range in random fashion from 3 to 6. Isomer Ic gave similar results (runs 3 and 16). The absence of any trends in these results indicates that both the *cis* and competing *trans* or non-stereospecific elimination reactions possess the same type of rate dependence on the polarity and basicity of the medium.

The rates of the transformations are also very insensitive to the dissociating power of the medium. The kinetic data of Table V indicate that the values of the rate constants decrease only by factors that are distributed between 3.4 and 3.7 for the four diastereomers as solvent is changed from dioxane to 50% dioxane–50% methanol. Similarly, as solvent is changed from dioxane to dimethylformamide, the rate constants for Ia and Id decrease only by factors of 3.7 and 2.0, respectively. The yield patterns of the reactions run in dioxane and dimethylformamide as solvent (compare runs 13 and 24, and runs 17 and 25, Table II) are very similar, and therefore the ratio of rates of the *cis* and *trans* reactions must change little with changes in the dissociating power of the solvent. The small decrease in rate observed for both reactions as the solvent is made more polar suggests that the starting state is more solvated than the transition state for both reactions. *Clearly, none of the mechanisms operative can involve processes in which either carbonium ions or carbanions are made in the rate-controlling stage of the reaction.* Otherwise, a much greater sensitivity to medium effects would have been observed.

In pure methanol, the value of the rate constant for isomer Ib decreased by more than a factor of 10^3 as compared to the rate in dioxane. The results of runs 28 and 30 (Table II) indicate that a decrease of the same order of magnitude must apply to isomer Ia, but that the rate decrease for isomer Id is about a factor of 18. An explanation for these observations is as follows.

The tendency of sulfoxides to enter into hydrogen bonds is well established.[11a,21,22] If only the non-hydrogen-bonded sulfoxide molecules undergo the elimination reaction, and if equilibrium between hydrogen-bonded and non-hydrogen bonded species is established faster than reaction occurs, the observed rate of reaction is the product of the equilibrium constant, K, and the rate constant, k (see equation 1). In pure methanol, K for isomers Ia and Ib might possess a low value due to extensive hydrogen-bonding, and as a result k_{obs} would be slow. This hydrogen-bonding effect might not be as apparent in dioxane–methanol mixtures since the dioxane and sulfoxide are in competition with one another for the methanol molecules. Open-chain diastereomeric alcohols show different tendencies to enter into intermolecular hydrogen bonding,[23] and steric inhibition of hydrogen-bonding could result in higher values for K for Id than for either Ia or Ib. The stereospecificity of the elimination reaction of Id in methanol (run 30) was about the same as in dioxane (run 4), although the yields indicate that the latter reaction was an order of magnitude faster than the former. Extrapolation of the rates of runs 42 and 43 to pure methanol as solvent leads to a similar rate factor. These facts suggest that all of the reactions that give the olefin involve non-hydrogen-bonded starting states.



(1) $k_{obs} = K \times k$

The data of Table V demonstrate that in both dioxane and 50% dioxane–50% methanol, $k_{Id} > K_{Ic} > K_{Ib} > K_{Ia}$, and that k_{Id}/k_{Ia} in both media is about 5.5. In dimethylformamide, k_{Id}/k_{Ia} is 10. Thus the diastereomers (Ic and Id) that go predominantly to the least thermodynamically stable olefin (*cis*-II) react faster than the diastereomers (Ia and Ib) which give the more stable *trans*-olefin. Furthermore, at 80°, the reactions of diastereomers Ia and Ib which give *trans*-olefin are no more stereospecific than those of Ic and Id which give *cis*-olefin (see Table II). Clearly the transition states for the rate-determining steps of these reactions must not resemble olefin, or an opposite trend in the rate data[17] and a more stereospecific reaction for isomers Ia and Ib would be expected.

The rates of the *cis* and *trans* or non-stereospecific reactions exhibit different temperature coefficients. In runs 11 and 14, 12 and 18, and 26 and 27, a re-

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(22) G. Briegleb, *Z. Elektrochem.*, **50**, 35 (1941).

(23) J. L. Mateos and D. J. Cram, THIS JOURNAL, **81**, 2756 (1959).

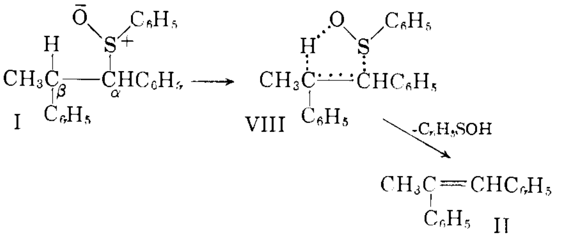
action temperature of 120° was employed (Table II). Isomer Ia gave from 3/1 to 8/1 predominance of *cis* over *trans* elimination (the more stable *trans*-olefin was the major product), whereas isomer Id gave from 1.7/1 to 3/1 predominance of *trans* over *cis* elimination. At 80°, both isomers in the same solvents (dioxane and dimethylformamide) gave from 3/1 to 9/1 predominance of *cis* elimination over *trans* elimination. Thus at 120°, the ratio, $k_{cis\text{-elim}}/k_{trans\text{-elim}}$ for Id decreases to values somewhat less than unity, whereas at 80° the same ratio was considerably greater than unity.

The data of Table VI demonstrate that in the reaction of Ib, $\Delta H^{\ddagger}$ varies about 5 kcal. per mole as the temperature is varied between the extremes of 70.15 and 108.7°. In the reaction of Ic, $\Delta H^{\ddagger}$ changes 1.5 kcal. per mole for a similar temperature range. The change of $\Delta H^{\ddagger}$ for Ib is well outside probable error. Although the values of $\Delta H^{\ddagger}$ for Ic are within probable error of one another, it is likely that the differences are real but less pronounced than for isomer Ib. *The lack of constancy of $\Delta H^{\ddagger}$ for changes of temperature in the pyrolytic reaction is strong evidence for the operation of at least two competing primary processes which lead to olefin.*

Over the range of 65 to 108°, the above reactions of Ib and Ic changed very little in their predominantly *cis* steric course in spite of the fact that a change in the balance of mechanisms was occurring as the temperature was raised. This result, coupled with the fact that at 120°, Id gives olefin by a predominantly *trans* steric course, indicates that the primary process favored at higher temperatures can assume either a *cis* or *trans* steric course. The primary process favored by lower temperatures appears to be *cis* in steric course.

Mechanisms of the Sulfoxide Elimination Reaction.—The mechanisms for the sulfoxide elimination reaction must satisfy the following requirements: (1) The reactions occur by at least two primary processes, both of which are unimolecular, and involve non-hydrogen-bonded sulfoxide as the starting state. (2) The rates of these primary processes are only slightly sensitive to the ionizing power of the solvent. (3) The primary process favored at lower temperatures is stereospecific and *cis* in steric course. The primary process favored at higher temperatures tends to be non-stereospecific, and the most thermodynamically stable olefin dominates in the product. (4) The reaction rates of those diastereomers that give the least stable olefin are higher than those which give the most stable olefin.

In the classical mechanism[24] that has been proposed for the internal elimination reaction (E_i reaction), the leaving group abstracts a hydrogen from C_β in a sort of intramolecular acid–base reaction. The simplest version of this mechanism involves a single, cyclic transition state which intervenes between reactant and product. As applied to the reaction at hand, this mechanism requires a transition state such as VIII for the production of olefin from sulfoxide. This mechanism meets the structural, kinetic and stereochemical requirements for that process which is favored by lower temperatures. The fact that the diastereomers leading to the less stable olefin react faster than those giving the more stable olefin indicates that the relative energies of the starting state governs the activation energies more than the relative energies of the products. In other words, the shapes of the starting and transition states resemble one another more than the shapes of the transition states and products.



A mechanistic scheme which is consistent with the requirements for the processes favored at higher temperatures is formulated in Chart I. Starting material, A, in the rate-determining step undergoes homolytic cleavage to give a radical-pair, C. This discrete intermediate partitions between *cis* and *trans* elimination reaction paths without the two radicals ever completely leaving the solvent cage. Intermediate C goes to E (*cis* elimination) by transfer of a hydrogen atom from the hydrocarbon radical to the sulfoxyl radical before the original pseudo-diastereomeric character of the radical pair is lost. Intermediate C goes to F (*trans* elimination) through a second radical pair (D) as an intermediate, whose pseudo-diastereomeric configuration is different from that of C with respect to the relative positions in space of the two radicals. Similarly, D is formed directly from B, and partitions between E and F. In this scheme, the steric course of the over-all reaction is governed by the ratio, $k_c k_{-e}/k_d k_e$, if k_e and k_{-e} are very much greater than k_c and k_d. This condition might be approached at higher temperatures where the two diastereomeric starting materials give largely *trans*-olefin (E) as product. In this circumstance, k_c is expected to be greater than k_d since eclipsing effects in the transition state leading to E would be much less than those leading to F. Similarly, $k_{-e} > k_e$, since C is less internally sterically hindered.

At lower temperatures, this mechanism might favor over-all *cis* elimination for the following reasons. If $k_c > k_e$, then A would provide largely E. Similarly, if $k_d > k_{-e}$, then B would give mainly F. Since the sulfoxide group is bulky, the conformation favored for the starting material is likely to place that group near the hydrogen bound to C_β, as in A and B. The relative rates of k_a and k_b would be governed by the relative stabilities of the starting sulfoxides A and B and would be unrelated to the relative stabilities of the olefinic products. *Since both the classical Hurd mechanism and the radical pair mechanism for the E_i reaction can assume a cis-steric course, neither the stereo-*

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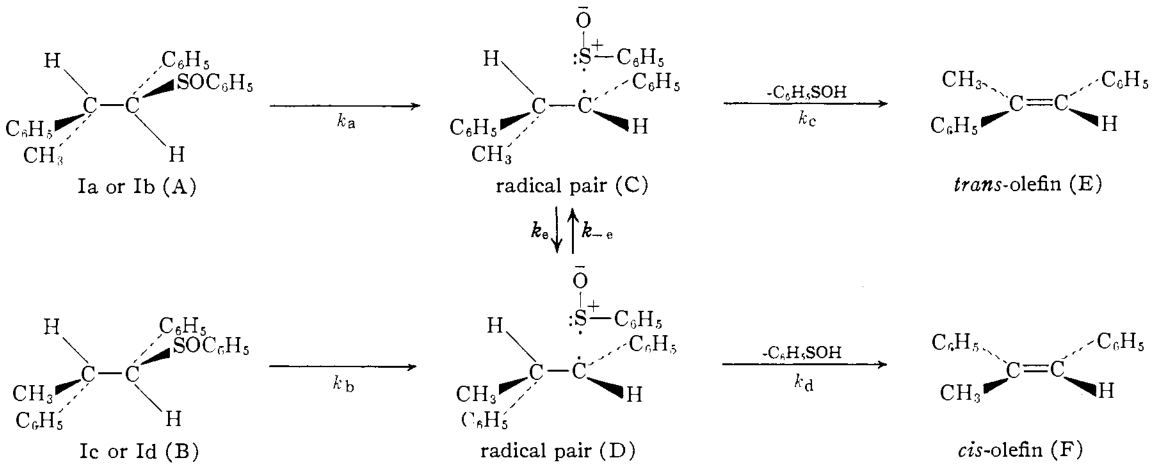
[24] (a) C. D. Hurd and F. H. Blunck, THIS JOURNAL, **60**, 2419 (1938); (b) references to more refined proposals are summarized by D. J. Cram in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 305–314.

CHART I



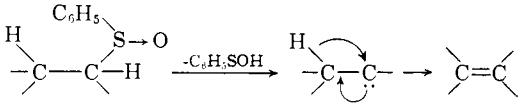
chemistry nor the kinetics taken separately can be used to differentiate between these mechanisms.

The entropies of activation recorded in Table VI suggest the above mechanistic picture for the E_i reaction. These data indicate that the mechanism predominant at lower temperatures possesses a negative entropy, whereas the mechanism favored at higher temperatures has a positive entropy. The entropies of activation associated with reactions whose rate-determining transition states involve the making of five or six-membered rings and whose starting states are neutral have been found to range from −2 to −17 e.u.[25] The Hurd mechanism also satisfies these criteria, and the small negative entropy associated with the low temperature E_i reaction correlates with the entropies observed for other reactions involving cyclic transition states. On the other hand, homolytic processes such as that involved in the radical-pair mechanism would be expected to display a positive entropy of activation, as is observed for the high temperature E_i reaction in runs 46 and 47.

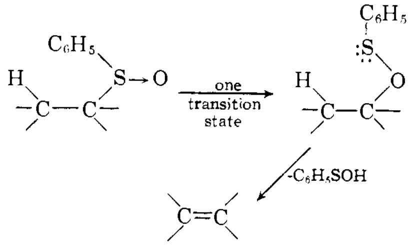
Two other possible mechanisms for the E_i reaction are outlined below, both of which would follow first-order kinetics and would be insensitive to the polarity of the medium. The carbene mechanism (1,1-elimination) would be non-stereospecific, whereas the second stage of the rearrangement mechanism could be either stereospecific or non-stereospecific, depending on whether the Hurd or the radical-pair process applied. Although neither of these mechanisms can be ruled out, they are both considered improbable, particularly the carbene mechanism.

Correlations of Reactivity and Relative Configurations of the Diastereomeric Sulfoxides.—Although the relative configurations of the two asymmetric carbon atoms in the four diastereomers of I were established by their mode of synthesis, the relative configurations about the asymmetric sulfur atom has not been discussed. In this section, provisional assignments of relative configuration to the three asymmetric centers of isomers Ia, Ib, Ic and Id will be made.

Carbene mechanism



Rearrangement mechanism



In both dioxane and 50% dioxane–50% methanol at 80°, $k_{Ib}/k_{Ia} \cong 3$, and $k_{Id}/k_{Ic} \cong 2$ (see Table V). Since the least stable isomer of each pair is presumed to react the faster, the relative configurations about sulfur in each isomer can be assigned if the relative stabilities of each diastereomeric pair can be deduced through examination of molecular models. With the aid of scale models and principles developed previously,[13,23,26] the rotomers formulated were selected as the most stable for each of the four diastereomers. Within each of the *erythro* and *threo* series, the formula at the left should be more stable and less reactive than the one on the right, because of the steric interactions between the substituents on the β-carbon and on the sulfur atoms. Thus the configurations of the isomers can be tentatively assigned as indicated, and the reactivity order, $k_{Id}>k_{Ic}>k_{Ib}>k_{Id}$, is correlated with the structures of the starting materials.

If isomer Id is the most internally strained, it might be expected to exhibit the highest degree of steric inhibition of resonance of the sulfoxide with the attached phenyl group. Indeed, λ_{max} in the

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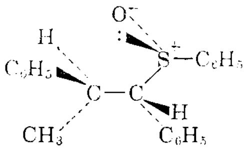
[25] (a) Calculated from the data from E. L. Eliel in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 116; (b) S. Winstein, E. Grunwald, R. E. Buckles and C. J. Hanson, THIS JOURNAL, **70**, 811 (1948); (c) R. Heck and S. Winstein, *ibid.*, **79**, 3106, 3114, 3432 (1957); W. N. White, P. Gwynn, P. Schlitt, C. Girard and W. Fife, *ibid.*, **80**, 3271 (1958); (d) H. L. Goering and R. L. Jacobson, *ibid.*, **80**, 3277 (1958); (e) S. Winstein, L. Goodman and R. Boschan, *ibid.*, **72**, 4669 (1950).

[26] (a) F. A. Abd Elhafez and D. J. Cram, *ibid.*, **75**, 339 (1953); (b) D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957).



erythro, Ia, m.p. 184°
(more stable)

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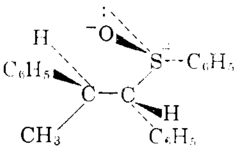
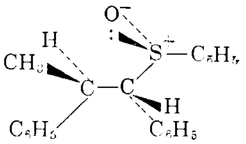


erythro, Ib, m.p. 132°
(less stable)



threo, Ic, m.p. 155°
(more stable)

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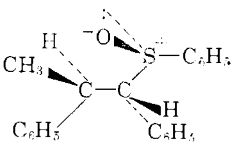

threo, Id, m.p. 75°
(less stable)

ultraviolet spectrum of this isomer occurs at 3 $m\mu$ shorter wave length and with lower intensities than the corresponding band in the spectra of the other three isomers (see Table I).

Mechanisms of Other Pyrolytic Elimination Reactions.—The results of this investigation may have implications with regard to the mechanisms of other E_i reactions. Most of these exhibit partial stereospecificity in the *cis* direction, exhibit first-order kinetics and are not subject to important medium effects.[27] Substituent effects on reaction rate both with respect to the leaving group and the α-carbon operate in a direction consistent with what might be expected of either of the Hurd mechanism or the homolytic cleavage as a rate-determining step. The reactions are usually free of molecular rearrangements with respect to the carbon skeleton,[28] but occasionally exhibit rearrangements with respect to leaving group.[29] When xanthate or carboxylate esters which contain no β-hydrogen are pyrolyzed, the products are suggestive of a free radical process.[30] In the amine oxide pyrolyses of systems which contain two different kinds of non-benzyl β-hydrogens, the hydrogen lost was not subject to important polar effects, but was largely controlled by steric and statistical factors.[19] The same is true of acetate pyrolysis.[31] All of these facts are consistent with the two general mechanisms outlined in this paper.

The steric course of these reactions deserves further comment. The Hurd mechanism accounts for only the product which arises by a *cis* elimination, yet none of the pyrolytic reactions are completely stereospecific. In fact, in some cyclic systems, chlorosulfite[18c] and xanthate pyrolyses[32] assume a predominantly *trans* steric course. The radical-pair mechanism provides a means of obtaining either stereochemistry, *cis* or *trans*. The leaving groups in most of the E_i reactions are bulky, and in open-chain systems at lower temperatures tend to be distributed in conformations gauche to β-hydrogens (small groups). As a result, the radical-pair produced possesses a conformation favorable to a *cis*-hydrogen abstraction process, which can proceed without conformational readjustments. In general, the reactions which involve the bulkier leaving groups and lower temperatures tend to give the more stereospecific results.

The authors are much indebted to Professor G. S. Hammond for valuable discussions and suggestions concerning this investigation.

Experimental

***erythro*-1,2-Diphenyl-1-propyl Phenyl Sulfide (IVa).**—To 200 ml. of absolute ethanol in a nitrogen atmosphere was added (in pieces) 1.86 g. (0.081 mole) of sodium metal. After the reaction was complete, 8.9 g. (0.081 mole) of thiophenol was added dropwise, and the resulting solution was stirred for one hour. To this solution was added as a solid, 7.2 g. (0.027 mole) of *threo*-1,2-diphenyl-1-propyl chloride.[14] The mixture was stirred under nitrogen for 48 hours at about 50° (a precipitate of sodium chloride appeared after about 6 hours). The reaction mixture was cooled, filtered, and the filtrate was extracted with ether. The ether solution was washed with water, dried and evaporated to a small volume. The solid (IVa) that separated as white crystals amounted to 7.1 g. (87% yield), m.p. 103–104.5°. A small portion of this material was recrystallized twice from ether for analysis, m.p. 103.5–104°.

A similar reaction with *erythro*-1,2-diphenyl-1-propyl chloride[14] gave 2.8 g. (46% yield) of *cis*-α-methylstilbene, m.p. 44–46°, undepressed by admixture with an authentic sample.[14]

***threo*-1,2-Diphenyl-1-propyl Phenyl Sulfide (IVb).**—A solution of 3.0 g. (0.014 mole) of *threo*-1,2-diphenyl-1-propanol[12] in 16.0 g. (0.145 mole) of thiophenol and 0.3 ml. of concentrated hydrochloric acid was heated to 120–130° under nitrogen for 60 hours. Small amounts (0.3 ml.) of additional concentrated hydrochloric acid were added at intervals. The reaction mixture was cooled and shaken with a mixture of 100 ml. of ether and 100 ml. of cold 5% sodium hydroxide solution. The aqueous phase was washed with ether, and the combined ether extracts were washed with water, dried and evaporated to an oil. Solid separated (1.0 g. or 23% yield) which proved to be IVa, m.p. 104–106°. The remaining oil was chromatographed on 50 g. of neutral, activity I alumina.[33] The oil eluted with pentane crystallized on standing at 0°, and was recrystallized three times from pentane to give 0.61 g. (14% yield) of IVb, m.p. 41.5–43°. A similar procedure in which *p*-toluenesulfonic acid was substituted for hydrochloric acid worked somewhat better.

Preparation of *erythro*-1,2-Diphenyl-1-propyl Phenyl Sulfoxides, Ia and Ib.—To a solution of 2.0 g. (0.0056 mole) of *erythro*-1,2-diphenyl-1-propyl phenyl sulfide (IVa) in 25 ml. of chloroform at 5° was added a solution of 1.10 g. (0.0056 mole) of perbenzoic acid in 3 ml. of chloroform. The resulting mixture was allowed to come to room temperature, and was stirred for three days. The chloroform solution was then washed with 50 ml. of dilute sodium carbonate solution, with water, and was dried. Solvent was evaporated, and the residue was fractionally crystallized from ether–chloroform by the triangle method. Isomer Ia proved to be the more insoluble, and was obtained in 28% yield (0.59 g.), m.p. 184–185°. Isomer Ib was isolated in 15% yield (0.320 g.), m.p. 132–133°.

A similar run with 30% hydrogen peroxide as the oxidizing reagent gave a 15% yield of Ia, a 3% yield of Ib, and a 38% recovery of starting material. Another run in which peracetic acid was employed gave a 30% yield of Ia and a 13% yield of Ib.

Preparation of *threo*-1,2-Diphenyl-1-propyl Phenyl Sulfoxides, Ic and Id.—To a solution of 10.8 g. (0.0355 mole) of *threo*-1,2-diphenyl-1-propyl phenyl sulfide (IVb) in 125 ml. of chloroform at −5° under nitrogen was added dropwise with stirring 300 ml. of a 0.12 M solution of perbenzoic

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[27] G. L. O'Connor and H. R. Nace, THIS JOURNAL, **74**, 5454 (1952), and **75**, 2118 (1953), in their kinetic study of the pyrolytic elimination reaction of a series of xanthates, carbonates and esters of cholesterol in the absence of solvent observed good first-order kinetics for the reaction even though the medium in effect was changing from that of starting material to that of product as the reaction proceeded.

[28] See, *e.g.*, W. Formin and N. Sochanski, *Ber.*, **46**, 246 (1913).

[29] D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, **49**, 60 (1951).

[30] See, *e.g.*, G. Bulmer and F. G. Mann, *J. Chem. Soc.*, 666 (1945).

[31] (a) D. H. Froemsdorf, C. H. Collins, G. S. Hammond and C. H. DePuy, THIS JOURNAL, **81**, 643 (1959); (b) W. J. Bailey and W. F. Hale, *ibid.*, **81**, 647, 651 (1959).

[32] F. G. Bordwell and P. S. Landis, *ibid.*, **80**, 2450 (1958).

[33] H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1951).

acid in chloroform.[34] The reaction mixture was then stirred for 4 days at room temperature. The resulting solution was washed with 150 ml. of dilute aqueous sodium carbonate, with water, and was dried. Evaporation of the solvent under reduced pressure gave an oil which crystallized from ether after 6 days at 0°. The resulting material was fractionally crystallized by the triangle method to give as the more insoluble isomer, 0.95 g. (8% yield) of Ic, m.p. 150–151°, and as the more soluble isomer, 3.03 g. of Id, m.p. 74–76°, 28% yield. Portions of these materials were recrystallized 4 to 6 times from ether to give Ic, m.p. 155–155.5°, and Id, m.p. 75.5–76°. A second run made on a smaller scale gave a similar ratio of products.

threo-**1,2-Diphenyl-1-propyl Phenyl Sulfone (Vb).**—To a solution of 0.100 g. (0.00315 mole) of Ic in 6 ml. of chloroform at −5° was added dropwise with stirring 10 ml. (0.0015 mole) of 0.15 *M* solution of perbenzoic acid in chloroform.[34] The solution was stirred at 25° for 10 hours and then at 40° for one hour. The resulting solution was washed with dilute aqueous sodium carbonate, with water, and was dried and evaporated at reduced pressure. The resulting solid (0.08 g., m.p. 132–135°) was recrystallized four times from ether to give 0.040 g. (30% yield) of *threo*-sulfone Vb, m.p. 138–139°.

By a similar procedure, 0.100 g. (0.000315 mole) of Id was oxidized with 10 ml. of 0.15 *M* solution of perbenzoic acid (the reaction mixture was ultimately refluxed for 2 hours). Isolation of the product gave 0.033 g. of *threo*-sulfone Vb, m.p. 136–137°, undepressed by admixture with Vb prepared above.

By a similar procedure, 1.00 g. (0.00033 mole) of *threo*-sulfide IVb was oxidized with 0.88 g. (0.0066 mole) of perbenzoic acid to give 0.5 g. (45% yield) of sulfone Vb, m.p. 138–139°, undepressed by admixture with either of the above samples.

erythro-**1,2-Diphenyl-1-propyl Phenyl Sulfone (Va).**—The same procedure that was used for the preparation of Vb from Id (see above) was used here. From 0.100 g. (0.00031 mole) of Ia and 0.153 g. (0.00062 mole) of perbenzoic acid was obtained 0.91 g. (87% yield) of Va (recrystallized from ether), m.p. 183–184.6°.

Similarly, 0.030 g. (0.000094 mole) of Ib was oxidized with 0.050 g. (0.0009 mole) of perbenzoic acid to give 0.022 g. of Va, m.p. 182–183°, undepressed by admixture with sulfone prepared from Ia.

By the same procedure, from 0.80 g. (0.0027 mole) of sulfide IVa and 1.94 g. (0.008 mole) of perbenzoic acid was obtained 0.71 g. (79% yield) of sulfone Va, m.p. 183–184°, undepressed by admixture with either of the above samples.

Solvents Employed in Product Analyses and Kinetic Runs.—Methanol (J. T. Baker Analyzed Reagent Grade) was dried by distillation from barium oxide. Dimethylformamide (Eastman Kodak Co. White Label Grade) was similarly purified. Diethylene glycol diethyl ether was purified by distillation from sodium and redistillation from lithium aluminum hydride. Dioxane (Eastman Kodak Co. White Label) was refluxed 10 hours with hydrochloric acid, the water and acid were absorbed with solid potassium hydroxide, and the resulting dioxane was refluxed with sodium and distilled. Pyridine (Karl Fischer reagent) was used without purification.

Procedure for a Typical Kinetic Run (40).—Dry clean test-tubes were prepared for sealing. The stock solution was prepared from 0.3500 g. (0.001092 mole) of Ic and 20.048 ml. of purified dioxane to give a 0.0545 *M* solution. The ampules were flushed with dry, pure nitrogen, and 1.983 ml. of the stock solution was added to each tube which was subsequently sealed. The tubes were placed in a constant temperature oil-bath, at 79.70 ± 0.05°, and removed at intervals. The tubes were opened, the contents were transferred quantitatively to a chromatograph column containing 60 g. of neutral activity I alumina.[33] The column was washed with purified pentane (500 ml.), and the eluate was carefully evaporated through a packed column. The residue was quantitatively transferred to a 100-ml. volumetric flask and dissolved in spectral grade 95% ethanol. One ml. of this solution was diluted to 10 ml. in a second volumetric flask and the ultraviolet spectrum was taken. Product composition and yield were calculated as described previously.

Since α-methylstilbene was destroyed by unknown means upon prolonged heating, points could be taken to the end of the third half-life on the faster rates, but only through the second half-life of the slow rates. In run 34 points were taken only during the first half-life.

Pyrolysis of Sulfoxide Id (Run 19).—A solution of 0.300 g. (0.000938 mole) of Id in 25 ml. of purified dioxane and 0.15 ml. (0.0019 mole) of pyridine was placed in a dried pressure tube, and the system was flushed with dry pure nitrogen. The tube was sealed and heated at 80° for 60 hours. The tube was then cooled, the solvent was evaporated under a nitrogen atmosphere, and the residue was chromatographed on 40 g. of activity I neutral alumina.[33] Olefin was eluted with pentane, 10-ml. fractions being taken. Residues from the first 12 fractions crystallized to give 0.128 g. (73% yield) of *cis*-α-methylstilbene, m.p. 44–46°, undepressed by admixture with an authentic sample. Fractions 13–19 also solidified, 0.048 g., m.p. 50–54°. This material gave an ultraviolet spectrum with λ_{max} 265 mμ, which demonstrates the presence of both *cis*- and *trans*-olefins.

Pyrolysis of Sulfoxide Ia (Run Not Recorded in Table II).—A solution of 0.300 g. (0.0094 mole) of Ia in 25 ml. of dioxane and 0.115 g. (0.0019 mole) of pyridine was sealed in a glass tube and heated at 95° for 36 hours. Solvent was removed under reduced pressure (nitrogen), and the residue was chromatographed on 60 g. of activity I neutral alumina.[33] The column was eluted with pentane, and the solid residue was fractionally recrystallized by the triangle method to give 0.102 g. of *trans*-α-methylstilbene, m.p. 79–81° (undepressed by admixture with an authentic sample), and 0.024 g. of *cis*-α-methylstilbene, m.p. 44–46° (undepressed by admixture with an authentic sample), 66% combined yields. Other small fractions with intermediate melting range were also obtained.

Pyrolysis of Sulfoxides with Special Analysis of Products.—Ultraviolet spectra were taken of a series of mixtures of known composition of *cis*- and *trans*-α-methylstilbene. A plot of molar extinction coefficient *vs.* precentage composition was linear over the entire composition range. A plot of wave length *vs.* percentage composition deviated somewhat from linearity near 100% *trans*-olefin.

In a typical run (4), a solution of 0.030 g. (0.000094 mole) of Id in 2.5 ml. of purified dioxane was sealed under nitrogen in an ampule, and heated at 80° for 60 hours. The contents of the tube were transferred quantitatively to a chromatograph column which contained 70 g. of neutral activity I alumina.[33] The column was eluted with 800 ml. of pure pentane, and the pentane was evaporated through a column. The residue was quantitatively transferred to a volumetric flask and diluted to either 500 or 1,000 ml. with spectral 95% ethanol. The ultraviolet spectrum showed λ_{max} 264 mμ (ε 12,600) which corresponds to 86% *cis*- and 14% *trans*-α-methylstilbene, and a 100% yield of olefin.

Pyrolyses of *threo*- **and** *erythro*-**1,2-Diphenyl-1-propyl Phenyl Sulfone (Va and Vb).**—A solution of Va in dioxane when heated at 135° for 7 days gave back only 75% of starting material and produced no olefin. A similar treatment at 190° for 3 days in tetraethylene glycol as solvent produced no detectable amount of α-methylstilbene. A solution of Vb in dioxane was heated at 120° for 52 hours, and a 73% yield of starting material was recovered. No olefin was detected.

Controls on Stability of α-Methylstilbene.—A 0.030 *M* solution of *cis*-α-methylstilbene in dioxane (0.15 *M* in pyridine) in a sealed ampule under nitrogen was heated at 120° for 12 hours. Spectral analysis of the product demonstrated an 83% recovery of olefin after chromatography, 95% of which was *cis*- and 5% *trans*-α-methylstilbene.

In a second experiment, a solution of 0.0302 g. of Ia, and 0.100 g. of *cis*-α-methylstilbene in 2.5 ml. of dioxane was heated at 123° for 2.25 hours. Spectral analysis of the product after chromatography indicated that 99% of the total olefin was accounted for, 82% of which was *cis*-α-methylstilbene and 18% was the *trans* isomer.

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[34] G. Braun in H. Gilman's, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 431.