ORGANIC AND BIOLOGICAL CHEMISTRY

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Elimination Reactions. VII. A Comparison of Some Eliminations in Open-chain and Cyclic Systems

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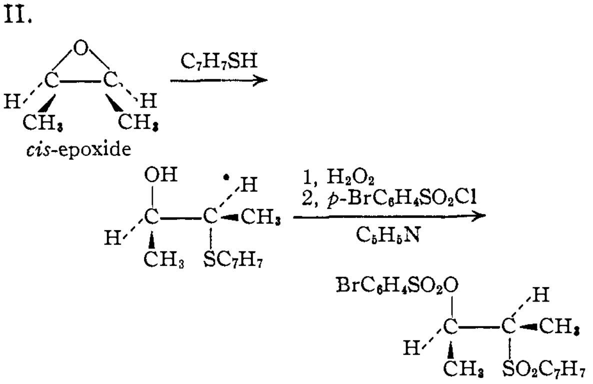
The brosylates of the *dl-threo* and *dl-erythro* forms of 3-*p*-tolylsulfonyl-2-butanol (I and II) each react with trimethylamine or hydroxide ion in 50% aqueous dioxane solution by stereoselective *trans* elimination forming *trans*- and *cis*-2-*p*-tolylsulfonyl-2-butenes, respectively. Carbanion intermediates of any but extremely short half-life are ruled out by these experiments. The brosylate of *trans*-2-*p*-tolylsulfonylcyclopentanol underwent *cis* elimination under comparable conditions at a rate seven times that of I and three times that of II. The activation energy of the *cis* elimination was of comparable magnitude to the *trans* elimination of I and II. It is concluded that relatively rapid *cis* eliminations, such as this, do not proceed by energetically unfavorable two-stage mechanisms involving carbanion intermediates.

In previous papers[2] it has been established that the high ratio of *trans/cis* elimination rates for adjacent H– and –Y groups, which has been demonstrated to exist in some cyclic systems,[3] is markedly reduced when H– is activated by an arylsulfonyl grouping. The *trans/cis* rate ratio in our activated systems was found to depend on the base used, the ring size and the solvent. In 50% aqueous dioxane the ratios of *trans/cis* rates for arylsulfone tosylates in the cyclohexane series are 435, 116 and 25 for the bases hydroxide ion, triethylamine and trimethylamine, respectively. In the cyclopentane series the rate ratios for these bases in the same solvent are 20, 6.6 and 1.2.

The *trans* and *cis* eliminations with trimethylamine were shown to be general base catalyzed, and it was concluded from this that carbanion intermediates[3] with half-lives of more than about 10^{-8} sec. cannot be present.[2] It is still possible that very short-lived carbanions may be formed, but the small *trans/cis* rate ratios observed with trimethylamine did not seem to justify the assumption that *cis* elimination might proceed by an energetically unfavorable two-stage mechanism. In open-chain systems formation of a carbanion intermediate should lead to a non-stereoselective elimination. The elimination reactions of the brosylates of the diastereoisomeric *dl*-3-*p*-tolysulfonyl-2-butanols have now been examined in order to test this point[4] and to obtain additional evidence on the relative rates of *trans* and *cis* eliminations in various systems.

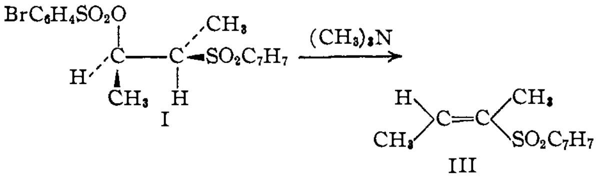
Starting from *trans*- and *cis*-2-butenes the *trans*- and *cis*-2-butene epoxides were prepared by way of the chlorohydrins. A rough determination of the rate of ring closure was obtained by measuring the amount of epoxide formed during various time intervals. The *trans*-epoxide was formed at a rate about ten times that at which the *cis*-epoxide is formed, which is in line with expectations on the basis of the *cis* effect.[5]

The *cis*- and *trans*- epoxides were converted in the series of steps shown (for the *cis* compound) to the *dl-threo*- and *dl-erythro*-sulfone brosylates I and II.



I (*threo* isomer)

Elimination of H-$OSO_2C_6H_4Br$ from I and II under the influence of trimethylamine in 50% aqueous dioxane was found to occur stereoselectively to give two different sulfones III and IV. Assuming *trans* elimination, the *trans* isomer III should be formed from the *threo* isomer I.



The isomeric relationship of III and IV was established by hydrogenation of each to *sec*-butyl *p*-tolyl sulfone, which was synthesized independently. The relationships of the methyl groups in III and IV were proved by syntheses from *trans*- and *cis*-2-bromo-2-butenes.

Recently Dreiding and Pratt[6] have shown that formation and carbonation of *cis*- and *trans*-2-butenyl-2-lithium occurs predominantly with main-

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[2] See J. Weinstock, R. G. Pearson and F. G. Bordwell, THIS JOURNAL, **78**, 3473 (1956), and references cited therein. Paper VI in this series is J. Weinstock, S. N. Lewis and F. G. Bordwell, *ibid.*, **78**, 6072 (1956).

[3] S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951), found *trans/cis* rate ratios of the order of 10^4–10^6 for dehydrohalogenation of benzene hexachlorides. See also E. D. Hughes, C. K. Ingold and R. Pasternak, *J. Chem. Soc.*, 3832 (1953).

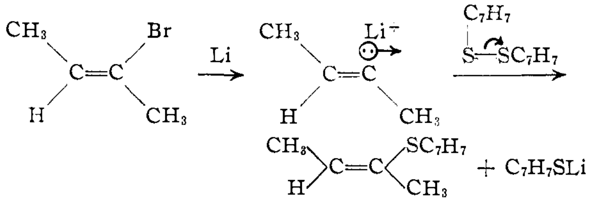
[4] After this work was completed, we received a manuscript from Professor P. S. Skell describing similar experiments with the diastereoisomeric 3-benzenesulfonyl-2-iodobutanes. Fortunately, the two pieces of work are complementary and led to the same conclusions; see P. S. Skell and J. H. McNamara, THIS JOURNAL, **79**, 85 (1957).

[5] D. Y. Curtin, Abstracts 13th National Organic Symposium of Am. Chem. Soc., Ann Arbor, Mich., June, 1953; D. Y. Curtin and D. B. Kellom, THIS JOURNAL, **75**, 6011 (1953).

[6] A. S. Dreiding and R. J. Pratt, *ibid.*, **76**, 1902 (1954).

tenance of configurations giving tiglic and angelic acids, respectively. In our work the *dl*- and *meso*-2,3-dibromobutanes were prepared from pure samples of *cis*- and *trans*-2-butenes, and (*trans*) dehydrobromination was effected using the method of Dreiding and Pratt.[6,7]

The lithium derivatives of *cis*- and *trans*-2-bromo-2-butenes were prepared at −40° by reaction with lithium metal, and these were treated (separately) with *p*-tolyl disulfide to give 50–60% yields of the corresponding *cis*- and *trans*-2-*p*-tolylthio-2-butenes (IIIa and IVa). These reactions may be looked on as nucleophilic displacements of the 2-butenyl-2-carbanion (configuration maintained) on one of the sulfur atoms of *p*-tolyl disulfide. The infrared spectrum of *trans*-2-*p*-tolylthio-2-butene (IIIa) agreed for the most part with that reported by Truce and Simms[8] for this compound.



IIIa

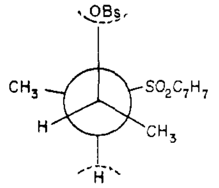
Little or no change in refractive index or infrared spectra of either of the sulfides was observed on standing, indicating no isomerization under these conditions.

Oxidation of IIIa and IVa with hydrogen peroxide gave the corresponding sulfones (III and IV), which were purified by crystallization. The *trans*-sulfone III has a strong peak at 14.7 μ, which is lacking in the *cis* isomer. Using this peak as a basis of analysis, it was determined that crude sulfide IIIa yields about 25% of IV and 75% of III on oxidation and sulfide IVa gives 85% of IV and 15% of III on oxidation. It is doubtful that isomerization occurs during or after oxidation so these percentages reflect the purities of IIIa and IVa. Dreiding and Pratt[7] reported 75% retention of configuration on formation and carbonation of *cis*-2-butenyl-2-lithium and 91% retention for carbonation of the *trans* isomer at −15°. Our results agree well with theirs. Curtin and coworkers[9] have found that vinyllithium compounds react with a high degree of stereoselectivity and have suggested that loss of configuration[6] may occur during the reaction of lithium with *cis*- and *trans*-2-bromo-2-butene. To test this point the reaction was run using butyllithium, as well as with lithium metal. Essentially no difference was observed in the degree of stereoselectivity.

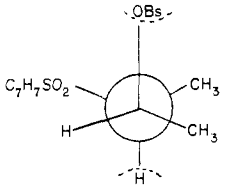
In another experiment, using lithium and *cis*-2-bromo-2-butene, part of the lithium derivative was treated immediately after its formation with *p*-tolyl disulfide, and part was allowed to stand for 2 hr. prior to treatment with *p*-tolyl disulfide. The relative proportion of *cis* and *trans* isomers formed in these two instances was found to be the same.

Our experiments indicate that isomerization occurs neither during the formation of the lithium derivative by the reaction of *cis*- and *trans*-2-bromo-2-butenes with lithium metal or butyllithium nor by isomerization of the lithium derivative after it is formed. Apparently a partial interconversion of the *cis*- and *trans*-2-bromo-2-butenes occurs prior to formation of the lithium derivative. These results support Curtin's conclusion[9] that the formation and reactions of vinyllithium derivatives are highly stereoselective.

The structure assignment for III and IV is further supported by the observation that the rate of formation of IV from II by reaction with trimethylamine is over twice as fast as that of III from I. As indicated in the conformation diagrams, *trans* elimination for I requires that $C_7H_7SO_2$– and –CH_3 be brought into the same plane, as the double bond is formed.



I



II

Since there is good evidence to indicate a large steric effect for $C_7H_7SO_2$–,[2,10] the *cis* effect between this group and methyl should be greater than between the two methyl groups of II, and the rate of formation of III should be less than that of IV.

The 14.7 μ band proved useful also in checking the stereoselectivity of the eliminations with II (to form IV), since the presence of small amounts of III in IV can be detected by this means. The spectra indicate that little or no III is produced from II in eliminations with hydroxide ion and trimethylamine. The evidence concerning the stereoselectivity of the reaction of I → III is not so clear-cut, but the spectra indicate predominant stereoselective elimination here also.

The fact that eliminations from I and II in 50% aqueous dioxane under the influence of trimethylamine occur stereoselectively rules out the possibility of an intermediate carbanion of any but very short half-life. Since product analysis shows that *trans* elimination has occurred to the extent of at least 95%, the *trans*/*cis* ratio for the open-chain systems must be at least 20 and may be much higher. This is to be compared with ratios of 25 and 1.2 for the cyclohexane and cyclopentane analogs, respectively. One factor believed to favor *cis* elimination with trimethylamine in cyclic systems is the fact that the electrostatic attraction between the positive charge developing on the base and the negative charge developing on the leaving brosylate group may partially offset the repulsive forces between the electrons of the two leaving groups.[2] This would be possible also for

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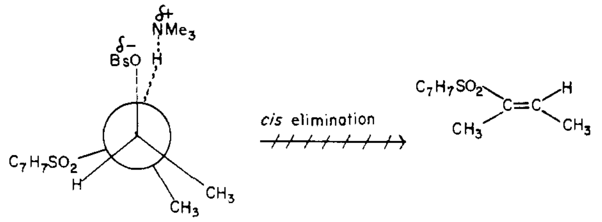
[7] The credit for recognizing that eliminations of this type are *trans* rather than *cis* appears to belong to A. Michael (*J. prakt. Chem.*, **52**, 289 (1895)) rather than to P. Pfeiffer or P. F. Frankland.[6]

[8] W. E. Truce and J. A. Simms, This Journal, **78**, 2759 (1956).

[9] See D. Y. Curtin, H. W. Johnson, Jr., and E. G. Steiner, *ibid.*, **77**, 4566 (1955).

[10] F. G. Bordwell and G. D. Cooper, *ibid.*, **73**, 5184 (1951).

cis eliminations in open-chain systems, as illustrated for the *threo* isomer I.



I (*threo*) IV

Coplanar *cis* elimination would be unlikely, since this would require an eclipsed conformation in the transition state. Repulsive forces no doubt would be very large[11] in such a transition state. There is evidence to indicate that transition states in *trans* eliminations from open-chain systems occur at an early state in the reaction (before such repulsions get very large), since eliminations to produce *cis* stilbenes are not much more difficult than those to produce *trans*-stilbenes, despite a difference in stabilities of the stilbene isomers of about 6 kcal. per mole.[5,12,13]

On the other hand, *cis* elimination from a non-eclipsed conformation should be possible and should be somewhat comparable to *cis* eliminations in cyclic systems. However, from our data this type of elimination appears to be less favored relative to *trans* elimination than in the C_5 or even C_6 cyclic systems. One possible explanation for this is that such a *cis* elimination would require approach of Me_3N to hydrogen between either $OSO_2C_6H_4Br$ and CH_3 or $OSO_2C_6H_4Br$ and H, whereby hindrance might be somewhat greater than in *trans* elimination, where the approach is between CH_3 and H. This steric factor is similar in basis to that leading to the steric control of asymmetric induction,[14] but its application to our system is not nearly so clearcut or convincing.

The results of a comparison of the rates of elimination reactions of I and II with those of the *trans*- and *cis*-cyclopentane analogs (V and VI) are given in Table I.

The rates were measured conductometrically by the method described earlier.[2] All reactions were found to be general base catalyzed. The ratio of *trans*/*cis* elimination rates for VI and V was found to be 1.3, which agrees well with the previous ratio of 1.2 for the tosylates.[2]

It is of particular interest to note that *cis* elimination for V is seven times faster than *trans* elimination for I and three times faster than *trans* elimination for II. Furthermore, the activation energy for the *cis* elimination is of the same order of magnitude or smaller than for the *trans* eliminations. On the basis of a much lower rate and about 12 kcal. higher activation energy for *cis* elimination in the benzene hexachloride system Cristol suggested a two-stage mechanism for *cis* eliminations. He has since generalized this viewpoint to include other *cis* eliminations.[15] Our data provide no such basis for the assumption of an energetically unfavorable two-stage mechanism for *cis* eliminations. The early observations[2] that the *cis* eliminations are general base catalyzed, and the present observation that comparable *trans* eliminations in open-chain systems are stereoselective[4] show that any carbanion intermediates formed must be of very short half-life. The information on hand points to some kind of a concerted mechanism for *cis* as well as for *trans* eliminations in our systems.

TABLE I

RATES, ACTIVATION ENERGIES AND ACTIVATION ENTROPIES FOR ELIMINATIONS IN OPEN-CHAIN AND CYCLIC SYSTEMS AS INITIATED BY TRIMETHYLAMINE IN 50% AQUEOUS DIOXANE

Brosylate	Type of elim.	T, °C.	k_2, mole^{-1} sec.$^{-1}$	Rel. rate (25°)	E_a, kcal./mole	$\Delta S^{\ddagger}$, e.u.
threo-2-*p*-Tolylsulfonyl-3-butyl (I)	*trans*	25	3.29×10^{-3}	1.0	14.5	−23.6
		40	1.06×10^{-2}			
		50	2.20×10^{-2}			
erythro-2-*p*-Tolylsulfonyl-3-butyl (II)	*trans*	25	7.62×10^{-3}	2.3	12.8	−27.6
		40	2.17×10^{-2}			
		50	4.10×10^{-2}			
trans-2-*p*-Tolylsulfonylcyclopentyl (V)	*cis*	25	2.42×10^{-2}	7.0	11.8	−26.4
		40	6.24×10^{-2}			
		50	1.13×10^{-1}			
cis-2-*p*-Tolylsulfonylcyclopentyl (VI)	*trans*	25	3.19×10^{-2}	9.7	12.1	−27.2
		40	9.90×10^{-2}			
		50	1.58×10^{-1}			

Since the activation of the α-hydrogen by the arylsulfonyl group is favorable for carbanion formation, it seems likely to us that many other *cis* eliminations will proceed without carbanion formation. However, with further activation of the hydrogen atom and/or changes in the nature of the leaving group, systems which will undergo two-stage eliminations should be arrived at. Activation of hydrogen by a carbonyl group and bromine atom in *erythro*-benzalacetophenone dibromide appears to be just sufficient to give a borderline case, where elimination of hydrogen bromide under the influence of potassium acetate occurs to the extent of 34% by a concerted *trans* mechanism and to the extent of 66% by carbanion formation.[16] The *threo* form, where the *cis* effect is smaller, reacts only by the concerted path.[16]

Investigations of the effect of the arylsulfonyl group on the rates and mechanisms of elimination reactions in other types of systems are under investigation.

Experimental[17]

trans-Butene-2-epoxide—*dl*-*erythro*-3-Chloro-2-butanol (30.5 g., 0.282 mole), prepared according to the method of Lucas and Gould,[18] was added with stirring to 100 g. of potassium hydroxide in 50 ml. of water, which was heated in a water-bath at 65°. The epoxide was allowed to distil from the reaction mixture into a graduated side-arm takeoff trap

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[11] However, orbital overlap should be as favorable for coplanar *cis* elimination as for coplanar *trans* elimination.

[12] R. Otto and F. Stoffel, *Ber.*, **30**, 1799 (1897).

[13] See D. J. Cram, F. D. Green and C. H. Depuy, THIS JOURNAL, **78**, 790 (1956), for an excellent discussion of this point.

[14] D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5828 (1952).

[15] See S. J. Cristol and W. P. Norris, *ibid.*, **76**, 3005 (1954), and papers cited therein.

[16] R. E. Lutz, D. F. Hinkley and R. H. Jordan, *ibid.*, **73**, 4647 (1951).

[17] Microanalyses were by Miss Hilda Beck.

[18] H. J. Lucas and C. W. Gould, THIS JOURNAL, **63**, 2541 (1941).

and the amount collected in tared receivers. Redistillation of the crude epoxide gave 17.6 g. (81%) of material, b.p. 53–55°, n^{20}_{D} 1.3724. Lucas and Wilson[19] reported b.p. 53.6–54.1° (747 mm.), n^{20}_{D} 1.3736. Plotting the rate of formation of epoxide at 65° against time gave a crude first-order rate constant of 8.5×10^{-3} sec.$^{-1}$.

cis-**Butene-2-epoxide.**—Using the method described for *trans*-butene-2-epoxide gave 78% yield of *cis*-butene-2-epoxide, b.p. 57–58°, n^{20}_{D} 1.3802. Lucas and Wilson[19] reported b.p. 59.9–60.4° (747 mm.), n^{20}_{D} 1.3826. An approximate rate constant obtained as above was 9.0×10^{-4} sec.$^{-1}$.

dl-erythro-**3-*p*-Tolylthio-2-butanol.**—*trans*-Butene-2-epoxide (7.2 g., 0.1 mole) was added to a stirred solution of 12.4 g. (0.1 mole) of *p*-thiocresol and 4.4 g. of sodium hydroxide in 30 ml. of 50% ethanol. After stirring for 2 hr. at 30°, the solution was extracted with 30 ml. of chloroform, the extract dried over anhydrous sodium sulfate and the solvent removed on the steam-bath. Vacuum distillation of the residue gave 13.7 g. (70%) of a viscous, colorless oil, b.p. 99–102° (0.2 mm.), n^{20}_{D} 1.5534.

Anal. Calcd. for $C_{11}H_{16}OS$: C, 67.30; H, 8.21. Found: C, 67.83; H, 7.98.

dl-threo-**3-*p*-Tolylthio-2-butanol.**—Addition of *p*-thiocresol as above to *cis*-butene-2-epoxide gave 74% yield of a viscous oil, b.p. 103–104° (0.4 mm.), n^{20}_{D} 1.5529.

Anal. Calcd. for $C_{11}H_{16}OS$: C, 67.30; H, 8.21. Found: C, 66.94; H, 7.95.

dl-erythro-**3-*p*-Tolylsulfonyl-2-butanol.**—*erythro*-3-*p*-Tolylthio-2-butanol (7.8 g., 0.04 mole) was dissolved in 20 ml. of glacial acetic acid, 15 ml. of 30% hydrogen peroxide was added cautiously and the mixture heated at 85° for 2 hr. The mixture was poured into water, the acetic acid neutralized with sodium carbonate solution and extracted with chloroform. The extract was dried over anhydrous sodium sulfate and evaporated to give a solid residue, m.p. 70–72°. Recrystallization from hexane gave 7.4 g. (86%) of colorless crystals, m.p. 71–72°.

Anal. Calcd. for $C_{11}H_{16}O_3S$: C, 57.86; H, 7.06. Found: C, 57.88; H, 7.08.

dl-threo-**3-*p*-Tolylsulfonyl-2-butanol.**—Oxidation of 6.0 g. (0.031 mole) of the *threo*-sulfide with hydrogen peroxide in acetic acid gave 5.8 g. (95%) of viscous oil, b.p. 164–165° (0.2 mm.), n^{20}_{D} 1.5377.

Anal. Calcd. for $C_{11}H_{16}O_3S$: C, 57.86; H, 7.06. Found: C, 57.98; H, 6.84.

dl-erythro-**3-*p*-Tolylsulfonyl-2-butyl Brosylate (*p*-Bromobenzenesulfonate).**—*dl-erythro-p*-Tolylsulfonyl-2-butanol (3.3 g.) was added to 3.7 g. of *p*-bromobenzenesulfonyl chloride in 15 ml. of dry pyridine at 0°. The clear solution was allowed to stand at 0° for three days after which the liquid was decanted into 100 ml. of water. The mixture was extracted with chloroform, the extract dried over anhydrous sodium sulfate and evaporated to give 4.2 g. (67%) of solid ester. After crystallization from hexane the ester melted at 100–101°.

Anal. Calcd. for $C_{17}H_{19}O_5S_2Br$: C, 45.64; H, 4.28. Found: C, 45.74; H, 4.28.

The tosylate (*p*-toluenesulfonate) prepared in an analogous manner melted at about 12–15°.

dl-threo-**3-*p*-Tolylsulfonyl-2-butyl Brosylate.**—Esterification of 10.7 g. of the *threo*-sulfone alcohol with 13 g. of *p*-bromobenzenesulfonyl chloride at 0–5° gave 13.4 g. (64%) of colorless crystals, m.p. 142–145°. Recrystallization from hexane raised the melting point to 144–145°.

Anal. Calcd. for $C_{17}H_{19}O_5S_2Br$: C, 45.64; H, 4.28. Found: C, 45.88; H, 4.12.

The tosylate was prepared in 67% yield by a similar procedure, m.p. 93–94°.

cis-**2-*p*-Tolylsulfonyl-2-butene.**—A solution of the *erythro*-brosylate (4.5 g., 0.011 mole) in 40 ml. of dioxane containing 8 ml. of 5 *N* sodium hydroxide was stirred and heated on the steam-bath for 1 hr. The solution was poured into 100 ml. of water and the mixture was extracted with chloroform. Distillation of the solvent gave 2.6 g. of an oil which crystallized on standing. After several crystallizations from hexane 2.1 g. (91%) of material, m.p. 52–53°, remained.

Anal. Calcd. for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71. Found: C, 63.06; H, 6.64.

Comparison of the intensity of the 14.7 μ peak (absent in the pure *cis* isomer) with that of a sample of pure *trans* isomer (see below) indicated the presence of no more than 5% of *trans* isomer in the crude *cis* product; $\lambda^{\mathrm{KBr}}_{max}$ 6.02(m), 6.20(m), 6.65(w), 6.88(m), 7.10(w), 7.72(s), 8.50(s), 8.78(s), 9.16(m), 9.78(w), 10.95(w), 12.20(m), 12.44(w), 13.98(s), 14.38(s), 15.44(s).

trans-**2-*p*-Tolylsulfonyl-2-butene.**—Treating 0.45 g. of the *threo*-brosylate with 1 ml. of 5 *N* NaOH in 5 ml. of dioxane at 80° for 1 hr., the solution poured into 50 ml. of water and the mixture extracted with chloroform gave 0.20 g. (95%) of crystals which melted at 45–47° after recrystallization from hexane. Repeated recrystallization raised the melting point to 48–49°; $\lambda^{\mathrm{KBr}}_{max}$ 6.02(m), 6.20(m), 6.65(w), 6.88(m), 7.10(w), 7.72(s), 8.50(s), 8.78(s), 9.16(m), 9.60(w), 9.78(w), 12.18(m), 12.44(w), 14.00(s), 14.38(m), 14.70(s), 15.44(m).

Anal. Calcd. for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71. Found: C, 62.66; H, 6.48.

2-*p*-Tolylsulfonylbutane.—*sec*-Butyl bromide (21 g., 0.15 mole) was added with stirring to a solution 19.0 g. (0.15 mole) of *p*-thiocresol and 4 g. of sodium hydroxide in 20 ml. of water and 50 ml. of ethanol. The solution was refluxed for 3 hr. during which a second phase separated. The upper layer was diluted with 50 ml. of ether, washed twice with 10% aqueous sodium hydroxide and with water. The ether solution was dried over anhydrous magnesium sulfate, filtered and the ether evaporated. Vacuum distillation of the residue gave 13.0 g. of 2-*p*-tolylthiobutane, b.p. 81–83° (0.3 mm.), n^{20}_{D} 1.5338.

Anal. Calcd. for $C_{11}H_{16}S$: C, 73.27; H, 8.94. Found: C, 73.03; H, 8.75.

Oxidation of the sulfide with 30% hydrogen peroxide in acetic acid solution gave 2-*p*-tolylsulfonylbutane, m.p. 41–42°.

Anal. Calcd. for $C_{11}H_{16}SO_2$: C, 62.23; H, 7.59. Found: C, 62.18; H, 7.45.

trans-2-*p*-Tolylsulfonyl-2-butene (0.5 g.) in 25 ml. of ethanol was hydrogenated in a Parr apparatus at 25 p.s.i. using 0.25 g. of 10% palladium-on-charcoal. After removal of the catalyst and solvent, the residue was vacuum distilled and 0.40 g. of an oil, b.p. 175–177° (4 mm.), was collected. On standing the oil crystallized to a solid, m.p. 40–43°. After crystallization from hexane the melting point was 41–43° and did not depress the m.p. of the synthetic sample of 2-*p*-tolylsulfonylbutane. The infrared spectra were also identical. Repetition of the experiment starting with *cis*-2-*p*-tolylsulfonyl-2-butene gave comparable results.

cis-**2-Bromo-2-butene.**—*meso*-2,3-Dibromobutane was prepared by adding bromine dropwise with efficient stirring to *trans*-2-butene (Phillips 99% grade) which was cooled at −20°. Distillation gave a product boiling at 73–74° (47 mm.), n^{28}_{D} 1.5080.[20] Two hundred grams (0.93 mole) of *meso*-2,3-dibromobutane in 150 ml. of ethylene glycol was placed in a 1-l. flask fitted with a stirrer, thermometer, dropping funnel and a reflux take-off device. With the flask contents heated to 115°, 68.5 g. (1.2 moles) of 85% KOH in 250 ml. of ethylene glycol was added in 45 min. using rapid stirring. Product distilled into the take-off device along with a small amount of water. The crude product was dried over anhydrous calcium chloride and distilled in a 24-inch helices-packed column collecting 108 g. (86%), b.p. 91–92.5°, n^{28}_{D} 1.4585; reported[21] b.p. 93.9°, n^{20}_{D} 1.4620.

trans-**2-Bromo-2-butene.**—Bromination of *cis*-2-butene (Phillips 99% grade) at −20° gave *dl*-2,3-dibromobutane, b.p. 67.5–68.5° at 32 mm., n^{28}_{D} 1.5105.[20] Dehydrohalogenation of 216 g. of the dibromobutane using the above procedure gave 110 g. (81%), b.p. 83.5–84°, n^{28}_{D} 1.4540; reported[21] b.p. 85.5°, n^{20}_{D} 1.4579.

trans-**2-*p*-Tolylthio-2-butene.**—Lithium (1.4 g., 0.2 g. atom) was cut into small pieces and placed in a 3-neck flask containing 200 ml. of dry ether. The temperature was held at −40 to −45° as 13.5 g. (0.1 mole) of freshly prepared *trans*-2-bromo-2-butene was added with stirring. The addi-

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[19] H. J. Lucas and C. E. Wilson, THIS JOURNAL, **58**, 2398 (1936).

[20] W. G. Young, R. T. Dillon and H. J. Lucas, *ibid.*, **51**, 2528 (1929), report b.p. 72.7–72.9° at 50 mm., n^{20}_{D} 1.5116, n^{25}_{D} 1.5092 for *meso*-2,3-dibromobutane and b.p. 75.6–75.8° at 50 mm., n^{20}_{D} 1.5147, n^{25}_{D} 1.5125 for *dl*-2,3-dibromobutane.

[21] M. Lepingle, *Bull. soc. chim.*, [4] **39**, 741 (1926).

tion required about 1 hr., and after an additional hour at −40° all the lithium appeared to have reacted. The temperature was kept at −40° during the hour required for the addition, with stirring, of a solution of 24.6 g. (0.1 mole) of *p*-tolyl disulfide in 60 ml. of ether. The mixture was allowed to warm to room temperature and was filtered through cotton. The ether solution was extracted five times with 50-ml. portions of water, dried over anhydrous magnesium sulfate and the solvent removed on the steam-bath. Vacuum distillation of the 25.5-g. residue gave 9.2 g. (52%) of a fraction boiling at 78–80° (0.3 mm.), $n^{28}\text{D}$ 1.5600. Truce and Simms[8] reported b.p. 83–86° (2 mm.), $n^{20}\text{D}$ 1.5634. The infrared spectrum of our product, which is contaminated with *cis* isomer, matched most of the peaks listed by Truce and Simms.[8]

Oxidation of 3.0 g. of *trans*-2-*p*-tolylthio-2-butene with 30% hydrogen peroxide in acetic acid gave 2.90 g. of crystals, m.p. 44–46°. Recrystallization gave material identical with that obtained by treating I with base. Infrared analysis indicates that the original mixture contained 90% of *trans*- and 10% of *cis*-2-*p*-tolylsulfonyl-2-butene.

***cis*-2-*p*-Tolylthio-2-butene.**—Using a procedure identical with that as above, 14 g. (0.103 mole) of *cis*-2-bromo-2-butene was converted to the lithium compound and treated with *p*-tolyl disulfide. Vacuum distillation gave 11.0 g. (62%) of crude *cis*-2-*p*-tolylthio-2-butene, b.p. 67–69° (0.3 mm.), $n^{28}\text{D}$ 1.5580.

Anal. Calcd. for $C_{11}H_{14}S$: C, 74.09; H, 7.86. Found: C, 73.90; H, 7.76.

Oxidation of 3.0 g. (0.017 mole) of crude *cis*-*p*-tolylthio-2-butene with 10 ml. of 30% hydrogen peroxide in 30 ml. of acetic acid for 1 hr. at 70–80° was enough to eliminate the yellow color of the sulfide. The solution was poured into 100 ml. of ice-water and the resulting white crystals, collected on a filter, were washed and dried. The crude material melted at 44–47°, and infrared analysis showed that it consisted of 75% of *cis*- and 25% *trans*-2-*p*-tolylsulfonyl-2-butene.

***trans*- and *cis*-2-(*p*-Tolylsulfonyl)-cyclopentyl Brosylates. (V and VI).**—These esters were prepared from the corresponding sulfone alcohols and *p*-bromobenzenesulfonyl chloride by the method described above.

trans-2-(*p*-Tolylsulfonyl)-cyclopentyl *p*-bromobenzenesulfonate melted at 130–131°.

Anal. Calcd. for $C_{18}H_{19}O_5S_2Br$: C, 47.06, H, 4.16. Found: C, 46.69; H, 3.81.

cis-2-(*p*-Tolylsulfonyl)-cyclopentyl *p*-bromobenzenesulfonate melted at 136–137°.

Anal. Calcd. for $C_{18}H_{19}O_5S_2Br$: C, 47.06; H, 4.16 Found: C, 47.16; H, 3.94.

Kinetic Measurements.—Pseudo first-order rates were measured conductometrically using a large excess of trimethylamine in 50% aqueous dioxane buffered with amine salt. Second-order rate constants were obtained by plotting the observed first-order rate constants from three different dilutions of buffer stock against amine concentration. The slope of such a plot is equal to the second-order rate constant. A typical set of data is given in Table II for the reaction of V at 50°. The concentration of trimethylamine used in this run is 0.0222 *M*. The trimethylamine *p*-toluenesulfonate concentration was 0.0002 *M*. Using the value 3000 ohms as the infinity reading a plot of time *vs.* log $(R/R - R_\infty)$ gave a slope of 1.09×10^{-3}; $k_1 = 2.303 \times 1.09 \times 10^{-3} = 2.50 \times 10^{-3}$ sec.$^{-1}$.

TABLE II

REACTION OF *trans*-2-*p*-TOLYLSULFONYLCYCLOPENTYL BROSYLATE WITH TRIMETHYLAMINE IN 50% AQUEOUS DIOXANE AT 50°

Time, sec.	Resistance ohms	log $(R/R - R_\infty)$	Time, sec.	Resistance ohms	log $(R/R - R_\infty)$
34	7400	0.226	211	4800	0.426
55	6900	.248	250	4550	.468
70	6600	.264	303	4300	.520
85	6250	.284	351	4100	.572
116	5800	.316	405	3900	.638
140	5450	.347	500	3700	.723
177	5100	.384	1019	3210	.723
			∞	3000	1.185

Similar runs with amine concentrations of 0.0645 and 0.0443 *M* gave k_1 values of 7.54×10^{-3} and 4.96×10^{-3}, respectively. A plot of these k_1 values against amine concentrations gave a straight line with a slope equal to 1.13×10^{-1}. The second-order constants for V at 25 and 40° were 2.42×10^{-2} M^{-1} sec.$^{-1}$ and 6.24×10^{-2} M^{-1} sec.$^{-1}$, respectively.

A plot of the logarithm of these second-order rate constants against the reciprocal of the absolute temperature gave a line with a slope of 2.58×10^3; $E_a = 4.58 \times 2.58 \times 10^3 = 11.8$ kcal.

$$\Delta S\ddagger = -R\left[\ln\frac{kT}{h} - \ln k_2 - \left(\frac{E_a - RT}{RT}\right)\right] = -26.4 \text{ e.u.}$$

EVANSTON, ILLINOIS

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

Correlation of Solvolysis Rates. V.[1] α-Phenylethyl Chloride[2]

BY ARNOLD H. FAINBERG AND S. WINSTEIN

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Rates of solvolysis of α-phenylethyl chloride are reported for an extensive series of solvent compositions. These are employed for a detailed examination of the scope and limitations of the linear free energy relationship for the correlation of solvolysis rates, $\log k = \log k_0 + mY$. The data are not fit very satisfactorily by a single log *k* *vs.* Y line. However, there is a strong tendency for dispersion into rather satisfactory separate lines for each binary solvent set. The linearity of these lines appears to depend in part on roughly linear relations between the enthalpy and entropy of activation of α-phenylethyl chloride and the corresponding quantities for *t*-butyl chloride, respectively.

Introduction.—In the present article are reported the results of a study of the rates of solvolysis of α-phenylethyl chloride in an extensive series of solvents to disclose more clearly the scope and limitations of the linear free energy relationship[3] represented by equation 1.

$$\log k = \log k_0 + mY \qquad (1)$$

In this equation, k and k_0 are the first-order solvolysis rate constants for a certain substance, RX, in a solvent and in the standard solvent, 80%

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[1] Previous papers in this series, A. H. Fainberg and S. Winstein: (a) (III) THIS JOURNAL, **78**, 2770 (1956); (b) (IV), in press.

[2] (a) Research sponsored by the Office of Ordnance Research, U. S. Army; (b) some of the material of this paper was presented before the 128th Meeting of the American Chemical Society at Minneapolis, Minn., Sept. 16, 1955, p. 52R, Abstracts of Papers.

[3] (a) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948); (b) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).