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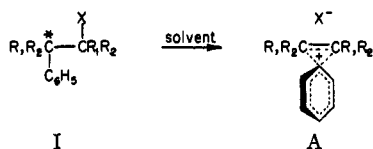
Studies in Stereochemistry. XIX. The Question of the Structure of the Phenonium Tosylate Ion-Pairs That Occur as Intermediates in the Solvolyses of the Stereoisomeric 4-Phenyl-3-hexyl Tosylates¹

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RECEIVED NOVEMBER 22, 1952

The *L-threo*- and *L-erythro*-4-phenyl-3-hexyl tosylates have been solvolyzed in dry formic and acetic acids, the products have been quantitatively examined, and the rates in the case of the *L-threo*-isomer have been measured. In the acetolysis of the *L-threo* isomer at 75°, of the 27% of acetate produced by a simple substitution reaction, a 5 to 1 ratio of retention to inversion of configuration was observed, whereas of the 18% of formate similarly produced in the formolysis of the same isomer, a 13 to 1 ratio was found. From the amounts of ester product that arose from symmetrical phenonium tosylate ion-pairs (or their stereochemical equivalent), it has been calculated that in acetic acid at 75°, about six out of seven of the bridged ion-pairs formed collapsed to *D,L-threo*-tosylate, and one exchanged its anion to go to *D,L-threo*-acetate. In formic acid at 25°, about all of the bridged ion-pairs formed went directly to formate. In both the acetolysis and formolysis of the *L-erythro*-tosylate, about 7% of the ester product arose by simple substitution with inversion of configuration. The large predominance of retention over inversion of configuration in the simple substitution reaction in the *threo* series indicates that: (1) the formation of *threo* ester from open ions (or ion-pairs) is much favored over *erythro* ester for steric reasons; or (2) unsymmetrical phenonium ions intervene as intermediates in a system at least theoretically capable of producing symmetrical phenonium ions.

The first evidence for the existence of phenonium ions (A) as intermediates in the solvolytic reactions of systems such as I was obtained in the 3-phenyl-2-butyl tosylate system^{3a} (I, R₁ = CH₃, R₂ = H). The symmetry properties of the bridged carbonium ions produced from this starting material offer particular advantages for the extraction of information concerning the mechanism of the Wagner-Meerwein rearrangement,^{3a,3b} and the accompanying intramolecular isomerization reaction.^{3c,3d} The 3,4-dimethyl-4-phenyl-3-hexyl *p*-bromobenzoate system



(I, R₁ = CH₃ and R₂ = C₂H₅) which possesses similar symmetry properties with respect to both starting material and bridged ion has also been investigated in connection with the solvolytic elimination reaction.⁴ The solvolytic reactions of systems possessing quite different symmetry properties such as 2-phenyl-3-pentyl tosylate⁵ (II) and 3-phenyl-2-pentyl tosylate⁵ (III) have also been of use in the study of the solvolytic reactions that involve the collapse of phenonium ions to give both skeletally rearranged and unrearranged products, whereas the 1,2-diphenyl-1-propyl tosylate system (IV) allowed studies to be made of phenonium ions



- II (R₁ = CH₃, R₂ = H, R₃ = C₂H₅ and R₄ = H)
 III (R₁ = C₂H₅, R₂ = H, R₃ = CH₃ and R₄ = H)
 IV (R₁ = CH₃, R₂ = H, R₃ = C₆H₅ and R₄ = H)

(1) This work was supported by the Office of Ordnance Research, U. S. Army.

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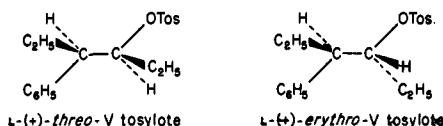
(3) (a) D. J. Cram, *THIS JOURNAL*, **71**, 3863 (1949); (b) D. J. Cram, *ibid.*, **74**, 2129 (1952); (c) D. J. Cram, *ibid.*, **74**, 2159 (1952); (d) S. Winstein and K. Schreiber, *ibid.*, **74**, 2165 (1952).

(4) D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952).

(5) (a) D. J. Cram, *ibid.*, **71**, 3875 (1949); (b) D. J. Cram, *ibid.*, **74**, 2159 (1952).

that collapse only in the direction from which they are made.⁶

Although the 4-phenyl-3-hexyl tosylate system (V) of the present study⁷ possesses the same symmetry properties as the 3-phenyl-2-butyl tosylate system,³ the steric constraints involved in the formation of *cis*-phenonium ions in which two ethyl groups are eclipsed should be greater than those in which two methyl groups are eclipsed. The pres-



ent investigation was undertaken to determine if these steric factors are important enough to seriously affect the course of the solvolytic substitution reaction, possibly to permit the stereochemistry of the *simple substitution reaction*⁸ to be studied in a system capable of producing symmetric phenonium ions.

The Kinetics of the Solvolyses of *L-threo*-4-Phenyl-3-hexyl Tosylate

The kinetics of both the acetolysis and formolysis of *L-threo*-4-phenyl-3-hexyl tosylate (*L-threo*-V tosylate) were studied in a manner analogous to the previous kinetic study of the solvolyses of *threo*-3-phenyl-2-butyl tosylate.⁹ Both the titrimetric and polarimetric solvolytic rate constants (k_t and k_p , respectively) of the reactions of *L-threo*-V tosylate with dry acetic acid were determined at two temperatures and found to be clearly first order. Likewise, the polarimetric solvolytic rate constant in dry formic acid was determined at 25° and found to be first order. Table I records these constants and the conditions under which they were obtained.

(6) F. A. Abd Elhafez and D. J. Cram, *ibid.*, **75**, 339 (1953).

(7) The preparation, resolution and determination of the relative configurations of the stereoisomers of 4-phenyl-3-hexanol and their tosylate esters have been previously reported [Paper XVIII of this series, *ibid.*, **75**, 2293 (1953)].

(8) By "simple substitution" is meant that reaction whose ester products do not involve immediate precursors that partition directly between molecularly rearranged and unrearranged product.

(9) The details of the method employed are found in ref. 3d, and are not elaborated here.

TABLE I

RATE CONSTANTS AND THE CONDITIONS FOR THEIR DETERMINATION OF *L-threo*-4-PHENYL-3-HEXYL AND *L-threo*-3-PHENYL-2-BUTYL TOSYLATES

Solvent	Concn. ester, mole/l.	Salt added	Concn. salt, mole/l.	Proc.	T, °C.	Rotations α_D^{25}		k , sec. ⁻¹
						Initial	Final	
Solvolyses in 4-phenyl-3-hexyl system								
AcOH ^b	0.0882	KOAc	0.105	Tit.	74.64	$(1.68 \pm 0.03) \times 10^{-4}$
AcOH ^b	.0882	KOAc	.105	Pol.	74.64	-1.47°	-0.06°	$(5.48 \pm .19) \times 10^{-4}$
AcOH ^b	.0900	KOAc	.120	Tit.	50.08	$(1.01 \pm .02) \times 10^{-6}$
AcOH ^b	.0900	KOAc	.120	Pol.	50.08	-3.08°	0.09°	$(3.19 \pm .09) \times 10^{-6}$
HCOOH ^c	NaOOCH ^c	...	Pol.	25.2	-1.44°	0.06°	$(3.90 \pm .10) \times 10^{-4}$
Solvolyses in 3-phenyl-2-butyl system ^d								
AcOH	0.0957	NaOAc	0.116	Tit.	74.91	$(6.72 \pm 0.16) \times 10^{-5}$
AcOH	.0957	NaOAc	.116	Pol.	74.91	0.53°	-0.01°	$(3.33 \pm .10) \times 10^{-4}$
HCOOH	.0696	None	...	Tit.	24.98	$(2.28 \pm .03) \times 10^{-4}$
HCOOH	.1161	None	...	Pol.	25.12	3.92°	-.04°	$(2.65 \pm .12) \times 10^{-4}$

^a Rotations were taken in a 4-dm. tube. ^b Solutions contained 1% acetic anhydride. ^c The solution was prepared by mixing 0.4063 g. of tosylate ester, 3.00 ml. of pure CHCl₃, 0.120 g. of dry NaOOCH and 10 ml. of dry formic acid with one another. ^d These data were taken from S. Winstein and K. Schreiber, ref. 3d.

Although the titrimetric formolysis rate constant of *L-threo*-V tosylate was not determined, its correspondence within experimental error to the polarimetric rate constant was demonstrated. The formolysis was carried out under the conditions of run 5 (Table III) for one polarimetric half-life, and the unreacted *L-threo*-V tosylate was almost quantitatively recovered in an optical form essentially indistinguishable from that of the starting material.

In Table II are compared ΔH^\ddagger and ΔS^\ddagger for the solvolysis of *L-threo*-4-phenyl-3-hexyl tosylate and *L-threo*-3-phenyl-2-butyl tosylate^{3d} in acetic acid.¹⁰

TABLE II

ΔH^\ddagger AND ΔS^\ddagger FOR ACETOLYSES OF *L-threo*-4-PHENYL-3-HEXYL TOSYLATE (H) AND *L-threo*-3-PHENYL-2-BUTYL TOSYLATE (B)

Compound	Calcd. from	ΔH^\ddagger , kcal./mole	ΔS^\ddagger , e.u.
H	k_t	24.9	-4.5
H	k_α	25.2	-1.2
B ^a	k_t	26.3	-2.9
B ^a	k_α	25.9	-1.1

^a Data taken from S. Winstein and K. Schreiber, ref. 3d.

The similarities in structure between the phenylbutyl and phenylhexyl systems as well as the proximity of the ΔH^\ddagger 's and ΔS^\ddagger 's for the processes that occur in acetic acid make particularly valuable a comparison of the distributions of products obtained in the two systems.

It is interesting that the higher value of k_t for the phenylhexyl as compared to the phenylbutyl system is parallel to the relationship between the relative titrimetric rates obtained for the acetolyses^{11a} and formolyses^{11b} of the *p*-bromobenzenesulfonates of 2-butanol and 2-propanol, respectively. In both acetic and formic acids the rates of appearance of the sulfonic acid are higher in the systems repre-

sented by R-CH-C₂H₅ than in the systems repre-

sented by R-CH-CH₃ by a factor of from 1.4-2.5,

in spite of the fact that phenyl becomes involved in the solvolyses in one set of systems and not in the other.

The Products of Solvolysis of the Optically Pure Diastereomeric 4-Phenyl-3-hexyl Tosylates

The solvolytic reactions were carried out under the conditions reported in Table III, and the mixtures of acetate (formate) and olefin formed as product were converted to mixtures of 4-phenyl-3-hexanol and olefin which were separated through chromatographic procedures. The alcohols were then analyzed for the distributions of each diastereomer and enantiomer of 4-phenyl-3-hexanol in the mixtures. In the infrared spectra of *L-threo*- and *L-erythro*-isomers, enough differences exist in the optical densities of the two isomers (a factor of from about 2-3) to allow analyses of mixtures of the two components to be made with an accuracy of about $\pm 1\%$.¹² Figure 1 records plots of optical density vs. % composition of known mixtures of *L-threo*- and *L-erythro*-alcohols at the four wave lengths most advantageous for analysis, and in each case the plots are linear. The percentages of *erythro* and *threo* alcohols in the final mixtures were calculated by solving two sets of two simultaneous equations in two unknowns, and the results are recorded in Table III. The final mixtures from the solvolyses were also subjected to polarimetric analyses, both as the free alcohols and as their respective acetates. From these values, the values of the rotations of the optically pure alcohols⁷ and acetates (see experimental) and the infrared analyses, the relative amounts of each of the four isomers in each mixture are estimated in Tables III and IV.

Discussion

The data at hand for the solvolytic behavior of

(12) The spectra of racemic and optically pure material were found to be identical for each diastereomer.

(10) The only difference in the experimental conditions used for the two sets of acetolyses at 50° is that for the phenylbutyl system, base was absent whereas for the phenylhexyl system base was present. At 75° in acetic acid, the presence of base had only a minor effect on the solvolytic rate constant for the phenylbutyl system (ref. 3d).

(11) (a) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, THIS JOURNAL, **74**, 1113 (1952); (b) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

TABLE III
RESULTS OF SOLVOLYSES OF OPTICALLY PURE DIASTEROBOMERIC 4-PHENYL-3-HEXYL TOSYLATES

Run no.	Starting material ^a	Sol.	T, °C.	Tm., hr.	Yld. ol. %	Yld. alc. %	n_D^{20} , alc.	$[\alpha]_D^{20}$, alc.	n_D^{20} , alc.	α_D^{20} , alc.	n_D^{20} , acet.	α_D^{20} , acet.	n_D^{20} , Total	α_D^{20} , Total	n_D^{20} , <i>threo</i>	α_D^{20} , <i>erythro</i>	Total
1	L- <i>erythro</i> -Tos.	AcOH ^f	75	66	28	62	1.5079	27.6°	54.5°	27.2°	1.4855	7	94	101	6	95	101
2	L- <i>threo</i> -Tos.	AcOH ^f	75	66	40	50	1.5070	...	5.91°	2.06°	1.4852	96	5	101	97	4	101
3	D- <i>threo</i> -Tos.	AcOH ^f	75	66	39	48	1.5072	...	-7.42°	-2.54°	1.4851	95	4	99	94	5	99
4	L- <i>erythro</i> -Tos.	HCOOH ^h	75	0.08	31	57	1.5079	26.6°	52.9°	1.4857	5	94	99	7	95	102
5	L- <i>erythro</i> -Tos.	HCOOH ^h	25	66	5	90	1.5079	28.1°	54.0°	1.4855	8	93	101	6	95	101
6	L- <i>threo</i> -Tos.	HCOOH ^h	75	0.08	36	54	1.5071	...	1.30°	0.48°	1.4851	100	0	100	100	1	101
7	L- <i>threo</i> -Tos.	HCOOH ^h	25	66	11	80	1.5070	...	4.30°	1.80°	1.4852	100	0	100	99	1	100

^a For preparation and properties, see ref. 7. ^b c 5%, CHCl₃. ^c Homogeneous. ^d Taken on liquid films, 0.03 mm. thick, with Beckman infrared spectrophotometer Model IR2T (NaCl cells). Standards and unknowns taken in the same cells within an hour of each other. Slit widths (mm.) equal: ^e0.549; ^f0.599; ^g0.923; ^h0.962. ⁱ Initial concentration ROTos. = 0.200 M, KOAc = 0.240 M, excess Ac₂O = 1%. ^j Initial concentration ROTos. = 0.0882 M, KOAc = 0.105 M, excess Ac₂O = 1%. ^k Initial concentration ROTos. = 0.200 M, NaOOC = 0.240 M. ^l The tosylate went into solution over a period of one hour.

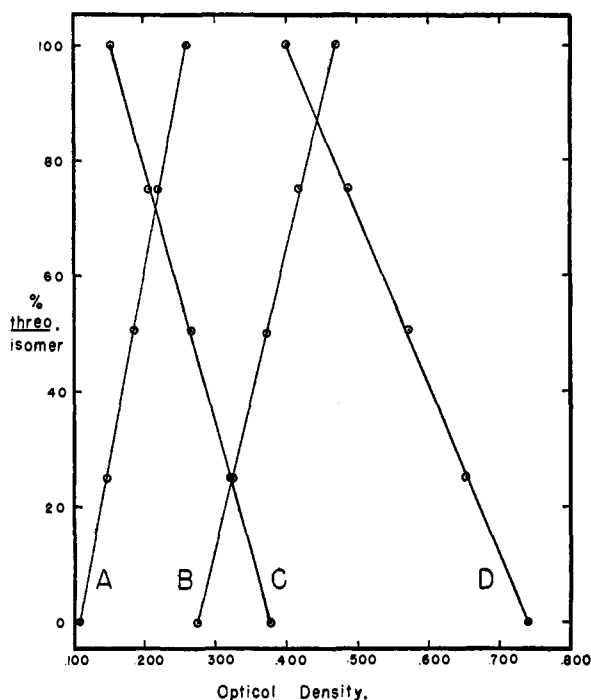


Fig. 1.—Plots of optical density vs. % composition of known mixtures of L-*threo*- and L-*erythro*-4-phenyl-3-hexanol (homogeneous films, 0.03 mm. thick, NaCl prism) at various wave lengths in the infrared (Beckman spectrophotometer, Model IR2T): curve A, λ 12.14 μ (slit = 0.599 mm.); curve B, λ 13.55 μ (slit = 0.962 mm.); curve C, λ 11.80 μ (slit = 0.549 mm.); curve D, λ 13.32 μ (slit = 0.923 mm.).

both the active *threo*-4-phenyl-3-hexyl and *threo*-3-phenyl-2-butyl tosylates permit a thorough analysis of the relative importance of the various processes to be made. In the following kinetic scheme (Chart I) for the solvolysis reactions,¹³ k_0 is the rate of formation of olefin; k_r is the rate of formation of total *threo*-OS (retention of configuration) by a simple substitution reaction⁸; k_i is the rate of formation of total *erythro*-OS (inversion of configuration) by a simple substitution reaction⁸; k_p is the rate of formation of symmetrically bridged ion-pairs⁸ (or their stereochemical equivalent); k_c is the rate of collapse of these bridged ion-pairs to racemic tosylate; and k_e is the rate of exchange of the bridged ion-pairs with solvent to form racemic acetate (or formate). The polarimetric rate constant (k_a), and the titrimetric rate constant (k_t) are broken down into their component rate constants in equations 1 and 2. Combination of equations 1 and 2 gives equation 3 in which the relative rates of partition of symmetrical phenonium tosylate between the reaction giving racemic alkyl tosylate and that giving racemic alkyl acetate are defined.¹⁴

(13) This kinetic scheme only summarizes the processes distinguishable in terms of products that occur during the solvolytic reactions at hand. Detailed mechanisms for many of these types of processes have been discussed elsewhere [e.g., I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 173 (1946); C. G. Swain and W. P. Lansdorf, Jr., *THIS JOURNAL*, **73**, 2813 (1951); S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951); D. J. Cram, ref. 3a and *ibid.*, **74**, 2137 (1952)].

(14) These equations are based on the assumption that all of the rate constants are first order, and that the intermediate ions do not accumulate.

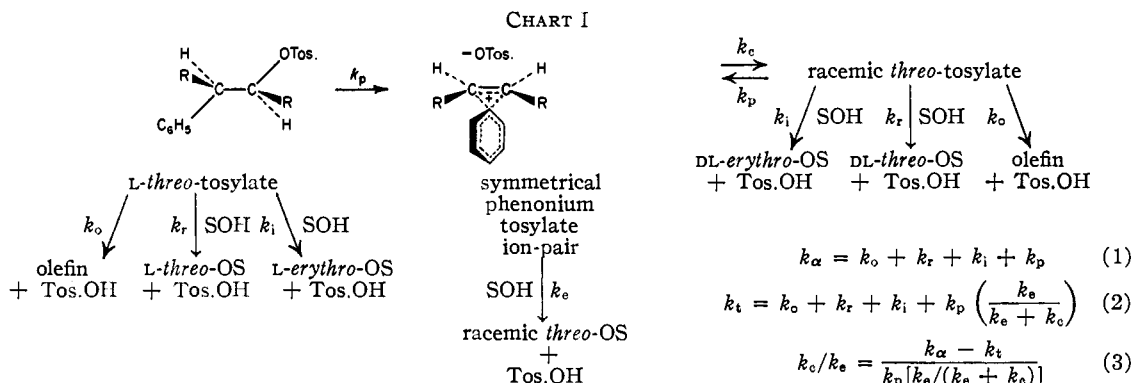
TABLE IV

DISTRIBUTIONS OF PRODUCTS IN ALCOHOL-OLEFIN MIXTURES ULTIMATELY OBTAINED FROM SOLVOLYSES OF TOSYLATES OF 4-PHENYL-3-HEXYL (H) AND 3-PHENYL-2-BUTYL (B) SYSTEMS

Run no. ^a	Starting material	Sol.	Temp., °C.	Yield, % al. + ol.	Ol. in mixt., % ^c	% active <i>threo</i> alc. in mixt. based on α acet. ^e		% alc. in mixt. arising by simple substitution with	
						α alc. ^d	α acet. ^e	Retention ^f	Inversion ^g
1	L- <i>erythro</i> -H-Tos.	AcOH	75	90	31	4.5
2	L- <i>threo</i> -H-Tos.	AcOH	75	90	44	3.5 ^h	3.8	12	2.5
3	D- <i>threo</i> -H-Tos.	AcOH	75	87	45	4.7	4.9	14	2.5
4	L- <i>erythro</i> -H-Tos.	HCOOH	75	88	35	3.9
5	L- <i>erythro</i> -H-Tos.	HCOOH	25	95	5	6.7
6	L- <i>threo</i> -H-Tos.	HCOOH	75	90	40	0.8	0.8	0.8	0.3
7	L- <i>threo</i> -H-Tos.	HCOOH	25	91	12	5.5	4.8	5.1	0.4
8 ⁱ	L- <i>erythro</i> -B-Tos.	AcOH	75	91	24	3.4
9 ⁱ	L- <i>threo</i> -B-Tos.	AcOH	75	88	40	0.4	...	1.8	2.1
10 ⁱ	L- <i>erythro</i> -B-Tos.	HCOOH	25	90	21	0.0
11 ⁱ	L- <i>threo</i> -B-Tos.	HCOOH	25	89	21	0.0	...	0.0	0.0

^a Run numbers 1-7 correspond to those of Table III. ^b ROTos. = 100%. ^c Final olefin + final alcohol = 100%. ^d Based on magnitudes of rotations of optically pure, homogeneous alcohols as follows (ref. 7): *threo*, α_D²⁰ 26.4°, *erythro*, α_D²⁰ 28.2° (*l* = 1 dm.). ^e Based on magnitudes of rotations of optically pure homogeneous acetates as follows (see Experimental): *threo*, α_D²⁰ 75.6°, *erythro*, α_D²⁰ 54.2° (*l* = 1 dm.). ^f Total alcohol arising by simple substitution⁸ with retention of configuration = active *threo* × (*k*_α/*k*_t). ^g Calculated from infrared data of Table III. ^h Sample calculation is as follows. Total *erythro* isomer present in alcohol = 4.5% (Table III). Active *erythro* alcohol = 4.5% × (*k*_t/*k*_α) = 1.36%. Contribution of this material to rotation of alcoholic mixture = 0.0136 × 28.2° = 0.38°. Residual rotation due to active *threo* isomer = 2.06° - 0.38° = 1.68°. Amount of optically pure *threo* material in alcohol mixture = 1.68°/26.4° = 0.0636, and amount of optically pure *threo* material in alcohol-olefin mixture = 0.035. ⁱ Product data taken from papers V (ref. 3b) and VI (THIS JOURNAL, 74, 2137 (1952)) of this series, and *k*_t and *k*_α taken from data of S. Winstein and K. Schreiber (ref. 3d).

The ratio *k*_c/*k*_e can be evaluated, since *k*_α and *k*_t pure *threo*-tosylates of the 4-phenyl-3-hexyl and 3-phenyl-2-butyl systems. have been measured directly, and *k*₀, *k*_i and *k*_r can



be estimated making use of the yield data for the processes which these latter constants defined. Since *k*_t is the sum of several first-order rate constants, the component rate constants are proportional to the respective yields¹⁵ of the products produced in the component rate processes. The yields of olefin and of total *erythro*-OS have been measured directly by gravimetric and infrared methods whereas the yields of L-*threo*-OS coming from unracemized L-*threo*-tosylate by the process defined by *k*_r has been measured polarimetrically. Since the total yield of *threo*-OS arising by *k*_r is equal to (*k*_α/*k*_t × yield L-*threo*-OS),¹⁶ then *k*_r can be evaluated along with *k*₀ and *k*_p [*k*_e/(*k*_e + *k*_c)]. Table V records the ratios of *k*_α/*k*_t, *k*_c/*k*_e, *k*_r/*k*_i, *k*_p/(*k*_o + *k*_i + *k*_r) and *k*_p/*k*_i for the solvolyses of optically

(15) The amount of starting material accounted for in terms of final olefin and alcohol product was about 90% in each run. In the calculations of Table V, it is assumed that the 10% loss is proportionally divided between the olefin and alcohol products.

(16) This relationship has been derived previously [S. Winstein and D. Trifan, *ibid.*, 74, 1157 (1952)] and applied to the *threo*-3-phenyl-2-butyl system (ref. 3d).

The values of *k*_c/*k*_e (Table V) provide a quantitative picture of the partition of the phenonium tosylate ion-pairs between the collapse (to tosylate) and exchange (to acetate) reactions. Thus in acetic acid at 75° in the *threo*-4-phenyl-3-hexyl system, *k*_c/*k*_e ≅ 5.7 whereas in the *threo*-3-phenyl-2-butyl system under the same set of conditions, *k*_c/*k*_e ≅ 7.1.¹⁷ Since the anion exchange reaction of the bridged ion-pairs probably occurs by a dissociation mechanism,^{3b} it seems reasonable to expect that the more sterically constrained phenonium ion-pairs of the *threo*-4-phenyl-3-hexyl system (VII) would dissociate more readily than those of the less constrained *threo*-3-phenyl-2-butyl system (VI). These results and their interpretation are consistent with the previous observation that the more sterically favorable *trans*-phenonium tosylate (VIII) produced from L-*erythro*-2-phenyl-3-pentyl (or L-*erythro*-3-phenyl-2-pentyl) tosylate exchanges its

(17) If *k*₀, *k*_i and *k*_r are disregarded as contributors to *k*_t (the titrimetric rate constant) as was done previously (ref. 3b and 3d), then *k*_α/*k*_t = *k*_o/*k*_e + 1.

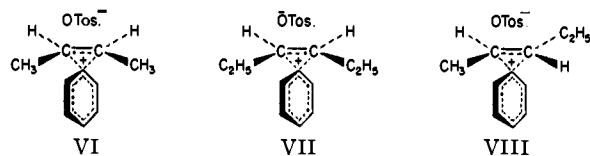
TABLE V

RELATIVE RATES OF PROCESSES THAT OCCUR DURING SOLVOLYSIS OF *L-threo*-TOSYLATES OF 4-PHENYL-3-HEXYL (H) AND 3-PHENYL-2-BUTYL (B) SYSTEMS

Run no. ^a	Sys-tem	T, °C.	Solvent	k_{α}/k_{β}	k_e/k_a	k_r/k_i	$\frac{k_p/k_i + (k_e/k_a + k_r/k_i)d}{k_i}$	k_p/k_i
2 ^e	H	75	AcOH	3.3	5.4	4.8	4.6	107
3 ^e	H	75	AcOH	3.3	5.9	5.6	4.3	106
6	H	75	HCOOH	≈ 1	≈ 0	≈ 2.7	≈ 1.4	≈ 150
7	H	25	HCOOH	~ 1	~ 0	~ 13	~ 4.7	~ 270
9 ^f	B	75	AcOH	5.0	7.1	0.9	10.3	220
11 ^g	B	25	HCOOH	1.2	0.2	...	4.5	200

^a These run numbers correspond to those of Tables III and IV. ^b Calculated from kinetic data of Table I. ^c Calculated through the use of the data of Tables I and IV and equation (3). ^d Calculated with equations (2) and (3). ^e The only differences in these runs were that the starting materials were enantiomeric, and different concentrations of KOAc were employed in the two runs. ^f The kinetic data (ref. 3d) were gathered in solution, 0.1155 M in NaOAc, whereas the product data were taken from a run 0.228 M in NaOAc. Apparently the concentration of base has little effect on the course of the reaction (ref. 3b and 3d). ^g The kinetic data (ref. 3d) were gathered in the absence of NaOOCH, whereas the product data were taken from a run, 0.190 M in NaOOCH (ref. 3b).

anion less readily than its *cis* counterpart.^{5b} The striking decrease in the value of k_c/k_e in passing from acetic to formic acid observed in the 3-phenyl-2-butyl system^{5b} also applies to the 4-phenyl-3-hexyl system, a fact which further illustrates the vastly superior ionizing power of the latter solvent.

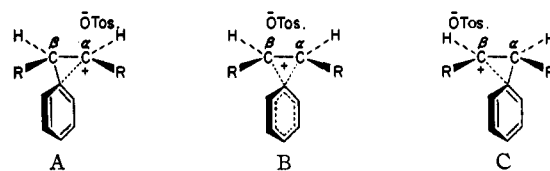


The most remarkable feature of the solvolyses of the *threo*-4-phenyl-3-hexyl system is the marked predominance of the rate of the simple substitution reaction⁸ that gives retention of configuration over that which gives inversion. The values of k_r/k_i (Table V) range from about 5 or 6 in acetic acid at 75° to a value of about 13 in formic acid at 25°. These values are in marked contrast to that of the *threo*-3-phenyl-2-butyl system (acetic acid at 75°) where $k_r/k_i = 0.9$ (in formic acid the ratio could not be evaluated). Since in other simple S_N1 reactions, $k_r/k_i \leq 1$,¹⁸ the predominance of retention over inversion in the system at hand appears to demand an extraordinary explanation.

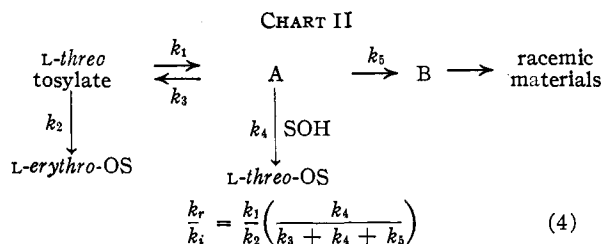
Two alternative explanations are suggested for this phenomenon, the first and more attractive of which is arrived at by substituting for the symmetrical phenonium ion B, a dynamic equilibrium between two unsymmetric ions, A and C, a further possibility being that B is an intermediate intervening between the two unsymmetrical intermediates.¹⁹ In these schemes, B is considered to have a

(18) For instance, W. Doering and H. Zeiss, Abstracts of Meeting of the American Chemical Society, Philadelphia, Pa., April, 1950, p. 7L; H. Zeiss, Abstracts of Meeting of the American Chemical Society, Chicago, Ill., September, 1950, p. 50N; J. Steigman and L. P. Hammett, THIS JOURNAL, **59**, 2536 (1937).

(19) These possibilities have been previously mentioned [S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952)] without any experimental evidence being brought to bear on the point.



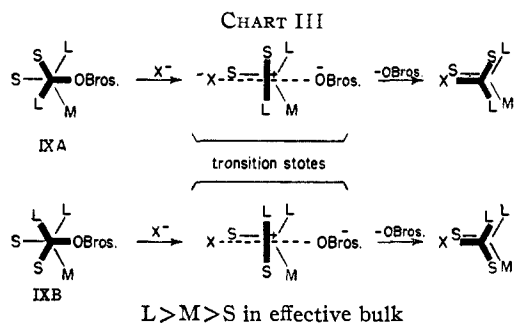
rather rigid geometry (whether intermediate or transition state), the two R groups being pressed into a totally eclipsed conformation, whereas in A and C, the relative weakness of the longer bond (which would be more directed toward the benzene ring as a whole) should give the three-membered ring a more flexible character, permitting a partially staggered arrangement for the two R groups. Since the arguments are similar with B either as an intermediate or a transition state, B is assumed to be an intermediate for purposes of simplification, as is indicated in the following kinetic scheme. Equation (4)¹⁴ relates the ratio k_r/k_i (see Table V) to the various processes of Chart II. The data of Table IV indicate that if such a mechanistic scheme ap-



plies, then $k_1/k_2 \gg 1$ in both the 4-phenyl-3-hexyl and 3-phenyl-2-butyl systems. Since $k_4/(k_3 + k_4 + k_5) < 1$, the value of k_r/k_i in equation (4) is controlled by the actual balance between these two opposing factors. Each of these factors would be sensitive to steric effects, and to the nucleophilicity and ionizing power of the solvent, and therefore the variation in values of k_r/k_i (Table V) in passing from acetic to formic acid and from the 4-phenyl-3-hexyl to the 3-phenyl-2-butyl systems is not surprising in terms of such a reaction scheme. Thus the values of k_2 and k_5 relative to k_4 might diminish as steric effects become more important, and the value of k_r/k_i would increase, as has been observed in passing from the phenylbutyl to the phenylhexyl system (compare runs 3 and 9 of Table V). One might expect further that k_1 and k_4 would increase relative to k_2 in passing from a solvent of lower to one of higher ionizing power (and a solvent of higher to one of lower nucleophilicity), and as a consequence the value of k_r/k_i would increase. Such an increase is observed in runs 3 and 7 (Table V) in passing from acetic to formic acid as the reaction solvent.

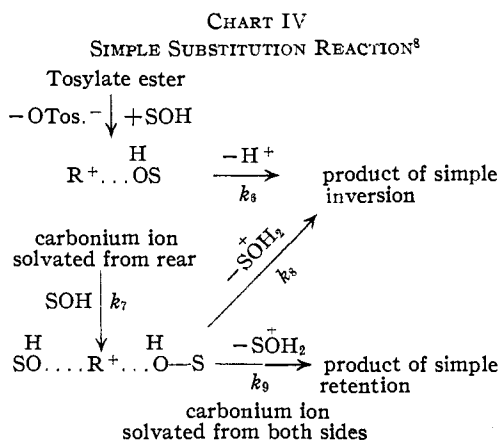
The yield data for the material arising in the solvolyses by simple substitution with inversion of configuration (Table IV) give a rough indication as to the relative contributions these processes make to the titrimetric rate constants (k_t), and in each case (compare runs 1 and 2, 4 and 6, 5 and 7, 8 and 9) k_i for the *threo* isomer appears to be markedly lower than the corresponding rate constant would be for the *erythro* isomer. An explanation for this difference is found in the different steric require-

ments for simple inversion occurring in the two diastereomeric systems. Thus it has been previously demonstrated in S_N2 reaction sequences such as are shown in Chart III, that diastereomer IXA reacts markedly faster than diastereomer IXB.²⁰ This



difference in rate was attributed to the probability that if (as is likely) the preferred conformations for the reactions are those in which the displacing group (X^-) comes in across the smallest group (S) attached to the adjacent asymmetric carbon atom, then the transition state from IXA should be stabler than that from IXB.²¹ A somewhat similar explanation might apply to the results at hand. Thus the transition states for that part of the simple substitution reaction⁸ occurring with inversion of configuration might well be similar to those of Chart III in which SOH is substituted for X^- . If this is the case, then IXA would be a model for *erythro*-4-phenyl-3-hexyl tosylate and IXB a model for the *threo*-isomer, and the *erythro*-isomer should be more amenable to simple inversion than the *threo*-isomer, as has been observed. Smaller differences were found between the *threo* and *erythro* isomers of the 3-phenyl-2-butyl system with respect to the amount of product arising through a simple substitution reaction⁸ occurring with inversion of configuration, a fact compatible with the less importance of steric effects in this as compared to the 4-phenyl-3-hexyl system.

A second possible explanation for the fact that $k_r/k_i > 1$ (see Table V) is outlined in the kinetic



(20) D. J. Cram and F. A. Abd Elhafez, *THIS JOURNAL*, **74**, 5851 (1952).

(21) Very little difference exists in the energies of IXA and IXB. On the other hand, in the transition state from IXA, the $L > < M$ and $L > < S$ steric repulsions should be less important than the $M > < S$ and $L > < L$ steric repulsions associated with the transition state from IXB.

scheme of Chart IV. Equation (5) sets forth the relationships between k_r , k_i and the component rate constants of Chart IV.¹⁴ In such a scheme, the value of k_8/k_9 should be rather insensitive to both the nucleophilic character and ionizing power of the

$$\frac{k_i}{k_r} = \frac{k_8}{k_9} + \frac{k_8}{k_7} \left(1 + \frac{k_8}{k_9} \right) \quad (5)$$

solvent, and should be largely controlled by the steric situation. In a system containing only one asymmetric carbon atom (e.g., α -phenylethyl chloride), $k_8/k_9 = 1$, and the departure of this value from unity in a system containing two asymmetric carbon atoms should become more marked as steric effects become more controlling. The value of k_8/k_7 should increase with increased nucleophilicity and decrease with increased ionizing power of the solvent, and should also be sensitive to the steric situation. The results are compatible with such expectations. Thus with *L-threo*-4-phenyl-3-hexyl tosylate as starting material, in run 7 with formic acid as solvent ($T = 25^\circ$), $k_i/k_r \cong 0.08$ whereas in run 3 with acetic acid as solvent ($T = 75^\circ$), $k_i/k_r \cong 0.18$.²² Furthermore, $k_i/k_r = 1.1$ for run 9 (*L-threo*-3-phenyl-2-butyl tosylate + acetic acid at 75°), a value much closer to unity than that observed in the parallel reaction (run 3) in the more sterically constrained 4-phenyl-3-hexyl system. The fact which is the most difficult to explain in terms of the above kinetic scheme is the very low value of k_i/k_r (0.08) in run 7 (*L-threo*-4-phenyl-3-hexyl tosylate + formic acid at 25°). For $k_i/k_r \ll 1$, both k_8/k_9 and k_8/k_7 would have to be much less than unity, and in run 7, $k_8/k_9 < 0.08$. In other words, the disolvated 4-phenyl-3-hexylcarbonium ion would have to favor collapse to *threo* over *erythro* product by a factor of more than thirteen, and it is difficult to believe that steric effects alone could account for such a large difference.

Of these two alternative explanations for the fact that the simple substitution reaction⁸ of the *threo*-4-phenyl-3-hexyl system occurs largely with retention of configuration, the former rests on polar and the latter on steric grounds. Although other explanations are possible, they are variations of general schemes of which the above detailed mechanisms are illustrative.

A completely satisfactory measure of the ability of phenyl *vs.* solvent to participate in the solvolytic substitution reactions at hand must await decisions between the alternate mechanisms of this paper as well as a further clarification of the mechanism of the solvolytic elimination reaction discussed previously.²³ However, the values for $k_p/(k_0 + k_i + k_r)$ and k_p/k_i in Table V (see Chart I) probably describe the outer limits for the ratio of phenyl to solvent participation in these reactions. Whichever ratio is taken, the ability of phenyl to participate seems to be greater for the 3-phenyl-2-butyl than for the 4-phenyl-3-hexyl system in acetic acid, whereas in formic acid this ability is about the same. Actually these values vary surprisingly little from system to system and from solvent to solvent. Certainly if the production of olefin is disregarded, the

(22) Formic acid is a much better ionizing solvent and poorer nucleophile than acetic acid.

(23) D. J. Cram, *ibid.*, **74**, 2137 (1952).

stereochemistry of the reactions is largely governed by the intervention of the phenyl group rather than the solvent in the substitution reactions.

These same effects are currently being studied in the still more hindered 2,5-dimethyl-4-phenyl-3-hexyl system.

Experimental Part

Kinetic Measurements.—The solutions of acetic acid were prepared from C.P. acetic acid, potassium carbonate (C.P. anhydrous) and enough acetic anhydride to react with the water produced and leave a 1% excess of anhydride. For the kinetic runs at 50 and 75° (both titrimetric and polarimetric) the ampoule technique was used. The titrations were made by methods described previously,^{3d} and the polarimetric readings were taken in a one-dm. tube held at 25° through use of a thermostated jacket. The solutions of formic acid were prepared by weighing out the tosylate ester, dissolving it in pure (ethanol free) chloroform, and adding this solution to a solution of anhydrous sodium formate in pure formic acid (100.02% by titration with Karl Fischer reagent). The polarimetric rate was followed in a 4-dm. jacketed polarimeter tube thermostated at 25°. The solvolyses were followed to 80–90% completion, and the mean deviations in first-order rate constants are shown in Table I.

Formolysis of L-threo-4-Phenyl-3-hexyl Tosylate for One Polarimetric Half-life.—This reaction was carried out in a fashion identical to the kinetic run (polarimetric run at 25° in formic acid) described in Table I, except that the reaction was interrupted after 30 minutes (one polarimetric half-life). The mixture was poured onto ice and extracted immediately with ether. The ether layer was washed twice with water, once with sodium carbonate solution, and was dried. The solution was evaporated to a heavy oil under reduced pressure at room temperature (most of the chloroform distilled), and this oil was crystallized from cold pentane (two crops) to give a 48% yield of recovered L-threo-4-phenyl-3-hexyl tosylate, $[\alpha]^{25}_D -21.1^\circ$ (*c* 12% in CHCl_3). For the starting tosylate, $[\alpha]^{25}_D -21.5^\circ$ (*c* 8% in CHCl_3).

The Acetates of the Isomers of 4-Phenyl-3-hexanol.—The acetates were prepared by the pyridine-acetic anhydride method.^{3b} After the reaction mixtures were decomposed with ice-water, the products were extracted into pure pen-

tane, the pentane layers were washed with dilute acid, dilute base and finally with water. The pentane layers were dried, the solvent was evaporated through a short column, and the residual oils were twice flash-distilled at 20 mm. of pressure to give colorless oils which were analyzed directly. Table VI records these analyses and the physical properties of these substances (the yields in each case were from 91–95%).

Acetolysis of L-threo-4-Phenyl-3-hexyl Tosylate at 75° (run 2) for Products.—The results of runs 1–7 which were carried out for product analyses are recorded in Table III. The method used in these runs will be illustrated with a record of run 2.

A solution of 6.66 g. of L-threo-4-phenyl-3-hexyl tosylate⁷ (0.02 mole) in 100 ml. of C.P. glacial acetic acid (in which had been dissolved 1.52 g. of anhydrous potassium carbonate and 3 ml. of acetic anhydride) was held at 75° for 66 hours and cooled to room temperature. This solution was shaken with 200 ml. of pure pentane and 500 ml. of ice-water, the organic layer was washed well with water, with sodium carbonate solution, and was dried. The solvent was evaporated through a short column, and the residual oil was added dropwise to a slurry of 0.3 g. of lithium aluminum hydride and 30 ml. of ether. The resulting mixture was cautiously mixed with ice-water, acidified with dilute sulfuric acid, and the ether layer was separated, washed with water, with dilute base, and it was then dried. The solvent was evaporated through a short column, and the residual oil was submitted to chromatographic absorption on a column of basic alumina (10 by 40 cm.) made up in pure pentane. The olefinic fraction was washed through with pure pentane until a 400-ml. portion of the eluate was completely free of material. The pentane was evaporated through a short column, and the residual oil was twice flash-distilled at 20 mm. of pressure to give 1.30 g. of olefin. The chromatographic column was then eluted with methanol, and the methanol was evaporated through a short column to a low volume. The residual oil was shaken with a mixture of pure pentane and water, the pentane solution was washed with water, dried, and the pentane was evaporated through a short column. The residual oil was flash-distilled twice at 20 mm. pressure, wt. 1.75 g. This material was used directly for the polarimetric and infrared analyses, and also for preparation of the acetate derivative.

The control experiments carried out for the 3-phenyl-2-butyl system^{3b} are considered applicable to the 4-phenyl-2-hexyl system, with the possible exception of runs 4 and 6 (formic acid at 75°). Since the data of these runs were only used in a supplementary way, controls were not run for these solvolyses.

Acknowledgment.—The authors take pleasure in acknowledging the value of stimulating discussions concerning the content of this paper with Dr. W. G. McMillan.

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TABLE VI

ANALYSES AND PHYSICAL PROPERTIES OF THE ISOMERIC 4-PHENYL-3-HEXYL ACETATES

Isomer	n^{25}_D	α^{25}_D (<i>l</i> = 1 dm.)	Mol. form.	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
D,L-threo	1.4851		$\text{C}_{14}\text{H}_{20}\text{O}_2$	76.32	76.45	9.15	9.30
D,L-erythro	1.4855		$\text{C}_{14}\text{H}_{20}\text{O}_2$	76.32	76.46	9.15	9.74
L-threo	1.4852	+75.6°	$\text{C}_{14}\text{H}_{20}\text{O}_2$	76.32	76.46	9.15	9.35
D-erythro	1.4855	-54.2°	$\text{C}_{14}\text{H}_{20}\text{O}_2$	76.32	76.47	9.15	9.44
L-erythro	1.4855	+54.1°	$\text{C}_{14}\text{H}_{20}\text{O}_2$	76.32	76.24	9.15	9.24