gen uptake, and the hydrocarbon was recovered through shaking the reduced mixture with water and pure pentane. The pentane layer was washed with water, dried and passed through 20 g. of activated alumina. The column filtrate was evaporated through a column and the residue was flash-distilled. This product (0.364 g., $n^{25}\text{D}$ 1.4861) was submitted directly to infrared analysis.

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

Studies in Stereochemistry. IX. Phenonium Sulfonate Ion-pairs in the Substitution and Elimination Reactions in the 2-Phenyl-3-pentanol and 3-Phenyl-2-pentanol Systems

BY DONALD J. CRAM

The products of the solvolyses in glacial acetic acid of the *p*-toluenesulfonates of the stereoisomers of 3-phenyl-2-pentanol and 2-phenyl-3-pentanol have been analyzed. With regard to the acetate products of the reaction, the sulfonate ester of D-*erythro*-3-phenyl-2-pentanol and D-*erythro*-2-phenyl-3-pentanol give essentially the same mixture of 58% D-*erythro*-2-acetoxy-3-phenylpentane and 42% D-*erythro*-3-acetoxy-2-phenylpentane. Analogously, the sulfonate ester of D-*threo*-3-phenyl-2-pentanol gives about the same mixture of 58% D-*threo*-2-acetoxy-3-phenylpentane and 42% L-*threo*-3-acetoxy-2-phenylpentane as does the sulfonate ester of L-*threo*-2-phenyl-3-pentanol. Simple solvolysis reactions without involvement of the phenyl group account for only minor amounts of acetate product. These facts are interpreted in terms of phenonium sulfonate ion-pairs as intermediates in these reactions.

The production of widely differing balances of olefinic products in the solvolyses of the four sulfonate esters provides evidence that the olefin and acetate products arise through at least two different primary processes. The presence of rearranged olefin (both conjugated and unconjugated) among the products in each experiment is interpreted as evidence for an isomerization reaction, the *p*-toluenesulfonate of D-*erythro*-3-phenyl-2-pentanol giving the *p*-toluenesulfonate of D-*erythro*-2-phenyl-3-pentanol and *vice versa*, and the *p*-toluenesulfonate of D-*threo*-3-phenyl-2-pentanol giving the *p*-toluenesulfonate of L-*threo*-2-phenyl-3-pentanol and *vice versa*. Different ratios of conjugated to unconjugated 2-phenylpentene were obtained from the *p*-toluenesulfonates of D-*erythro*-2-phenyl-3-pentanol and D-*threo*-2-phenyl-3-pentanol. These differences are interpreted in terms of the steric requirements for the formation of a phenyl *vs.* a hydrogen-bridge from materials of the *erythro* as compared to the *threo* configuration.

Paper III of this series[1] reported the results of the solvolyses in glacial acetic acid of the *p*-toluenesulfonates of the stereoisomers of IIIA, IVA, VA and VIA.[2] Only a qualitative study of the nature of the acetate products was reported, and no examination of the products of the elimination reaction was made. The present investigation deals with a quantitative study of the acetate and olefinic products of the solvolysis reactions.

Methods and Results

The solvolysis reactions and methods of isolation of the alcoholic and olefinic fractions from the reaction mixtures were carried out by procedures analogous to those reported in Papers V[3a] and VI[3b] in which the solvolyses of the *p*-toluenesulfonates of the isomers of 3-phenyl-2-butanol were studied. Table I reports the analyses and rotations of the acetates, propionates and benzoates of the optically pure isomers of 3-phenyl-2-pentanol and 2-phenyl-3-pentanol. The yields of the olefinic and alcoholic products from the solvolysis reactions are reported in Table II, along with the rotations of the alcoholic products obtained in the various runs. The acetates, propionates and benzoates of the alcoholic mixtures from the solvolysis experiments were also prepared and their rotations are reported in Table II.

Figure 1 reports the infrared spectra of IIIB, IVB, VB and VIB, and Table III reports the optical densities of the substances at the eight wave lengths which were most amenable to the analysis of mixtures of these four compounds (or of their enantiomers). The differences in the optical densities

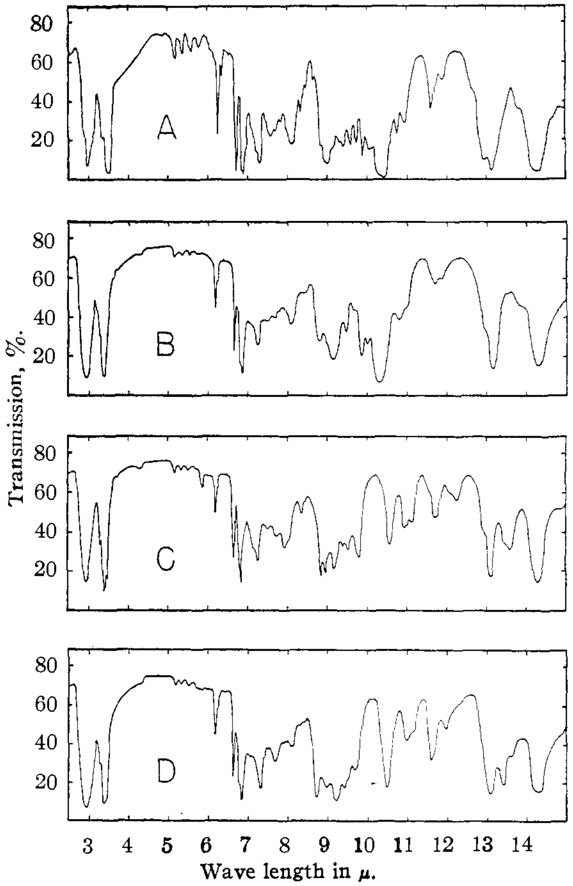

Fig. 1.—Infrared spectra, homogeneous samples, NaCl prism: A, D-*threo*-2-phenyl-3-pentanol (IIIB), cell thickness = 0.03 mm.; B, D-*erythro*-2-phenyl-3-pentanol (IVB), cell thickness = 0.01 mm.; C, D-*threo*-3-phenyl-2-pentanol (VB), cell thickness = 0.01 mm.; D-*erythro*-3-phenyl-2-pentanol (VIB), cell thickness = 0.01 mm.

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[1] D. J. Cram, THIS JOURNAL, **71**, 3871 (1949).

[2] The numbering system for these isomeric pentanols has been maintained from paper to paper. The relationships of all of the configurations of the substances to D-glyceraldehyde are reported in Paper VII [*ibid.*, **74**, 2149 (1952)] of this series.

[3] (a) D. J. Cram, *ibid.*, **74**, 2129 (1952); (b) *ibid.*, **74**, 2137 (1952).

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF DERIVATIVES OF THE STEREOISOMERS OF 3-PHENYL-2-PENTANOL AND 2-PHENYL-3-PENTANOL[a]

Compound	n^{25}D	α^{25}D[b]	Mol. form	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
IIIA Acetate	1.4872	−27.7°	$C_{13}H_{18}O_2$	75.68	75.64	8.79	9.08
IVB Acetate	1.4868	+35.3	$C_{13}H_{18}O_2$	75.68	75.97	8.79	9.04
VA Acetate	1.4869	−66.3	$C_{13}H_{18}O_2$	75.68	75.65	8.79	8.96
VIB Acetate	1.4864	+54.5	$C_{13}H_{18}O_2$	75.68	75.52	8.79	8.96
IIIA Propionate	1.4852	−32.3	$C_{14}H_{20}O_2$	76.32	76.22	9.15	9.26
IVB Propionate	1.4860	+36.5	$C_{14}H_{20}O_2$	76.32	76.21	9.15	9.31
VA Propionate	1.4838	−57.2	$C_{14}H_{20}O_2$	76.32	76.50	9.15	9.16
VIB Propionate	1.4840	+49.7	$C_{14}H_{20}O_2$	76.32	76.17	9.15	9.07
IIIA Benzoate	1.5417	+13.9	$C_{18}H_{20}O_2$	80.57	80.35	7.51	7.70
IVB Benzoate	1.5420	+57.9	$C_{18}H_{20}O_2$	80.57	80.33	7.51	7.71
VA Benzoate	1.5403	−33.8	$C_{18}H_{20}O_2$	80.57	80.30	7.51	7.82
VIB Benzoate	1.5412	+59.9	$C_{18}H_{20}O_2$	80.57	80.32	7.51	7.60

	IIIB Tos.	IVB Tos.	VB Tos.	VIB Tos.
M.p., °C.	101–102	86–87	72–73	40–41
$[\alpha]^{22}$D[c]	51.08°	−4.90	−25.4	+19.0

[a] Derivatives were prepared from alcohols (ref. 4) of the following rotations (l = 1 dm.): IIIA, α^{25}D +12.1°; IIIB, α^{25}D −11.4°; IVA, α^{25}D −7.25°; IVB, α^{25}D +7.34°; VA, α^{25}D −16.8°; VB, α^{25}D +16.2°; VIA, α^{25}D −20.2°; VIB, α^{25}D +20.3°. [b] l = 1 dm., (liq.). [c] Benzene solution, $c \cong 5\%$.

TABLE II

THE OXYGEN-CONTAINING PRODUCTS OF SOLVOLYSIS

Run no.	Config. st. mat.	Yld. alc., %	Yld. olefin, %	α^{25}D Alcoholic mixtures and deriv. of mixtures[a] alc.	acet.	prop.	benz.	Composition	Synthetic mixtures α^{25}D, homogen. (l = 1 dm.) alc.	acet.	benz.
1[b]	IIIB	51	37	−12.8°	.....	.....	.....				
2[c]	IIIB	56	39	−12.7	−27.9°	−23.3°	−23.4°	42% IIIB and			
3[b]	VB	52	37	+13.0	.....	.....	.....	58% VA	−12.7°	−26.6	....
4[c]	VB	58	36	+13.0	+28.2	+22.6	+25.0				
5[b]	IVB	61	23	+14.3	.....	.....	.....				
6[c]	IVB	68	24	+14.8	+43.7	+42.1	+56.4	42% IVB and			
7[b]	VIB	65	21	+15.2	.....	.....	.....	58% VIB	+16.9	+45.6	+58.1
8[c]	VIB	71	22	+15.2	+44.8	+42.5	+57.2				

[a] Homogeneous (l = 1 dm.). [b] In these runs, KOAc = 0.78 mole (starting material = 1 mole), hence in about the last quarter of the run the solution was acidic. [c] In these runs, KOAc = 1.2 moles (starting material = 1.0 mole), hence the solution was never acidic.

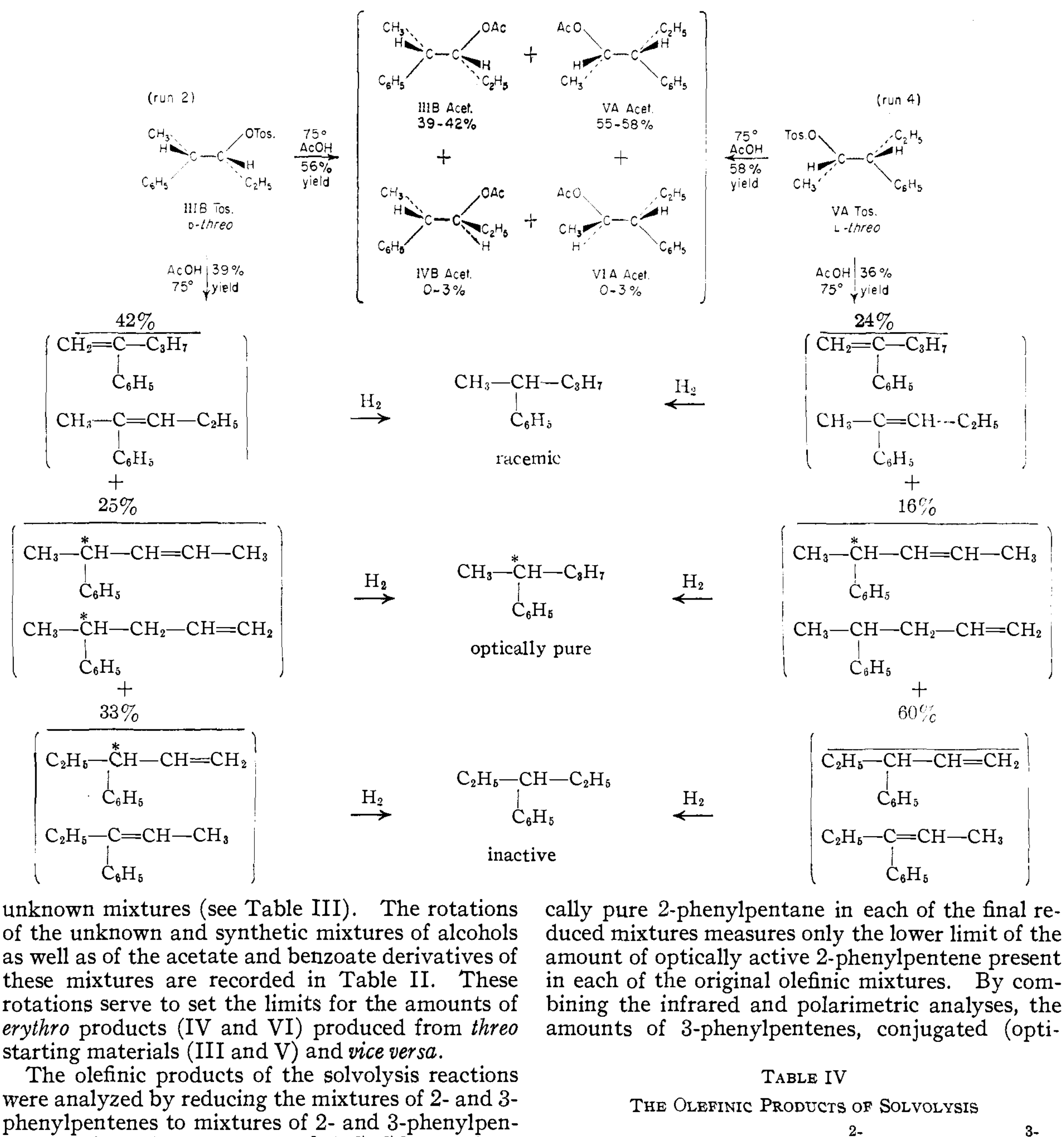
TABLE III

INFRARED ANALYSES OF THE ALCOHOLIC PRODUCTS OBTAINED FROM THE SOLVOLYSES[a]

Compounds	Optical densities[b] at wave lengths (μ) used for analyses λ = 10.03	λ = 10.30	λ = 10.73	λ = 11.56	λ = 11.90	λ = 12.17	λ = 13.38	λ = 13.58
Pure alcohols								
IIIB	0.737	1.27	0.500	0.304	0.168	0.074	0.521	0.249
IVB	.860	1.39	.603	.251	.178	.100	.460	.292
VB	.237	0.242	.295	.345	.209	.352	.616	1.04
VIB	.214	.290	.249	.810	.414	.208	1.22	0.640
Alcohols, run no.[c]								
2	0.459	0.792	0.379	0.330	0.197	0.239	0.599	0.728
1st. model[d]	.469	.842	.386	.349	.202	.238	.627	.728
2nd. model[e]	.457	.800	.381	.330	.192	.242	.599	.740
4	.450	.778	.374	.331	.192	.233	.590	.713
6	.517	.957	.406	.588	.320	.160	.975	.501
1st. model[f]	.494	.932	.396	.589	.314	.164	.977	.511
2nd. model[g]	.498	.926	.396	.606	.319	.162	.995	.508
8	.499	.922	.392	.596	.321	.163	.985	.510

[a] A Model IR2, Beckman spectrophotometer with a NaCl prism was used. Homogeneous samples in a cell of 0.03 mm. were employed. [b] Slit width = 0.92 mm. for all wave lengths except λ = 10.30, where slit width = 2.82 mm. [c] Run numbers are the same as in Table II. [d] Synthetic mixture: 39.0% IIIB; 3.5% IVB; 54.6% VA; 3% VIA. [e] Synthetic mixture: 42.0% IIIB; 58.0% VA. [f] Synthetic mixture: 2.7% IIIB; 38.8% IVB; 2.5% VB; 56.0% VIB. [g] Synthetic mixture: 42.0% IVB; 58.0% VIB.

of the four compounds allow accurate analyses for *erythro*- and *threo*-3-phenyl-2-pentanol (V and VI) as separate components, and for the two isomeric 2-phenyl-3-pentanols (III and IV) as a single component (the spectra of III and IV are almost identical). Corrections for deviations from Beer's law were made through the use of synthetic mixtures whose compositions approximated those of the



unknown mixtures (see Table III). The rotations of the unknown and synthetic mixtures of alcohols as well as of the acetate and benzoate derivatives of these mixtures are recorded in Table II. These rotations serve to set the limits for the amounts of *erythro* products (IV and VI) produced from *threo* starting materials (III and V) and *vice versa*.

The olefinic products of the solvolysis reactions were analyzed by reducing the mixtures of 2- and 3-phenylpentenes to mixtures of 2- and 3-phenylpentane with hydrogen over a Pd–$CaCO_3$ catalyst. This alkylbenzene mixture was then submitted to the infrared analytical scheme worked out in Paper VIII of this series[4] for 2- and 3-phenylpentane mixtures. The results of these analyses are recorded in Table IV.

The amount of unconjugated and hence optically active 2-phenylpentene in each of the unknown mixtures was determined by polarimetric analysis of the final alkylbenzene mixture.[5] Since a small amount of racemic 2-phenylpentane was probably produced from optically active 4-phenyl-2-pentene during the reduction reaction,[6] the amount of optically pure 2-phenylpentane in each of the final reduced mixtures measures only the lower limit of the amount of optically active 2-phenylpentene present in each of the original olefinic mixtures. By combining the infrared and polarimetric analyses, the amounts of 3-phenylpentenes, conjugated (opti-

TABLE IV

THE OLEFINIC PRODUCTS OF SOLVOLYSIS

Run[a] no.	Config. st. mat.	Yld. olef., %	$\alpha^{25}D$,[b] olef.	2-Phenyl-[c] pentenes, %	2-Phenylpentenes, % conj.[d]	Unconj.[d]	3-Phenyl-[c] pentenes, %
1	IIIB	37	− 4.97°	66	41	25	34
2	IIIB	39	− 4.99	67	42	25	33
3	VB	37	+ 1.80	40	23	17	60
4	VB	36	+ 1.80	40	24	16	60
5	IVB	23	−51.64	84	41	43	16
6	IVB	24	−54.17	86	34	52	14
7	VIB	21	−41.58	68	30	38	32
8	VIB	22	−42.70	67	24	43	33

[a] These run numbers correspond with those of Table II. In runs 1, 3, 5 and 7, KOAc = 0.78 mole (st. mat. = 1.0 mole), and in runs 2, 4, 6 and 8 KOAc = 1.2 mole (st. mat. = 1.0 mole). [b] Homogeneous (l = 1 dm.). [c] These values were calculated from infrared measurements made on the mixtures of 2- and 3-phenylpentane obtained when the olefinic mixtures were reduced. [d] These values were calculated from the amounts of optically active 2-phenylpentane present in the reduced mixture.

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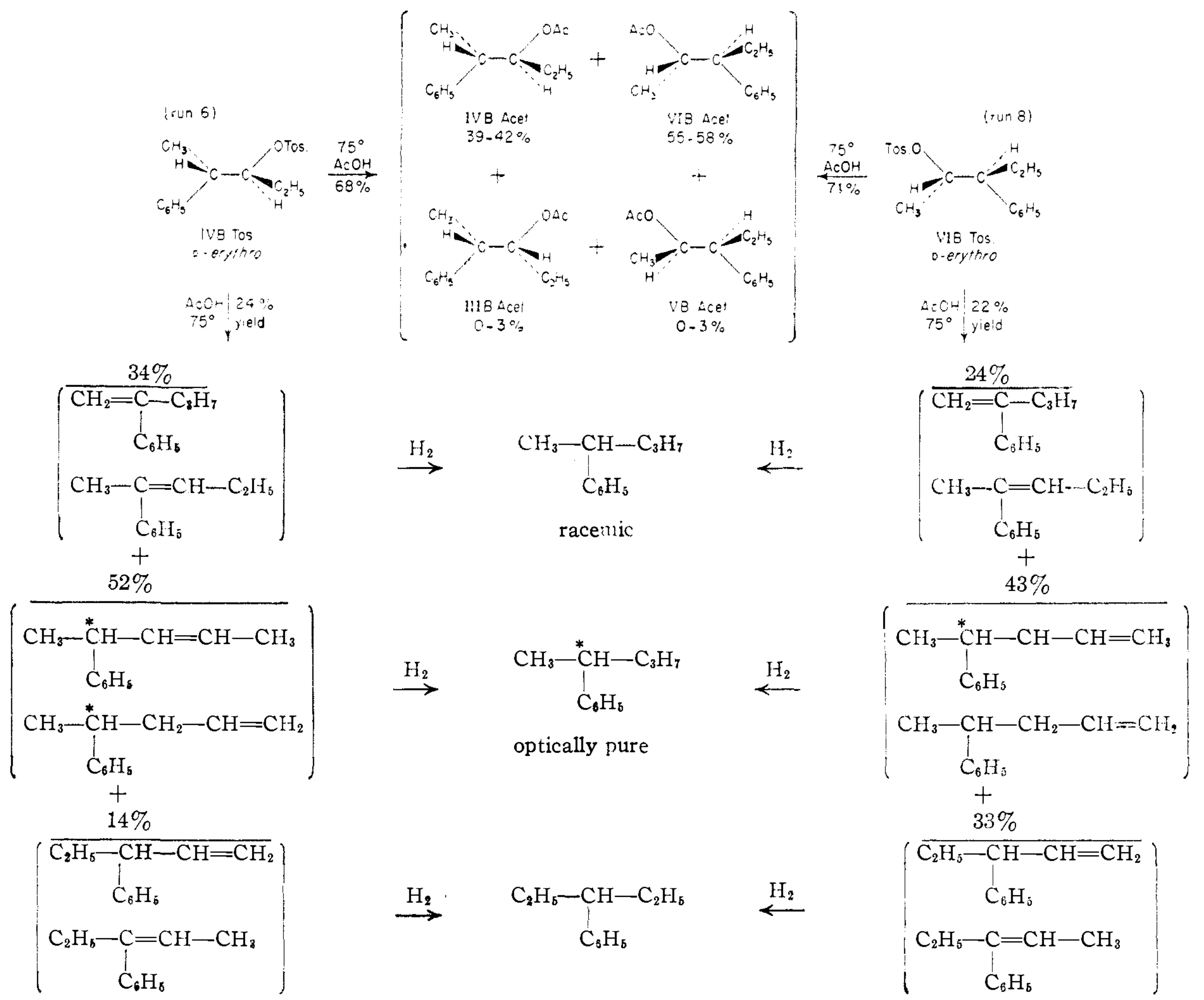
(4) D. J. Cram, THIS JOURNAL, **74**, 2152 (1952).

(5) A plot of composition *vs.* rotation of solutions made up of optically pure 2-phenylpentane in 3-phenylpentane appears in Paper VIII of this series (ref. 4).

(6) When optically pure 3-phenyl-1-butene was reduced with the same catalyst as that used in this investigation, from 1 to 10% racemized 2-phenylbutane was produced (unpublished results).



cally inactive) 2-phenylpentenes and unconjugated (optically active) 2-phenylpentenes can be determined, and the results of the analyses are recorded in Table IV.

The correspondence between the results obtained in those experiments that involve the same starting materials provides evidence that the procedures employed are reproducible and that the variables were controlled. The slightly greater yield of alcohol obtained in those runs that never became acidic (runs 2, 4, 6 and 8 of Table II) is due to the use of a refined isolation procedure employed in these as compared to the other runs. The difference in the relative amounts of unconjugated and conjugated 2-phenylpentane found in runs 5 and 7 as compared to runs 6 and 8, respectively, is probably due to partial isomerization of unconjugated to conjugated olefin caused by the strong acid present in the former runs.[7] These results are summarized in the formulations.[8]

Discussion

The acetate ion present in these solvolyses probably plays no mechanistic role in the reactions. The pentanol systems of the present investigation are analogous to the butanol system already studied[3b] in which the reactions giving rise to both olefin and acetate were demonstrated to occur without the assistance of acetate ion. Furthermore, the lack of marked differences between the results obtained in runs 1, 3, 5 and 7 as compared to runs 2, 4, 6 and 8 where concentrations of acetate ion were higher support this conclusion.

With respect to the acetate products of solvolysis, the results indicate the reactions to have been highly stereospecific in nature, a total of 0–6% of the acetate products having arisen by non-stereospecific processes. The results seem to be analogous to those obtained in the 3-phenyl-2-butanol system,[3a] and undoubtedly analogous phenonium sulfonate ion-pairs are involved as intermediates in the stereospecific process giving rise to acetate, as well as in the isomerization reaction (*e.g.*, IVB Tos. ⇄ VIB Tos.). The fact that the phenonium acetate ion-pair collapses more often to the carbon atom bearing the methyl group than to the carbon atom bearing the ethyl group (ratio of 3 to 2) is probably a consequence of the smaller bulk of a methyl *vs.* an ethyl group. It is interesting that the same ratio is observed when the methyl and ethyl groups are *cis* as when they are *trans* in the cyclic intermediate.

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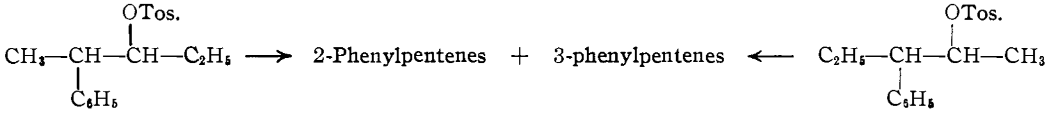
[7] An analogous isomerization of 3-phenyl-1-butene to 2-phenyl-2-butene was demonstrated to occur slowly under these same conditions (unpublished results).

[8] Although in run 4 the starting material was of the VB configuration the formulations of this paper employ the VA configuration since this change results in a conservation of space. Since VA and VB are enantiomorphically related, this change in no way modifies the ideas or results.

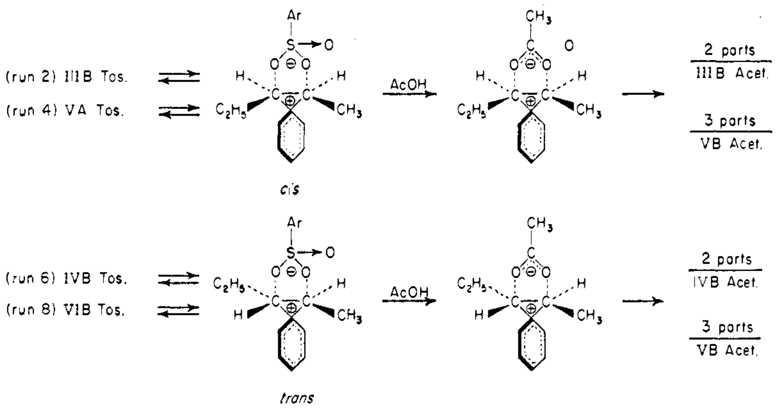
Unlike the acetate products of solvolysis, the ratios of the different olefinic products vary considerably with the starting material in question. The data of Table IV show that although the *p*-toluenesulfonates of IIIB and VA give about the same acetate products, each gives a preponderance of unrearranged olefin over rearranged olefin. The *p*-toluenesulfonates of IVB and VIB give balances of olefinic products that are much closer together, but still in a direction that indicates a larger amount of a given olefin is realized when produced without rearrangement than when produced only with rearrangement. These observations support the evidence presented in Paper VI[3b] against any mechanism for olefin production that involves a phenonium sulfonate ion-pair as an *immediate* precursor of olefin. It is highly probable however that the rearranged olefin in each case is produced through the isomerization reaction (*e.g.*, IVB Tos. ⇄ VIB Tos.) which itself involves bridged ion-pairs as intermediates. Thus phenonium sulfonate ion-pairs are in a sense precursors of rearranged olefin, but ordinary *p*-toluenesulfonate esters intervene between these bridged ions and the olefinic products.



$$CH_3-\underset{C_6H_5}{CH}-\overset{OTos.}{CH}-C_2H_5 \longrightarrow \text{2-Phenylpentenes} + \text{3-phenylpentenes} \longleftarrow C_2H_5-\underset{C_6H_5}{CH}-\overset{OTos.}{CH}-CH_3$$

IIIB Tos. (run 2)	67%	33%	....
....	40%	60%	VB Tos. (run 4)
IVB Tos. (run 6)	86%	14%	....
....	67%	33%	VIB Tos. (run 8)

The similarity in the balance of yields between rearranged and unrearranged olefin from IVB Tos. and VIB Tos. as compared to the balance obtained from IIIB Tos. and VB Tos. points to a higher degree of equilibration between material of the IV and VI configuration before the reaction spends itself than was attained with materials of the III and V configurations. Although this difference in the degree of equilibration represents a composite of a large number of different rate constants, it qualitatively correlates with the stereochemistry of the phenonium sulfonate ion-pairs that are intermediates in the isomerization (equilibration) reaction. Thus when the methyl and ethyl groups are *cis* to one another in the bridged ion-pairs, the transition state leading to such a configuration should be of higher energy because of the steric repulsions between the methyl and ethyl group than when these two groups are distributed *trans* to one another. An analogous observation was made in paper VIII of this series[4] in which the *p*-toluenesulfonates IIIB, IVB, VB and VIB were treated with lithium aluminum hydride. In those experiments considerably more rearranged phenylpentane was obtained from materials of the IV and VI than from those of the III and V configurations.



The rates of appearance of *p*-toluenesulfonic acid from the sulfonate esters of *threo*- and *erythro*-2-phenyl-3-pentanol are very close, and a similar relationship exists for the *p*-toluenesulfonates of 3-phenyl-2-pentanol.[9] As a consequence of these facts, and the probability that materials of the *erythro* configuration (IV and VI) go further toward equilibrium during solvolysis than the materials of the *threo* configuration (III and V), it can be concluded that a bigger fraction of phenonium sulfonate ion-pairs go to acetate when the configuration of the bridged cycle is *cis* (from *threo* materials) than when it is *trans* (from *erythro* materials). In other words, the value of the ratio of k_c to $k_{-a} + k_{-b} + k_c$ is higher than the value of the ratio of k_t to $k_{-m} + k_{-n} + k_t$.

$$\begin{tikzcd}
\text{(run 2) IIIB Tos.} \arrow[r, shift left, "k_a"] \arrow[d, "k_1"] & \textit{cis}\text{ ion-pairs} \arrow[l, shift left, "k_{-a}"] \arrow[r, shift right, "k_{-b}"'] \arrow[d, "k_c"] & \text{(run 4) VA Tos.} \arrow[l, shift right, "k_b"'] \arrow[d, "k_2"] \\
\text{olefin + acetate + acid} & \text{acetate + acid} & \text{olefin + acetate + acid} \\
\text{(run 6) IVB Tos.} \arrow[r, shift left, "k_m"] \arrow[d, "k_3"] & \textit{trans}\text{ ion-pairs} \arrow[l, shift left, "k_{-m}"] \arrow[r, shift right, "k_{-n}"'] \arrow[d, "k_t"] & \text{(run 8) VIB Tos.} \arrow[l, shift right, "k_n"'] \arrow[d, "k_4"] \\
\text{olefin + acetate + acid} & \text{acetate + acid} & \text{olefin + acetate + acid}
\end{tikzcd}$$

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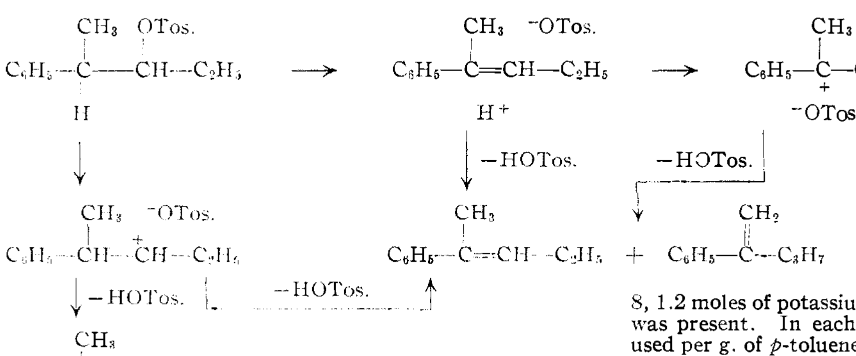
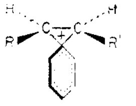
[9] Private communication from S. Winstein. An analogous situation exists in the 3-phenyl-2-butanol series.

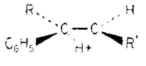
The suggestion has been made earlier[3a] that the reaction, ion pair → acetate, takes place through the dissociation of the phenonium sulfonate ion-pairs into phenonium and sulfonate ions, and that new ion-pairs (*e.g.*, phenonium acetates) are formed which then collapse to stable products. The above conclusions support this hypothesis since the greater steric repulsions in *cis* ion-pairs would tend to produce a higher degree of dissociation into separate ions than would be expected with a *trans* configuration.

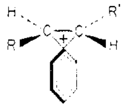
Strong evidence that the 2-phenylpentenes in runs 2 and 4 arise from a common precursor, and that an analogous situation holds for the 2-phenylpentenes in runs 6 and 8 is found in the values of the ratios of unconjugated to total 2-phenylpentene obtained in these runs. The values (unconjugated to total 2-phenylpentenes) are as follows: run 2, 0.37; run 4, 0.40; run 6, 0.61; run 8, 0.64. The values are almost the same in runs 2 and 4, which fact offers strong evidence that both sets of olefins (2-phenylpentenes) arise from the *p*-toluenesulfonate of IIIB. Similarly both sets of olefins in runs 6 and 8 must have come from the sulfonate ester of IVB. Furthermore, the difference in the values of the ratios in runs 2 and 4 on the one hand and in runs 6 and 8 on the other is clear evidence that a single precursor cannot be common to all four runs. These results are in complete harmony with those obtained in similar experiments in the 3-phenyl-2-butanol system[3b] where at least two primary processes operated in the production of olefin from sulfonate ester. The first of these involved simple ionization of the C–O bond of the sulfonate ester to produce a carbonium ion which collapsed to both conjugated and unconjugated olefin. The second involved participation of a hydrogen (attached to the benzyl carbon atom) in the displacement of the sulfonate ester and formation of a hydrogen-bridged ion. This ion then either liberated a proton directly to give conjugated olefin or collapsed to a tertiary carbonium ion which in turn gave conjugate olefin. This mechanism as applied to the present results is outlined below.

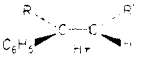


An examination of the absolute yields of olefin (see Table IV) produced from the various isomeric starting materials indicates that sulfonate esters of the *threo* configuration (I,[3b] III and V) always give more olefin than those of the *erythro* configuration (II,[3b] IV and VI). This difference in each case can be accounted for largely by the difference in yield of conjugated rather than unconjugated olefin. In the cases when the *p*-toluenesulfonates of I (*threo*) and II (*erythro*) were employed as starting material,[3b] a substantial amount of hydrogen migration was involved in the production of conjugated olefin. Analogous rearrangements undoubtedly occur in the pentanol system. Since a considerable fraction of conjugated olefin probably arises by processes that involve hydrogen bridges, the differences in yields of conjugated olefin as one passes from *threo* to *erythro* starting materials might well measure the differences in the amounts of hydrogen bridge formed. If this is true, then phenyl-bridge formation predominated over hydrogen-bridge formation to a greater extent in the *erythro* than in the *threo* system. The stereochemistry of the bridged ions provides an explanation for this phenomenon. The processes of phenyl- and hydrogen-bridge formation compete with one another. Of the four bridged ions involved, the phenyl-bridge from *erythro* starting materials is the only one in which bulky groups are not arranged *cis* to one another. Therefore in the *erythro* system phenyl-bridging should predominate more than in the *threo* system. Thus the greater yield of olefin from compounds of the *threo* configuration is not incompatible with the stereochemical relationships of the systems involved.









Experimental Part

Preparation of Acetates, Propionates and Benzoates of the Various Stereoisomers of 2-Phenyl-3-pentanol and 3-Phenyl-2-pentanol.—In each case, to a mixture of one part of alcohol and five parts of dry pyridine was added 1 mole (alcohol = 1 mole) of acid chloride. After standing for eight hours at room temperature the mixture was shaken with a mixture of pure pentane and dilute sulfuric acid. The organic layer was washed successively with water, sodium carbonate solution and water. The pentane solution was then dried, evaporated to a small volume, and the residue was passed through a small column of basic alumina suspended in pentane. The column eluate (pentane was used as a developer) was evaporated and the residue was flash-distilled to give pure ester.

The Solvolysis Experiments.—The solvolysis experiments were carried out in dry glacial acetic acid that contained one per cent. of acetic anhydride. In runs 1, 3, 5 and 7, 0.78 mole of potassium acetate (sulfonate ester = 1 mole) was present, whereas in runs 2, 4, 6 and 8, 1.2 moles of potassium acetate (sulfonate ester = 1 mole) was present. In each case 20 ml. of reaction solvent was used per g. of *p*-toluenesulfonate ester, and the reaction was carried out for 30 hours at 75°. During this period all but about one per cent. of starting material had been dissipated. The olefin and alcoholic products were isolated through procedures that are completely analogous to those reported for similar experiments in the 3-phenyl-2-butanol system.[3]

The Reduction of the Mixtures of 2- and 3-Phenylpentenes to Mixtures of 2- and 3-Phenylpentanes.—In all cases the reductions were carried out at atmospheric pressure and room temperature in ethanol (6 ml. per 1.0 g. of olefin) as solvent.

The catalyst employed (1.0 g. per 1.0 g. of olefin) was 5% palladium supported on calcium carbonate. The product was isolated by evaporation of the solvent and distillation of the residue. The hydrogen uptake was in each case theory ±2%. The mixture of 2- and 3-phenyl-pentane isolated had an index of refraction of $n^{25}\text{D}$ 1.4860 ± 0.0001 (for pure 2-phenylpentane, $n^{25}\text{D}$ 1.4858; for pure 3-phenylpentane, $n^{25}\text{D}$ 1.4861[4]).

Acknowledgment.—The author takes pleasure in acknowledging the value of stimulating conversations concerning the content of this paper with Dr. W. G. McMillan.

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Neighboring Carbon and Hydrogen. XII. Internal Rearrangement in Solvolysis of 3-Phenyl-2-butyl *p*-Toluenesulfonate[1]

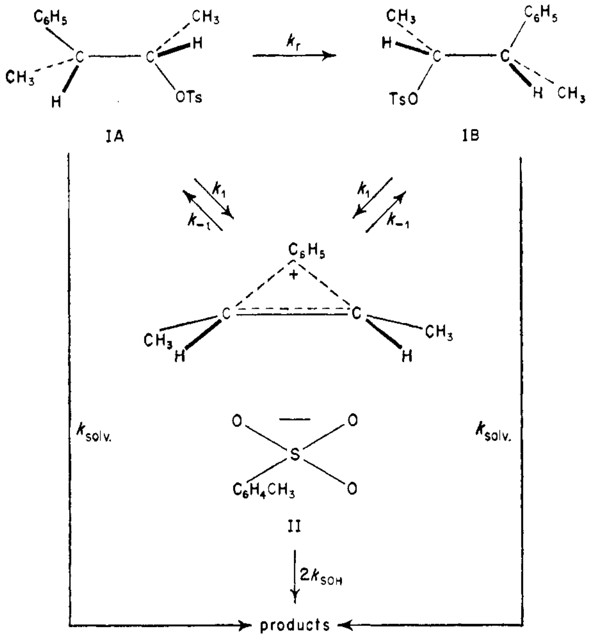
BY S. WINSTEIN AND KURT C. SCHREIBER

The same kind of polarimetric and titrimetric rate scrutiny as in the case of *exo*-norbornyl *p*-bromobenzenesulfonate has now been given the solvolysis of 3-phenyl-2-butyl *p*-toluenesulfonate IA. For the latter substance, polarimetric and titrimetric rate constants show good first order behavior, the polarimetric rates exceeding the titrimetric by factors of 2, 4.5–5, and 1.18 in ethanol, acetic acid and formic acid, respectively. Other details of the observed kinetics in the presence of added solutes show convincingly that the excess racemization is due to an internal pheonomenon, and the results are discussed along with those for *exo*-norbornyl *p*-bromobenzenesulfonate. The rate of internal excess racemization of 3-phenyl-2-butyl *p*-toluenesulfonate is nearly as sensitive to change in solvent as the solvolysis rate, and there is suggested the probability of a common intermediate, essentially an ion-pair, for both internal racemization and solvolysis. This intermediate can give racemic *p*-toluenesulfonate by "internal return" or can go on to products. Analogous internal phenomena may be generally important in a number of connections.

The discovery that polarimetric rate constants were 1.4 to 3.5 times as large as titrimetric rate constants in the solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate[2] III brought to light a phenomenon of considerable importance to our understanding of molecular rearrangements. In principle, this kind of complication can be present in all studies of neighboring group participation.

The same kind of polarimetric and titrimetric scrutiny as in the case of *exo*-norbornyl *p*-bromobenzenesulfonate (III) has been given the solvolysis of 3-phenyl-2-butyl *p*-toluenesulfonate (IA). In this system, representing another symmetrical case, the rate[3] is convenient for extension of the measurements over a larger solvent range, including formic acid. Thus the system is especially worthwhile in seeking information on the nature of the reaction responsible for the excess racemization accompanying solvolysis. Further, the system represents a case of control of the stereochemistry[4] of replacement by neighboring phenyl.[5] However, the completeness of this control can be assessed more accurately with a knowledge of the excess racemization accompanying solvolysis. The results of the measurements on 3-phenyl-2-butyl *p*-toluenesulfonate are reported in this paper and discussed along with the results on *exo*-norbornyl *p*-bromobenzenesulfonate[2] and some related matters.

One of the optically active modifications of the 3-phenyl-2-butyl *p*-toluenesulfonate diastereomer labeled I by Cram[4] was obviously the material to be studied. Since the 3-phenyl-2-butyl acetates from the two diastereomeric types of toluenesulfonate (I and II) are very largely different,[4] it was already clear that any changes in the *p*-toluenesulfonate concurrent with formation of acetolysis product would keep the toluenesulfonate I within the I classification. The phenomenon analogous to the one accompanying solvolysis of *exo*-norbornyl *p*-bromobenzenesulfonate[2] would, in the case of IA, also give rise to a racemization rate (k_α) in excess of a titrimetric solvolysis rate (k_t).



Polarimetric acetolysis rate constants determined at 50° or 75° indeed exceeded the previously determined titrimetric rate constants.[3] Table I lists the previously determined titrimetric rate constants, k_t, in acetic acid at a concentration of *ca.* 0.03 M and also titrimetric constants determined at the higher concentration (*ca.* 0.1 M) necessary for the polarimetric work. The agreement is good. Table II shows the good first order behavior of the data in a typical titrimetric run. Table I also

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[1] Research supported by the Office of Naval Research.

[2] Winstein and Trifan, THIS JOURNAL, **74**, 1154 (1952).

[3] Winstein, *et al.*, *ibid.*, **74**, 1113 (1952).

[4] (a) Cram, *ibid.*, **71**, 3863 (1949); (b) Cram, *ibid.*, **71**, 3883 (1949).

[5] Winstein, Schreiber, Brown and Schlesinger, *ibid.*, **74**, 1140 (1952).