[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]
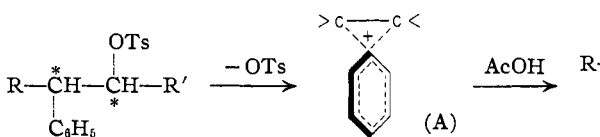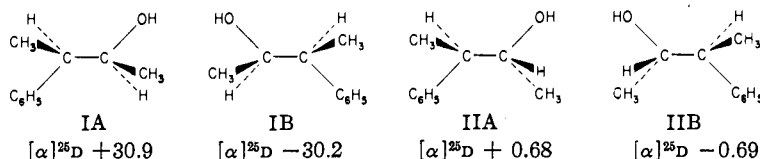
## Studies in Stereochemistry. V. Phenonium Sulfonate Ion-pairs as Intermediates in the Intramolecular Rearrangements and Solvolysis Reactions that Occur in the 3-Phenyl-2-butanol System

### BY DONALD J. CRAM

When the $p$-toluenesulfonates or $p$-bromobenzenesulfonates of the stereoisomers of 3-phenyl-2-butanol are dissolved in ionizing solvents (acetic and formic acids or acetonitrile) an intramolecular rearrangement occurs in which the phenyl and the $p$-toluenesulfonate (or $p$-bromobenzenesulfonate) groups exchange places. A comparison of the stereochemical structures of the products and reactants indicates the rearrangement to be highly stereospecific. When the reaction of the $p$-bromobenzenesulfonate is carried out in the presence of a large concentration of $p$-toluenesulfonate ion, minor amounts of $p$-toluenesulfonate of the same configuration as the $p$-bromobenzenesulfonate product are obtained. The configurations of the recovered $p$-bromobenzenesulfonates (or $p$-toluenesulfonates) are in each case qualitatively the same as the configurations of the solvolyzed products (acetates or formates). These facts are rationalized in terms of a series of reversible reactions between starting material, bridged ion-pairs (phenonium $p$-toluenesulfonates or $p$-bromobenzenesulfonates) and rearranged $p$-toluenesulfonate or $p$-bromobenzenesulfonate products. The solvolysis reaction is interpreted as going by an exchange reaction between phenonium sulfonate ion-pairs and solvent to give new ion-pairs which collapse to product.

In Papers I and III[1] of this series evidence was presented for the existence of a cyclic bridged ion (A)[2] as a discrete intermediate in the phenyl migration that occurs during the solvolyses of the tosylates ($p$-toluenesulfonates) of the various stereomers of 3-phenyl-2-butanol, 2-phenyl-3-pentanol and 3-phenyl-2-pentanol. In Paper IV[3] the stereochemical structures of the four stereo-

IA    $[\alpha]^{25}D +30.9$

IB    $[\alpha]^{25}D -30.2$

IIA    $[\alpha]^{25}D + 0.68$

IIB    $[\alpha]^{25}D -0.69$

mers of all three compounds were interrelated, and structural assignments were made on the basis of both the stereochemistry of the rearrangement reaction[1] and of the Chugaev elimination reaction.[4] The numbering system (IA and IB representing one set of enantiomorphs and IIA and IIB designating the second pair) adopted in the previous papers is maintained here.

$$ \text{R—}\overset{*}{\underset{\underset{\text{C}_6\text{H}_5}{|}}{\text{CH}}}\text{—}\overset{\underset{*}{}}{\underset{}{\overset{\text{OTs}}{|}}{\text{CH}}}\text{—R}' \xrightarrow{-\text{OTs}} \text{(A)} \xrightarrow{\text{AcOH}} \text{R—}\overset{*}{\underset{\underset{\text{C}_6\text{H}_5}{|}}{\text{CH}}}\text{—}\overset{\overset{\text{OAc}}{|}}{\underset{*}{\text{CH}}}\text{—R}' $$

$$ \text{R—}\overset{}{\underset{\underset{\text{C}_6\text{H}_5}{|}}{\underset{*}{\text{CH}}}}\text{—}\overset{\overset{\text{OAc}}{|}}{\underset{*}{\text{CH}}}\text{—R}' $$

$+$

olefin

(1) D. J. Cram, THIS JOURNAL, **71**, 3863, 3875 (1949).

(2) This type of ion subsequently will be referred to as a "phenonium ion."

(3) D. J. Cram, THIS JOURNAL, **71**, 3883 (1949).

(4) Further substantiation of the correctness of these assignments will be found in Papers VII and VIII of this series.

The present investigation deals with a more detailed study of the mechanism of the solvolysis reaction, and with the concomitant transformations. This paper reports the results that pertain to the reactions giving rise to the oxygen containing products, whereas Paper VI in this series will deal with the mechanism by which the olefinic products are produced.

### Methods

The physical properties and analyses of the starting materials are reported in Table I. The tosylates, brosylates ($p$ - bromobenzenesulfonates) and acetates as well as the alcohols (IA, IB, IIA and IIB) from which these derivatives were prepared were synthesized by methods that have already been reported.[1] The brosylate of IIA was inordinately unstable, and had to be used as soon as prepared and, when obtained as a product, its properties had to be recorded without delay. Table II records the

Table I

Physical Properties and Analyses of Starting Materials

| Compound | $n^{25}D$ | M.p., °C. | Rotation, $[\alpha]D$ | Mol. form. | Calcd. Carbon | Calcd. Hydrogen | Found Carbon | Found Hydrogen |
|---|---|---|---|---|---|---|---|---|
| IA tosylate[a] | .... | 62–63 | +16.97[o,b] | .......... | ... | .. | ... | .. |
| IB tosylate[c] | .... | 62–63 | −16.89[b] | $C_{17}H_{20}O_3S$ | 67.08 | 6.62 | 66.97 | 6.59 |
| I tosylate | .... | 46–47 | ....... | $C_{17}H_{20}O_3S$ | 67.08 | 6.62 | 67.22 | 6.77 |
| IIA tosylate[d] | .... | 36–37[f] | −17.41[b] | .......... | ... | .. | ... | .. |
| IIB tosylate[e] | .... | 46–47[f] | +17.72[b] | $C_{17}H_{20}O_3S$ | 67.08 | 6.62 | 67.07 | 6.77 |
| IA acetate[a] | 1.4877 | .... | − 8.08[g,i] | $C_{12}H_{16}O_2$ | 74.96 | 8.38 | 74.89 | 8.65 |
| IIB acetate[e] | 1.4877 | .... | +32.55[g,i] | $C_{12}H_{16}O_2$ | 74.96 | 8.38 | 74.89 | 8.57 |
| IB brosylate[c] | .... | 74–75[h] | −21.7[b] | $C_{16}H_{17}O_3SBr$ | 52.03 | 4.93 | 51.73 | 4.77 |
| I brosylate | .... | 93–94 | ....... | $C_{16}H_{17}O_3SBr$ | 52.03 | 4.93 | 51.98 | 4.63 |
| IIA brosylate[d] | .... | 57–58 | −19.6[b] | $C_{16}H_{17}O_3SBr$ | 52.03 | 4.93 | 52.02 | 4.64 |

[a] Prepared from alcohol IA, $[\alpha]^{23}D$ +32.1°. IA tosylate was previously reported (ref. 1). [b] Benzene solution, $c =$ 5%; $T = 23$–25°. [c] Prepared from alcohol IB, $[\alpha]^{23}D$ −31.8°. [d] Prepared from alcohol IIA, $[\alpha]^{23}D$ 0.36°. IIA tosylate was previously reported but was erroneously labeled IB (see Table I, ref. 1). [e] Prepared from alcohol IIB. $[\alpha]^{23}D$ −0.51°. [f] These enantiomers were each isolated in two polymorphic forms, one set melting at 36–37°, the other at 46–47°. [g] These rotations were taken on the pure liquid sample, $l = 1$ dm., $\lambda =$ D, $T = 23°$. [h] The compound seemed to solidify and remelt at 77–78°. [i] $\alpha D$.

conditions of each experiment and the results.

The sulfonate esters were isolated from the reaction medium through extraction and crystallization procedures. The carboxylate esters and olefins were first isolated by distillation as mixtures, which were converted by lithium aluminum hydride to mixtures of alcohol and olefin. These two classes of components were then quantitatively separated by chromatographic methods with alumina. The alcohols were submitted to infrared analysis. Figure 1 records the infrared spectra of the two diastereomeric 3-phenyl-2-butanols (I and II) and of 2-phenyl-2-butanol,[5] and enough differences



Fig. 1.—Infrared spectra of the two diastereomeric 3-phenyl-2-butanols (I and II, the numbers designating the configurations as in text) and 2-phenyl-2-butanol (III). Spectra were taken on liquid films (0.01 mm. thickness) in NaCl cells on a Baird Spectrophotometer.

(5) This alcohol could have arisen in the reaction by migration of a hydrogen instead of a phenyl group during the course of solvolysis. Evidence that such a process does indeed take place is presented in paper VI of this series.

between the spectra exist to allow analyses for the three components. Table III reports the results of this analysis taken at the most advantageous wave lengths. The absence of any 2-phenyl-2-butanol in the mixtures (as shown by inspection of the optical densities of the pure substances and unknown mixtures at all four wave lengths) resolved the problem into an analysis of a two-component system (carbinols I and II).

The results of conducting the solvolysis reaction with the brosylates of IB and IIA in acetic acid and in the presence of ten parts (brosylate = 1 part) of tosylate ion are recorded in Table IV. In these experiments the acetate products were not examined, attention being given to only the analysis of the brosylate–tosylate mixtures that were isolated after about two thirds of the ester had solvolysed. The vast differences between the percentage of carbon and of bromine in the tosylates and brosylates of the isomers ($\Delta = 15.05\%$ for carbon and $\Delta = 21.64\%$ for bromine) allow two independent methods of analysis for the balance between the two derivatives in the crystalline products. The identity of these products was determined from their rotatory power, and from a series of mixed melting point experiments.

Results

A high degree of stereospecificity for the reaction that produces the acetates is apparent in runs 3–6. Both IA and IB tosylates (runs 3 and 4) give ultimately alcoholic products, 96% of which possess the I configuration and 4% the II configuration. It is clear from the low rotation of the alcoholic fraction ($\alpha^{23}D$ 0.20°, $l = 1$ dm.) that the component belonging to the I series is almost completely racemic. Thus the small residual rotation in the alcoholic product of run 3 amounts to $\alpha D = +0.20°$ ($l = 1$ dm.), and must be due to a preponderance of IA over IB to the extent of 0.64%.[6] The maximum contribution that the IIA present could make to the rotation is 0.002° and this value is within the experimental error. From the rotations of the

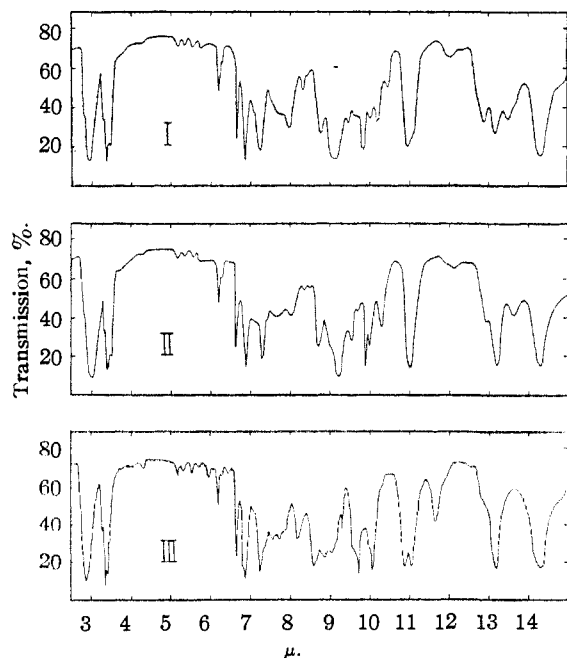(6) In this and subsequent calculations of a similar sort, the assumption has been made that the rotational contributions of the two components are additive. The structural similarity of the two diastereomeric alcohols lends substance to this assumption.

TABLE II:  THE OXYGEN-CONTAINING PRODUCTS OF SOLVOLYSIS

| Run no. | Start. mat. Config. tos. | Start. mat. Wt. g. | Solution | Moles base added | Temp. °C | Time hr. | Yld. alc. | $\alpha D$ alc. | $\alpha D$ acet. | %I mixt. | %II mixt. | 1st crop rec. tos. Yld. % | 1st crop M.p. °C | 1st crop $[\alpha]D$ | 2nd crop rec. tos. Yld. % | 2nd crop M.p. °C | 2nd crop $[\alpha]D$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | IA | 10 | Gl. acetic | 0.8 | 75 | 36 | 43 | +0.14° | .. | .. | .. | 0 | .. | .. | .. | .. | .. |
| 2 | IIB | 10 | Gl. acetic | 0.8 | 75 | 36 | 58 | -1.92 | -0.43° | .. | .. | 0 | .. | .. | .. | .. | .. |
| 3 | IA | 14 | Gl. acetic | 1.2 | 75 | 33 | 53 | +0.20 | .. | 96 | 4 | 0 | .. | .. | .. | .. | .. |
| 4 | IB | 12 | Gl. acetic | 1.2 | 75 | 33 | 53 | -0.19 | .. | 96 | 4 | 0 | .. | .. | .. | .. | .. |
| 5 | IIA | 12 | Gl. acetic | 1.2 | 75 | 33 | 68 | +1.91 | +32.49 | 5 | 94 | 0 | .. | .. | .. | .. | .. |
| 6 | IIB | 14 | Gl. acetic | 1.2 | 75 | 33 | 69 | -1.82 | .. | 5 | 94 | 0 | .. | .. | .. | .. | .. |
| 7 | IA | 5 | Gl. acetic | 1.2 | 75 | 3½ | .. | .. | .. | .. | .. | 30 | 46-49 | +1.09° | 0.5 | 47-49 | .. |
| 8 | IIB | 5 | Gl. acetic | 1.2 | 75 | 3½ | .. | .. | .. | .. | .. | 32 | 46-47 | +18.1 | 2.1 | 46-47 | .. |
| 9 | IA | 5 | Dry formic | 1.2 | 25 | 24 | 70 | +0.03 | -0.01 | .. | .. | 0 | .. | .. | .. | .. | .. |
| 10 | IIB | 5 | Dry formic | 1.2 | 25 | 24 | 71 | .73 | +33.50 | .. | .. | 0 | .. | .. | .. | .. | .. |
| 11 | IA | 2.5 | Dry formic | 1.2 | 25 | 0.72 | 33 | .. | .. | .. | .. | 40 | 55-59 | +13.9 | Trace | Oil | .. |
| 12 | IB | 5 | Acetonitrile | 2 | 82 | 67 | 0 | .. | .. | .. | .. | 52 | 45-46 | -6.43 | 3.6 | 42-45 | -16.67° |
| 13 | IIA | 5 | Acetonitrile | 2 | 82 | 67 | 0 | .. | .. | .. | .. | 45 | 45-46 | -17.56 | 7 | 45-48 | -4.31 |
| 14 | IA | 1.0 | Acetonitrile + TosOH (1 mole) | 0 | 82 | 2 | 0 | .. | .. | .. | .. | 40 | 45-48 | -4.33 | 15 | .. | .. |
| 15 | IA | 0.5 | Chloroform | 0 | 62 | 53 | 0 | .. | .. | .. | .. | 92 | 62-63 | +16.77 | .. | .. | .. |

* Starting material = 1 mole.  In runs 1–8 the base was added in the form of potassium carbonate along with more than enough acetic anhydride to consume the water produced. Anhydrous sodium formate was employed in runs 9–11, and anhydrous potassium carbonate was present as a second phase in runs 12–15.  ᵇ In each case the solvent was preheated.  ᶜ For every sample of alcohol, $n^{25}D$ 1.5168 ± 0.0006.  ᵈ Pure sample, l = 1 dm., T = 23–25°.  ᵉ Values obtained from infrared data (see Table III).  The spectrophotometer cannot distinguish between the enantiomorphs in each racemate series.  ᶠ C = 5% (benzene), T = 23–25°.  ᵍ For every sample of acetate, $n^{25}D$ 1.4877 ± 0.0003.  ʰ M.m.p. with I tosylate

(racemic) 46–48°.  ⁱ M.m.p. with authentic sample of IIB tosylate, 46–47°.  ʲ This material was converted to the acid phthalate, 1st crop, yield 62%, 2nd crop, yield 3%, m.p. (both crops) 130–131°, not depressed by admixture with an authentic sample.  The residue was extracted into NaHCO₃ solution, acidified, and a trace of material crystallized, m.p. 128–130°, not depressed by admixture with IA acid phthalate.  ᵏ Converted to the acid phthalate: 1st crop, yield 64%, $[\alpha]^{25}D$ +65.6° (c 3%. in ethanol), m.p. 101–102°, m.m.p. with an authentic sample of the acid phthalate of IIB, 101–102°; residue extracted into NaHCO₃ solution, acidified, and a trace of material crystallized, m.p. 98–100° (not depressed by admixture with the first crop).  ˡ M.m.p. with IA tosylate, 58–62°.  ᵐ M.m.p. with tosylate of I (racemic), 45–47°.  ⁿ M.m.p. with authentic IIA tosylate, 45–46°.  ° M.m.p. with IIA tosylate, 44–46° (filtrates produced 5% yield of non-distillable, non-acidic oil).  ᵖ M.m.p. with I tosylate (racemic), 45–47°.  M.m.p. with IA tosylate 62–63° (filtrates produced a 4% yield of non-distillable, non-acidic oil).  ᵍ M.m.p. with IA tosylate, 62–63°.

TABLE III

INFRARED ANALYSES FOR THE DIASTEREOMERIC 3-PHENYL-2-BUTANOLS AND 2-PHENYL-2-BUTANOL

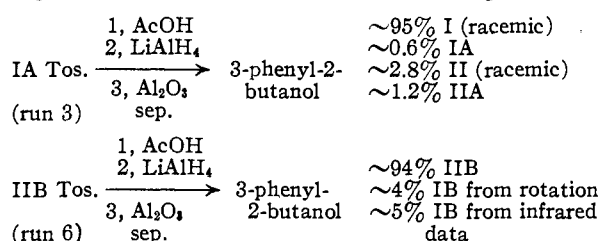| Sample[a] alcohol | Optical density (Cell thickness = 0.03 mm., slit = 0.92 mm.) | | | | % I[b] | % II | % Total[b] |
|---|---|---|---|---|---|---|---|
| | $\lambda = 8.10\,\mu$ | $\lambda = 8.60\,\mu$ | $\lambda = 10.38\,\mu$ | $\lambda = 11.67\,\mu$ | | | |
| I | 1.11 | 0.322 | 0.589 | 0.190 | .. | .. | .. |
| II | 0.806 | .399 | 1.01 | .211 | .. | .. | .. |
| 2-Phenyl-2-butanol | .609 | 1.29 | 0.330 | .821 | .. | .. | .. |
| 50% I, 50% II | .920 | 0.373 | .783 | .204 | 46 | 51 | 97 |
| From run 3 | 1.09 | .334 | .598 | .189 | 95.5 | 3.5 | 99 |
| From run 4 | 1.09 | .333 | .598 | .186 | 95.5 | 3.5 | 99 |
| From run 5 | .816 | .391 | .981 | .189 | 4.9 | 94.6 | 99.5 |
| From run 6 | .815 | .392 | .984 | .202 | 4.5 | 94.9 | 99.4 |

ᵃ No solvent was employed.  ᵇ These values were calculated using the data at $\lambda = 8.10\,\mu$ and $\lambda = 10.38\,\mu$, assuming that Beer's law holds, and that no 2-phenyl-2-butanol was present.  That the first assumption is valid is shown by the facts that the sum of I and II are very close to 100% and that the deviation from Beer's law at 50% I, 50% II is small (and hence much smaller at low concentrations of I in II or II in I).  The second assumption is demonstrated to be valid by the values of the optical density at $\lambda = 8.60\,\mu$ and $\lambda = 11.67\,\mu$.

TABLE IV

SOLVOLYSES OF BROSYLATES OF IA AND IIB IN PRESENCE OF HIGH CONCENTRATIONS OF TOSYLATE IONS[a]

| | | | 16 | 17 |
|---|---|---|---|---|
| Run no. | | | 16 | 17 |
| Bros.[b] | | | IB | IIA |
| % yld., ac. + ol.[c,d] | | | 63 | 59 |
| Wt. %[d] recov. | cryst. mat. | | 25 | 27 |
| | non.-cryst. mat.[e] | | 2 | 1 |
| Crystalline material recrystallized | 1st crop | Wt. %[d] yld. | 19 | 20 |
| | | $[\alpha]D^f$ | -2.05[e] | -18.8 |
| | | M.p., °C | 79-86[i] | 43-50[i] |
| | | Wt. %[g] tos. {Brom. | 15 | 26 |
| | | {Carb. | 16 | 25 |
| | 2nd crop | Wt. % yld.[d] | 1.5 | 4.3 |
| | | $[\alpha]D^f$ | .... | -17.8[e] |
| | | M.p., °C | 43-45[i] | 42-44[i] |
| | | Wt. %[g] tos. {Brom. | 87 | 48 |
| | | {Carb. | 91 | 50 |
| Over-all yields,[h] % | {Bros. | | 16 | 17 |
| | {Tos. | | 5 | 9 |

ᵃ Ten moles of KO Tos. to one of brosylate in dry glacial acetic acid (see Experimental).  ᵇ See Table I for properties.  ᶜ Yields are calculated on the assumption that the ratios of acetate to olefin are the same as those found in runs 3 and 5 (Table II and unpublished results).  ᵈ Wt. starting material = 100%.  ᵉ This material was non-acidic.  ᶠ T = 23–25°, c 5%, in benzene.  ᵍ These wt. %'s are based on bromine and carbon analyses for the mixtures, total crop = 100%.  ʰ These are yields of recrystallized material including both crops, and take into consideration the difference in molecular wt. of the tosylate and brosylate esters.  ⁱ See experimental part for mixed melting point determinations.

acetate made from the alcohol mixture of run 3 and the rotations of the acetates of pure IA and IIA, it is evident that of the 4% of material of the II configuration in the mixture, 2.8% is II (racemic) and 1.2% is IIA. The data are summarized below. A similar treatment of the data from run 6 produces the results shown in the diagram.

Ratio of about 3.7 to 1

IB Bros. (run 16) $\xrightarrow[\text{1.5 half-lives}]{\text{O Tos.}^- \text{ CH}_3\text{COOH}}$ 15% I Bros. + 1.5% IB Bros. + 4.5% I Tos. + acetate, olefin
(racemic)   (optically pure)   (racemic)

ratio of about 2 to 1

IIA Bros. (run 17) $\xrightarrow[\text{1.5 half-lives}]{\text{O Tos.}^- \text{ CH}_3\text{COOH}}$ 17% IIA Bros. + 9% IIA Tos. + acetate, olefin
(optically pure)  (optically pure)

IA Tos. (run 3) $\xrightarrow[\substack{3,\ \text{Al}_2\text{O}_3 \\ \text{sep.}}]{\substack{1,\ \text{AcOH} \\ 2,\ \text{LiAlH}_4}}$ 3-phenyl-2-butanol

~95% I (racemic)
~0.6% IA
~2.8% II (racemic)
~1.2% IIA

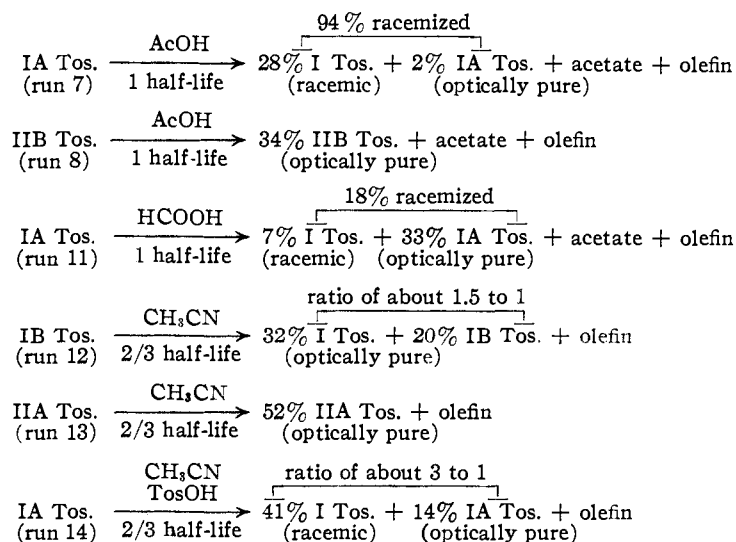IIB Tos. (run 6) $\xrightarrow[\substack{3,\ \text{Al}_2\text{O}_3 \\ \text{sep.}}]{\substack{1,\ \text{AcOH} \\ 2,\ \text{LiAlH}_4}}$ 3-phenyl-2-butanol

~94% IIB
~4% IB from rotation
~5% IB from infrared data

An even higher degree of stereospecificity for the solvolysis reactions that were conducted in formic acid was experienced.

IA Tos. (run 9) $\xrightarrow[\substack{3,\ \text{Al}_2\text{O}_3}]{\substack{1,\ \text{HCOOH} \\ 2,\ \text{LiAlH}_4}}$ 3-phenyl-2-butanol

~100% I (racemic)
< 0.02% IA (calcd. from rot. of alcohol)
< 0.01% IIA (calcd. from rot. of acetate)

IIB Tos. (run 10) $\xrightarrow[\substack{3,\ \text{Al}_2\text{O}_3}]{\substack{1,\ \text{HCOOH} \\ 2,\ \text{LiAlH}_4}}$ 3-phenyl-2-butanol

~100% IIB
~0.5% IB
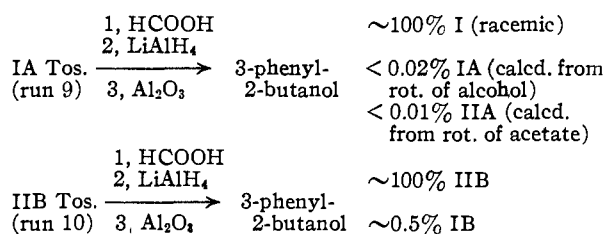
A new feature of the solvolysis reaction was brought to light when IA tosylate was recovered from a partially acetolyzed mixture. This sulfonate ester had undergone *94% racemization* during the period of one solvolytic half-life. The tosylate of IIA was recovered optically pure in a similar

94 % racemized

IA Tos. (run 7) $\xrightarrow[\text{1 half-life}]{\text{AcOH}}$ 28% I Tos. + 2% IA Tos. + acetate + olefin
(racemic)   (optically pure)

IIB Tos. (run 8) $\xrightarrow[\text{1 half-life}]{\text{AcOH}}$ 34% IIB Tos. + acetate + olefin
(optically pure)

18% racemized

IA Tos. (run 11) $\xrightarrow[\text{1 half-life}]{\text{HCOOH}}$ 7% I Tos. + 33% IA Tos. + acetate + olefin
(racemic)   (optically pure)

ratio of about 1.5 to 1

IB Tos. (run 12) $\xrightarrow[\text{2/3 half-life}]{\text{CH}_3\text{CN}}$ 32% I Tos. + 20% IB Tos. + olefin
(optically pure)

IIA Tos. (run 13) $\xrightarrow[\text{2/3 half-life}]{\text{CH}_3\text{CN}}$ 52% IIA Tos. + olefin
(optically pure)

ratio of about 3 to 1

IA Tos. (run 14) $\xrightarrow[\text{2/3 half-life}]{\substack{\text{CH}_3\text{CN} \\ \text{TosOH}}}$ 41% I Tos. + 14% IA Tos. + olefin
(racemic)   (optically pure)

experiment. When formic acid was used as solvent, the unreacted IA tosylate was racemized to the extent of 18% during one solvolytic half-life.[7]

(7) The half-lives in formic and acetic acids were calculated from the rate data obtained by S. Winstein, *et al.*, [S. Winstein, B. Morse, E. Grunwald, K. Schreiber and J. Corse, *ibid.*, **74**, 1113 (1952)]. The
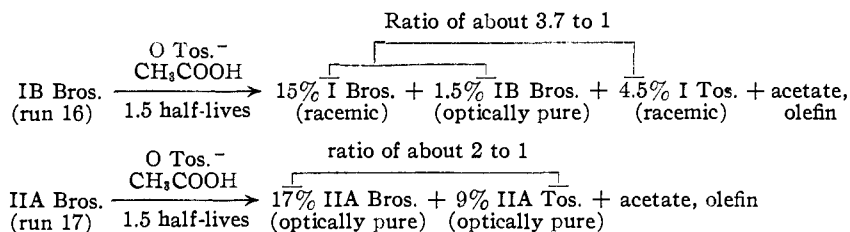
When the esters were heated in acetonitrile, a non-solvolytic medium, a slow reaction to give olefins took place. Again IA tosylate was shown to undergo racemization more rapidly than elimination. Both reactions were found to be strongly catalyzed by *p*-toluenesulfonic acid.

Since it was of interest to learn whether or not the racemization of IA tosylate involves the separation of tosylate ion from the molecule, the partial solvolysis of the corresponding brosylate was carried out in the presence of a high concentration of tosylate ion. Both tosylate and brosylate esters were isolated from the reaction mixture, and both sulfonate esters had approximately the same configuration.

## Discussion

Evidence has been accumulated in the foregoing experiments that exclusive of olefin formation, four discrete sets of products can be realized when tosylate or brosylate esters of 3-phenyl-2-butanol are allowed to react in glacial acetic acid. Although several of the reactions undoubtedly have common intermediates, they can best be discussed in terms of names which refer more to the product than to the mechanism by which the product comes into being. In the present discussion the four reactions will be referred to as follows: the solvolysis reaction (C) in which sulfonate esters are converted to carboxylate esters, both asymmetric carbon atoms being involved in the process, the isomerization reaction (D) in which tosyl and phenyl groups exchange places in half of the molecules; the exchange reaction (E) in which a tosylate anion outside of the molecule exchanges with a brosylate group within the molecule, with or without stereoisomerization of the system, and the simple replacement reaction (F) in which a tosyl group is replaced by an acetoxy group, the stereochemistry of no carbon atom other than the one at the seat of reaction being involved in the process.

The Solvolysis Reaction.—In view of the recently discovered isomerization reaction of IA tosylate to I tosylate (runs 7 and 11)[8] the evidence presented

author is indebted to S. Winstein for suggesting the use of formic acid as a solvolytic medium.

(8) Such a reaction was considered improbable until W. G. Young, S. Winstein and H. L. Goering [*ibid.*, **73**, 1958 (1951)] discovered the somewhat similar intramolecular rearrangement of α,α-dimethylallyl chloride in acetic acid. The experiments were conducted by the author to ascertain the existence of an isomerization in the tosylate of IA after S. Winstein and D. Trifan had made the observation that the rate of loss of optical activity was greater than the rate of appearance of *p*-bromobenzenesulfonic acid during the solvolysis of active *exo*-norbornyl brosylate in acetic acid [S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952)].

in Papers I and III[1] of this series for a bridged ionic intermediate (a phenonium ion) in the solvolysis reaction requires elaboration. If $k_i$, the rate of isomerization, is much greater than $k_s$, the rate of solvolysis, then the racemic nature of the I acetate produced (*e.g.*, in runs 3 and 4) could be explained without recourse to mechanisms involving bridged ions as intermediates in the solvolysis reaction. The results of the present

$$\text{IA Tos.} \xrightarrow{k_i} \text{I Tos. (racemic)}$$

|  | | $\downarrow k_s$ | $\downarrow k_s$ |
|---|---|---|---|
|  |  | I Acetate | I Acetate |
| In acetic acid | | 20% | 80% |
| In formic acid | | 75% | 25% |

investigation remove this ambiguity from the former interpretation. Thus in runs 3 and 4 in glacial acetic acid (the reaction went to completion) the preponderance of IA over IB in the final product was negligible. Yet in experiment 7, where the reaction was run for one solvolytic half-life, the isomerization reaction had passed through about four half-lives (the recovered tosylate of I was 94% racemized). Therefore in acetic acid the isomerization reaction must be four times as fast as the solvolysis reaction, or $k_i/k_s = 4/1$. Since the solvolysis reaction is irreversible and the isomerization is in effect irreversible (I Tos.—✕→IA Tos.), then the ratio of I acetate produced directly from IA tosylate to I acetate produced *via* I tosylate must be one to four. In other words, 20% of I acetate must have arisen by a route not involving I tosylate as an intermediate. Clearly the isomerization reaction in itself cannot account for the virtually racemic character of the solvolysis product.

Similar reasoning applied to the data obtained in formic acid (runs 9 and 11) reveals that in this solvent $k_i/k_s = 1/3$, and that 75% of I formate produced must not have involved I tosylate as an intermediate. Therefore the argument previously advanced[1] for a phenonium ion intermediate, internally compensated in the I series, but asymmetric in the II series becomes valid.

**The Isomerization and Exchange Reactions.—** Four general mechanisms are compatible with the stereochemistry of the isomerization reaction.

$$\text{IA Tos.} + {}^{-}\text{OTos.} \rightleftharpoons \text{IB Tos.} + {}^{-}\text{OTos.} \quad (1)$$

IA Tos. ⟶ [dissociated ions] + ⁻OTos ⟶ I Tos. (racemic) (2)

$$\text{IA Tos.} \rightleftharpoons \text{IB Tos.} \quad (3)$$

IA Tos. ⟶ ⟶ I Tos. (racemic) (4)

Experiment 16 in which IB brosylate was solvolyzed in the presence of ten moles of tosylate ion (starting material = one mole) gave after about 1.5 solvolytic half-lives a ratio of about 3.7 to 1 of recovered brosylate to tosylate, both substances being almost completely racemic. Thus the isomerization reaction took place in the presence of large amounts of a different but very similarly constituted ion without that ion being involved in the isomerization process to any large degree. Had the reaction been intermolecular, conditions would have been favorable for the production of predominantly tosylate ester.[9] Mechanisms 1 and 2 are therefore incompatible with the evidence.

If mechanism 3 applies then the transition state would have to be somewhat like (S), in which a phenyl group bridges two atoms on one side and the tosyl group does the same on the other side of the carbon–carbon bond. Yet in the solvolysis process a somewhat similarly constituted species (a pheno-

(S)

nium ion) was shown to be a distinct intermediate and not a transition state. Furthermore, the rates of solvolysis and isomerization are very close together indicating that the activation energies for the rate-controlling steps are similar. If mechanism 3 were operating no ionic bonds would be formed in the isomerization, whereas in the solvolysis reaction a covalent bond is being broken and a largely ionic bond being formed. Mechanism 3 also lacks the virtue of explaining the exchange reaction, and requires that the exchange take place by some independent process.

In contrast to the other three, mechanism 4 offers an internally consistent explanation of not only the isomerization but also the solvolysis and exchange reactions. In this mechanism a distinct intermediate exists between the starting material and product in the isomerization reaction. This intermediate is an ion-pair (a phenonium tosylate or brosylate) which sometimes exchanges its anion for a solvent molecule (solvolysis) or a solvent anion (acetate or formate anions), sometimes it exchanges its anion for either a different anion that has been dissolved in the solvent (exchange reaction) or the same anion that has previously been liberated by the solvolytic process, and sometimes the ion-pair collapses to sulfonate ester (isomerization reaction). With such a mechanism the rate of formation of the ion-pair would be very sensitive to the ionizing power of the solvent. Thus the rates of ion-pair formation have been found to fall off rapidly in going from formic acid to acetic acid

(9) At the beginning of the reaction the ratio of tosylate to brosylate ion was infinity, and after one half-life the ratio was 20:1. The tosylate ion is probably somewhat more nucleophilic than the brosylate ion as evidenced by the higher acidity of *p*-bromobenzenesulfonic acid as compared to *p*-toluenesulfonic acid and by the fact that brosylate esters solvolyze about three times as fast as tosylate esters. Were the isomerization reaction mainly intermolecular, tosylate ester would accumulate very rapidly and the only brosylate ester recoverable would be optically active and unisomerized starting material.

to acetonitrile to chloroform. The distribution of products once the ion-pair had formed should be sensitive to both the ionizing power and nucleophilic character of the solvent. The greater the ionizing power of the solvent, the greater the tendency of the ion-pair to dissociate, thereby allowing the solvent or dissolved anions to assert their nucleophilic tendencies in more open competition with the nucleophilic properties of the anion of the original ion-pair. In the experiments at hand it was found that in acetic acid, roughly for every five ion-pairs formed, four collapsed to tosylate ester, and one went to acetate. In formic acid on the other hand, for every four ion-pairs formed, only one collapsed to tosylate ester and the other three went to formate. Since acetic acid is more nucleophilic than formic, the ionizing power seems to be more important than the nucleophilic character of the solvent in determining the fate of an ion-pair.

The roughly thirty-fold increase in the rate of the isomerization reaction when carried out in the presence of $p$-toluenesulfonic acid in acetonitrile (run 14) is an interesting example of acid catalysis, and suggests that the conjugate acid of the tosylate might be the species involved in at least the initiating stage of the isomerization reaction.[10] Although about the same amount of tosylate ester had been consumed in runs 12 and 14, in the acid catalyzed experiment the isomerization reaction had progressed about twice as far. Thus although the acid catalyzes both the isomerization and the competing reactions (those leading to olefins), the isomerization reaction is enhanced twice as much as the competing reactions.

The mechanism of the exchange reaction has a bearing on the fate of the initially formed ion-pair.
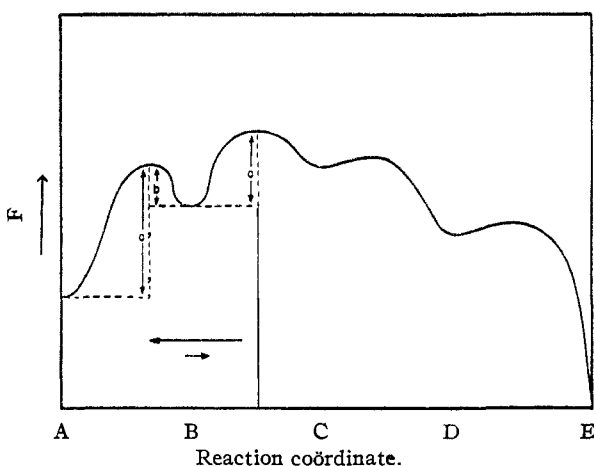


Fig. 2.—Energy–reaction coördinate diagram for the solvolysis reaction in acetic acid: A = tosylate or brosylate ester; B = phenonium tosylate (or brosylate) ion pair; C = hypothetical dissociated or partially dissociated ions; D = phenonium acetate; a = activation energy for the isomerization reaction; b = activation energy for the collapse of phenonium tosylate (or brosylate) to starting material; c = activation energy for the dissociation (or partial dissociation) of phenonium tosylate (or brosylate).

(10) In paper I of this series (ref. 1) a similar suggestion was mistakenly made for the solvolysis reaction in acetic acid.

The fact that an exchange reaction took place at all is evidence in favor of a second reversible reaction in which one ion-pair goes to a second. In experiment 16 since phenonium brosylate went to phenonium tosylate (and probably to a very small extent in the reverse direction), it seems likely
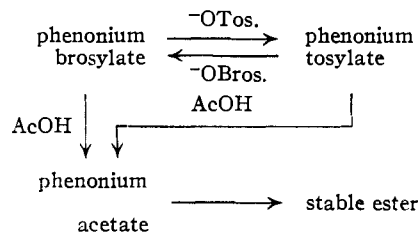


that the solvolysis reaction takes place through the formation of a second ion-pair (phenonium acetate) which then collapses to stable ester. Two limiting mechanisms can be envisioned to account for the conversion of one ion-pair to a second: the second ion-pair could be formed by either a dissociation of the first ion-pair and combination of the appropriate species (two transition states), or by a concerted displacement reaction (one transition state). Either possibility is consistent with the greater importance of the ionizing power of the solvent over the nucleophilic character of the solvent. In the first case, the dissociation of the first ion-pair would certainly be favored in the more ionizing solvent. In the second case, the more ionizing the solvent, the more ionic the character of the bond holding the ion-pair together, and the more amenable the anion of the pair would be to nucleophilic displacement, and vice versa.

Figure 2 is a crude plot of free energy vs. reaction coördinate for the solvolysis, isomerization and exchange reactions in acetic acid, and represents a mechanism, in part speculative, and in part substantiated by experiment. That B (phenonium tosylate ion-pair) is produced reversibly is well substantiated. The minima in the curve represented by C (partially or fully dissociated ions) and D (phenonium acetate) are suggested as reasonable but as yet unsubstantiated further stages in the reaction. The question of whether a minimum can intervene between A (starting tosylate ester) and B seems to be at least partially answered by the stereochemistry of the reaction. Such a minimum would represent a carbonium tosylate ion-pair, and to make the stereochemistry of the reaction compatible with the existence of such an "open" ion-pair would necessitate the following assumptions: first, that the configuration of the carbon atom involved in the open ion-pair was almost completely preserved throughout the lifetime of the species; second, that the anion of the open ion-pair can be displaced by the phenyl group only from the rear. Such a stage in the mechanism is not necessitated by any experimental evidence in the present investigation.

It is interesting to note that although the isomerization reaction could not be detected when IIA (or IIB) brosylate (or tosylate) was solvolyzed because collapse of the ion-pair gave back sulfonate of the same configuration as that of the starting material, yet the exchange reaction was detected

in this system (run 17).  Although IB and IIA brosylates were solvolyzed in the presence of tosylate ion (runs 16 and 17) under identical conditions, with the former starting material the ratio of recovered brosylate to tosylate ester was about 3.7 to 1 whereas with the latter the ratio was 2 to 1.  Other than in these experiments, the yields and product balances seem to be comparable from either stereomeric starting material.  The mechanistic argument is summarized in the following formulation.

(0.6%) produced in run 3 (IA Tos. completely solvolyzed in acetic acid) gives a means of estimating the extent to which acetate of I configuration was produced by a simple $S_N1$ mechanism.  If $k_r$ is the rate at which IA tosylate goes to IA acetate (or I tosylate goes to I acetate) by an $S_N1$ mechanism, then $k_s/k_r = 20/0.6 = 80/2.4$.  Therefore about 2.4% of the I acetate produced must have come from I tosylate by an $S_N1$ mechanism, and a total of about 3% of acetate of I (A and B)
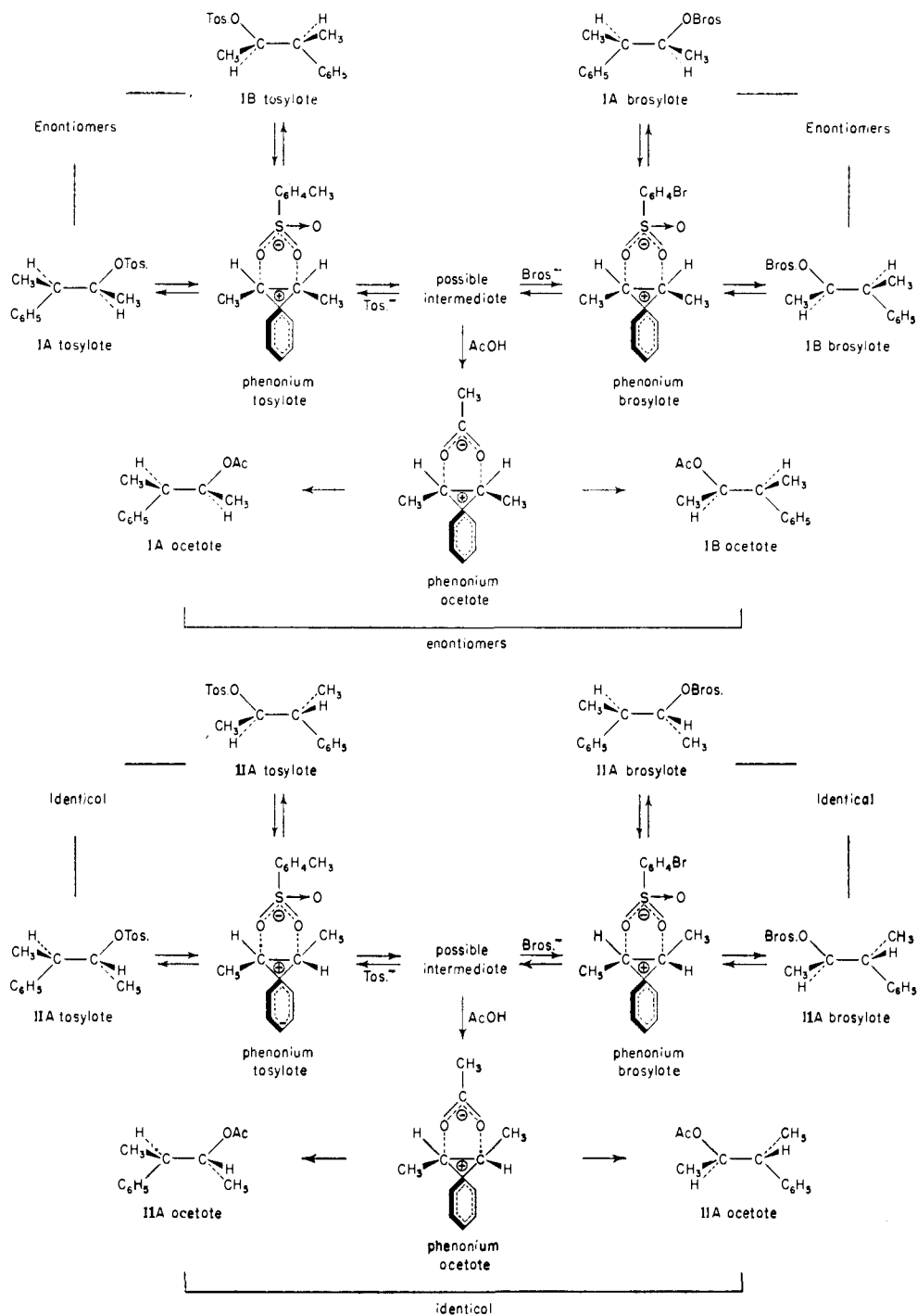


**The Simple Substitution Reaction.**—The small excess of acetate of configuration IA over that of IB

configuration must have been produced by an $S_N1$ mechanism.

Since the simple $S_N1$ process would also be expected to produce amounts of acetate of the II configuration (run 3) of the same order of magnitude as those of acetate of the I configuration, it is probable that the acetate of II configuration produced also arose by the simple $S_N1$ process. The ratio of II to IIA acetate found in run 3 is about two and one-half to one which is not highly divergent from the ratio of four to one which would be expected. A small amount of acetate of the II configuration might also have been produced by an $S_N2$ reaction of acetate ion with IA and I tosylates, but it seems improbable that more than a trace of acetate arose by such a path. It is interesting that the amounts of diastereomeric material produced from IA tosylate (run 3) and IIB tosylate (run 6) were approximately equal.

The absence of diastereomeric products when the solvolyses were conducted in formic acid is attributable to the weaker nucleophilic character and the enhanced power to dissociate ion-pairs of this acid as compared to acetic acid. Noteworthy in this connection is the relative freedom from noncrystallizable material of the tosylate recovered from the formic acid solvolysis (run 11) as compared to that material recovered from the experiments conducted in acetonitrile (runs 12 and 13).

The possible general implications of the existence of ion-pairs as intermediates in these reactions are many. First, the isomerization reaction can be looked upon as an aromatic substitution in which one methylene group is displaced by electrophilic attack on the benzene ring of a second methylene group bearing an incipient positive charge. Possibly many of the aromatic substitution reactions, both those occurring by intramolecular processes (*e.g.*, the Claisen rearrangement) and those involving intermolecular mechanisms (*e.g.*, the Friedel–Crafts reaction) go through similarly constituted ion-pairs as distinct intermediates in the reaction sequence. Second, the solvolysis reaction can be looked upon as an $S_N1$ replacement reaction, and the possibility that many $S_N1$ replacement reactions go through ion-pairs as intermediates is suggested by the present investigation. Third, the isomerization reaction is an intramolecular rearrangement, and the intermediate ion-pair of this reaction suggests that many molecular rearrangements (*e.g.*, the pinacol, Beckmann and allied rearrangements) may go through analogous intermediate stages.

### Experimental

**Solvolyses of Tosylates (Runs 1–8) in Acetic Acid.—**Anhydrous potassium carbonate (14.1 g.) was allowed to react with 1000 ml. of glacial acetic acid and 25 ml. of acetic anhydride. The solution (20 ml. per g. of tosylate) was warmed in a constant temperature bath (75°) for one-half hour, tosylate was added, and the mixture was allowed to stand for the times specified in Table II (in runs 1 and 2 the proportion was 13 ml. of solution to 1 g. of tosylate). At the end of this time the mixture was quenched in an icebath, diluted threefold with water, and the aqueous solution was extracted three times with pure pentane. In the cases where tosylate was to be recovered (runs 7 and 8) a 75% pentane–25% ether mixture was employed. The organic extracts were combined, washed twice with water, twice with bicarbonate solution, again with water, dried, and the solvent was removed at atmospheric pressure through a column (without a small column olefin losses amount to 10–20%) until a volume of 20 ml. remained. In runs 1–6,

this solution was added dropwise to a mixture of 30 ml. of dry ether and 1 g. of lithium aluminum hydride, and the resulting mixture was decomposed in a mixture of sodium hydroxide solution and ice. The organic layer was separated, the aqueous suspension was extracted twice with ether, the extracts were combined, dried, the solvent was removed at atmospheric pressure through a column, and the residue was flash distilled at 20 mm. (the mixture was never heated above 100° at any point). This mixture was submitted to separation on an alumina column (80 g. of alumina per g. of mixture) made up in pentane. The olefin fraction appeared in the column eluate, and the alcohol remained on the alumina when pentane was used as a developer. The alcohol was removed by elution with methyl alcohol. The pentane eluate was evaporated (through a column) and flash-distilled at 20 mm. to give the olefin fraction. This material was set aside.

The methyl alcohol was removed by distillation through a column, and the alcohol fraction was flash-distilled at 20 mm. This material was used directly for infrared analysis and preparation of acetate. In every case where either the olefin, alcohol or a mixture of the two was distilled, the small residue left in the pot was not acidic.

In those runs where tosylate was recovered (7 and 8), the concentrated solution (from the extractions) was cooled, and the crystalline tosylate was collected, further material being crystallized from the filtrates. When no more crystalline tosylate could be obtained the filtrates were combined, evaporated and submitted to distillation at 0.1 mm., the pot temperature never getting above 80°. Additional amounts of tosylate ester were recovered from the still residue. All tosylate ester fractions were combined and recrystallized, and two crops were taken. All filtrates when combined and evaporated gave only traces of a non-acidic residue.

**Solvolysis of Tosylates (Runs 9–11) in Formic Acid.—**These experiments were conducted in a manner analogous to those reported above except that the solvolysis solution was prepared by dissolving 2.52 g. of anhydrous sodium formate in 200 ml. of anhydrous formic acid, 20 ml. of solution per g. of tosylate being employed. The isolation procedures were completely analogous to those reported above.

**Reaction of Tosylates (Runs 12–14) in Acetonitrile.—**Mixtures made in the proportions of 10 ml. of acetonitrile to 1 g. of tosylate to 0.45 g. of anhydrous potassium carbonate (runs 12 and 13) were held at reflux, cooled, shaken with four volumes of water and one volume of a 50%-ether-50%-pentane mixture, and the layers were separated. The aqueous layer was again extracted with the ether mixture, the extracts were combined, washed three times with water, once with dilute acid, once with dilute base, and again with water. From here the isolation procedure was completely analogous to that used in runs 7, 8 and 11.

In run 14, in place of the potassium carbonate was added one mole (based on tosylate) of anhydrous *p*-toluenesulfonic acid (prepared from the monohydrate, the water being eliminated by azeotropic distillation with toluene). The isolation procedure was analogous to the other runs.

**Solvolyses of Brosylates (Runs 16 and 17) in the Presence of Tosylate Ion.—**Anhydrous potassium carbonate (84.20 g.) was allowed to react with a mixture of 207 g. of *p*-toluenesulfonic acid monohydrate, 600 ml. of glacial acetic acid and 286 ml. of pure acetic anhydride. The resulting mixture was made up to 1000 ml. with acetic acid (glacial) and 25 ml. of this solution per g. of brosylate was used in the solvolysis experiments. The solvent was preheated to 75°, the brosylate was added, and after 40 minutes the reaction mixture was quenched. The products were isolated in exactly the same manner as in runs 7 and 8. In each case the sulfonate ester products were identified through their rotations (see Table IV) and through the following mixed melting point experiments. About equal amounts of each component were used, and whenever IIA Tos. was involved, the polymorphic form melting at 46–47° was employed. Melting points of mixtures of knowns: Bros. I and Bros. IB, 87–92°; Bros. I and Tos. I, 45–75°; Bros. IB and Tos. IB, 66–68°; Bros. IB and Tos. I, 43–67°; Bros. IIA and Tos. IIA, 40–42°; Bros. I and Tos. IIB, 41–65°; Bros. IB and Tos. IIB, 34–41°; Bros. IIA and Tos. IA, 37–45°. Melting points of mixtures of knowns and sulfonate esters from runs 16 and 17: run 16, 1st crop and Bros. I, 88–92°; run 16, 1st crop and Bros. IB, 68–73°; run 16, 1st crop and Tos. I, 44–60°; run 16, 1st crop and Tos. IB, 60–64°; run 16, 2nd

crop and Tos. I, 45–47°; run 17, 1st crop and Bros. IIA, 44–56°; run 17, 1st crop and Tos. IIA, 39–41°; run 17, 2nd crop and Bros. IIA, 43–54°; run 17, 2nd crop and Tos. IIA, 40–42°. In run 17, the first crop gave oils when mixed with Bros. I, Bros. IB, Tos. IB or Tos. I; the second crop gave oils with Bros. I, Bros. IB, Tos. IB and Tos. I.

**Control Experiments.**—Demonstration of the complete separation of the olefinic and alcoholic products was accomplished by mixing 2 parts of IA alcohol $\alpha^{25}$D +31.5° ($l = 1$ dm.) with one part of an equimolar mixture of the four 2-phenyl-2-butenes and by submitting the resulting mixture (3.0 g.) to the chromatographic separation described above, followed by distillation of each fraction: alcohol fraction, $\alpha^{23}$D +31.6° ($l = 1$ dm.); olefin fraction, $\alpha^{23}$D 0.02° ($l = 1$ dm.). Thus there is no detectable contamination of olefin with alcohol, and less than 0.1% contamination of alcohol with olefin.

To ascertain whether experiments 12 and 13 were carried out in the presence of base, a large excess of finely divided potassium carbonate was refluxed for four hours with 500 ml. of dry acetonitrile, the mixture was filtered quickly while still at the boiling temperature, and the solvent was removed by distillation. No weighable residue remained in the flask. Water was added to the flask and titration of the resulting solution with dilute acid gave no more acid consumption than a blank run. It can be concluded that the reaction was conducted in the absence of base. To determine whether secondary acetate could be produced from olefin, and whether the acetates of 3-phenyl-2-butanol once formed were stable under the conditions of the acetolysis, a mixture of 2 g. of the acetate of IA ($\alpha^{23}$D −8.08°, $l = 1$ dm.) 1 g. of cis-2-phenyl-2-butene⁴ and 1 g. of trans-2-phenyl-2-butene⁴ and 1 g. of 3-phenyl-1-butene⁴ were held at 75° in the acetic acid solvolysis mixture for 36 hours. The acetate–olefin mixture that was recovered was reduced with lithium aluminum hydride, the alcohol and olefin separated (see above procedure), and the alcohol recovered ($\alpha^{23}$D +31.5°, $l = 1$ dm.), wt. 1.48 g.

---

# Studies in Stereochemistry. VI. The Mechanisms of the E₁ and Hydrogen Migration Reactions in the 3-Phenyl-2-butanol System

BY DONALD J. CRAM

The p-toluenesulfonates or p-bromobenzenesulfonates of the stereomers of 3-phenyl-2-butanol when allowed to react in either acetic acid or acetonitrile give substantial amounts of mixtures of cis- and trans-2-phenyl-2-butene, 2-phenyl-1-butene and 3-phenyl-1-butene. When acetic acid is the solvent both 3-acetoxy-2-phenylbutane and 2-acetoxy-2-phenylbutane are also produced. Analyses of these products based on infrared and polarimetric methods have been developed. The simple E₁ reaction has been shown to go by at least two mechanisms: one stereospecific and trans in steric direction, the other non-stereospecific. The migration of a hydrogen from carbon-3 to carbon-2 in the 3-phenyl-2-butanol system has been demonstrated to be a transformation concomitant to the simple elimination and solvolysis reactions. This rearrangement has been shown to be intramolecular, and to involve a symmetric intermediate, probably the methylethylphenylcarbonium ion. A comparison of the abilities of hydrogen and phenyl to participate in an intramolecular displacement reaction has been made, and these abilities have been correlated with the geometry of the transition states for the reactions involved.

In the preceding paper of this series evidence was adduced for the existence of a phenonium sulfate ion-pair as a discrete intermediate intervening between the starting p-toluenesulfonates of the isomers of 3-phenyl-2-butanol and their non-olefinic solvolysis products (acetates).¹ The present in-

$$CH_3—CH—CH—CH_3 \longrightarrow \underset{\oplus}{[C—C]} \xrightarrow{AcOH} CH_3—CH—CH—CH_3$$
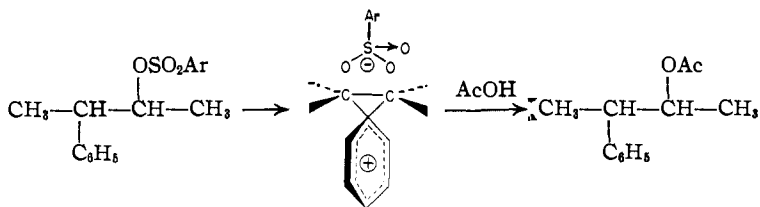
vestigation is concerned with the mechanism by which the 2-phenylbutenes come into being as an accompanying set of products of the same starting materials.

The use of the 3-phenyl-2-butanol system for the study of the E₁ reaction (and accompanying rearrangement–elimination reactions) offers several unique and distinct advantages over systems that have been used in the past for analogous studies.²

The presence of two asymmetric carbon atoms in the starting material and the existence of cis and trans isomerism in the 2-phenyl-2-butene products allows a determination of the stereochemistry of the E₁ reaction. Carbon atoms two and three are not part of a ring structure, and hence each stereomeric starting material can assume whatever rotational conformation is the most compatible with the steric requirements of the elimination reaction. An examination of the stereochemistry of the hydrogen migration is possible through a comparison of the configuration of the starting material and that of the 2-acetoxy-2-phenylbutane which is produced (along with 2-phenyl-1-butene) as a product of rearrangement. A

(1950)] that the 3-phenylcyclohexene used in the former investigation as a standard was contaminated with a considerable amount of 1-phenylcyclohexene. If the index of refraction for 3-phenylcyclohexene obtained by the latter investigators is applied to the data of Price, et al., it appears that when conjugated olefin can be produced by a trans elimination, the reaction largely assumes such a course (88% conjugated, 12% unconjugated olefin). However, when the conjugated olefin cannot be formed by a trans elimination reaction, cis elimination accounts for about half the product, the steric course of the reaction giving rise to the rest of the product not being clear. If one takes into consideration the probability that both the phenyl and hydrogen become involved in migrations from one carbon to the other in a manner analogous to those found in the 3-phenyl-2-butanol system (ref. 1), few conclusions can be reached without a thorough study of the immediate precursors of the two phenylcyclohexenes.

(1) D. J. Cram, THIS JOURNAL, **74**, 2129 (1952).

(2) The conclusion of C. C. Price and J. V. Karabinos [ibid., **62**, 1159 (1940)] that a predominantly trans elimination of the elements of water occurs when either cis- or trans-2-phenylcyclohexanol is heated with phosphoric acid has become somewhat equivocal by the recent findings of E. R. Alexander and A. Mudrak [ibid., **72**, 1810