boiling point of 122–123° (762 mm.) and a picrate melting at 170°.[13]

1,2-Dimethylpiperidine was prepared by the methylation of 2-methylpiperidine[9] with formaldehyde and formic acid by the procedure used for 1-methyl-2-ethylpyrrolidine and boiled at 124–125°. The picrate melted at 240–242°. The literature reports values of 126–127° (720 mm.) and 240–241°, respectively.[14]

Cyclization of N-Chlorodihexylamine.—N-Chlorodihexylamine, prepared from dihexylamine (37 g.), was irradiated for 24 hours in 150 ml. of 85% sulfuric acid. The mixture separated into two layers. The upper layer (97.3 g.) at 0°, when poured into water at 0°, gave a white waxy precipitate. A yield of 12 g. was obtained from 30 g. of the layer after one crystallization from acetone. The compound, after two further crystallizations from acetone, melted at 158–159° and analyzed for 4-chlorodihexylammonium bisulfate.

Anal. Calcd. for $C_{12}H_{28}O_4NSCl$: C, 45.34; H, 8.88; S, 10.07; neut. equiv., 159. Found: C, 46.31; H, 9.14; S, 10.64; neut. equiv., 156.

The upper layer (36.1 g.), when cyclized in the usual manner, gave N,N-dihexylbenzenesulfonamide (6.0 g.), b.p. 164–168° (1.5 mm.), and a tertiary amine fraction (6.25 g.) boiling at 104° (14 mm.), $n^{24.5}\text{D}$ 1.4465.

The methiodide of the tertiary amine fraction, after two crystallizations from ethyl acetate containing a little ethanol, gave prisms melting at 97.5–99°.

Anal. Calcd. for $C_{13}H_{28}NI$: C, 48.00; H, 8.68; N, 4.30. Found: C, 47.82; H, 8.47; N, 4.58.

The lower layer (320 g.), when cyclized in the usual way, gave N,N-dihexylbenzenesulfonamide (2.68 g.) and 0.7 g. of a tertiary amine fraction.

A second run starting with 37.0 g. of dihexylamine, when cyclized without separating the layers, gave 14.8 g. of tertiary amines boiling at 105–107° (14 mm.).

The tertiary amine, when chromatographed on a polypropylene oxide column using a Perkin–Elmer model 154 Vapor Fractometer at 140° and a flow rate of 51 ml./min. of helium at a pressure of 20 p.s.i. gave two peaks. The peaks separated with times of 33.4 and 35.7 minutes from the air peak and had relative areas of 95.6 and 4.4%, respectively. Addition of pure 1-*n*-hexyl-2-methylpiperidine increased and shifted the second peak at 37.3 minutes. At low concentration the peak occurred at 36 sec. Dihexylamine, when added, caused a third peak to appear at 51.1 minutes.

1-Hexyl-2-ethylpyrrolidine.—A mixture of 2-ethylpyrrolidine[10] (12.6 g.), hexyl bromide (25.1 g.) and potassium carbonate (10.7 g.) was heated at 140° with stirring for five hours. The mixture was added to dilute hydrochloric acid and the excess hexyl bromide removed with ether. The amine, when liberated with alkali, gave 1-hexyl-2-ethylpyrrolidine (14.5 g.) boiling at 104–105° (14 mm.), $n^{24.5}\text{D}$ 1.4473.

Anal. Calcd. for $C_{12}H_{25}N$: C, 78.69; H, 13.66. Found: C, 78.05; H, 12.90.

The methiodide melted at 97–98° and did not depress the melting point of the product obtained by cyclizing dihexylamine.

1-Hexyl-2-methylpiperidine.—A mixture of 2-methylpiperidine[9] (9.9 g.), hexyl bromide (16.5 g.) and powdered potassium carbonate (13.8 g.) was heated for five hours at 140°. The product, when treated in a manner similar to that given for 1-hexyl-2-ethylpyrrolidine, gave 12.0 g. of 1-hexyl-2-methylpiperidine, b.p. 104° (14 mm.), $n^{21.0}\text{D}$ 1.4581.

Anal. Calcd. for $C_{12}H_{25}N$: C, 78.68; H, 13.75. Found: C, 78.53; H, 13.46.

The methiodide melted at 188–189°.

Anal. Calcd. for $C_{13}H_{28}NI$: C, 48.00; H, 8.68. Found: C, 47.78; H, 8.35.

Cyclization of N-Chloro-N-ethylamylamine.—N-Chloro-N-ethylamylamine prepared from ethylamylamine[15] (28.8 g.) after irradiation in 135 ml. of 85% sulfuric acid at 25° for 24 hours, gave after treatment with alkali and a Hinsberg separation, a tertiary amine fraction (10.85) distilling at 118–120°. The picrate melted at 192–193.5°. The literature[16] reports values of 119–120° and 193–194°, respectively, for 1-ethyl-2-methylpyrrolidine.

The product when chromatographed on a tetraethylene glycol dimethyl ether column at a temperature of 60° using a flow rate of 51 ml./min. of helium at a pressure of 15 p.s.i., gave only one sharp peak at 18.6 minutes after the air peak.

1-Ethylpiperidine[7] had a migration time of 21.2 minutes at 70° while 1-ethyl-2-methylpyrrolidine gave a value of 14.0 minutes at this temperature.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF IOWA STATE COLLEGE]

Benzyl Tosylates. VII. Capture of Intermediates by Foreign Anions

BY GEORGE S. HAMMOND,[1] JOHN PELOQUIN, FABIAN T. FANG AND JAY K. KOCHI

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Solvolysis of benzyl tosylates in the presence of nitrate or chloride ions does not result in release of the theoretical amount of acid. Since the rates of destruction of the tosylates are not accelerated by the anions in question, the result is attributed to capture of intermediate carbonium ions by the foreign anions. This behavior is observed with *m*-halotosylates, indicating that the non-linear relationship between log *k* and σ^+ is not due to the appearance of a non-carbonium ion mechanism, with the less reactive compounds.

The first-order hydrolysis of *m*- and *p*-substituted benzyl tosylates does not follow either the Hammett equation[2–4] or a modified version of the equation using Brown's σ^+-parameter.[4–6] Brown and Okomoto[5] suggested that the failure of the rate data to correlate with σ^+ might be due to the operation of two distinctly different solvolytic mechanisms. The more reactive compounds, which react at rates which can be fitted to a σ^+-plot with only modest curvature, were believed to react by a carbonium ion mechanism. The less reactive compounds might react by a "direct displacement" mechanism, presumably a reaction between water and the substrate analogous to the second-order,

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Menshutkin reaction between amines and alkyl halides or sulfonates.

We have previously pointed out[4] that the behavior of substituent effects with changing reaction medium does not encourage resolution of the reactions into two discrete mechanisms. We have further investigated the problem by showing that the addition of nitrates and chlorides to the reaction mixture diverts a considerable fraction of the reaction to a path other than hydrolysis. Kinetic analysis indicates that the effect is most easily explained in terms of the capture of intermediate carbonium ions by the foreign anions, *even in the cases of the "slow substrates."*

Results and Discussion

Table I shows data which were collected during the early period of our study with benzyl tosylat- itself. The difference between the theoretical amount of acid produced and that actually observed is attributed to reaction 2. In the presence of lithium perchlorate, or in the absence of any added electrolyte, the theoretical amount of strong acid is produced.

TABLE I

SALT EFFECTS ON SOLVOLYSIS OF BENZYL TOSYLATE IN ACETONE-WATER AT 25°

Vol. acetone/ vol. water	Electrolyte	Concn. of electrolyte	% theoretical acid produced	$k \times 10^5$, sec.$^{-1}$
2.70	KCl	0.183	35	[a]
2.00	KNO_3	.250	63	6.70
2.00	KNO_3	.125	82	7.09
2.00	$LiClO_4$	.222	97–100	6.84
1.00	KNO_3	.378	71	36.3
1.44	KNO_3	.308	76	14.8
1.44	$LiClO_4$	.222	97–100	15.3
1.27	KNO_3	.222	87	24.1
1.27	$LiClO_4$	.222	100	22.9
1.27	None		99	23.4

[a] Not measured.

$$C_6H_5CH_2OTs + H_2O \longrightarrow C_6H_5CH_2OH + HOTs \quad (1)$$

$$C_6H_5CH_2OTs + X^- \longrightarrow C_6H_5CH_2X + OTs^- \quad (2)$$

Reaction rates were monitored by intermittent titration of the strong acid produced by solvolysis. Rate constants were calculated in the usual manner for runs carried out in the presence of lithium perchlorate since the rates of ester consumption and acid production were equal. Data for runs with added nitrates were analyzed by calculating the amount of ester destroyed during each increment. Data for the yield of acid at $t = \infty$ were used to establish the relationship between the rates of ester consumption and acid production in runs with nitrates. The constants obtained were very close to those observed in the runs with perchlorate. The results are most easily rationalized by the view that reactions 1 and 2 have a common, rate-determining step.

The results with benzyl tosylate itself do not bear strongly on the question of duality of mechanism since the point for the unsubstituted compound lies near the intersection of the two straight lines in a separated Hammett plot.[4] However, the rates of the *m*-halotosylates are much faster than would be predicted by the linear relationship defined by a plot of the data for the fast compounds against σ^+. Since the deviation is of the order of one log unit in k, the dual mechanism hypothesis predicts that only about 10% of the reaction would involve carbonium ions. For this reason, we investigated the effect of nitrate on the solvolysis of three *m*-halotosylates. In experiments in which solvolyses were allowed to proceed to completion without monitoring, extensive inhibition of acid production was found. Acid production was essentially theoretical in the presence of lithium chlorate. Relatively massive amounts of electrolyte were used in order to accentuate reaction 2. The data are summarized in Table II.

TABLE II

SOLVOLYSIS OF BENZYL TOSYLATES IN 1.25:1.00 ACETONE-WATER AT 25°

Tosylate	Electrolyte[a]	% theoretical acid produced
m-Bromobenzyl	KNO_3	56, 55
m-Bromobenzyl	$LiNO_3$	54
m-Bromobenzyl	$LiClO_4$	99
m-Iodobenzyl	KNO_3	55, 54, 55
m-Fluorobenzyl	KNO_3	60, 59, 58
m-Fluorobenzyl	$LiClO_4$	100

[a] Concn. = 1.04 *M*.

In order to show that the extensive capture by nitrate did not involve an SN2 reaction, the rates of the reaction of *m*-bromobenzyl tosylate were measured in the presence of the various electrolytes. The values obtained are shown in Table III and are compared with the value measured earlier[3] in the presence of a lower concentration of lithium perchlorate.

TABLE III

ELECTROLYTE EFFECTS ON RATE OF SOLVOLYSIS OF *m*-BROMOBENZYL TOSYLATE IN 1.27:1.00 ACETONE-WATER AT 25°

Electrolyte	Concentration of electrolyte	$k \times 10^5$, sec.$^{-1}$
KNO_3	1.04	2.14
KNO_3	1.04	2.32
$LiNO_3$	1.04	2.89
$LiClO_4$	1.04	2.72
$LiClO_4$	0.22	2.05

It is evident that electrolyte effects on the rate are small in this medium, and there is no evidence of acceleration by nitrate. Coincidental circumstances can be imagined in which a depression in the rate constant for the direct displacement by water is reduced in the presence of nitrates in such a way as to camouflage a contribution to the rate from an SN2 reaction with nitrate. However, such an explanation would require that the rate of hydrolysis be depressed by nitrates to a value lower than that observed in solutions containing no added electrolyte. We do not consider this a likely possibility and conclude that the reactions of even the slow substrates proceed by way of carbonium ion intermediates.

The one experiment in which chloride was used as the electrolyte is interesting. As would be expected, chloride is more efficient than nitrate in diverting the reaction from hydrolysis. However, the fact that chloride and nitrate can even be compared when present in comparable concentrations indicates that they are competing for a very unselective species since the nucleophilicity of chloride is very much greater than that of nitrate.[7] This in itself is clearly indicative of the carbonium ion mechanism with benzyl tosylate itself.

All available data indicate that a carbonium ion mechanism persists throughout the solvolyses of benzyl tosylates that have been studied. The fact that the reaction rates do not correlate with σ^+ surely indicates that the parameter is not universally useful for quantitative correlation of all electrophilic reactions occurring at an aromatic side chain. This conclusion is not intended to disparage the use of σ^+ as a correlative parameter since the wide scope of its applicability has been demonstrated. We do, however, believe that σ^+ cannot be used as a unique probe in establishment of a mechanism in all electrophilic reactions.

Dewar and Sampson[8] have recently studied the correlation of the rates of solvolysis of arylmethyl chlorides with calculated changes in delocalization energy accompanying ionization. Their results indicate that variation in the medium can result in variation of the proportionality constants relating log k to the calculated values of $\Delta E_{\text{ionization}}$. Since different linear relationships existed in the various solvents, they concluded that the variations did not reflect abrupt changes in mechanism but were due to variation in the extent to which the charge, formally assigned to a carbonium ion in the transition states, is transferred to solvent. As has been previously stated,[4] it is our view that such variations are evident in the solvolysis of benzyl tosylates, and the present study confirms the notion that variation in sensitivity to substituent effects need not imply a departure from the carbonium ion mechanism.

Experimental

The preparation of materials and general techniques have been described in earlier papers.[2-4] Unlike some of the more reactive benzyl tosylates, the *m*-halo compounds can be stored indefinitely in the solid state at room temperature without detectable changes in their solvolysis equivalents. In runs designed to measure the extent of carbonium ion capture, solutions were prepared as usual, allowed to stand in the constant temperature bath for periods equal to 20–30 half-lives and then titrated with standard triethylamine solution. Such samples were frequently allowed to stand for an additional few hours to confirm the assumption that no additional acid was produced. The kinetic runs with benzyl tosylate were carried out by the intermittent titration method.[2] Those with *m*-bromobenzyl tosylate were carried out by essentially the same technique except that the reaction was allowed to proceed in the absence of base and the solution was titrated to neutrality with triethylamine solution at appropriate intervals. The rate of destruction of tosylate in the presence of nitrate salts was calculated by using the observed infinity titers and the titers at intermediate points in the integrated form of the first-order rate expressions. Since the nitrates were present in large excess, it was assumed that the fraction of the tosylate converted to nitrate was constant throughout a run. Values of the constants calculated from individual points usually increased slightly and then fell off slightly during the course of runs. The average of such values did not vary by more than 10% from values calculated by the method of least squares. High-melting (<300°) crystalline precipitates separated from the reaction mixtures in the runs with nitrates during late stages of the runs. Qualitative tests showed the presence of nitrate ion and the absence of nitrite in the solid. The melting points were, however, too high to correspond to those of pure lithium or potassium nitrate. Runs were terminated when such precipitates were first noticed. Data for a typical run are shown in Table IV.

TABLE IV

SOLVOLYSIS OF *m*-BROMOBENZYL TOSYLATE IN 50 ML. OF 1.27:1.00 ACETONE–WATER CONTAINING 1.04 *M* $LiNO_3$ AT 25°; WEIGHT OF TOSYLATE 175.2 MG.; TRIETHYLAMINE 0.1042 *N*

Time, seconds	Triethylamine,[a] ml.	$k_1 \times 10^5$, sec.$^{-1}$
0	0	
3,600	0.23	2.47
5,400	.35	2.57
7,200	.50	2.72
9,000	.62	2.89
10,800	.73	2.91
12,600	.85	3.00
14,400	.95	3.00
16,200	1.04	2.89
18,000	1.14	3.03
19,800	1.23	3.06
21,600	1.30	3.01
26,040	1.46	2.96
28,800	1.56	2.98
30,600	1.62	2.98
32,400	1.68	2.97
36,000	1.77	2.94
43,200	1.93[b]	2.76
89,000	2.65[c]	
	Av.	2.89

[a] Calculated theoretical total triethylamine required 2.76 ml. (55% acid produced; see Table II). [b] Precipitate visible. [c] Considered reasonable approach to 2.76 ml. calculated as end-point for 56% theoretical total acid.

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