SOLVOLYSIS OF BICYCLIC BROSYLATES

by

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STATEMENT BY AUTHOR

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May 15, 1968

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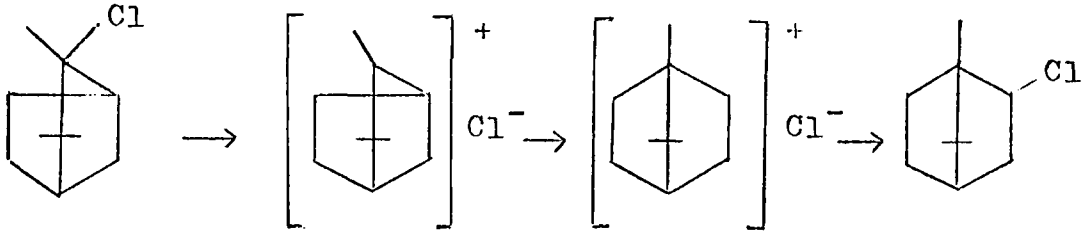
ABSTRACT

7-Norbornyl brosylate and 7-deuterio-7-norbornyl brosylate were prepared and solvolyzed in formic acid at 95°C. Rate constants for the two compounds were determined, a smaller rate constant being obtained for the deuterated compound. Implications of these results in connection with the non-classical carbonium ion theory are discussed.

HISTORY

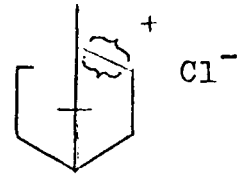
A great deal of controversy can be found in the literature of recent years concerning the existence or non-existence of non-classical carbonium ions in the solvolytic reactions of various derivatives of the norbornane compounds. The controversy has its foundations in the observed conversion of camphene hydrochloride to isobornyl chloride.[1]



1 2 3 4

This reaction, discovered and studied by Meerwein and van Emster, displayed a rearrangement of ring structure that was at first assumed to occur via a simple carbonium ion mechanism. The same ionic characteristics and orders of reaction that are general for carbonium ion mechanisms were observed in the above reaction.[2]

The first to suggest a carbonium ion of delocalized structure rather than a simple carbonium ion were Nevell, de Salas and Wilson.[3] Since the solvolysis reaction is highly stereospecific, they suggested that the intermediate carbonium ion might be a resonance hybrid and could be represented as 5.



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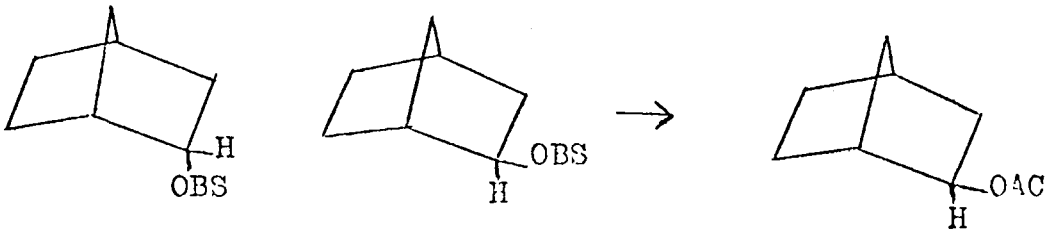
Most of the work supporting, exploring and refining the non-classical carbonium ion theory has been done by Winstein and co-workers. Winstein and Trifan proposed neighboring group participation in the solvolyses of norbornyl compounds such as is involved with reactions in which a phenyl or halide group is adjacent to the carbon with the developing positive charge.[4] Justification for this proposal is based primarily on the rates and stereochemistry of the solvolysis reactions.

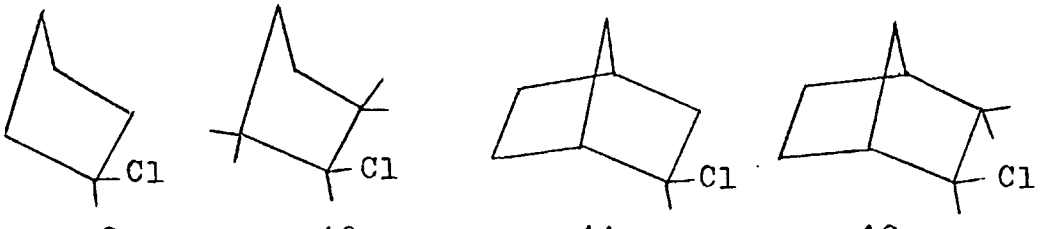
The reaction rates of exo-norbornyl derivatives were found to be 350 times greater than that of the endo-norbornyl derivatives, which were found to be comparable to the rates of cyclohexyl derivatives. This difference was attributed to anchimeric acceleration of the exo form due to participation by the C_6 of the norbornyl nucleus. Also Winstein has shown that both the endo and the exo forms of norbornyl p-bromobenzenesulfonate on solvolysis in acetic acid gave only the exo-norbornyl acetate in the product.



6 7 8

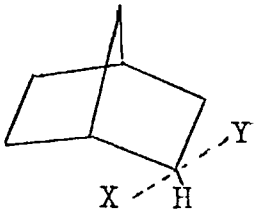
These phenomena have been studied and rationalized by Winstein on the basis of the non-classical carbonium ion theory.[5] The experimental evidence is, as Winstein and co-workers have said, most simply explained by the non-classical carbonium ion intermediates, but in actuality there has never been any definite proof for their existence.

H. C. Brown has also studied the problems of rate and stereospecificity in the norbornyl system.[6,7] He made rate comparisons of the norbornyl and cyclopentyl systems pointing out that the ring strain involved in the norbornyl system more closely resembles the cyclopentane system than the cyclohexane or t-butyl systems previously used for rate comparisons.[6]



	9	10	11	12
Relative rate:	1	82	5.4	206

It was found that the rate of solvolysis of the exo-norbornyl compound was only 5.4 times faster than the cyclopentyl analog while being 13,600 times faster than the t-butyl compound, and that increasing the substitution on the systems increases the reactivity. Brown attributed the rate differences between the exo and endo forms to the inhibition of the endo form as the desired path of the leaving group comes very close to the endocyclic system.[7]



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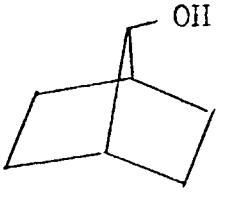
The predominance of the exo form in the solvolysis products of either isomer was explained by Brown on the basis of crowding of the endo position by the solvent anion of the ion pair in the reaction solution.[7]

Further support for the non-classical carbonium ion theory was cited by Winstein in the solvolytic reaction of the toluenesulfonates of 7-norborneol and that of anti-7-norbornenol.[8]



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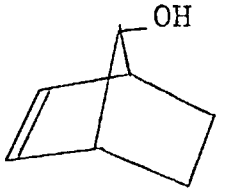

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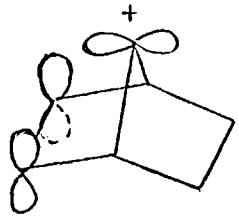
The reaction rate of the latter was found to be 10^{11} times greater than that of the former. Winstein pointed out that the geometry of the norbornyl system is uniquely unfavorable for stabilization of a cationic center at C_7. He attributed the large rate enhancement in the presence of the double bond to powerful anchimeric assistance to ionization at C_7 involving the C_2-C_3 π electron cloud. It was suggested that the vacant orbital on C_7 could overlap the p-orbital system of the double bond to form intermediate 17.[9]



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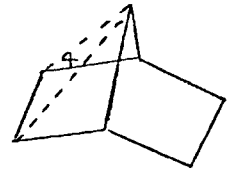

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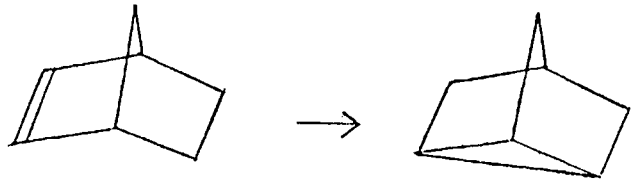
This double bond participation would also explain the complete retention of configuration found in the product.

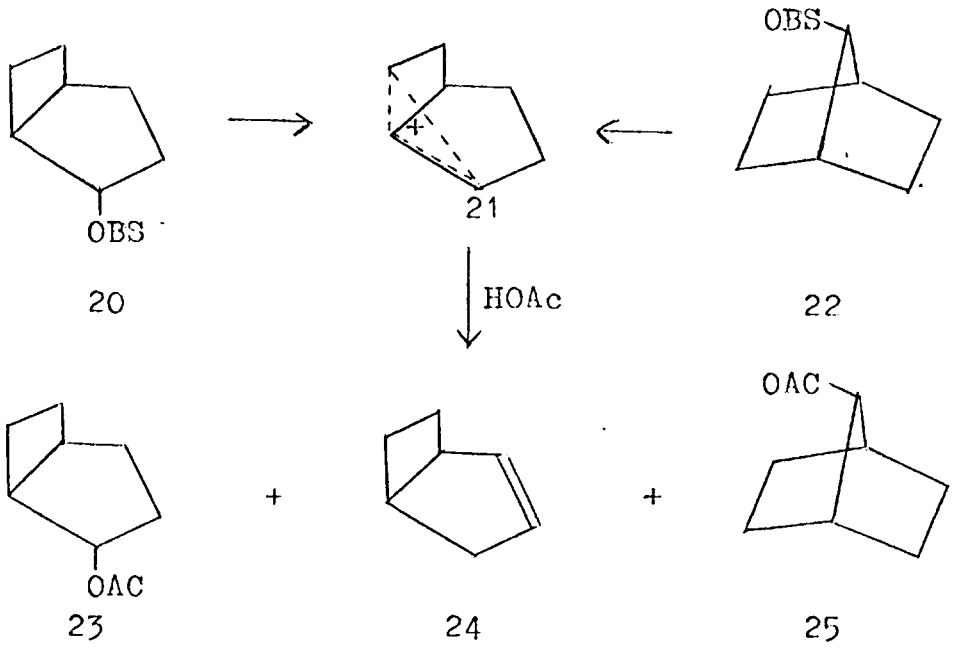
In a study of the ring strain of the norbornyl system, Schleyer has shown that nortricyclene is more stable than norbornene.[10]



18 19

Other evidence that the double bond in norbornene is highly strained is demonstrated by complexation with silver nitrate, large heat of hydrogenation and frequency in the IR region as compared with cyclobutadiene. Schleyer attributed the strain to angle strain in the rigid bicyclic molecule and also suggested that it might provide the driving force in the reaction which Winstein attributed to anchimeric acceleration due to participation of the double bond.

In a more recent study, Winstein proposed that although the p-bromobenzenesulfonate derivatives of 7-norbornanol solvolyzed at a rate comparible with that calculated according to the standard procedure developed by Foote[11] and Schleyer[12], a non-classical carbonium ion is still involved as an intermediate.[13] It was shown experimentally that trans-2-bicyclo [3.2.0] heptyl p-bromobenzenesulfonate 13 and 7-bicyclo [2.2.1] heptyl p-bromobenzenesulfonate 15 solvolyzed to give the same products with very nearly equal product distributions. In acetic acid, most of the product was 7-bicyclo [2.2.1] heptyl acetate, only 5-7% of the trans-2-bicyclo [3.2.0] heptyl acetate being formed and 1-2% of the unsaturated product being formed. These results seem to indicate the formation of the common bridged ion 21 as an intermediate.



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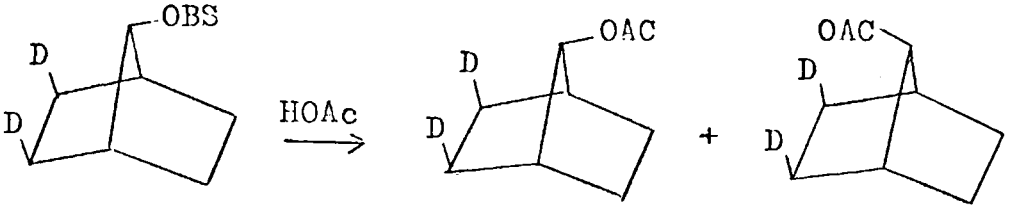
23 24 25

In addition, the trans-2-bicyclo[3.2.0]heptyl p-bromobenzenesulfonate was solvolyzed at a rate 100 times greater than the cis isomer, which suggests carbon participation by C_2.

In a more recent study, F. B. Miles found the percentage of retention of the acetolysis products of anti-2,3-dideuterio-7-norbornyl p-bromobenzenesulfonate to be 80-90% regardless of reaction conditions.[14]



26 27 28

80-90% 10-20%

Anything other than a 50-50 mixture is purportedly in-

compatible with a simple carbonium ion which would be expected to give equal amounts of the anti and syn isomers. The observed 80-90% retention product, however, cannot be explained wholly by the non-classical carbonium ion. The result is the necessity of modifying the latter by postulating "leakage" into a classical carbonium ion to explain the inversion product, or else, in classical terms, of invoking a predominant "front side collapse" of an ion pair with the solvent, which has been observed in cases for which there is steric hindrance to the back side. In this case it would be hard to imagine any hindrance to the back side of an ion pair unless the three bonds to C_7 are not coplanar, as Miles has suggested.[14]

PURPOSE

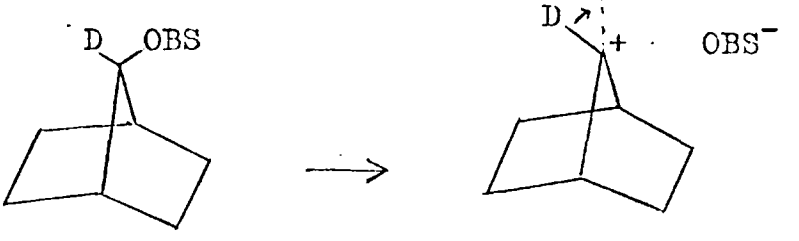
In the face of such opposing evidences and arguments, it is the purpose of this paper to throw some new light on the controversy of the non-classical carbonium ion intermediate versus the classical carbonium ion in the case of 7-norbornyl brosylate. The solvolysis of this particular compound does not involve any rate enhancement and the mechanism is therefore open to question even more than most norbornyl systems. Winstein proposed a non-classical intermediate when he found that the solvolysis of trans-2-bicyclo [3.2.0] heptyl brosylate and that of 7-bicyclo [2.2.1] heptyl brosylate lead to the same product distribution.[9] This led him to believe that there was an intermediate involved which had a structure intermediate to those of the two reactants. He reasoned that the trans-2-bicyclo [3.2.0] heptyl brosylate evidently is anchimerically assisted by participation as the rate constant of the trans isomer was found to be 100 times greater than that of the cis isomer. It doesn't seem to this author, however, that rearrangement of one ring system into another alone can be justifiably used as a reason for invoking a non-classical explanation, as rearrangement is a well known phenomenon of the classical carbonium ion. Carbonium ions are

known to rearrange whenever a 1,2 shift of a hydrogen or an alkyl group can cause the formation of a more stable carbonium ion.

The observed 80-90% retention in the product of solvolysis of 7-norbornyl brosylate noted in a recent paper by Miles[12] cannot be adequately explained on the basis of the non-classical carbonium ion intermediate. On the other hand, a 50% mixture in the products would be expected if a normal simple carbonium ion mechanism were involved. Miles has suggested the possibility of an explanation based on the front side collapse of a classical carbonium ion although he could not supply adequate explanation for a steric hindrance to prevent back side collapse. That the ring strain involved in the norbornyl system is considerable, however, is known from infra-red results of 7-norbornanone. It seems feasible that the geometry of the strained ring system of the 7-norbornyl brosylate may be such as to hinder the attainment of a completely planar system at C_7 which would indeed favor front side collapse.

If a classical carbonium ion were involved, however, it would definitely attempt to achieve the planar trigonal configuration characteristic of carbonium ions, and if this were the case, the reaction would exhibit an α-deuterium effect on the rate of reaction, as the heavier deuterium atom would tend to slow down

the attainment of the desired geometry and therefore the rate of reaction.



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RESULTS AND DISCUSSION

7-Norbornenone was catalytically hydrogenated to the saturated ketone in one case and to the completely reduced norbornyl alcohol in the second case. The ketone was then reduced by lithium aluminum deuteride to give the corresponding deuterated norbornyl alcohol. The alcohols were then converted to the brosylates with p-bromobenzenesulfonyl chloride in pyridine. After sufficient purifications, the deuterium content of the deuterated compound was found to be 94.3%.[15]

Cyclohexyl brosylate was obtained in a similar manner from reagent grade cyclohexanol. Cyclohexyl brosylate was solvolyzed in formic acid at 25°C., the procedure used being patterned after that reported by Winstein and Marshall.[16] The average rate constant obtained was 1.01×10^{-4} sec^{-1} which shows good agreement with the reported values of 1.07×10^{-4} at 25.0° and 0.988×10^{-4} at 24.4°.[17]

Tables 1,2 and 3 show computations giving the average rate constant for non-deuterated 7-norbornyl brosylate, while tables 4,5 and 6 show the computations for the rate constants for the deuterated compound. These determinations are also shown graphically in figures

1-6. The averages of the values are 1.935×10^{-6} sec^{-1} for the undeuterated compound and 1.700×10^{-6} sec^{-1} for the deuterated compound. The measurements in all cases were only carried out as far as about 70% reaction, and only the measurements as far as 50% reaction for the deuterated compound were considered in the rate constant calculations for this compound as the values gradually increase after 50% reaction. The higher values toward the end of the reaction might possibly be due to the slow conversion of the deuterated reactant to a rearranged compound that solvolyzes at a faster rate. From these results, it can be seen that there is a definite difference in the rate constants of the two forms of norbornyl p-bromobenzenesulfonate.

It has been calculated that for an isolated carbonium ion, the α-deuterium isotope effect of k_H/k_D = 1.4 would be expected, but the observed value is k_H/k_D = 1.15, probably due to interaction with the leaving group which impedes the bending motion, lowering the isotope effect.[18] In direct displacement reactions the isotope effect is virtually non-existent and the presence of any entering group at the rear of the reacting molecule reduces the isotope effect. Participation of a neighboring group should influence the α-deuterium isotope effect in the same manner as any entering group at the rear. Formic acid solvolysis of 2-phenylethyl-1,1-d_2

tosylate is known to proceed with anchimeric assistance and shows the reduced isotope effect of $k_H/k_D = 1.08$.[18] Experimental results found in this investigation for 7-deuterio-7-norbornyl brosylate show an α-deuterium effect of $k_H/k_D = 1.14$. This would seem to indicate the formation of a classical carbonium ion as opposed to the influence of neighboring group participation.

It has been shown, however, that the isotope effects in the cases of solvolysis of 2-p-anisylethyl tosylate and 2,2-diphenylethyl tosylate, for which the driving forces for anchimeric assistance are greater, smaller rate reductions of 1.12 and 1.10, respectively, were found.[18] The reason offered to explain this is that with greater stability in the bridged intermediate, there would be less bridging in the transition state leading to the intermediate and, therefore, less reduction of the isotope effect. Such an effect would not be expected in the case of 7-norbornyl brosylate, however, as the absence of any rate acceleration due to anchimeric assistance indicates that there is no great driving force leading to the formation of an exceptionally stable bridged intermediate. The observed α-deuterium effect of $k_H/k_D = 1.14$ would seem to give support to the presence of a classical carbonium ion as an intermediate in the formolysis of 7-norbornyl brosylate.

TABLE 1

Formolysis of 7-Norbornyl

p-Bromobenzenesulfonate

Kinetic Run #1

$T \times 10^4$ (sec)	% reax.	$C \times 10^{-2}$	log $(C_o - C)$	$k \times 10^{-6}$ (sec^{-1})
0.000	1.88	2.139(C_o)		
3.629	8.67	1.991	.0311	1.974
9.979	19.85	1.747	.0877	2.024
15.480	26.26	1.608	.1239	1.840
21.139	35.25	1.412	.1804	1.965
25.650	39.85	1.311	.2125	1.908
29.927	44.58	1.208	.2482	1.900
33.948	49.44	1.102	.2880	1.954
38.369	51.60	1.055	.3070	1.843
47.761	61.87	0.831	.4106	1.980
51.577	66.05	0.740	.4610	2.058
56.250	70.11	0.652	.5160	2.113

.3937 g. of 7-norbornyl brosylate was diluted to 60 ml. total volume with 88% formic acid, solvolysis at T = 95.0°C.

$k_{ave.} = 1.961 \times 10^{-6}$ sec^{-1}

TABLE 2

Formolysis of 7-Norbornyl

p-Bromobenzenesulfonate

Kinetic Run #2

$T \times 10^4$ (sec)	% reax.	$C \times 10^{-2}$	log $(C_o - C)$	$k \times 10^{-6}$ (sec^{-1})
0.000	2.98	2.156(C_o)		
3.539	8.74	2.028	.0266	1.731
9.907	19.55	1.788	.0813	1.889
17.586	27.66	1.607	.1277	1.906
21.060	36.17	1.418	.1820	1.990
25.607	41.20	1.307	.2174	1.955
29.862	47.03	1.178	.2626	2.025
33.851	50.602	1.098	.2931	1.994
38.279	54.31	1.015	.3273	1.969
47.657	62.26	0.839	.4099	1.981
51.541	66.90	0.735	.4671	2.087
56.221	69.02	0.688	.4958	2.031

.4013 g. of 7-norbornyl brosylate was diluted to 60 ml. total volume with 88% formic acid, solvolysis at T = 95.0°C.

$k_{ave.} = 1.996 \times 10^{-6}$ sec^{-1}

TABLE 3

Formolysis of 7-Norbornyl
p-Bromobenzenesulfonate
Kinetic Run #3

$T \times 10^4$ (sec)	% reax.	$C \times 10^{-2}$	log $(C_o - C)$	$k \times 10^{-6}$ (sec^{-1})
0.000	3.85	2.205(C_o)		
4.557	11.55	2.028	.0363	1.834
8.971	18.33	1.873	.0709	1.820
15.358	26.95	1.675	.1194	1.791
21.118	32.08	1.557	.1511	1.648
25.765	39.78	1.381	.2032	1.816
29.988	43.63	1.293	.2318	1.780
34.344	49.41	1.160	.2789	1.870
38.520	52.10	1.098	.3028	1.810
43.020	56.47	0.998	.3443	1.843
47.311	61.99	0.872	.4029	1.912
51.757	65.97	0.780	.4513	2.008
56.779	69.94	0.689	.5052	2.049

.4142 g. of 7-norbornyl brosylate was diluted to 60 ml. total volume with 88% formic acid, solvolysis at T = 95.0°C.

$k_{ave.} = 1.849 \times 10^{-6}$ sec^{-1}

TABLE 4

Formolysis of 7-Deuterio-7-Norbornyl p-Bromobenzenesulfonate
Kinetic Run #4

$T \times 10^4$ (sec)	% reax.	$C \times 10^{-2}$	log $(C_o - C)$	$k \times 10^{-6}$ (sec^{-1})
0.000	3.89	2.137(C_o)		
4.327	10.72	1.986	.0317	1.688
9.126	17.53	1.834	.0663	1.673
14.249	24.78	1.673	.1063	1.718
19.181	29.54	1.566	.1348	1.619
24.509	37.17	1.397	.1846	1.735
30.809	43.67	1.253	.2319	1.733
34.560	48.44	1.147	.2703	1.801
38.891	52.94	1.047	.3098	1.835
43.423	56.91	0.9583	.3483	1.847
48.031	60.61	0.8760	.3873	1.857
52.081	64.85	0.7817	.4368	1.932

.4030 g. of 7-deuterio-7-norbornyl brosylate was diluted to 60 ml. total volume with 88% formic acid, solvolysis at T = 95.0°C.

$k_{ave.}$ (to 50% reaction) = 1.710×10^{-6} sec^{-1}

TABLE 5

Formolysis of 7-Deuterio-7-Norbornyl p-Bromobenzenesulfonate
Kinetic Run #5

$T \times 10^4$ (sec)	% reax	$C \times 10^{-2}$	log $(C_o - C)$	$k \times 10^{-6}$ (sec^{-1})
0.000	4.66	2.096(C_o)		
4.320	11.65	1.942	.0332	1.770
9.090	22.10	1.712	.0879	2.227
14.184	24.11	1.668	.0992	1.611
19.145	31.34	1.509	.1427	1.717
24.469	37.21	1.380	.1815	1.708
30.798	44.60	1.218	.2357	1.763
34.481	50.23	1.094	.2824	1.886
38.891	55.05	0.988	.3162	1.872
43.362	59.60	0.888	.3730	1.981
47.970	66.97	0.726	.4605	2.211
51.984	70.99	0.638	.5166	2.289

.3982 g. of 7-deuterio-7-norbornyl brosylate was diluted to 60 ml. total volume with 88% formic acid, solvolysis at T = 95.0°C.

$k_{ave.}$ (to 50% reaction) = 1.742×10^{-6} sec^{-1}

TABLE 6

Formolysis of 7-Deuterio-7-Norbornyl p-Bromobenzenesulfonate
Kinetic Run #6

$T \times 10^4$ (sec)	% reax.	$C \times 10^{-2}$	log $(C_o - C)$	$k \times 10^{-6}$ (sec^{-1})
0.000	10.48	1.523(C_o)		
4.428	16.92	1.413	.0325	1.690
10.810	25.43	1.268	.0795	1.694
16.567	32.70	1.145	.1238	1.721
25.459	39.79	1.024	.1728	1.563
33.955	47.58	0.8917	.2323	1.576
38.455	54.50	0.7740	.2883	1.727
42.750	56.23	0.7446	.3107	1.674
55.361	65.74	0.5827	.4172	1.736
64.494	76.47	0.4003	.5802	2.072
72.961	75.26	0.4209	.5584	1.763

.2569 g. of 7-deuterio-7-norbornyl brosylate was diluted to 50 ml. total volume with 88% formic acid, solvolysis at T = 95.0°C.

$k_{ave.}$ (to 50% reaction) = 1.649×10^{-6} sec^{-1}

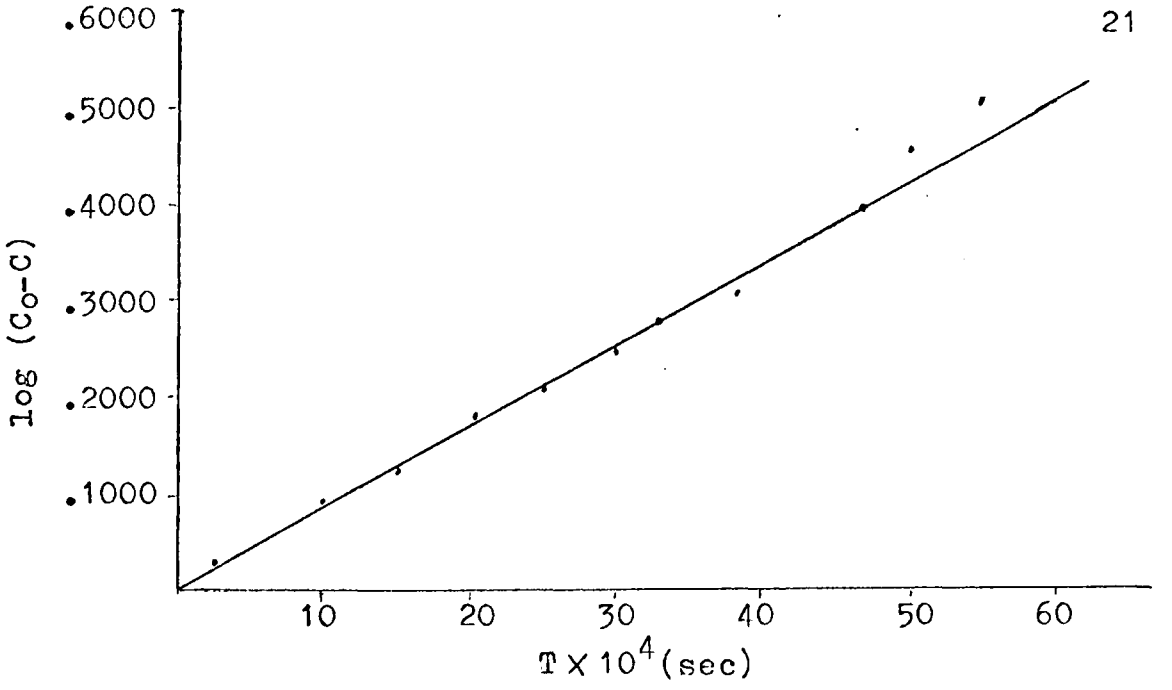

Figure 1- Formolysis of 7-Norbornyl p-Bromobenzenesulfonate, Kinetic Run #1

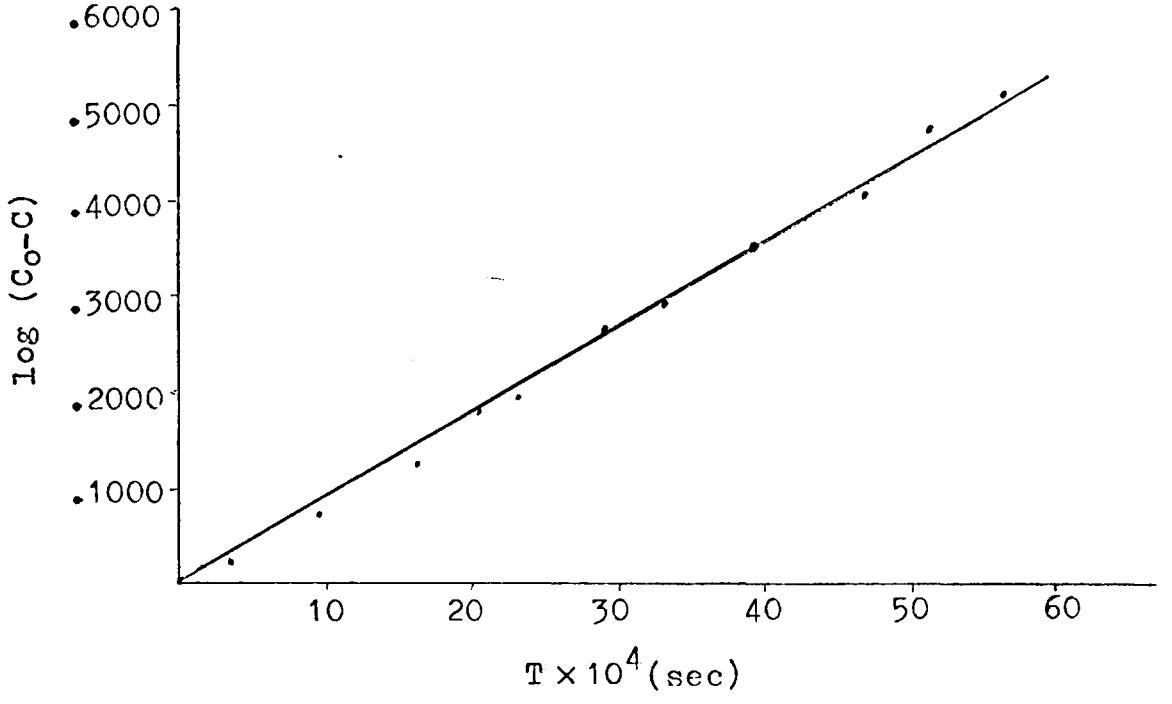

Figure 2- Formolysis of 7-Norbornyl p-Bromobenzenesulfonate, Kinetic Run #2

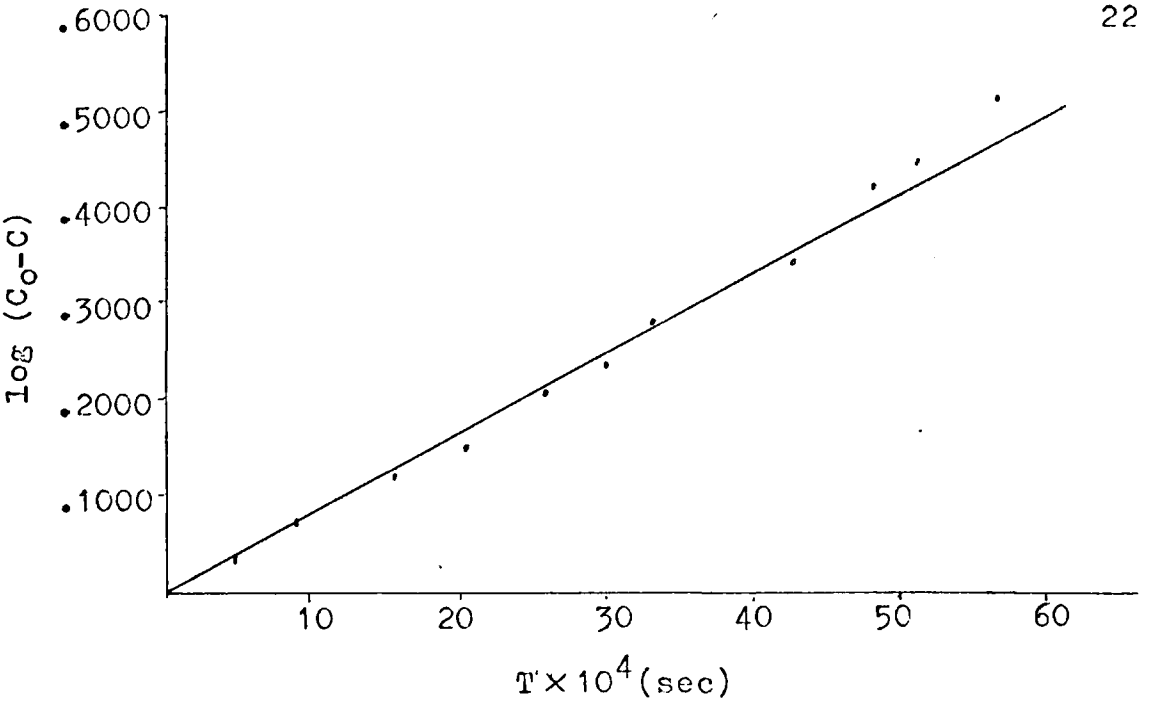

Figure 3- Formolysis of 7-Norbornyl p-Bromobenzenesulfonate, Kinetic Run #3

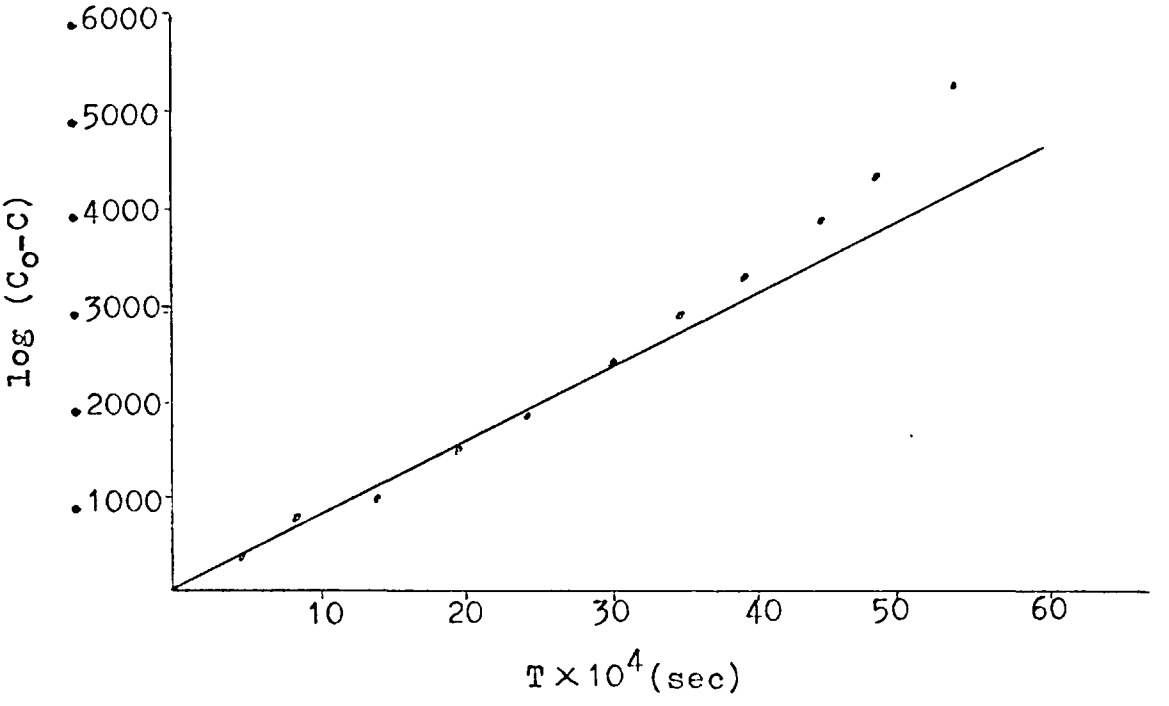

Figure 4- Formolysis of 7-Deuterio-7-Norbornyl p-Bromobenzenesulfonate, Kinetic Run #4

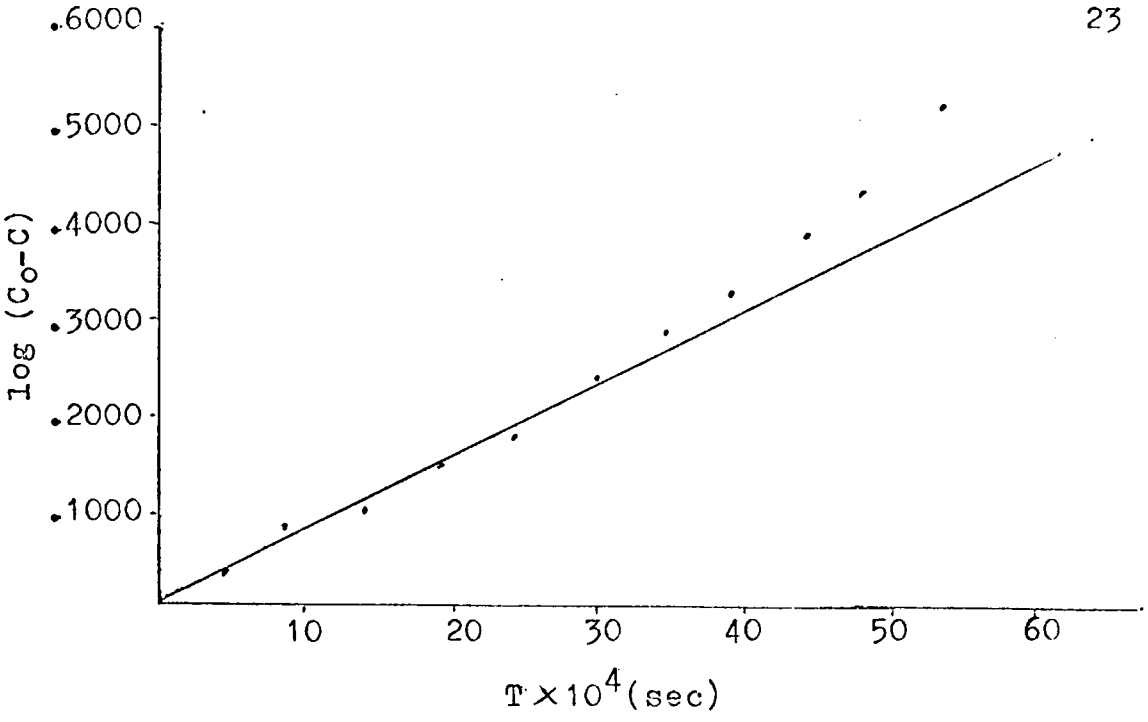

Figure 5- Formolysis of 7-Deuterio-7-Norbornyl p-Bromobenzenesulfonate, Kinetic Run #5

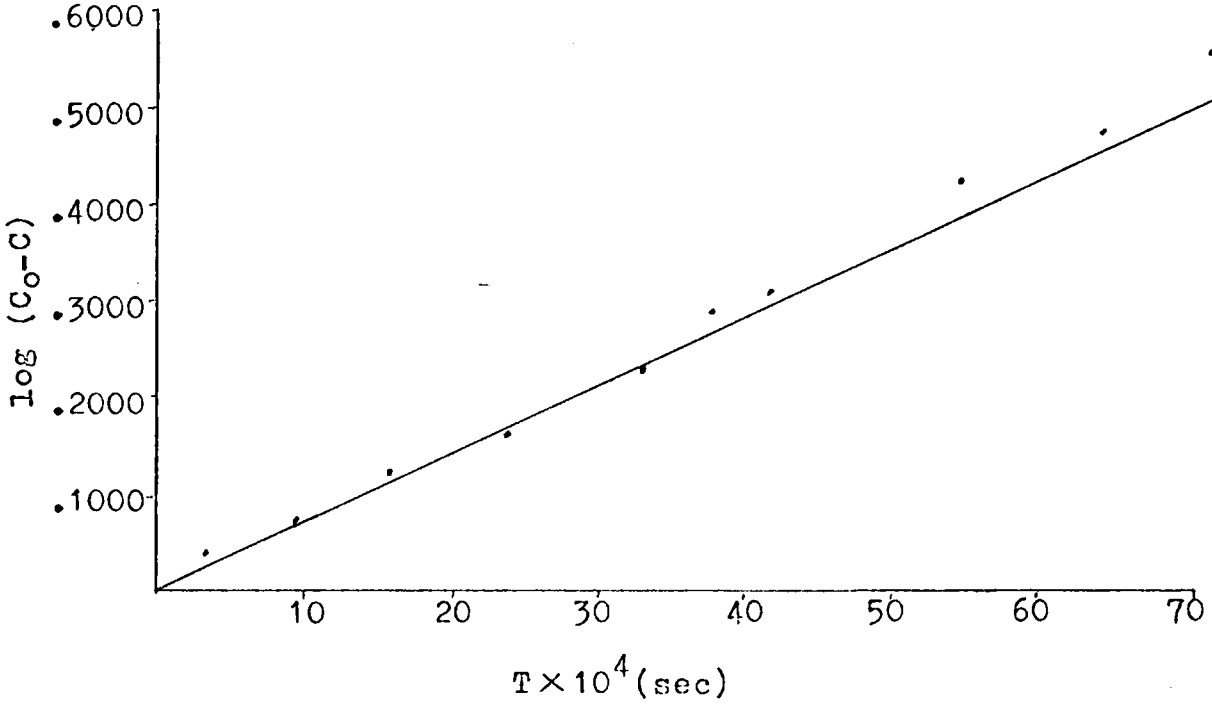

Figure 6- Formolysis of 7-Deuterio-7-Norbornyl p-Bromobenzenesulfonate, Kinetic Run #6

EXPERIMENTAL

1. Method and Materials

The starting material for the norbornyl derivatives made was 7-norbornenone which had been previously prepared from 1,2,3,4-tetrachloro-5,5-dimethoxy-cyclopentadiene according to the procedure by Gassman and Pape.[19] Products were analyzed on Perkin Elmer 337 Grating Infrared Spectrometer, Varian Model A60 Nuclear Magnetic Resonance Spectrometer. Mass spectra of the final products, deuterated and undeuterated 7-norbornyl brosylate, show the compounds to be very pure. Deuterium analysis showed the percent deuterium in the deuterated product to be 94.3%.[15] Formic acid used for the solvolyses was Mallinkrodt 88% analytical grade and the acetic acid used in the titrations was Mallinkrodt glacial analytical grade and the sodium acetate used as the titrant was Bakers analyzed analytical reagent. All acetic acid used was treated with acetic anhydride to remove traces of water.

2. 7-Norbornyl Ketone

The partial reduction of 7-norbornenone (3.0 g., 0.0278 m.) to the saturated ketone was achieved by catalytic hydrogenation in 15 ml. ethyl acetate at room

temperature and atmospheric pressure over platinum oxide. The reaction solution was rapidly stirred and reduced for two hours and fifteen minutes. The platinum black formed during the reaction was filtered off in a gravity filter and the solution was concentrated by distillation and evaporated to give the white crystalline product. Recrystallization from a 50% pentane ether solution yielded 2.9 g. (98.5%) of product.

3. 7-Deuterio-7-Norborneol

Lithium aluminum deuteride (0.5 g.) was put in a 200 ml. round bottom flask which was fitted with an addition funnel, a mechanical stirrer and a spiral condensor open to the atmosphere through a calcium chloride tube. The apparatus was flame dried before the catalyst was added to remove traces of water. Anhydrous ether (30.0 ml.) was added dropwise from the addition funnel with stirring and cooling of the reaction flask in an ice bath and with ice water running through the condensor, forming a light grey slurry with the lithium aluminum deuteride. The ketone (2.9 g., 0.0264 m.) was dissolved in 50 ml. anhydrous ether and the ketone ether solution was then added dropwise from the addition funnel to the slurry, slowly turning the solution from light grey to milky white. An additional 20 ml. ether was added from washings of the flask. Stirring and

refluxing of the reaction mixture was continued for twenty-four hours at 32°C.

After twenty-four hours, a 2,4-DNP test was negative. Hydrolysis was accomplished by the dropwise addition of 1.5 ml. water followed by the dropwise addition of 0.5 ml. 50% sodium hydroxide. The resultant mixture contained traces of water in the bottom of the flask. Most of the water was removed with a micropipette. The addition of anhydrous magnesium sulfate removed the last traces of water. The solution was carefully decanted and repeatedly washed with anhydrous ether and decanted before the solid material was put through a gravity filter and again washed. After treatment of the ether solution with anhydrous magnesium sulfate to remove any remaining traces of water, it was concentrated by distillation and evaporated to dryness to give 2.8 g. (94.0%) of product, m. p. 148-150°.

4. 7-Deuterio-7-Norbornyl Brosylate

After purification, the product (2.8 g., 0.0260 m.) was dissolved in 15 ml. dry pyridine (dried by distillation over calcium chloride) and chilled. A 5% excess of p-bromobenzenesulfonyl chloride (7.0 g.) was added to the solution and it was refrigerated for forty-eight hours. The resultant solution containing crystals of pyridine hydrochloride was put in 10% sulfuric acid

and the product was extracted with ether. The ether extracts were successively washed with 6N hydrochloric acid, saturated potassium bicarbonate and finally with water. The ether solution was concentrated by distillation and evaporated to give a white crystalline product. Recrystallization in 60% pentane ether and final drying in a vacumm desiccator resulted in 3.2 g. (43.3%) of product, m. p. 85-87°.

5. 7-Norborneol

The complete reduction of 7-norbornenone (3.0 g., 0.0278 m.) to 7-norborneol was achieved by catalytic hydrogenation in 15 ml. ethyl acetate at room temperature and at atmospheric pressure over platinum oxide. The reaction was allowed to continue with stirring until no further hydrogen was taken up. The first equivalent of hydrogen was taken up in two hours. The remainder was taken up at a rate of about 25 ml. per hour. The reaction flask was allowed to stir under hydrogen for a total of forty-six hours. The platinum black formed during the reaction was filtered off on a gravity filter. The ethyl acetate solution was concentrated by distillation and evaporated to give the white crystals of saturated alcohol. Recrystallization in 50% pentane ether gave 2.8 g. (90%) and 1.9 g. (61%) of product, m. p. 147-149°.

6. 7-Norbornyl Brosylate

After purification, the product (4.7 g., 0.0420 m.) was dissolved in 15 ml. dry pyridine and chilled. A 5% excess of p-bromobenzenesulfonyl chloride (12.0 g.) was added to the cold solution and it was left in the cold for twenty-four hours. To the solution was added 10% sulfuric acid, the product was extracted with ether and the ether extracts were washed with 6N hydrochloric acid, saturated potassium bicarbonate and water. The ether solution was concentrated by distillation and evaporated to give the white crystalline product. Recrystallization in 75% pentane ether and final drying in a vacumm desiccator gave 6.3 g. (49.5%) of product, m. p. 86-88°.

7. Cyclohexyl Brosylate

Cyclohexanol (4.0 g., 0.0364 m.) was dissolved in 20 ml. cold dry pyridine. p-Bromobenzenesulfonyl chloride (10.2 g.) was added and dissolved and the mixture was allowed to stand in the cold for twelve hours. To the solution was added 10% sulfuric acid, the product was extracted with ether and the ether extracts were washed with 6N hydrochloric acid, saturated potassium bicarbonate and finally with water. The ether extracts were distilled until no more ether came over and the result was a very thick liquid which would not crystal-

lize except after two days of standing in freezing temperatures. The white waxy solid obtained was mashed and spread on filter paper to remove liquid impurities. The powdery material obtained was dried in a vacumm desiccator and recrystallized several times from pentane. This process was repeated using a more pure grade of ether for extraction. The products obtained were 1.8 g. (16%) and 5.8 g. (50%) of white crystalline solid, m. p. 48-50° (lit.[20] m. p. 48.1-48.6°).

8. Methods of Rate Measurements

For solvolysis in formic acid, the procedure reported by Winstein and Marshall[16] was used. The starting materials were weighed out and made up to volume with formic acid at 23-25°C. The volumetric flasks were heated sufficiently so that the brosylate was completely in solution and the contents were then transferred to stoppered round bottom flasks, 10 ml. more formic acid was added with a pipette, and the flasks were immersed in the temperature bath at 95°. About six ml. samples were withdrawn with a 10ml. pipette at various intervals, cooled to room temperature over ice for 45 seconds, five ml. of which was pipetted into a 100 ml. beaker containg 50 ml. of anhydrous acetic acid to be titrated potentiometrically as described below. After the reaction had reached about 40% reaction, about

four ml. samples were removed from the reaction flasks with a five ml. pipette, cooled on ice to room temperature for twenty seconds and three ml. of the solution was titrated in the same way. The time of delivery onto the ice was used in the rate calculations, the time of delivery of the first sample called zero time.

The same method was used for runs at 25° except that five ml. samples were delivered directly into a 100 ml. beaker with 50 ml. anhydrous acetic acid and the time of that delivery was used in the rate calculations.

9. Potentiometric Titration

A Beckman pH meter, model G with standard glass and calomel electrodes was employed for the titrations. The electrodes were immersed in the stirred solution to be titrated, the solution was titrated with 0.00883 N potassium acetate in anhydrous acetic acid and the m. v. readings were plotted against the volume of added base. The potassium acetate was standardized with a standard solution of perchloric acid in acetic acid. Titrations of very low concentrations of generated acid were unsteady, at least a 5% reaction concentration needed for a good titration. Titrations of higher concentrations gave a more pronounced point of inflection on the titration curves when three ml. rather than five ml. aliquots were titrated.

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