Carbonium Ions. II. Mechanism of Acetolysis of 2-Phenylethyl Tosylate[1]

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Abstract: The acetolysis of 2-phenylethyl tosylate has been examined in the presence and absence of buffers. The acetolysis in the absence of buffers has been divided quantitatively into the k_Δ (anchimerically assisted) and k_s (anchimerically unassisted) paths and the rate constants for these two mechanisms have been determined at two temperatures. The rate constants were found to be $k_\Delta^{90} = 1.18 \times 10^{-6}$ sec^{-1} and $k_\Delta^{115} = 1.29 \times 10^{-5}$ sec^{-1} for the anchimerically assisted route and $k_s^{90} = 8.92 \times 10^{-7}$ sec^{-1} and $k_s^{115} = 7.93 \times 10^{-6}$ sec^{-1} for the anchimerically unassisted route. The entropy of activation for the k_Δ route was found to be -14.6 eu and for the k_s route was found to be -21.5 eu. The inductive effect of the phenyl group on k_s ($k_s^{75} = 2.07 \times 10^{-7}$ sec^{-1}) is compared to the rate constant for ethyl tosylate ($k_t^{75} = 7.72 \times 10^{-7}$ sec^{-1}). The electronic effect of a methoxy group in 2-*p*-anisylethyl tosylate ($k_\Delta^{75} = 2.6 \times 10^{-5}$ sec^{-1}) is compared with the effect of hydrogen in 2-phenylethyl tosylate ($k_\Delta^{75} = 2.39 \times 10^{-7}$ sec^{-1}) in the anchimerically assisted reaction. The rate constant for ion-pair return has been found to be $k_{14}^{90} = 8.00 \times 10^{-7}$ sec^{-1} and $k_{14}^{115} = 8.06 \times 10^{-6}$ sec^{-1}. The per cent retention of configuration on acetolysis expected from the above results is calculated and found to be in agreement with that which is reported. The meaning of these results is discussed.

The nature of intermediate steps in the solvolysis of 2-arylethyl tosylates has been the subject of rather extensive investigations. The questions which must be answered are: (1) what factors cause aryl participation to occur in the ionization step; (2) when aryl participation is observed to what extent is it important; and (3) when an aryl-bridged species is formed what is its nature (*i.e.*, is it an intermediate or a transition state and what is the nature of the bonding)? Evidence regarding these questions has been summarized in two recent reviews.[2,3] In simple 2-arylethyl tosylates[4] there are three types of evidence which are most often cited in discussing the mechanism of solvolysis: isotopic scrambling, rate acceleration, and entropies of activation. Only the first of these, isotopic scrambling, is completely unequivocal in the sense that if scrambling is observed in the product then aryl bridging must have occurred at some stage of the solvolysis. Isotopically labeled 2-arylethyl tosylates have been studied by a number of workers[5] with the observation that scrambling varies from slight to complete depending on the aryl group and the solvent.

Rate acceleration has often been used as evidence for aryl participation[2,3] and this appears to be valid in some cases where the rate acceleration is large. However, as has been pointed out very clearly[6] lack of large rate acceleration (as measured by titrimetric rate constants) is still compatible with aryl participation (arylonium ion formation) being one of several possible pathways to product. In fact, as will be shown in the present work, little or no rate acceleration and even rate deceleration (as measured by k_t) can be compatible with arylonium ion formation being one of the major pathways to product. It seems to us that failure to recognize that 2-arylethyl tosylates may undergo solvolysis by two simultaneous but distinct paths (the so-called k_Δ and k_s routes elucidated by Winstein and coworkers[6]) is the very crux of what has been called[3,7] a "serious inconsistency in theory" of carbonium ion chemistry. If one accepts these two distinct paths (k_Δ and k_s) as operating simultaneously then the inconsistency disappears because the term "anchimeric assistance"[8] is not synonymous with the term "anchimeric acceleration." It appears that even some proponents of the stable arylonium ion theory have needlessly emphasized acceleration in searching for neighboring group participation.[2]

In 2-arylethyl tosylates the entropies of activation for formolysis and acetolysis have been observed to fall in the range -10 ± 2 eu or -18 ± 2 eu.[5f,8,9] The -10-eu range has been found to correspond to solvolysis with a high degree of isotopic scrambling in the product while the -18-eu range corresponds to a

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[2] D. J. Cram, *J. Am. Chem. Soc.*, 86, 3767 (1964).

[3] H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, 87, 2137 (1965).

[4] In order to avoid confusion we wish to make it clear that the only system which will be examined or discussed in this paper is of the type Ar–CH_2–CH_2–OTs.

[5] (a) C. C. Lee, G. P. Slater, and J. W. T. Spinks, *Can. J. Chem.*, **35**, 1417 (1957); (b) W. H. Saunders, Jr., S. Asperger, and D. H. Edison, *J. Am. Chem. Soc.*, 80, 2421 (1958); (c) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, 41, 807 (1958); (d) C. C. Lee, R. Tkachuk, and G. P. Slater, *Tetrahedron*, 7, 206 (1959); (e) J. W. Clayton and C. C. Lee, *Can. J. Chem.*, **39**, 1510 (1961); (f) D. J. Cram and L. A. Singer, *J. Am. Chem. Soc.*, **85**, 1075 (1963); (g) L. Eberson, J. P. Petrovich, R. Baird, D. Dyckes, and S. Winstein, *ibid.*, 87, 3504 (1965); (h) W. H. Saunders, Jr., and R. Glaser, *ibid.*, 82, 3586 (1960); (i) C. C. Lee and A. G. Forman, *Can. J. Chem.*, 43, 3387 (1965); (j) C. C. Lee and A. G. Forman, *ibid.*, 44, 841 (1966); (k) C. C. Lee and L. Noszko, *ibid.*, 44, 2481 (1966); (l) C. C. Lee and L. Noszko, *ibid.*, 44, 2491 (1966); (m) J. E. Nordlander and W. G. Deadman, *Tetrahedron Letters*, 4409 (1967); *J. Am. Chem. Soc.*, 90, 1590 (1968).

[6] See ref 5g for a good summary of this, including prior references.

[7] (a) H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Am. Chem. Soc.*, 87, 1280 (1965); (b) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967); (c) H. C. Brown, *Chem. Eng. News*, 45, 87 (Feb 13, 1967).

[8] S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953).

[9] S. Winstein and R. Heck, *ibid.*, 78, 4801 (1956).

Table I. Per Cent Rearrangement in 2-Phenylethyl Acetate Isolated from Treatment of $C_6H_5CH_2C^*H_2OX$ with Acetic Acid at 115°

Run	$C_6H_5CH_2C^*H_2OX$ concn, *M*	Added solute concn, *M*	Solvent, %	Reaction time, hr	% rearrangement
1	Tosylate, 0.5	NaOAc, 0.5	HOAc, 99.7	17	9.3
2	Tosylate, 0.5	KOAc, 0.5	HOAc, 99.7	20	7.2
3	Tosylate, 0.5	Urea, 0.5	HOAc, 99.7	17	16.2
4	Tosylate, 0.5	Urea, 0.5	HOAc, 100	17	21.6
5	Tosylate, 0.5	None	HOAc, 99.7	17	24.0
6	Tosylate, 0.5	None	HOAc, 99.7	74	32.6
7	Tosylate, 0.5	HOTs, 0.5	HOAc, 99.7	74	36.0
8	Brosylate, 0.5	None	HOAc, 99.7	5	25.2
9	Brosylate, 0.5	None	HOAc, 99.7	30	36.0
10	Acetate, 0.5	HOTs, 1.0	HOAc, 99.7	29	0.3

low degree of scrambling in the product.[5] Two different analyses of these results have been published. One of these is primarily due to Winstein and coworkers[6] and has as one of its essential features the idea that if there is participation (anchimeric assistance[8]) by the aryl group in the transition state for solvolysis of a 2-arylethyl tosylate then some of the developing positive charge is dispersed into the aryl group. This dispersal of charge requires less solvation and ordering of the solvent than if the charge dispersal had not occurred. This would then tend to make the $\Delta S^{\ddagger}$ more positive in cases where anchimeric assistance by an aryl group occurs. Also the k_Δ route would involve loss of rotational freedom in the transition state and the k_s route would be a bimolecular process involving the combination of two particles. Each of these would contribute to the $\Delta S^{\ddagger}$ for the two different processes. An alternate interpretation involving equilibrating ions has been offered by Brown and coworkers.[3] This interpretation assumes a pair of classical primary carbonium ions from a 2-arylethyl tosylate and depending on the stability of the intermediate bridged structure equilibration between the two classical ions is slow (if aryl is a poor bridging group such as phenyl) of fast (if aryl is a good bridging group). It is then proposed that if equilibration is slow the reaction will show a more negative $\Delta S^{\ddagger}$ because rapid equilibration of the aryl group would prevent participation by solvent and thereby make $\Delta S^{\ddagger}$ more positive.

It seemed that one approach to examining the solvolysis mechanism of 2-arylethyl tosylates would be to look at a case where isotopic rearrangement in the product was intermediate (neither close to the 50% maximum nor 0%). It has been found that solvolysis of a labeled 2-arylethyl tosylate often occurs with very little isotopic scrambling in the product and this is only consistent with no leakage from the k_s to the k_Δ route.[6] The k_s route is expected to be a normal SN2 displacement at a primary carbon[10] with the nucleophile being either some anion or a solvent molecule. This takes place with inversion of configuration[10] implying that as the tosylate group leaves the nucleophile attacks with over-all inversion. It has been proposed that there is no leakage from the k_Δ to the k_s route.[11] All of these arguments indicate that the k_Δ and k_s routes can be treated as simultaneous but independent reactions and each should show its own characteristic thermodynamic constants. By proper choice of labeled starting materials and analysis of all compounds involved as a function of temperature and time one should be able to quantitatively determine the rate constants and thermodynamic functions for each solvolysis route, k_Δ and k_s, on a single compound in a single solvent. This has been done for 2-phenylethyl tosylate in acetic acid and the results are herein discussed.

In all previous work on the acetolysis of labeled 2-phenylethyl tosylate in which the degree of rearrangement in the product was determined either sodium or potassium acetate was added as a buffer.[5a,b,d] This is unfortunate because it appears that under these conditions a large part of the product comes about by the k_s route and since acetate ion is a better nucleophile than acetic acid the added acetate ion reduces the amount of rearrangement. Consistent with this is the fact that Winstein and coworkers observed an increase in titrimetric rate constant for 2-phenylethyl tosylate in acetic acid when potassium acetate was added[8] but only a normal salt effect when lithium perchlorate was added.[12] The lack of an observable special salt effect will be discussed later. Lee and coworkers[5a] observed 5.5% rearrangement on acetolysis (20 hr) with added potassium acetate and Saunders and coworkers[5b] observed 10% rearrangement on acetolysis (40 hr) with added sodium acetate. We have found (see Table I) 9.3% rearrangement[13] for acetolysis (17 hr) in the presence of added sodium acetate (0.5 *M*) (run 1) and 7.2% when Lee's conditions were repeated with potassium acetate (0.5 *M*) (run 2). All of these reactions were done at 115°. The slightly lower value observed by Lee and coworkers compared with our results in an attempt to repeat their conditions is not felt to be a significant difference. Our results are in satisfactory agreement with theirs. As will be clearly pointed out in this paper the observed extent of rearrangement is a function of the reaction temperature, extent of reaction, and concentration of any acetate ion and is therefore very difficult to duplicate unless great care is taken to control experimental conditions.

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[10] A. Streitwieser, Jr., *J. Am. Chem. Soc.*, 77, 1117 (1955).

[11] J. L. Coke, *ibid.*, **89**, 135 (1967).

[12] A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2767 (1956).

[13] The per cent rearrangement is found by oxidation of the compound to benzoic acid and then using the formula: % rearrangement = (activity of benzoic acid)(100)/(activity of original compound). Since a bridged ion can open at either carbon of the side chain the per cent bridging will equal twice the per cent rearrangement. The precision in determining the per cent rearrangement in a given sample is estimated to be ±0.2% or better and the relative accuracy is probably the same. However the absolute accuracy on a given sample is probably no better than ±1%.

In an effort to clarify exactly what factors were important in the acetolysis of 2-phenylethyl tosylate a number of preliminary experiments were run (Table I). These preliminary data were not used in calculation of the final thermodynamic parameters and rate constants because it was found that the precision and accuracy needed in these calculations required that all the data used in a given calculation be obtained from the same batch of labeled tosylate, by the same workers under rigorously controlled conditions. It was first necessary to show that *p*-toluenesulfonic acid did not catalyze rearrangement of the product of acetolysis. This was done by heating 2-phenylethyl-1-^{14}C acetate with 2 equiv of *p*-toluenesulfonic in acetic acid (99.7%) at 115° for 29 hr (approximately two half-lives for acetolysis) (run 10). The recovered acetate showed only 0.3% rearrangement. In order to test the effect of acetate ion on the solvolysis a sample of 2-phenylethyl-1-^{14}C tosylate (0.5 *M*) was heated at 115° in acetic acid (99.7%) for 17 hr with no acetate ion added (run 5). The 2-phenylethyl acetate which was isolated was found to have 24% rearrangement. With the appearance of an article by Bartlett and coworkers[14] it became possible to test the effect of the *p*-toluenesulfonic acid, produced during solvolysis in the absence of acetate ion, on this reaction to see if it might be catalyzing rearrangement in the starting tosylate. Using urea (0.5 *M*) as a buffer with 2-phenylethyl-1-^{14}C tosylate (0.5 *M*) in acetic acid (99.7%) at 115° for 17 hr (run 3) the 2-phenylethyl acetate was found to have 16.2% rearrangement. However, carbon dioxide was produced during the reaction and apparently the trace of water in the acetic acid was responsible for hydrolysis of the urea with subsequent production of carbon dioxide and ammonia. This ammonia would of course produce 1 equiv of acetate ion and this would result in a decrease in rearrangement. These deductions are supported by the fact that when these reaction conditions were repeated (17 hr, 115°) in anhydrous acetic acid (trace of acetic anhydride added) still using urea as a buffer (run 4) the acetate isolated was found to have 21.6% rearrangement. We feel this is close enough to the 24% rearrangement observed when *p*-toluenesulfonic acid was allowed to accumulate that it is strong evidence the starting tosylate is also stable to any catalytic effect of *p*-toluenesulfonic acid. The slight difference in rearrangement could be due to different rates of reaction under the slightly different reaction conditions since both reactions went only to partial completion and both were run for the same length of time. It could still be due to a trace of acetate ion present in the urea-buffered run, or it could be due to the *p*-toluenesulfonic acid which accumulates causing a greater extent of rearrangement than when it is buffered (to produce tosylate anion) with urea. It was shown that when the acetolysis of 2-phenylethyl tosylate was carried out in the initial presence of 0.5 *M* HOTs for 74 hr (greater than 96% reaction) (run 7) at 115° the rearrangement in the product was 36% as compared to 32.6% rearrangement when the same reaction was carried out without any initial HOTs. This is strong evidence that the *p*-toluenesulfonic acid is having a slight effect on the per cent rearrangement, tending to increase it. This would tend to cause a slight increase in per cent rearrangement as the reaction in the absence of buffer proceeds since *p*-toluenesulfonic acid accumulates. All of our solvolyses to determine rate data and per cent rearrangement for calculations of thermodynamic parameters were run in ordinary glacial acetic acid (99.7%) with no added buffers using 0.5 *M* 2-phenylethyl tosylate.

Using essentially the diagram of earlier workers[5c,e,k] with the added modification showing no crossover between the k_Δ and k_s routes[6,11] the acetolysis of 2-phenylethyl-1-^{14}C tosylate can be outlined (Scheme I). From the equations of Jenny and Winstein[5c] (1, 2, and 3) one can arrive at eq 4 from 1 and 3. From eq 2 and 4 one can derive eq 5.

$$k_t = Fk_\Delta + k_s \tag{1}$$

$$k_{14} = (1 - F)k_\Delta \tag{2}$$

letting

$$X = \frac{k_\Delta}{k_s} = \frac{\%\ \text{rearrangement in acetate (time} = \infty)}{50 - \%\ \text{rearrangement in acetate (time} = \infty)} \tag{3}$$

$$k_\Delta = \frac{Xk_t}{1 + XF} \tag{4}$$

$$k_\Delta = \frac{Xk_t + Xk_{14}}{1 + X} \tag{5}$$

$$k_{14}t = 2.303 \log \frac{50}{50 - \%^{14}\text{C}_2} \tag{6}$$

From eq 6 used by earlier workers[5c,e] and the actual analysis of per cent scrambling in the starting material as a function of time and temperature (see Table II), k_{14} can be obtained. The calculated values are $k_{14}{}^{90} = 8.00 \times 10^{-7}$ sec^{-1} and $k_{14}{}^{115} = 8.06 \times 10^{-6}$ sec^{-1}. It should be noted that k_{14} appears to increase slightly at about two half-lives.

Table II. Per Cent Rearrangement in Starting 2-Phenylethyl Tosylate as a Function of Reaction Time and Temperature

Temp, °C	Reaction time, hr	% C-14 at C-2
90	0.0	0.4
	24.0	3.8
	48.5	7.1
	96.8	12.3
	144.5	18.6
115	0.0	2.4
	3.0	6.6
	5.5	9.2
	9.0	13.3
	12.0	16.4
	22.0	26.1

The titrimetric rate constants for acetolysis of 2-phenylethyl tosylate (0.5 *M*) in ordinary glacial acetic acid (99.7%) with no acetate ion added were determined by the method of Winstein and coworkers[8] and were found to be $k_t{}^{90} = 1.27 \times 10^{-6}$ sec^{-1} and $k_t{}^{115} = 1.27 \times 10^{-5}$ sec^{-1} and these values were used in all our calculations. The agreement between these values and

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(14) W. S. Trahanovsky, M. P. Doyle, and P. D. Bartlett, *J. Org. Chem.*, 32, 150 (1967).

Scheme I[15]

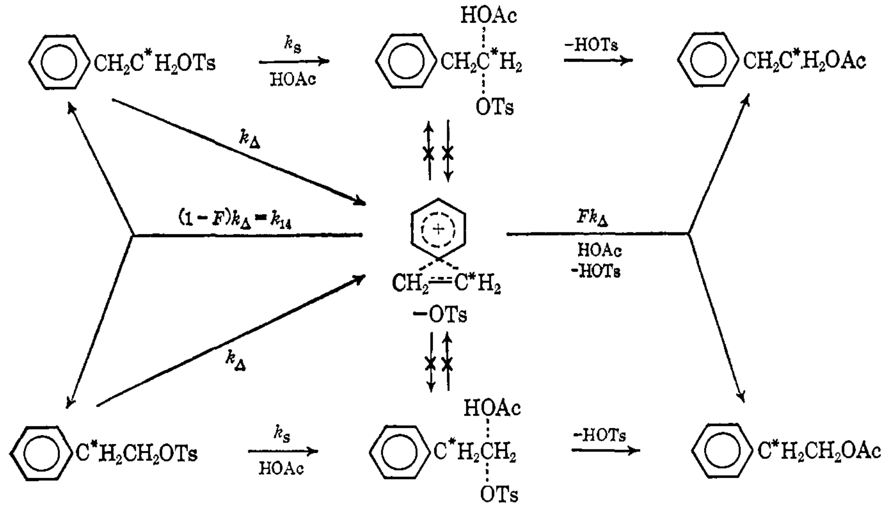

Table III. Per Cent Rearrangement in the 2-Phenylethyl Acetate Product as a Function of Per Cent Reaction and Temperature

Temp, °C	Point	Time, hr	% reaction (calcd)	% rearrangement[a]	
90	1	24.1	10.4	13.51	
	2	48.0	19.7	14.75	
	3	96.0	35.5	17.52	17.14
	4	145	48.4	18.98	19.02
	5	265	70.2	23.33	23.39
	6	432	86.1	27.57	27.30
	7	672	95.4	29.01	28.84
115	1	2.80	12.0	16.57	
	2	5.17	21.0	18.00	
	3	10.33	37.6	20.37	20.75
	4	14.08	47.5	22.31	22.29
	5	25.0	68.1	26.27	26.35
	6	50.0	89.8	31.00	30.94
	7	74.0	96.6	32.60	32.67

[a] Duplicate runs were made at each point except at points 1 and 2 where three runs were combined to obtain sufficient product to oxidize.

Table IV

Parameter or rate constant	Exptl value	Calcd by time = ∞ data	Calcd by time = O data	Av value
k_t^{90}	1.27×10^{-6} sec^{-1}			
k_t^{115}	1.27×10^{-5} sec^{-1}			
k_{14}^{90}	8.00×10^{-7} sec^{-1}			
k_{14}^{115}	8.06×10^{-6} sec^{-1}			
F^{90}		0.362	0.274	0.318
F^{115}		0.420	0.315	0.368
k_Δ^{90}		1.25×10^{-6} sec^{-1}	1.10×10^{-6} sec^{-1}	1.18×10^{-6} sec^{-1}
k_Δ^{115}		1.39×10^{-5} sec^{-1}	1.18×10^{-5} sec^{-1}	1.29×10^{-5} sec^{-1}
k_s^{90}		8.16×10^{-7} sec^{-1}	9.68×10^{-7} sec^{-1}	8.92×10^{-7} sec^{-1}
k_s^{115}		6.87×10^{-6} sec^{-1}	8.99×10^{-6} sec^{-1}	7.93×10^{-6} sec^{-1}

the values that can be calculated from Winstein's data[8] (calcd $k_t^{90} = 1.33 \times 10^{-6}$ sec^{-1} and $k_t^{115} = 1.31 \times 10^{-5}$ sec^{-1}) under anhydrous acetic acid conditions is indicative that the trace of water under our conditions does not materially affect the reaction. It should be pointed out that the k_t values do begin to increase slightly at about two half-lives.

Equations 1-5 require that the per cent rearrangement in the product be known when the reaction is complete (time = ∞), and this was found by constructing a plot (Figure 1) of the per cent rearrangement *vs.* the calculated per cent reaction (calculated on the basis of the experimental k_t and reaction time) (see Table III). The plot obtained was extrapolated to 100% reaction, and the rearrangement was found to be 33.4% at 115° (time = ∞) and 30.3% at 90° (time = ∞). From these results using eq 1-5 one can calculate F, k_Δ, and k_s at both 90 and 115° (time = ∞ data) and the results are shown in Table IV.

It is also true that from Scheme I one can write eq 7.

$$\frac{Fk_\Delta}{k_s} = \frac{\%\ \text{rearrangement in acetate (time = 0)}}{50 - \%\ \text{rearrangement in acetate (time = 0)}} \quad (7)$$

Equation 7 simply represents the path for forming product before the starting tosylate has had a chance to rearrange to any extent. Equation 7 requires that the per cent rearrangement at time = 0 be obtained and this can be found by extrapolation to 0% reaction as shown in Figure 1. The rearrangement was found to be 14.6% at 115° (time = 0) and 11.9% at 90° (time = 0). From these results using eq 1, 2, and 7 one can calculate F, k_Δ, and k_s at both 90 and 115° (time = 0 data) and the results are shown in Table IV.

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(15) The symbol used here for the ethylenephenonium ion is merely for convenience and has no special significance. We wish merely to show it as a bridged entity and reserve a discussion of the nature of the bonding for a future publication.

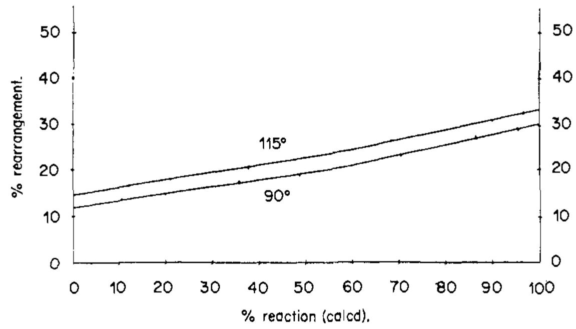

Figure 1. Per cent rearrangement in 2-phenylethyl acetate product as a function of per cent reaction and temperature.

Table V

Solvolytic route		Thermodynamic functions (calcd) From time $= \infty$ data	From time $= 0$ data	Av value
k_Δ	E^*, kcal/mol	26.9	26.5	26.7
	$\Delta H^\ddagger$, kcal/mol	26.1	25.7	25.9
	$\Delta F^\ddagger$, kcal/mol	31.6	31.7	31.7
	$\Delta S^\ddagger$, eu	−13.9	−15.3	−14.6
k_s	E^*, kcal/mol	23.9	24.9	24.4
	$\Delta H^\ddagger$, kcal/mol	23.1	24.2	23.7
	$\Delta F^\ddagger$, kcal/mol	32.1	31.9	32.0
	$\Delta S^\ddagger$, eu	−23.2	−19.8	−21.5
k_t	E^*, kcal/mol	25.8		
	$\Delta H^\ddagger$, kcal/mol	25.0		
	$\Delta F^\ddagger$, kcal/mol	31.6		
	$\Delta S^\ddagger$, eu	−17.0		

In principal the time = 0 and time = ∞ calculations should agree with each other and one should be able to predict the experimental observations of each from the other. In fact, however, there are some differences. We do not at present understand all of these differences but they are not large. It is felt that the most reliable way to handle the data is to use the average of both sets of calculations, time = 0 and time = ∞, and this has been done. In Tables IV and V the results of each individual calculation (time = 0 and time = ∞) are shown and the average of these is given in each case. In Table V are shown the thermodynamic parameters that can be calculated for each reaction path. Table VI shows our results calculated to 75° in order to compare the results with the work of others.

A number of rather interesting conclusions can be arrived at from the present results. Investigations by earlier workers[5f,8,9] would indicate that the k_Δ route would be expected to show a $\Delta S^\ddagger$ of about 8 eu more positive than a k_s route. We find that for 2-phenylethyl tosylate in acetic acid $\Delta S^\ddagger$ for the k_Δ route is about 7 eu more positive than for the k_s route. It is of interest to note that the $\Delta S^\ddagger$ for trifluoroacetolysis of 2-phenylethyl tosylate in the absence of buffer was −16.8 eu (this is of course based on k_t values).[5m] It appears from Nordlander's work[5m] and the present work that values for $\Delta S^\ddagger$ in the absence of solvent anion are somewhat more negative than the corresponding values for reactions run in the presence of solvent anion as a buffer. It is rather difficult to see how the present analysis of the $\Delta S^\ddagger$ for the two processes, k_Δ and k_s, on acetolysis of 2-phenylethyl tosylate can be accommodated by Brown's[3] explanation of why the values for $\Delta S^\ddagger$ fall into two different ranges. If Brown's explanation is correct it would seem that one would have to propose that the classical 2-phenylethyl cation is simultaneously rapidly rearranging and not rearranging or else one would have to propose that our analysis is simply fortuitous with no logical explanation. Our results are exactly what one would expect on the basis of earlier work by Cram[5f] and Winstein.[8,9]

Table VI. Comparison of Acetolysis Rate Data with Other Work

Compound	Acetolysis rate constants, sec^{-1}
CH_3CH_2OTs[a]	$k_t^{75} = 7.72 \times 10^{-7}$
$C_6H_5CH_2CH_2OTs$	$k_s^{75} = 2.18 \times 10^{-7}$ [b]
	$k_s^{75} = 1.96 \times 10^{-7}$ [c]
	$k_s^{75} = 2.07 \times 10^{-7}$ (av)
p-$CH_3OC_6H_4CH_2CH_2OTs$[5c]	$k_\Delta^{75} = 2.6 \times 10^{-5}$
$C_6H_5CH_2CH_2OTs$	$k_\Delta^{75} = 2.26 \times 10^{-7}$ [b]
	$k_\Delta^{75} = 2.51 \times 10^{-7}$ [c]
	$k_\Delta^{75} = 2.39 \times 10^{-7}$ (av)

[a] S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952). [b] Time = 0 data. [c] Time = ∞ data.

The data in Table VI allows for the first time an experimental estimate of the net effect (inductive, steric, etc.) of placing a phenyl group on the 2 position of ethyl tosylate. Our results indicate that in acetolysis at 75° the k_t value (essentially a k_s value) for ethyl tosylate is about 3.7 times as fast as the k_s value for phenylethyl tosylate (calculated from higher temperatures). This is the effect on a primary carbon undergoing direct displacement and cannot be compared directly with a similar displacement at secondary or tertiary carbon. We can also compare (Table VI) the effect of aryl substituents on the ability of the aryl group to participate in loss of the tosylate group from a primary carbon. Comparison of the k_Δ values for acetolysis at 75° of phenylethyl tosylate (calculated from higher temperatures) and 2-p-anisylethyl tosylate[5c] indicates that the p-methoxy substituent has an accelerating effect of about 109 times over hydrogen on the k_Δ values. The fact that 2-p-anisylethyl tosylate does not show a very large k_t value in acetic acid relative to the k_t for phenylethyl tosylate is in part due to the fact that F for the 2-p-anisylethyl tosylate is smaller[5c] (indicating a greater degree of return from the bridged ion) and in part to the fact that for 2-phenylethyl tosylate k_t is composed mostly of k_s. Our results also emphasize why one should not use k_t values in attempting to construct a Hammett type plot[7b] in systems like the one under study since it is only the k_Δ values that are a valid measure of the ability of an aryl group to participate.

Fainberg and Winstein[12] observed only a slight rate increase when lithium perchlorate was added to the acetolysis of 2-phenylethyl tosylate and they stated that a normal salt effect could easily account for this increase. The reason a special salt effect was not observed can be understood in terms of the work of Lee and coworkers[5d] and the present work. Even in the present work where k_Δ mades a larger contribution to k_t than in the earlier work[5d] the k_t that is observed for acetolysis of 2-phenylethyl tosylate at 115° is composed of about 63% k_s and 37% k_Δ. This means that a special salt effect on k_Δ would have only a small over-all rate increase on k_t. At lower temperatures the effect would be even less pronounced since at lower temperatures k_Δ makes a smaller contribution to k_t. In the case of 2-phenylethyl-1-^{14}C tosylate there is a more sensitive test for a special salt effect than using k_t *vs.* lithium perchlorate concentration[12] and this is the rearrangement ratio (per cent rearrangement in starting material over per cent rearrangement in product) in the absence or presence of lithium perchlorate. Lee and coworkers[5d] have checked this and found that added perchlorate ion causes the rearrangement ratio to decrease from about 0.4 to about 0.2 (at approximately one half-life). Even though their work was done in the presence of acetate ion which makes the observed per cent rearrangements in starting material and product fairly small and thereby subject to a relatively large error in measurement it appears that the difference between their two rearrangement ratios is well outside of experimental error. Their conclusion that added perchlorate ion is trapping a bridged intermediate and thereby showing a special salt effect in the rearrangement ratio by preventing some return to scrambled starting material seems justified. It has been shown[16] that acetate ion is not as efficient a trapping agent as perchlorate ion but the exact results expected under the conditions used by Lee and coworkers[5d] are difficult to analyze quantitatively.

Our analysis of the two routes, k_Δ and k_s, for acetolysis of 2-phenylethyl tosylate makes a prediction as to the stereochemistry expected on solvolysis. If one assumes that the bridged species is a symmetrical ion which is attacked with equal probability at either carbon of the ethylene group and if one makes the further assumptions that participation of the phenyl group to displace the tosylate group involves inversion at the primary carbon bearing the tosylate group and that opening of the bridged ion involves a second inversion, then the k_Δ path should involve net retention of configuration (*i.e.*, a double inversion at one carbon or a single inversion at two carbons). It seems reasonable also to assume that the k_s path involves a single inversion of configuration.[10] From the foregoing assumptions one would predict that the per cent bridging involved in direct formation of product which can be expressed by $(Fk_\Delta)(100)/(Fk_\Delta + k_s)$ should be the same as the per cent retention observed on acetolysis. Using the average values obtained in the present work from Table IV one would predict 37% bridging at 115° on acetolysis of 2-phenylethyl tosylate in the absence of buffers. This calculation assumes formation of bridged species and return to covalent tosylate would also involve net double inversion or two inversions and hence retention of configuration. This prediction has been examined experimentally by Professor Eugene Snyder[17] using *threo*-1,2-dideuterio-2-phenylethyl brosylate.[18] This compound has the characteristic of making internal return from the bridged ion unobservable if one assumes inversion on bridging followed by inversion on opening of the bridged ion. Snyder observes about 42% retention of configuration on acetolysis of the *threo*-1,2-dideuterio-2-phenylethyl brosylate at 115° for 40 hr (reaction virtually complete) in the absence of acetate ion as a buffer. In order to compare this number to our own work involving the tosylate we carried out runs 8 and 9 in Table I. From these two runs and the known k_t value of the brosylate[9] one can construct a per cent rearrangement *vs.* per cent reaction plot for 2-phenylethyl-1-^{14}C brosylate and it can be shown by comparison of this plot with the same kind of plot for the corresponding tosylate (Figure 1) that the brosylate gives slightly greater rearrangement (2–3%) or bridging (4–6%) than does the tosylate. Thus the value obtained by Snyder (42% retention using the brosylate) is in very good agreement with what we would predict (37% plus 4–6%) based on our tosylate and brosylate. Snyder[17] has also determined the per cent retention in the *threo*-1,2-dideuterio-2-phenylethyl brosylate on acetolysis in the presence of sodium acetate and finds 21% retention in the product at 115° after 20 hr reaction. Since it is now known that the brosylate gives slightly more bridging than the tosylate (see above) this value can be compared to some of our work. Run 1, Table I, indicates 9.3% rearrangement or 18.6% bridging in the product from the 2-phenylethyl tosylate in the presence of acetate at 115° for 17 hr (it would be slightly less at time = 0). Allowing for the difference between the brosylate and the tosylate our work is in very good agreement with that of Snyder.

Snyder[17] has also very recently completed work of the same type involving acetolysis of *threo*-1,2-dideuteruo-2-phenylethyl tosylate in the absence of acetate ion. He finds approximately 32% retention in the product at 115° between 10 and 40% reaction. This value lies between our observed time = 0 value for per cent bridging (29.2%) and the value predicted by our average calculations (37%), and the difference is probably well within the combined experimental error for a prediction of this type. We estimate an error of ±2% in absolute accuracy for measuring the per cent bridging and Snyder[17] estimates an error of similar magnitude in this work. However, here it should be realized we are predicting a per cent bridging based on rate constants and the error would be larger than in an actual measurement. One of the factors which could be causing the disagreement between our actual time = 0 experimental results and calculations based on data taken at later stages of the reaction might be the slight effect of accumulating *p*-toluenesulfonic acid (as indicated by results from run 7, Table I) and this would also affect Snyder's results. Also the fact that both k_t and k_{14} (and presumably k_Δ and k_s) show a slight upward drift after one to two half-lives and in our calculations based on time = ∞ data a constant value for k_t and k_{14} was assumed may contribute to this discrepancy. It is of interest to note that Snyder[17] also observes a very slight increase in retention of configuration at longer reaction times. It is the lack of understanding of the slight difference in the results of our two approaches to obtain the various rate constants which has led us to base our

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[16] S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *Chem. Ind.* (London), 664 (1954); S. Winstein and E. Clippinger, *J. Am. Chem. Soc.*, 78, 2784 (1956).

[17] E. I. Snyder, private communication. We wish to thank Professor Snyder for keeping us informed of his work and for numerous discussions involving our work.

[18] R. J. Jablonski and E. I. Snyder, *Tetrahedron Letters*, 1103 (1968).

discussion on the average values obtained by the time = 0 approach and the time = ∞ approach. Further work may clarify this problem. However if we base our discussions on the time = 0 data alone where complications cannot arise we arrive at basically the same conclusions. Considering that our method of determining k_Δ and k_s should lead to a slightly larger error in these rate constants than one normally observes in rate constants determined by titrimetric methods our use of the average of the two approaches seems justified since the average does not differ drastically from each value. We feel however that the values of each approach should also be recorded since future work may prove one approach more accurate than the other.

We feel that the present work provides overwhelming support for the dual mechanistic paths, k_Δ and k_s, for solvolysis of 2-arylethyl tosylates[4] and that in this system one will observe a wide range of situations involving competition between k_Δ and k_s as one varies the aryl group. The outcome of this competition will depend on such factors as the nature of the aryl group, the solvent or nucleophile, the leaving group, and the temperature of the solvolysis. The nature of the bridged species is currently being investigated in our laboratories by a Hammett-type treatment involving k_Δ values (determined by the present method) for a variety of phenyl-substituted 2-phenylethyl tosylates. This work will be published shortly.

Experimental Section

All melting points and boiling points are uncorrected. Distillations were done through a 2-ft Podbielniak-type column unless otherwise stated. Preparative gas chromatographic purifications were done on an Aerograph Autoprep Model A-700 with a 20-ft SE-30 (40%) column. The purity of all samples of 2-phenylethyl acetate were checked before oxidation on an F & M Model 5750 gas chromatograph with a 6-ft UCW-98 (10%) column and were of greater than 99% purity. Counting for radioactivity was done with a Nuclear Chicago Model 6860 liquid scintillation counter and samples were corrected for background and counter efficiency. Counter efficiency was 85% and this was determined by the channels ratio method and by internal standardization using toluene-^{14}C. A total of 15 ml of counting solution (0.5 g of PPO and 0.03 g of POPOP per 100 ml of toluene) was used for each sample counted.

Benzyl Cyanide-1-^{14}C. The general procedure of Friedman and Shechter[19] was used. A mixture of 1 mCi of potassium cyanide-^{14}C (69 mg) (purchased from Nuclear-Chicago Corp.), 30.4 g (0.62 mol) of sodium cyanide, and 245 ml of dry dimethyl sulfoxide was allowed to equilibrate overnight at 50° with stirring. The mixture was cooled to room temperature and 76 g (0.6 mol) of benzyl chloride was added with stirring over a period of 0.5 hr. The temperature of the reaction flask was maintained below 40° during the addition by external cooling. After the addition was complete the reaction mixture was stirred at room temperature for 6 hr and was then diluted with 900 ml of water. The aqueous mixture was extracted with 450 ml of ether in portions. The ether solutions were combined, washed with cold 6 N hydrochloric acid followed by water, and then dried and evaporated. Distillation of the resulting oil gave 60.3 g (85% of theory) of benzyl cyanide-^{14}C, bp 100–101° (8 mm) (lit.[20] bp 100–101° (8.5 mm)).

Ethyl Phenylacetate-1-^{14}C. The procedure of Adams and Thal[21] was used to hydrolyze 60.3 g (0.52 mol) of benzyl cyanide-^{14}C to the corresponding phenylacetic acid-1-^{14}C which was not purified but was simply dried and then was dissolved in a mixture of 300 ml of absolute ethanol and 3 ml of sulfuric acid. The resulting solution was heated at reflux for 2 hr and then was partially evaporated under vacuum. The resulting solution was cooled and diluted with water. The aqueous mixture was extracted with ether, and the ether solution was washed successively with water and saturated sodium bicarbonate solution. The ether solution was dried and evaporated and the resulting oil was distilled to yield 68 g (80% of theory) of ethyl phenylacetate-1-^{14}C, bp 114–117° (20 mm) (lit.[22] bp 103–107° (6 mm)).

2-Phenylethyl Alcohol-1-^{14}C. A total of 63 g (0.38 mol) of ethyl phenylacetate-1-^{14}C was added slowly with stirring to 19 g (0.5 mol) of lithium aluminum hydride in 500 ml of anhydrous ether. The resulting mixture was stirred at room temperature for 1 hr and then was decomposed by successive addition of 20 ml of water, 15-ml of 20% sodium hydroxide solution, and 70 ml of water. The solid was removed by filtration and was washed with ether. The ether solutions were combined, dried, and evaporated, and the resulting oil was distilled to give 40 g (85% of theory) of 2-phenylethyl alcohol-1-^{14}C, bp 108° (18 mm) (lit [23] bp 112° (18 mm)).

2-Phenylethyl-1-^{14}C p-Toluenesulfonate. The procedure of Tipson[24] was used to convert 35 g (0.28 mol) of 2-phenylethyl alcohol-1-^{14}C to the tosylate with the following modifications. Ether was used as the extraction solvent and care was taken to keep all wash solutions quite cold. The product isolated upon evaporation of the ether solvent was recrystallized from a mixture of petroleum ether (bp 30–60°) and a small amount of benzene to yield 53 g (69% of theory) of 2-phenylethyl-1-^{14}C p-toluenesulfonate, mp 39–40° (lit.[8] 35.5–36.6°). The combined recrystallized product from three preparations on the above scale was found to have an activity of 3.58×10^6 dpm/mmol (average of five separate determinations). The per cent rearrangement in this starting tosylate was determined by the procedure of Lee and coworkers[5a] and indicated 0.4% rearrangement (duplicate determinations). All the values shown in Table III and Figure 1 have been corrected for this rearrangement by subtracting the 0.4% from the observed per cent rearrangement in the acetate product. The tosylate used in obtaining all the data in Table III and the data in Table II for the 90° temperature was from the above combined batch of tosylate. The data in Table II for the 115° temperature was obtained using a different batch of tosylate that was more highly rearranged (2.4% rearrangement). Since in the k_{14} determinations it is only the rate of change of per cent rearrangement that is of interest the experimentally determined per cent rearrangements are recorded and plotted from Table II without correcting for the background per cent rearrangement in the starting tosylate,

Oxidation Procedures. The oxidation of 2-phenylethyl acetate was carried out as follows although the scale was varied from sample to sample. A mixture of 0.30 g (1.83 mmol) of 2-phenylethyl acetate, 1.2 g of sodium dichromate, 9.1 ml of concentrated sulfuric acid, and 24 ml of water was stirred and heated at reflux for 24 hr. The reaction mixture was cooled and the solid which formed was collected by filtration and was recrystallized from water and dried under vacuum to yield pure benzoic acid, mp 122°. This benzoic acid was then counted to determine its activity.

The oxidation of 2-phenylethyl p-toluenesulfonate was carried out in two steps by the method of Lee and coworkers [5a, 25] A mixture of 1.2 g (4.3 mmol) of 2-phenylethyl p-toluenesulfonate, 1.4 g (10 mmol) of sodium iodide, and 30 ml of acetone was stirred and heated at reflux for 25 min. The mixture was cooled and filtered, and the filtrate was diluted with 150 ml of water. The aqueous solution was extracted with ether in portions, and the ether solutions were combined, dried, and evaporated to yield 2-phenylethyl iodide as an oil. This compound was not purified but was oxidized directly as follows. A mixture of 0.4 g (1.73 mmol) of 2-phenylethyl iodide, 1.5 g of potassium permanganate, and 20 ml of water was stirred and heated at reflux for 24 hr. The mixture was cooled and filtered; the filtrate was acidified with concentrated hydrochloric acid. The solid which formed was collected by filtration and was recrystallized from water and dried under vacuum to yield pure benzoic acid, mp 122°. The benzoic acid was then counted to determine its activity.

In the determination of per cent rearrangement of a given sample

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(22) C. S. Leonard, *J. Am. Chem. Soc.*, **47**, 1774 (1925).

(23) R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 2548 (1947).

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(25) C. C. Lee and J. W. T. Spinks, *Can. J. Chem.*, **32**, 1005 (1954).

of a compound the sample was oxidized and then duplicate weighings and counting of each product benzoic acid were carried out. The per cent rearrangements reported are the average of these duplicate weighings and countings.

Kinetics and Per Cent Rearrangement Determinations. Titrimetric rate constants were determined at 90 and 115° at 0.5 *M* 2-phenylethyl *p*-toluenesulfonate (inactive) in 99.7% acetic acid (no buffer) in sealed ampoules in a constant-temperature bath according to the method of Winstein and coworkers.[8]

For the determination of per cent rearrangement in a given compound from a reaction the sealed ampoule method (above) was used with the conditions being specified in Tables I, II, and III (the data in Tables II and III represent runs with no added buffers and an initial concentration of 0.5 *M* 2-phenylethyl-1-^{14}C *p*-toluenesulfonate in 99.7% acetic acid). Sample size was usually 22 ml of 0.5 *M* 2-phenethyl-1-^{14}C *p*-toluenesulfonate solution. After the appropriate reaction time the ampoules were removed from the constant-temperature bath, cooled in ice, and opened. The contents were diluted with ice water, and the acetic acid was neutralized with a slight excess of sodium carbonate (cold). The basic mixture was extracted with two portions of 100 ml of ether, and the ether solutions were combined, washed with water, and dried. The ether was then removed and the remaining oil was heated with 70 ml of petroleum ether. After cooling, the radioactive 2-phenylethyl *p*-toluenesulfonate which had crystallized was collected by filtration and recrystallized from petroleum ether (bp 30–60°, mp 39–40°), prior to oxidation. The petroleum ether solution (containing the radioactive 2-phenylethyl acetate) from which the tosylate originally crystallized was concentrated and the resulting oil was purified by preparative gas chromatography or by distillation through a short-path column to yield the radioactive 2-phenylethyl acetate, bp 107–108° (12 mm) (lit.[5a] bp 109° at 18 mm), which was oxidized.

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Chemical Synthesis and Structure Proof of a Stereoregular Linear Mannan, Poly-α-(1→6′)-anhydro-D-mannopyranose[1]

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Abstract: Stereoregular poly-α-(1→6′)-anhydro-D-mannopyranose has been synthesized by the phosphorus pentafluoride initiated polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-mannopyranose at −78° in methylene chloride, followed by debenzylation of the polymeric derivative with sodium in liquid ammonia. The polymer, isolated as a hemihydrate, $[\alpha]^{30}\text{D}$ 121.5–122.8° (1% in DMSO), forms cloudy solutions in water and clear solutions in dimethyl sulfoxide. On periodate oxidation, this polymer consumes the theoretical amount of oxidant and produces the theoretical amount of formic acid. After oxidation the optical rotation of both the synthetic mannan and a synthetic stereoregular poly-α-(1→6′)-anhydro-D-glucopyranose are identical. Less stereoregular mannans have been synthesized from the corresponding triacetate and after oxidation show lower positive rotations.

Of all natural polymers, only the polysaccharides must be synthesized by a propagation or stepwise coupling process under complete steric control. Recent publications from this laboratory have described the chemical synthesis of the linear backbone of a bacterial dextran,[2–4] the complete stereoregularity of which has been confirmed independently by enzymic analysis (100% α, ~98% α-(1→6′)).[5] We wish now to demonstrate that the stereoregularity of this polymerization is duplicated with the corresponding mannose derivative in spite of the different configuration of the carbon atom (C_2) adjacent to the reaction site.

The monomer, 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-mannopyranose (mp 60–61°, $[\alpha]^{25}\text{D}$ −31.2–32° (1% in chloroform)), was synthesized *via* conventional benzylation of 1,6-anhydro-β-D-mannopyranose. The latter was prepared by pyrolysis of ivory nut meal[6] and isolated as the triacetate. Polymerization was accomplished using high vacuum technique in methylene chloride at −78° and initiation with 4–25 mol % phosphorus pentafluoride to monomer and 33–66 w/v % monomer to solvent ratios. The polymers produced had intrinsic viscosities in chloroform at 25° of 0.40–2.4 dl/g, proper elementary analyses, and specific rotations of $[\alpha]^{30}\text{D}$ +56–57° (1% in chloroform). An estimate of molecular size from a viscosity–number average molecular weight relationship derived for the corresponding tribenzylglucan[7] suggests that the benzylated mannan may have been prepared at $\overline{DP}_n$ values up to ~1050 or $\overline{M}_n$ values up to 450,000.

The highest viscosities obtained were about six times those previously reported for the glucan derivative,[2,3] and were obtained by taking pains to transfer only phosphorus pentafluoride from the decomposition products of *p*-chlorobenzenediazonium hexafluoro-

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[1] This paper is dedicated to Dr. E. Husemann in honor of her 60th birthday.

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