

Nonbenzenoid Aromatic Systems. IV.¹
 2-(1-Azulyl)ethyl Tosylate Buffered Acetolysis. An
 Exclusive k_{Δ} Process without Ion-Pair Return

Sir:

Ample evidence has recently been reported which demonstrates that two discrete, strongly assisted pathways, k_s (solvent assisted) and k_{Δ} (aryl assisted), compete without crossover in the solvolyses of primary² and secondary³ β -arylalkyl arenesulfonates. We wish to report the results of buffered acetolysis of 2-(1-azulyl)ethyl tosylate (**1a**) and certain derivatives which establish it as an *exclusive* k_{Δ} process *without* the complicating factor of ion-pair return. Preliminary results, to be reported later, indicate that this system will answer several questions about the k_{Δ} pathway and the importance of early *vs.* late transition states in present theory.

2-(1-Azulyl)ethanol was prepared by the method of Anderson.⁴ A number of substituents were introduced into the ring 3 position through electrophilic substitution by established procedures.⁵ Due to the basicity of the azulene nucleus buffered acetic acid was employed as the medium and due to the color of these substrates the kinetics were followed by potentiometric titrations^{6a} or by the conductivity method.^{6b} The rate data and activation parameters for these compounds and for 2-(*p*-anisyl)ethyl (**2**) and 2-phenylethyl tosylates (**3**) under these conditions are given in Table I.

The effect of the 3 substituents as well as the results of α -deuterium scrambling (to be discussed) show that the ionization step (k_1) is indeed rate determining.⁷

(1) (a) For paper III in this series see R. G. Cooks, R. N. McDonald, J. R. Curtis, and H. E. Petty, *Org. Mass Spectrom.*, in press. (b) Presented at the international symposium on "The Chemistry of Nonbenzenoid Aromatic Compounds," Sendai, Japan, Aug 1970.

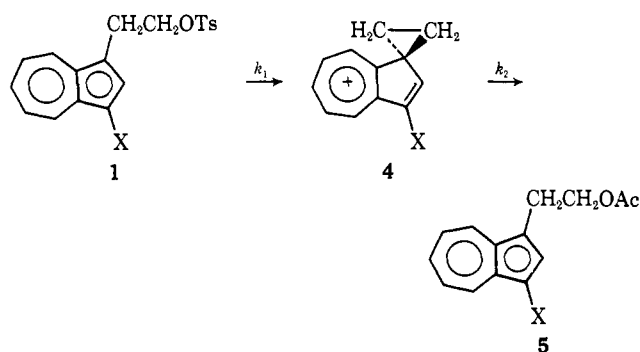
(2) (a) M. D. Bentley and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **92**, 3996 (1970); (b) J. M. Harris, F. L. Schadt, P. v. R. Schleyer, and C. J. Lancelot, *ibid.*, **91**, 7508 (1969); (c) R. J. Jablonski and E. I. Snyder, *ibid.*, **91**, 4445 (1969); (d) M. G. Jones and J. L. Coke, *ibid.*, **91**, 4284 (1969); (e) J. L. Coke, F. E. McFarlane, M. C. Mourning, and M. G. Jones, *ibid.*, **91**, 1154 (1969); (f) A. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 6546 (1968); (g) J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968).

(3) (a) H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92**, 5244 (1970); (b) A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969); (c) C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4291, 4296, 4297 (1969); (d) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *ibid.*, **91**, 4294 (1969); (e) C. J. Kim and H. C. Brown, *ibid.*, **91**, 4287, 4289 (1969); (f) J. A. Thompson and D. J. Cram, *ibid.*, **91**, 1778 (1969); (g) J. E. Nordlander and W. J. Kelley, *ibid.*, **91**, 996 (1969); (h) ref 1g. For references in β -aryl substituents in 2-norbornyl derivatives see ref 3c.

(4) A. G. Anderson, R. G. Anderson, and T. S. Fujita, *J. Org. Chem.*, **27**, 5435 (1962).

(5) The 3 substituents and their methods of substitution are: NO₂, A. G. Anderson, R. Scottoni, E. J. Cowles, and G. Fritz, *J. Org. Chem.*, **22**, 1193 (1957); COCH₃ and Br, A. G. Anderson, J. A. Nelson, and J. J. Tazuma, *J. Amer. Chem. Soc.*, **75**, 4980 (1953); and SCH₃, L. L. Repogle, R. M. Arluck, and J. M. Maynard, *J. Org. Chem.*, **30**, 2715 (1965). All new compounds gave satisfactory elemental analyses with the exception of **1a**. This is undoubtedly due to its high reactivity and relative instability when neat or as the solid TNB complex. The samples of **1a**·TNB used in this study were recrystallized to constant melting point and log ϵ ; infinity titers were 95+ % and the recovery of 2-(1-azulyl)ethyl acetate (**5a**) was 93 %.

(6) (a) A Metrohm E436 potentiograph was used; (b) this method employed the McDonald-Davis Mini-Cell^{8c} coupled to a Beckman RC-18A conductivity bridge; (c) available through Research Products, Inc., Manhattan, Kansas 66502.



- a, X = H
 b, X = NO₂
 c, X = COCH₃
 d, X = Br
 e, X = SCH₃

From the data in Table I, we see that a 3-nitro substituent, **1b**, in the azulene ring has k_t about the same as **2**. As we move down this series, the rate increases to a maximum in **1a** which has a titrimetric rate ratio, k_{1a}/k_3 , of 68,000. These results demonstrate the tremendous participating power of the azulene nucleus.

It is interesting that the ΔS^\ddagger for **1a-1e** are -4 to -10 eu. Although calculated from temperature ranges of only 10° in some cases, such values are consistent with those observed for the k_{Δ} process in 2-arylethyl derivative solvolyses.^{2b,2d,8} In accord with this and the rate accelerations was the observation that **1a-1e** gave no elimination products, but only the primary acetate **5** as the product of acetolysis.

One of our questions at the beginning of this study was how substituent groups at the various nonequivalent positions in **1a** would be correlated in this solvolysis. While poor correlations are obtained for these 3-substituents using σ and σ^+ constants, good correlations results with σ_m° ,⁹ σ_p° ,¹⁰ and σ° ¹¹ constants. One such correlation is shown graphically in Figure 1 using the σ_p° constants¹⁰ with $\rho = -3.60 \pm 0.20$ and a correlation coefficient of 0.995.

It is of interest that this ρ value is the same as that found for the acetolysis of neophyl brosylates, $\rho = -3.745$, using the relationship $\log(k/k_0) = \rho(\sigma^\circ + R\sigma_R^+)$; ¹⁰ with σ^+ constants, neophyl brosylate acetolysis has $\rho^+ = -2.96$ (75°)¹² and the k_{Δ} process in 2-phenylethyl tosylate acetolysis has $\rho^+ = -2.4$ (115°).^{2b} The 10^3 rate acceleration for **1a** compared to neophyl brosylate (extrapolated $k_t = 3.1 \times 10^{-8} \text{ sec}^{-1}$)¹² at 25° is presumably due to the greater polarizability of the π cloud in the five-membered azulene ring,¹³ even though

(7) E. Grovenstein and F. C. Schmalstieg (*J. Amer. Chem. Soc.*, **89**, 5084 (1967)) showed in the iodination of azulene the destruction of the intermediate (k_2) was rate determining.

(8) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956).

(9) P. R. Wells, "Linear Free Energy Relationships," Academic Press, New York, N. Y., 1968, p 15.

(10) Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jap.*, **39**, 2274 (1966).

(11) P. R. Wells, S. Ehrenson, and R. W. Taft, *Progr. Phys. Org. Chem.*, **6**, 147 (1968).

(12) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3432 (1957).

(13) Dewar^{2a} has reported that a plot of the self-polarizability (π_{rr}) *vs.* log relative rate for solvolysis of a number of alternate hydrocarbon

Table I. Buffered Acetolysis Rate Data of 2-Arylethyl *p*-Toluenesulfonates

	Temp, °C	$10^6 k, \text{sec}^{-1}$	$\Delta H, \text{kcal/mol}$	$\Delta S, \text{eu}$
3-NO ₂ -1-AzCH ₂ CH ₂ OTs (1b)	25.0 ^b	(5.4 × 10 ⁻³)		
	70.0	1.36 ± 0.05	24.3 ± 0.6	-10.2 ± 1.7
	90.0	10.2 ± 0.01		
	90.0	9.53 ± 0.03 ^d		
3-COCH ₃ -1-AzCH ₂ CH ₂ OTs (1c)	25.0 ^b	(0.128)		
	50.0	3.16 ± 0.07	23.9 ± 0.4	-5.2 ± 1.2
	70.0	29.5 ± 0.4		
3-Br-1-AzCH ₂ CH ₂ OTs ^c (1d)	25.0 ^b	(0.415)		
	35.0	1.58 ± 0.01	23.7 ± 0.7	-3.7 ± 2.2
	50.0	10.0 ± 0.1		
3-SCH ₃ -1-AzCH ₂ CH ₂ OTs ^c (1e)	25.0	1.95 ± 0.01	21.7 ± 0.2	-7.3 ± 0.8
	35.0	6.61 ± 0.06		
1-AzCH ₂ CH ₂ OTs ^c (1a)	25.0	6.09 ± 0.10	20.5 ± 0.5	-9.2 ± 1.4
	35.0	19.3 ± 0.02		
	35.0	19.4 ± 0.17 ^d		
<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂ CH ₂ OTs ^e (2)	25.0 ^b	(4.9 × 10 ⁻³)		
	75.0	2.01 ± 0.02	24.1 ± 0.5	-11.2 ± 1.3
	95.0	14.1 ± 0.50		
	95.0	11.3 ± 0.12 ^d		
C ₆ H ₅ CH ₂ CH ₂ OTs ^e (3)	25.0 ^b	(9.0 × 10 ⁻³)		
	110.0	0.987 ± 0.001	24.2 ± 0.2	-18.8 ± 0.4
	130.0	5.02 ± 0.01		

^a Rate studies with 0.010 *M* ROTs and 0.012 *M* KOAc. ^b Extrapolated from rates at higher temperatures. ^c Solvolyzed as *sym*-trinitrobenzene complex. Several of the compounds in this table were studied as their *sym*-trinitrobenzene (TNB) complexes. To establish that TNB has no effect on the acetolysis rates, the rate of acetolysis of 1a·TNB was determined in the presence of an additional equivalent of TNB. No change was observed titrimetrically.^{6a} ^d Rate determined conductometrically (0.00123 *M* KOAc and 0.00102 *M* ROTs). ^e Rate studies with 0.005 *M* ROTs and 0.006 *M* KOAc. ^f Rate constants were calculated using a computer program which gives essentially identical results as those from the LSKIN1 program (D. F. DeTar and C. E. DeTar in "Computer Programs for Chemistry," D. F. DeTar, Ed., Vol. I, W. A. Benjamin, New York, N. Y., 1968); the listed errors are those from the average of duplicate runs. ^g Only the titrimetric data were used.

the geometry of the transition state may well be early compared to those of 2, 3, and neophyl considering the stabilities of the respective intermediates.^{15,16}

Such arguments predict a reduced amount of ion-pair return, $(1 - F)k_{\Delta}$, for 1 compared to 2 and 3. We prepared 1a-*l*,*l*-*d*₂ and 1b-*l*,*l*-*d*₂ and subjected each to the buffered acetolysis conditions for one and ten half-lives. The results are summarized in Table II.¹⁷

Table II. Methylene Scrambling in the Buffered Acetolysis of 1a-*l*,*l*-*d*₂ (35.0°) and 1b-*l*,*l*-*d*₂ (90.0°)

Compound	Reaction time (t _{1/2})	Deuterium content ^a		% proton content ^a	
		C _α	C _β	C _α	C _β
1-AzCH ₂ CD ₂ OTs	0	1.68	0.10 ^b		
1-AzCH ₂ CD ₂ OTs	1	1.72	0.06		
1-AzCH ₂ (D ₂)CH ₂ (D ₂)OAc	1			51.1	48.9
1-AzCH ₂ (D ₂)CH ₂ (D ₂)OAc	10			51.5	48.5
3-NO ₂ -1-AzCH ₂ CD ₂ OTs	0	1.81	0.00		
3-NO ₂ -1-AzCH ₂ CD ₂ OTs	1	1.70	0.11		
3-NO ₂ -1-AzCH ₂ (D ₂)CH ₂ (D ₂)OAc	1			48.9	51.1
3-NO ₂ -1-AzCH ₂ (D ₂)CH ₂ (D ₂)OAc	10			49.3	50.7

^a These results are the average of duplicate experiments. The errors are considered to be about ± 1%. ^b This degree of scrambling occurred in preparation of the tosylate ester using the ether-KOH method [K. B. Wiberg and A. J. Ashe, *J. Amer. Chem. Soc.*, **90**, 63 (1968)].

2-arylethyl tosylates accounts for much of the data in these systems. However, he points out that π_{rr} provides "a poor guide to reactivity" in other than alternate hydrocarbons.¹⁴

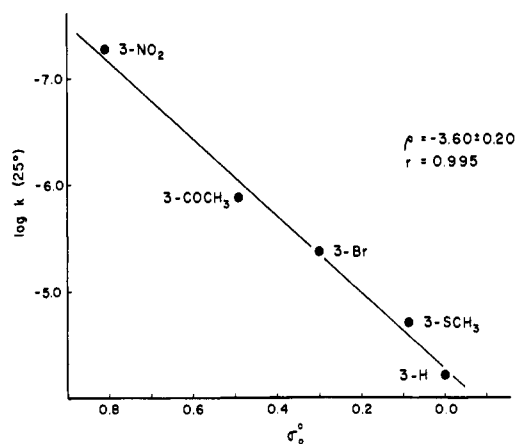
(14) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 363.

(15) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(16) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 175.

(17) A combination of mass and nmr spectroscopy was used to determine the C_α and C_β deuterium contents since both 1a- and 1b-*l*,*l*-*d*₂ rearrange in the mass spectrometer while the corresponding alcohols are stable.¹

From the analysis of the deuterium content at C_α and C_β of the ethyl side chain after one acetolysis half-life we find *no* ion-pair return from 4a to 1a and about 12% for 4b to 1b.¹⁸ Analysis of the product

Figure 1. Hammett plot of buffered acetolysis data of 1a-1e ($\log k$) vs. σ_p^o constants.¹⁰

acetates shows no variation in the results from the one and ten half-life experiments.

(18) These calculated *F* values are considered to be minimum estimates since the concentration of the special salt, KOAc, is constantly being depleted and replaced by the common ion salt KOTs.²⁰ We believe that determination of these values in the presence of such perturbing effects is best accomplished practically at about one solvolytic half-life. This change in direction in the *F* values is opposite to that obtained by Jenny and Winstein²¹ for the acetolysis of 2 in the presence of LiClO₄ where *F* increases with per cent reaction (*F* = 0.26, 0.28, and 0.33 at 10, 13.7, and 38% reaction, respectively) using the equation (per cent reaction)/[per cent reaction + 2(per cent label scramble in recovered tosylate)] = *F*, the relationship used in the present calculations. The increasing *F* for 2 probably reflects the decreasing ratio [ion-pair intermediate]/[LiClO₄] as a function of per cent reaction.

The F values (fraction of ion pairs going to product) for **1a** and **1b** are calculated to be 1.0 and 0.81, respectively, in buffered acetolysis after one $t_{1/2}$ assuming no secondary α -deuterium isotope effect in the reaction of **4b** with solvent.¹⁸ Since the reactivities of **1b** and **2** are nearly the same (Table I), a similarity in their F values would be expected; Coke^{2d} has assigned $F = 0.466 \pm 0.017$ for acetolysis of **2**. This apparent inconsistency is due to a special salt effect by KOAc for **2**¹⁸⁻²¹ which is also believed operating in the buffered acetolysis of **1b**. We believe that this is apparent when the titrimetric and conductometric data for **1a**, **1b**, and **2** (Table I) are compared.²²

From the deuterium scrambling data for **1b** (Table II), the acetate product shows about $2 \pm 1\%$ of the k_s pathway present. On the basis of 2% k_s , we calculate $k_s = 2 \times 10^{-6} \text{ sec}^{-1}$ (90°) under these conditions in good agreement with the value of Coke, $k_s = (3.5 \pm 3.1) \times 10^{-6} \text{ sec}^{-1}$, for **2** at 90° .^{2d} Since k_s has been shown to change little as a function of aryl ring substituent,^{2a,b} we conclude that **1a** and **1c-1e** undergo buffered acetolysis totally by the k_A pathway.

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(19) J. R. Curtis, Ph.D. Thesis, Kansas State University, 1971.

(20) S. Winstein, P. E. Klinedinst, and G. C. Robinson (*J. Amer. Chem. Soc.*, **83**, 885 (1961)) reported special salt effects for tetrabutylammonium acetate and lithium acetate in the acetolysis of 1-anisyl-2-propyl OTs and 3-anisyl-2-butyl OBs, respectively.

(21) Buffered acetolysis of **2-1,1-d₂** (0.010 M ROTs, 0.012 M KOAc) at 95.0° shows $8 \pm 1\%$ label scramble in recovered tosylate and $0 \pm 1\%$ of the k_s pathway after 50% reaction with $F \approx 0.76$. Unbuffered acetolysis of **2-1,1-d₂** showed $35 \pm 1\%$ label scramble in recovered tosylate after 46% reaction at 75.0° ($F \approx 0.40$) and $35 \pm 1\%$ label scramble after 50% reaction at 95.0° . E. F. Jenny and S. Winstein (*Helv. Chim. Acta*, **41**, 807 (1958)) reported that unbuffered acetolysis of **2-1-¹⁴C** (0.050 M ROTs) gave 38% label scramble after 38% reaction ($F = 0.33$) which was reduced to 5% after 49% reaction ($F = 0.83$) by addition of 0.010 M LiClO₄ at 75.0° . The disagreement in the scrambling data from the two methods at 75° in the absence of added salt is not understood.

(22) For **1a** we see the same rate in going from 0.010 M ROTs and 0.012 M KOAc (titrimetric) to 0.0010 M ROTs and 0.0012 M KOAc (conductometric). The same concentration change with **1b** leads to a 6-7% reduction in the rate constant while a smaller concentration change with **2** (0.005 M ROTs and 0.006 M KOAc for titrimetric data) is found to give a larger, $19 \pm 4\%$, rate reduction.²³ This should be reflected in the F values for **1b** and **2** in unbuffered acetolysis, the F for **1b** being larger than that of **2**. The present data allow only the observation that such appears to be the case.

(23) Generally, agreement in rate constants determined by these two methods has been excellent with the conductometric^{6b} k_t about 1% larger than the titrimetric^{6a} k_t in the absence of special effects;²⁴ R. N. McDonald and G. E. Davis, unpublished results.

(24) B. L. Murr and V. J. Shiner (*J. Amer. Chem. Soc.*, **84**, 4672 (1962)) have arrived at a similar conclusion.

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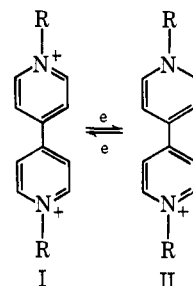
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Electron Transfer to Bipyridilium (Paraquat) Salts

Sir:

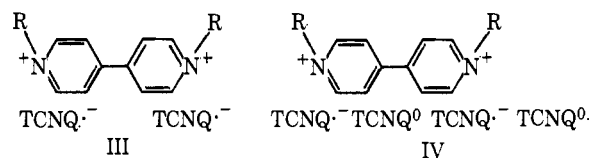
The high electron affinity of 4,4'-bipyridilium (paraquat) salts, well-known herbicides,¹ has been demonstrated already in 1933 by Michaelis and Hill² who have shown that bipyridilium bases can be reduced to form colored species. The colorless bivalent cation accepts an electron to form II, a violet univalent cation, and this process may be represented by the following equilibrium



where R is generally an aryl or alkyl group or a hydrogen atom and the counterion is omitted.

The ease of reduction of paraquat is attributed to its high electron affinity which is also responsible for the formation of a variety of charge-transfer complexes between paraquats and phenols, quinones, hydroquinones, etc.,³⁻⁵ the latter acting as electron donors and the paraquats as electron acceptors.

Bipyridils also form two types of electrically conducting salts when treated under suitable conditions with 7,7,8,8-tetracyanoquinodimethane (TCNQ) or its derivatives. These can be represented by structures III and IV where TCNQ⁻ denotes the radical anion



and TCNQ⁰ the neutral molecule. The TCNQ salts of mono- or polyammonium salts differ from charge-transfer complexes since in the latter an equilibrium is established between the donor, acceptor, and the complex, while in TCNQ salts, an unpaired electron is believed to be delocalized over the domains of TCNQ rings leading to a relatively high electrical conductivity. Structure III is formed by the reaction of two LiTCNQ⁻ molecules with one molecule of I and its specific resistivity is several orders of magnitude higher than the resistivity of structure IV which is formed when two neutral TCNQ molecules are added to III. The dramatic decrease in resistivity is attributed to the enhanced electron transport in the presence of neutral TCNQ and these facts are in agreement with previous results pertaining to a large number of TCNQ salts and their anisotropic conductivity which is highest in the direction perpendicular to the TCNQ rings.^{6,7}

(1) W. R. Boon, *Endeavour*, **26**, 27 (1967).

(2) L. Michaelis and E. S. Hill, *J. Gen. Phys.*, **16**, 859 (1933).

(3) A. J. MacFarlane and R. T. P. Williams, *J. Chem. Soc. A*, 1517 (1969).

(4) B. G. White, *Trans. Faraday Soc.*, **65**, 2000 (1969).

(5) A. Ledwith and H. J. Woods, *J. Chem. Soc.*, 1422 (1970).

(6) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).