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SOLVOLYSIS OF 9-SUBSTITUTED 10-ANTHRANYL SYSTEMS[1a, b]

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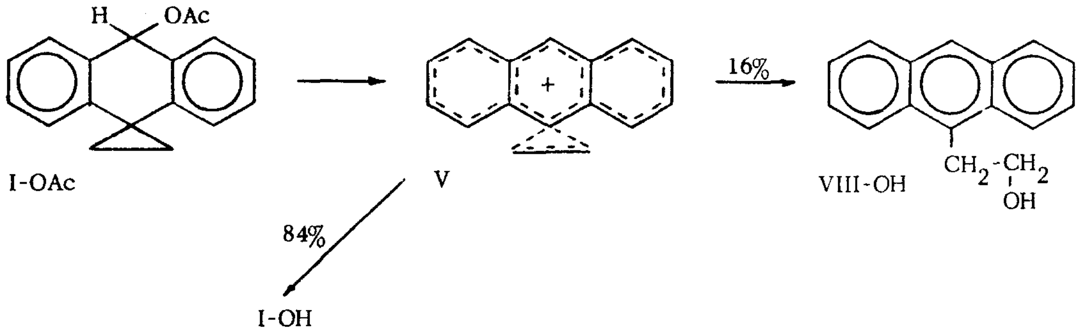
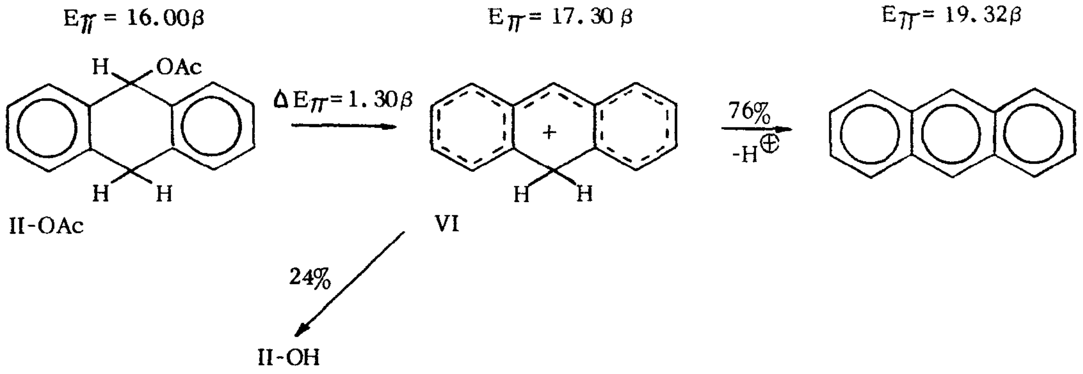
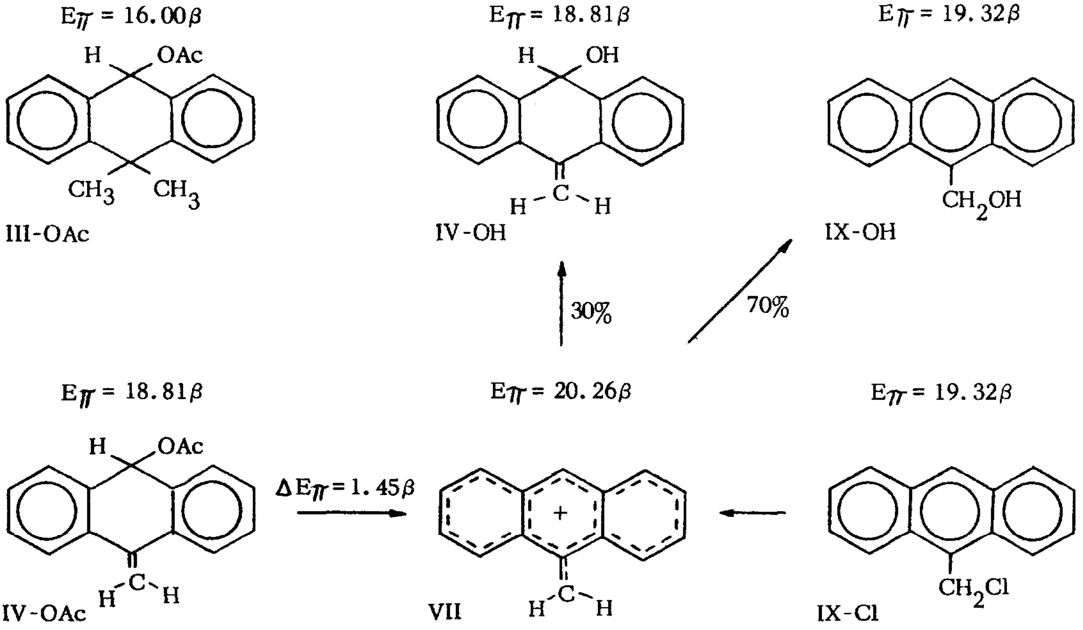
One of the most interesting and instructive 2-aryl-1-ethyl systems is β-(9-anthryl)-ethyl (VIII). In hydrolysis,[2a] kinetic product control from the bridged ion V leads mostly to spiro-alcohol I-OH containing a cyclopropane ring, along with the anthrylethanol VIII-OH. The bridged ion V, which is sufficiently stable for direct observation[2b] by nmr in SO_2-SbF_5, is generated in solvolysis solvents from suitable derivatives of the anthrylethyl (VIII) or spiro-anthranyl (I) types. It appeared to us that data of fundamental importance could be provided by a solvolytic comparison of the spiro-anthranyl system (I) with the three analogs containing two hydrogen atoms (II), two methyl groups (III) or an olefinic methylene group (IV) instead of the spiro-cyclopropane ring. Firstly, solvolysis rates would disclose the relative rate-enhancing effects of spiro-cyclopropane, H_2, $(CH_3)_2$ and methylene groupings on ionization rate. Secondly, in the methylene case (IV), the corresponding carbonium ion is the 9-anthrylmethyl benzyl type cation VII, and it is interesting to compare this cation with the 9-anthrylethyl bridged ion V as regards kinetic and thermodynamic product control. Such a study would provide the simplest example of "9-methyleneanthranyl-9-anthrylmethyl tautomerism" (e.g., X $\rightleftharpoons$ XI). Such tautomerism[3] was known long ago, but it appears to have been virtually forgotten by investigators between 1949 and nearly the present time. Recently, however, Bergson and Flynn[4] have carried out several elegant studies in this field.

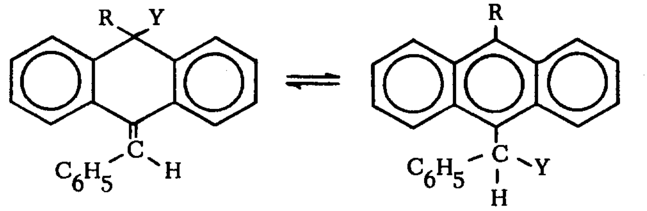

H
OAc
I-OAc
V
16%
VIII-OH
CH_2-CH_2
OH
84%
I-OH


Eπ = 16.00β
Eπ = 17.30 β
Eπ = 19.32β
H
OAc
ΔEπ = 1.30β
76%
-H⊕
H
H
II-OAc
VI
24%
II-OH


Eπ = 16.00β
Eπ = 18.81β
Eπ = 19.32β
H
OAc
H
OH
CH_3
CH_3
III-OAc
H
C
H
IV-OH
CH_2OH
IX-OH
30%
70%
Eπ = 18.81β
Eπ = 20.26β
Eπ = 19.32β
H
OAc
ΔEπ = 1.45β
IV-OAc
VII
CH_2Cl
IX-Cl

Most recently,[4b] they have studied the acid-catalyzed conversion of several substituted 9-methyleneanthranols (X; R = CH_3, C_6H_5; Y = OH) to the corresponding thermodynamically favored anthrylmethyl ethyl ethers (XI; R = CH_3, C_6H_5; Y = OEt) in ethanolic hydrogen chloride solution.[4c]

X



XI

Because of instability and general high reactivity, acetate derivatives were the most reactive esters we could manage and still compare the four systems I-IV with the same leaving group. The anthranyl acetate[5, 6a] II-OAc, mp 80-81°, and the 9,9-dimethylanthranyl analog[5] III-OAc, mp 107°, were prepared from anthranol and 9,9-dimethylanthranol, respectively, using pyridine-acetic anhydride at 0°. The 9,9-dimethylanthranol,[5] mp 79.5-80.5°, was obtained by lithium aluminum hydride reduction of the corresponding ketone. The spiro-anthranyl acetate[5, 6b] I-OAc, mp 62°, and the 9-methyleneanthranyl acetate,[5] mp 89.5-90.5°, were prepared from I-OH and IV-OH, respectively, using pyridine-acetic anhydride[6c] at ca. -20°. The 9-methyleneanthranol IV-OH, mp 96-98° (dec.), was prepared by lithium aluminum hydride reduction[6d] of the known 9-methyleneanthrone.

Satisfactory first order solvolysis rate constants were obtained for the four acetate esters in aqueous acetone solvents, a summary of the data being given in Table I. The products of solvolysis at 25° in 60% acetone (90% acetone in the case of I-OAc), containing added sodium bicarbonate, were collected and analyzed by nmr under conditions shown by control experiments to insure kinetic product control. From the 9,9-dimethylanthranyl ester III-OAc the corresponding anthranol III-OH was obtained. The unsubstituted anthranyl ester II-OAc formed 24% anthranol II-OH and 76% anthracene. From the spiro-acetate I-OAc was observed 84% spiro-alcohol I-OH and 16% anthrylethanol VIII-OH, essentially the same mixture observed previously from solvolysis of VIII-OTs in aqueous dioxane.[2a] The 9-methyleneanthranyl acetate IV-OAc also led to a mixture, 30% of methylene anthranol IV-OH and 70% of the 9-anthrylmethyl alcohol IX-OH. Essentially the same mixture, 28% IV-OH and 72% IX-OH, was observed from solvolysis of the known 9-anthrylmethyl chloride.[7]

TABLE I

Summary of Solvolysis Rates

Acetate	Solvent % Acetone	Temp. °C.	10^5 k (sec.$^{-1}$)	Rel. Rate 25°
I-OAc	90	25.0	113.8 ± 5.6	1150
II-OAc	60	25.0	38.2 ± 0.7	1.00
II-OAc	80	25.0	1.26 ± 0.04	
II-OAc	90	25.0[a]	0.099	
II-OAc	90	50.0	1.56 ± 0.03	
II-OAc	90	75.0	18.46 ± 0.41	
III-OAc	60	25.0	42.3 ± 0.4	1.09
IV-OAc	60	25.0	46.7 ± 0.2	1.22

[a] Extrapolated from data at higher temperatures

The rate data show the spiroanthranyl ester I-OAc to be more reactive than its counterparts II-OAc and III-OAc by three powers of ten.[9] The great rate enhancement due to the cyclopropane ring in I-OAc provides a clear kinetic demonstration of the extensive electron release from the spiro-"cyclopropane" group in phenonium ions. This demonstration is the first of its kind, since this is the first time we have been able to approach kinetically a bridged ion such as V from a structure which already incorporates the cyclopropane ring. The spiroanthranyl I-OAc is also some three powers of ten more reactive than the methylene anthranyl analog IV-OAc, providing another kind of example where the accelerating effect of a cyclopropane ring is greater than that of an olefinic group.[10]

The new information on kinetic product control in solvolysis of I-OAc, II-OAc and IV-OAc provides not only confirmatory evidence[2a] on the behavior of the anthrylethyl bridged ion V, but also completely new evidence regarding partitioning of the anthranyl and 9-anthrylmethyl cations VI and VII during hydrolysis. Thus, the anthranyl ion VI, which loses a 10-proton completely to yield anthracene in thermodynamic control, gives 24% of anthranol II-OH in kinetic control, only 76% of anthracene being formed by proton loss. The anthrylmethyl cation VII, which yields only anthrylmethanol IX-OH in thermodynamic control, yields a mixture of products in kinetic control, 70% from coordination of water at the methyl group cationic center and 30% from water attack at the C_{10}-cationic center. The anthrylmethyl cation, with its relatively low cationic charge at the CH_2^+ carbon atom of the $ArCH_2^+$ system, is obviously favorably disposed towards nucleophilic attack on the Ar group competitive with that at the CH_2^+ carbon. However, more information will be needed about other $ArCH_2^+$ systems before it is clear how best to correlate the partition factors in kinetic product control with various available theoretical parameters.

REFERENCES

1. (a) Research supported in part by the National Science Foundation; (b) Research sponsored in part by the U. S. Army Research Office (Durham); (c) Postdoctoral Fellow of the Fritz-Thyssen Foundation, Köln, Germany, 1965-1966; (d) Contribution # 2033.

2. (a) L. Eberson, J. P. Petrovitch, R. Baird, D. Dyckes and S. Winstein, J. Am. Chem. Soc. 87, 3504 (1965); (b) L. Eberson and S. Winstein, ibid. 87, 3506 (1965).

3. (a) J. W. Cook, J. Chem. Soc. 2798 (1928); (b) P. L. Julian, W. Cole, G. Diemer and J. G. Schafer, J. Am. Chem. Soc. 71, 2058 (1949).

4. (a) K. G. Flynn and G. Bergson, Acta Chem. Scand. 19, 756 (1965); (b) G. Bergson and K. G. Flynn, Arkiv Kemi, in press; (c) Since the reaction was followed by ultraviolet absorption, formation of any 9-methyleneanthranyl ether X by kinetic control was not observed.

5. This and the other indicated new compounds gave satisfactory carbon and hydrogen analyses.

6. (a) Rapid transformation to anthracene occurs on melting; (b) Above the mp, a slow but complete transformation to VIII-OAc, mp 88-90°, occurs; (c) When acetylation of the spiro-alcohol I-OH was performed at 0°, a mixture of I-OAc (80%) and VIII-OAc (20%) was obtained; (d) Under many reaction conditions, the attempted lithium aluminum hydride reduction led mainly to 9-methylanthracene. Using a 1.1 mole proportion of hydride, a very large volume of ether, and a 10 minute reaction period led to good results.

7. Solvolysis of 9-anthrylmethyl chloride (and α-9-anthrylethyl chloride) has been previously studied by several investigators in correlating reactivity of $ArCH_2Cl$ and $ArCHClCH_3$ with quantum mechanical quantities such as ΔE_π of ionization[8] Only 9-anthrylalkanol was observed as product, but no precautions were taken to insure kinetic product control.

8. See A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", John Wiley and Sons, Inc., New York, N.Y., 1961, pp. 367-379, for pertinent references and a good presentation of the rate data.

9. It is interesting to compare this rate ratio with the reported factors of 4 or 9 by which p-cyclopropylcumyl chloride solvolyzes more rapidly than the p-isopropylcumyl analog in aqueous acetone or dioxane. L. B. Jones and V. K. Jones, Tetrahedron Letters No. 14, 1493 (1966); H. C. Brown and J. D. Cleveland, J. Am. Chem. Soc. **88**, 2051 (1966).

10. The simple HMO π-electron energy change accompanying ionization (ΔE_π) is 1.45 β for IV-OAc, slightly greater than the value of 1.30 β for II-OAc and III-OAc. However, the calculated advantage of IV-OAc is apparently balanced by such factors as inductive, hyperconjugative and solvation effects.