

STEREOCHEMICAL REQUIREMENTS FOR THE BETA-DEUTERIUM  
ISOTOPE EFFECT IN THE  $SN^1$  DISPLACEMENT OF VINYL ESTERS

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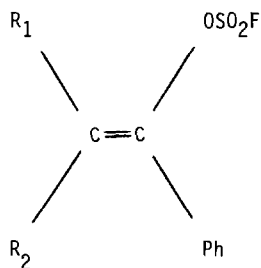
Available evidence<sup>(1)</sup> indicates that under normal  $SN^1$  solvolytic conditions a vinyl cation of linear configuration is the thermodynamically favored intermediate. The stereochemical course of the reaction path from product-forming intermediate to product is thus described. At this time no information is available on the stereochemistry of the first-formed intermediate (be it the same as the product-forming one or not) or of the transition state. Therefore the stereochemical course leading from vinyl reactant to the product-forming intermediate has not been resolved. Examination of this sequence would add much to the basic knowledge and understanding of these interesting, reactive intermediates.

Rate constants involving hyperconjugative effects are quite sensitive to transition state stereochemistry.<sup>(2)</sup> The maximum  $\beta$ -deuterium isotope effect is observed in  $SN^1$  solvolyses of saturated systems when a dihedral angle of  $180^\circ$  is maintained between the developing "p" orbital and the hyperconjugating group. Extrapolating to unsaturated systems, the maximum effect would be expected when a trans periplanar relationship exists between the leaving group and the hyperconjugating group.

$\beta$ -deuterium isotope effects have been reported in  $SN^1$  solvolyses in unsaturated systems<sup>(1)</sup>, but were used only to substantiate the intermediacy of a vinyl cation. In one instance, a positional influence on the isotope effect was found for monodeuterated cis-trans isomers of 1,2-dimethylethenyl triflate<sup>(3)</sup>. However, the difference in the  $\beta$ -isotope effect was attributed to a change in mechanism. Stereochemical requirements for the isotope effect in solvolyses leading to vinyl cations is unknown, and thus the configuration of the transition state can only be a matter of conjecture.

To investigate transition state geometry and its effect on solvolyses of vinyl systems, the  $\beta$ -deuterium isotope effect was measured in a model system, 1-phenylethenyl fluorosulfonate (1a). This compound and the 50:50 mixture of cis-trans monodeuterated fluorosulfonates were prepared

by the addition of fluorosulfuric acid to ethynyl benzene and ethynyl-d-benzene respectively, as previously reported (4) These compounds were subjected to  $S_N1$  acetolysis conditions, which led exclusively to the appropriate 1-phenylethenyl acetates. The reactions were followed by nmr,



1a,  $R_1 = R_2 = H$

b,  $R_1 = D, R_2 = H$

c,  $R_1 = H, R_2 = D$

and the rate data obtained from the peak areas in the vinyl region. This method enabled the determination of the rate constants of the two deuterio-isomers without prior separation of the mixture. The deuterated 1-phenylethenyl fluorosulfonates (5) possessed vinyl signals at 4.45  $\tau$  (s) and 4.63  $\tau$  (d,  $J = 1.0\text{Hz}$ ). The product acetates (cis-trans deuterio-isomers) exhibited vinyl signals at 4.63  $\tau$  (s) and 5.13  $\tau$  (s). Integration of the vinyl region made it possible to determine the relative amounts of the fluorosulfonates at any time during the reaction. Overlap of reactant and product peaks at 4.63  $\tau$  in no way hindered kinetic determinations, since the relative amount of fluorosulfonate remaining was given by dividing the respective fluorosulfonate vinyl peak area by one-half of the sum total of all vinyl peak areas. This analysis depended upon production of equimolar amounts of the two monodeuterated 1-phenylethenyl acetates, which was demonstrated by allowing the reaction to proceed for approximately one half-life, further reaction after addition of an equal volume of water to remove unreacted fluorosulfonate, and finally, nmr analysis of the vinyl peak area of the two acetates on a carbon tetrachloride extract.

The kinetic data on the three vinyl fluorosulfonates are reported in Table I. A substantial difference in the  $\beta$ -deuterium isotope effect between the two deuterio-isomers is observed. The rate constants for compound 1b and 1c may be designated as  $k_{D-cis}$  and  $k_{D-trans}$  respectively. Similar to saturated systems, it is apparent that a trans periplanar relationship is required for the maximum isotope effect to be observed. The low  $k_H/k_{D-cis}$  value ( $1.10 \pm 0.02$ ) for 1b and the

large  $k_H/k_{D-trans}$  value ( $1.57 \pm 0.07$ ) for 1c argues for a bent transition state. However, the

Table I.

Rate Constants for Acetolyses of 1-Phenylethenyl  
Fluorosulfonates <sup>a</sup>

Compd	$k \times 10^5, \text{sec}^{-1b,c}$	$k_{1a}/k$
1a	$8.43 \pm 0.33$	1
1b	$7.70 \pm 0.14$	$1.10 \pm 0.02$
1c	$5.38 \pm 0.27$	$1.57 \pm 0.07$

a Conditions for acetolysis were 52 °C, about 0.3 M in ester, and buffered with slight excess of sodium acetate. b Acetolysis kinetics followed by nmr. c At least three determinations for each rate constant.

observation of a  $k_H/k_{D-cis}$  value larger than unity may indicate some movement in the transition state in the direction of linear structure. The extent of this movement cannot be evaluated from these data, since it is not certain deuterium incorporation in the cis position would require movement in the direction of linearity to exert an isotope effect.

#### References

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- 3 P. J. Stang and R. H. Summerville, J. Amer. Chem. Soc., **91**, 4600 (1969).
- 4 W. M. Jones and D. D. Maness, ibid., **92**, 5457 (1970)
- 5 The stereochemistry of the deuterated fluorosulfonates was assigned by the chemical shift values in comparison to vinyl triflates reported in reference 6. The acetolysis rate constants supported this assignment.
- 6 R. H. Summerville and P. v. R. Schleyer, J. Amer. Chem. Soc., **94**, 3629 (1972)