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Correlation of Rates of Solvolysis of 2-Tricyclo[3.3.0.0^{3,7}]octyl Tosylate with the 2-Aryl p-Nitrobenzoates. Evidence for the Absence of Anchimeric Assistance

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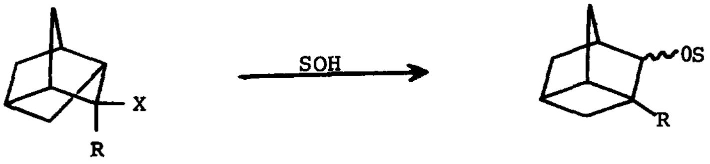
The 2-tricyclo[3.3.0.0^{3,7}]octyl system, **1**, undergoes solvolysis to give rearranged product, the 2-tricyclo[3.2.1.0^{3,6}] octyl system, **2**.[1]



1 **2**

It has been postulated that the secondary derivatives (**1**, R=H) solvolyze with anchimeric assistance.[1] The exact amount of assistance has been difficult to determine because of the lack of a suitable model system which solvolyzes without participation.[2]

Indeed, Sauers and O'Hara have concluded from the solvolysis of the tertiary aryl p-nitrobenzoates (**1**; R = aryl, X = OPNB) that the tertiary derivatives do not ionize with σ participation to form rearranged cations, but that their results were more consistantly interpreted in terms of formation of unrearranged tertiary cations which subsequently may rearrange.[3] Moreover, they suggest that their findings indicate that the estimated anchimeric assistance for the secondary system is in error.[3] Thus, the significance of anchimeric assistance in **1** is uncertain.

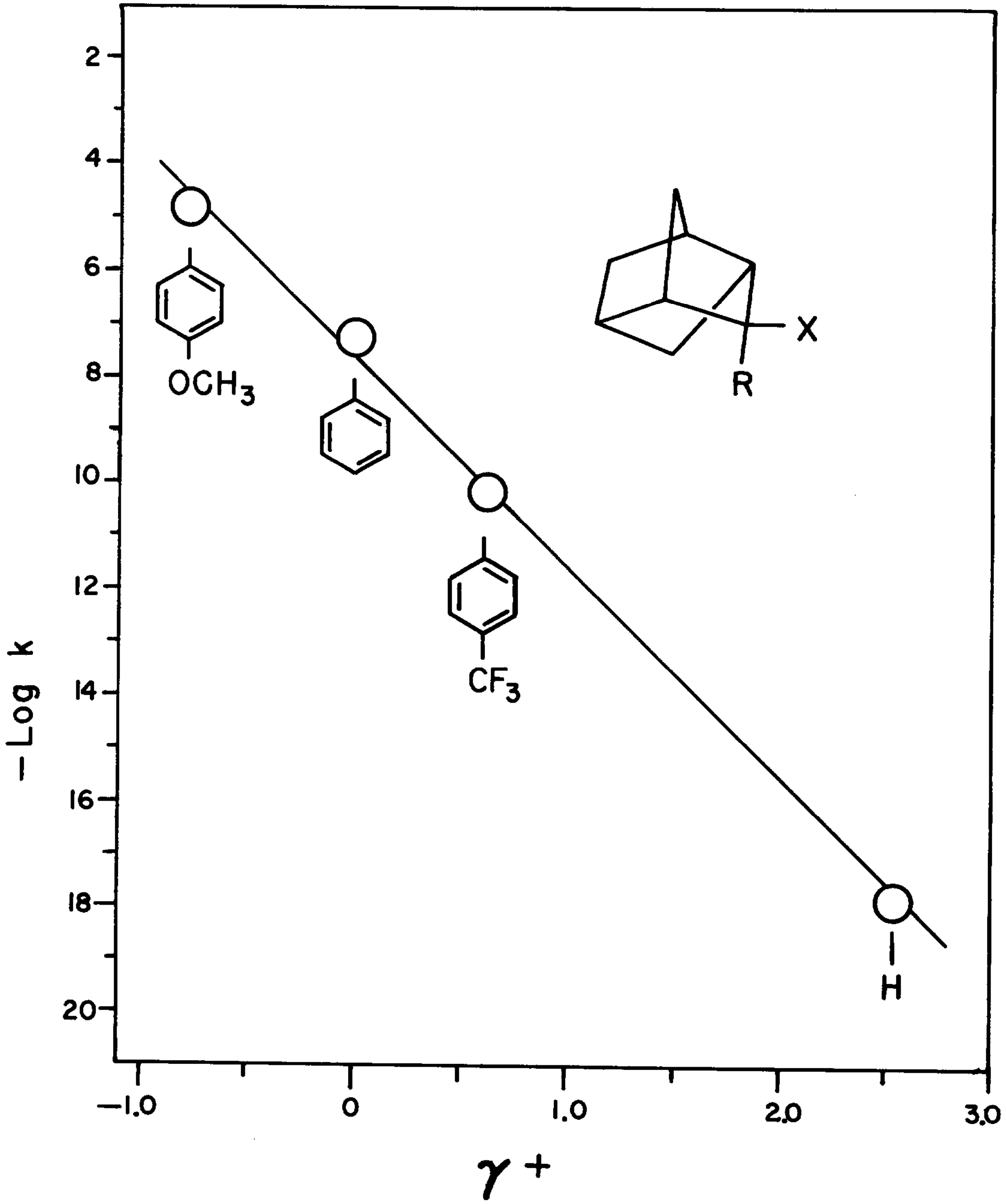
However, the $\rho\gamma^+$ relationship (1) has been recently applied to the elucidation of anchimeric assistance in various systems and was shown to be valuable in evaluating neighboring group effects.[4] The $\rho\gamma^+$ relationship permits the direct correlation of the rates of acetolysis of secondary tosylates with their corresponding tertiary benzylic derivatives.

$$\log \frac{k}{k_o} = \rho\gamma^+ \qquad (1)$$

The versatility of the $\rho\gamma^+$ relationship was shown in correlating rates of numerous tertiary benzylic chlorides and *p*-nitrobenzoates with the rate of acetolysis of the corresponding secondary tosylate. Indeed, the $\rho\gamma^+$ relationship is useful in elucidating both π and σ participation. For example,. with this technique rate enhancements as low as 18 can be assigned to anchimeric assistance in 2-*exo*-norbornenyl tosylate.[4] Therefore, this technique was applied to **1**. The results appear in Figure 1.

The rates of the tertiary aryl *p*-nitrobenzoates (**1**; R = aryl, X = OPNB) in 90% acetone at 25° were reported by Sauers and O'Hara.[3] The rate of acetolysis at 25° for the secondary tosylate (**1**; R = H, X = OTs), 1.19×10^{-7} $\sec^{-1}$,[5] was corrected to the rate of a *p*-nitrobenzoate in 90% acetone by multiplying the rate of acetolysis by 1.3×10^{-18} to give 1.54×10^{-11} $\sec^{-1}$.[6] The $\rho\gamma^+$ plot is shown in Figure 1.

FIGURE 1



The $\rho\gamma^+$ Relationship for the 2-tricyclo[3.3.0.0^{3,7}]octyl system

An excellent linear correlation was obtained with a rho of -4.00 (correlation coefficient 0.998). Clearly these results give no indication of any significant amount of anchimeric assistance in the secondary derivative. Thus, the formation of rearranged product, **2**, must occur after the rate determining step.

References and Notes

(1) (a) P. K. Freeman, R. B. Kinnel, and T. D. Ziebarth, Tetrahedron Let., 1059 (1970). (b) R. R. Sauers and B. R. Sickles, ibid., 1067 (1970).

(2) For a discussion on the importance of a suitable reference system see H. C. Brown and E. N. Peters, J. Am. Chem. Soc., **97**, 1927 (1975).

(3) R. R. Sauers and E. M. O'Hara, J. Am. Chem. Soc., **96**, 2510 (1974).

(4) E. N. Peters, J. Am. Chem. Soc., **98**, 5627 (1976).

(5) Rate at 25° was calculated from literature data: R. R. Sauers, K. W. Kelly, and B. R. Sickles, J. Org. Chem., **37**, 537 (1972).

(6) Correction factor was determined experimentally by P. G. Gassman and A. F. Fentiman, Jr., J. Am. Chem. Soc., **92**, 2549 (1970).