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Neighboring Group Participation in Solvolysis
of Organosulfur and Related Compounds

FINAL REPORT

Ernest L. Eliel, Ph.D.

August 31, 1985

U. S. ARMY RESEARCH OFFICE

DAAG29-82-R0184

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Neighboring Group Participation in Solvolysis
of Organosulfur and Related Compounds

Duration of project: September 1, 1982 - August 31, 1985

Personnel: 1) David E. Knox, graduate research associate, September 1, 1982 - August 10, 1984, full time. Mr. Knox earned his Ph.D. degree in August, 1984 through the research undertaken under the auspices of the Contract. He is now employed by Union Carbide Corporation, Bound Brook, NJ.

2) Ernest L. Eliel, Ph.D., W. R. Kenan, Jr. Professor, September 1, 1982 - August 31, 1985, part time.

3) Joy Carter, Secretary, September 1, 1982 - August 31, 1985, part time.

Publications: 1) "Neighboring Group Participation by Sulfur Involving Four-Membered-Ring Intermediates (RS-4)" Ernest L. Eliel and David E. Knox, J. Am. Chem. Soc., 107, 2964 - 2952 (1985).

2) "Neighboring Group Participation by Oxygen in the Solvolysis of Acyclic γ -Alkoxy Substituted *p*-Toluenesulfonates, Ernest L. Eliel, Leigh Clawson and David E. Knox, J. Org. Chem., 50, 2707 - 2711 (1985).

3) (in part) Rotational Conformation of the Phenyl Moiety in Geminally Substituted Phenylcyclohexanes with Equatorial Phenyl, Derek J. Hodgson, U. Rychlewska, Ernest L. Eliel, Muthiah Manoharan, David E. Knox and Edward M. Olefirowicz, J. Org. Chem., in press.

4) Solvolytic Displacement Reactions Involving the Formation

of Four-Membered Rings, David E. Knox, Ph.D. Dissertation,
University of North Carolina, Chapel Hill, NC 1984, viii +
155 pp.

No technical reports have been submitted.

Problem: Preliminary work [E. L. Eliel, W. H. Pearson, L. M. Jewell,
A. G. Abatjoglou, *Tetrahedron Letters*, 21, 331 (1980)] had
suggested that, whereas no neighboring group participation occurs
in the solvolysis of simple 3-thioalkyl or thioaryl substituted *p*-
toluenesulfonates, $\text{RSCH}_2\text{CH}_2\text{CH}_2\text{OTs}$, the situation is otherwise when
there are methyl substituents on the three-carbon chain intervening
between the tosylate and sulfur functions. Apparently a Thorpe-
Ingold effect in that case facilitates formation of a four-membered
ring intermediate (thietanium salt), as evidenced by the partial
or complete formation of rearranged products (Scheme 1).



Scheme 1

The purpose of the project was to determine the scope of this reaction,
to confirm the mechanism, to determine whether anchimeric assistance (rate
acceleration) occurs as well as rearrangement and to determine if oxygen can
participate in the same way as sulfur.

Summary of Results:

A- Sulfur compounds

- 1) It was verified that the methanolysis of not only 1- or 3- and 3,3-substituted but also that of 2- and 2,2-substituted tosylates (methyl substituent) of the type shown in Scheme 1 proceeds with partial or complete rearrangement. Although all efforts to isolate or prepare the thietanonium intermediate shown in Scheme 1 failed, there is little doubt that this intermediate does intervene in the reaction. Most of these experiments were carried out with R = benzyl.
- 2) Kinetic studies showed that the reaction involves rate acceleration relative to sulfur-free models. Thus there is anchimeric assistance as well as neighboring group participation (rearrangement).
- 3) When the substituent in position 3 is isopropyl or tert-butyl, rate acceleration (anchimeric assistance) is seen but no rearrangement. An ethyl substituent also induces anchimeric assistance, with some rearrangement (but less than with methyl). These results are explained on the basis of the partitioning of the thietanonium intermediate between the two possible (rearranged or unrearranged) products (cf. Scheme 1). Anchimeric assistance without rearrangement implies formation of the intermediate followed by return to unrearranged product.
- 4) When the substituent on sulfur (R in Scheme 1) is aryl or p-substituted aryl, there is less anchimeric assistance and rearrangement than when R = benzyl. The more electron-withdrawing the para substituent on the aryl group, the less neighboring group participation is seen and a very good correlation of k_{Δ} , the rate constant for the anchimerically assisted process, with σ^+ is found. The cases for R = n-butyl, sec-

butyl, tert-butyl were also studied; there is no systematic effect of group size, i.e. no palpable steric effect in R.

- 5) Anchimeric assistance may be substantially enhanced by solvent and salt effects. Thus more rearrangement is seen in aqueous methanol compared to dry methanol and considerably more rearrangement occurs in trifluoroethanol, $\text{CF}_3\text{CH}_2\text{OH}$, than in methanol, to the extent that even the straight-chain compound $\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{CH}_2\text{CD}_2\text{OTs}$ (the deuterium serves as a marker to manifest formation of a rearranged product) solvolyzes with 43% rearrangement signaling that 86% of the reaction proceeds via the thietanonium intermediate (Scheme 1). Enhanced rearrangement is also seen in methanol solvent in the presence of 0.1M lithium perchlorate (salt effect).

B - Oxygen Compounds

- 1) Neighboring group participation in the oxygen analogs of the above sulfur compounds, RO-C-C-C-OTs , is considerably more restricted than in the sulfur series. Only compounds with at least two geminal methyl substituents (at the 2- or 3-position) in the carbon chain show any evidence of rearrangement.
- 2) There is no evidence of anchimeric assistance (rate acceleration); i.e. the oxygen atom does not participate in the transition state or, if it participates, there is no effect on rate.
- 3) Salt effects (addition of lithium perchlorate) enhance the extent of rearrangement but still do not lead to rate enhancement.
- 4) The substrates needed for this study were prepared by novel applications of the solvomercuration - borohydride reduction sequence.

C - MM2 Calculations

It was hoped that the extent of neighboring group participation might be calculated in advance of experiment by the MM2 force field approach.

Unfortunately this did not prove feasible. However, in the attempt Mr. Knox acquired considerable expertise in the use of MM2 and became our internal consultant in this area. This explains his coauthorship of some work not directly related to the ARO-D project (publication #3).

Concluding Remarks

The objective proposed in the proposal for the contract, namely to explore in detail participation of sulfur (and, in less detail, that of oxygen) in solvolysis reactions via four-membered cyclic intermediates, has been achieved. In the process some potentially interesting observations concerning solvent and salt effects in these reactions have been recorded.