Tetrahedron Letters No. 5, pp. 339-342, 1963. Pergamon Press Ltd.
Printed in Great Britain.

σ-CARBON PARTICIPATION IN THE SOLVOLYSIS OF ORGANOMERCURIALS

Frederick R. Jensen, Robert J. Ouellette,
Gale Knutson and Donald A. Babbe
Department of Chemistry, University of California
Berkeley 4, California

(Received 21 November 1962)

THE rates of solvolysis of organomercurials are exceedingly sensitive to changes in structure,[1] and this reaction provides a dramatic way of demonstrating anchimeric assistance.

$$RHg^{+}Y^{-} \longrightarrow R^{+} + Hg^{\circ} + Y^{-}$$

Thus, the rates of reaction are greatly enhanced by phenyl participation in phenethyl derivatives.[2] The present paper is concerned primarily with σ-carbon participation in the solvolysis of organomercuric perchlorates, but other important aspects of the reaction are also included.

The rates of reaction of certain cyclic and bicyclic alkylmercuric perchlorates in acetic acid (containing a small amount of water) are given in Table I. In the case of exo-norbornyl, it was not found possible to quench this very fast reaction when the alkylmercuric perchlorate was

---

[1] F. R. Jensen and R. J. Ouellette, J. Am. Chem. Soc. **83**, 4777, 4778 (1961).

[2] Unpublished work.

fully formed, and, instead, the reaction was carried out under pseudo-zero order conditions.[1]

TABLE I

The Rates of Solvolysis of Selected Organomercurials in Acetic Acid at 25°

Compound	$k_1 \times 10^5$ $sec.^{-1}$	Relative Rate
Cyclopentyl	49.5	1
trans-4-*t*-Butylcyclohexyl	3.99	0.081 (equatorial)
cis-4-*t*-Butylcyclohexyl	79.6	1.61 (axial)
trans-4-Methylcyclohexyl	7.46	0.151
cis-4-Methylcyclohexyl	75.9	1.53
Cyclohexyl	40.8	0.82
endo-Norbornyl	1.66	0.0335
exo-Norbornyl	2700	54.5

The effect of ring size and conformation in the cyclopentyl and cyclohexyl compounds is dramatic. Assuming for the cyclohexyl compounds that the *t*-butyl group fixes the conformation and that the alkyl groups contribute in no other way to the observed rates of reaction,[3] the relative rates for *cis*- and *trans*-4-*t*-butylcyclohexylmercuric perchlorates give $k_{axial}/k_{equatorial} = 20$, the corresponding value for tosylates is about 3.5.[3] Cyclopentyl is 12 times as reactive as equatorial cyclohexyl but slightly slower than axial cyclohexyl. Using similar consideration, the

---

[3] S. Winstein and N. J. Holness, *J. Am. Chem. Soc.* **77**, 5562 (1955).

A-value for methyl is calculated as 1.8 kcal./mole, in excellent agreement with previous values.[4] More interestingly, the A-value for mercuronium ($-Hg^+$) is calculated as 0.0; previously, it has been shown that the conformational preference of bromomercuri (-HgBr) is also ∿0.[5]

Since minor changes in structure in cyclohexyl and cyclopentyl derivatives are reflected in substantial rate differences, even greater changes in rate should be expected for exo- and endo-norbornyl derivatives.

Endo-norbornylmercuric perchlorate undergoes reaction at 1/30 the rate of cyclopentyl and about 1/2 the rate of equatorial cyclohexyl. The observed changes in rate are thus greater between cyclopentyl and equatorial cyclohexyl than for endo-norbornyl and equatorial cyclohexyl.

On the other hand, exo-norbornylmercuric perchlorate undergoes reaction 54 times faster than cyclopentyl but 1600 times faster than endo-norbornyl. By comparison, exo-norbornyl brosylate undergoes solvolysis 15.8 times faster than cyclopentyl and 350 times faster than endo-norbornyl.[6]

The experimental methods have been described previously.[1] A number of runs were made at the indicated temperatures and the values were reproducible to about ±2% except for exo-norbornyl where the reproducibility was about ±4%. Melting

---

[4] F. R. Jensen and L. H. Gale, J. Org. Chem. **25**, 2075 (1960).

[5] F. R. Jensen and L. H. Gale, J. Am. Chem. Soc. **81**, 6337 (1959).

[6] A. Streitwieser, Jr., Chem. Revs. **56**, 698 (1956).

points of the new alkylmercuric acetates are as follows:[7] cyclopentyl, 53.3-53.8°; trans-4-t-butylcyclohexyl, 127.0-127.6°; cis-4-t-butylcyclohexyl, 89.6-90.2°; endo-norbornyl,[8] 70.4-71.0°; and exo-norbornyl,[9] 110.0-110.8°. The structures of the t-butylcyclohexyl and norbornylmercury compounds were proven through the stereospecific cleavage by bromine in pyridine[9] to the corresponding alkyl bromides.

This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society.

---

[7] Satisfactory elemental analysis were obtained for each of the compounds.

[8] We are indebted to Raymond Owyang for the preparation of the corresponding bromides.

[9] F. R. Jensen and L. H. Gale, J. Am. Chem. Soc. **81** 1261 (1959).