Tetrahedron Letters No.4, pp. 397-399, 1968. Pergamon Press. Printed in Great Britain.

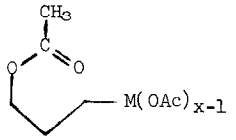
1,3-ACETOXYL PARTICIPATION IN THE SOLVOLYSIS OF ORGANOMERCURY COMPOUNDS (1)

Robert J. Ouellette and Richard D. Robins

Chemistry Department
The Ohio State University
Columbus, Ohio 43210

(Received in USA 2 October 1967)

In a report on the stereochemistry and direction of cleavage of bicyclo[n.1.0]alkanes by lead tetraacetate and thallium triacetate (2), we suggested that 1,3-acetoxyl participation in the decomposition of the intermediate organometallic derivatives of the general structure I might be important.



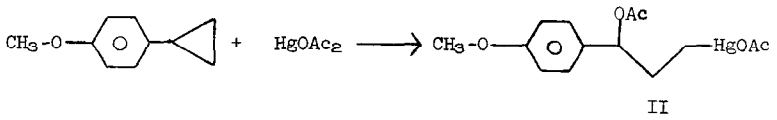
I

Such a 1,3-acetoxonium ion intermediate derived from the solvolysis of the carbon-metal bond seemed to be the most likely model with which to account for the observed stereochemistry in the two step oxidative cleavage mechanism proposed. However, while the analogy between 1,2-acetoxyl and 1,3-acetoxyl participation was considered a reasonable one, there was little independent experimental evidence that the latter had been observed previously (3).

In order to elucidate the decomposition pathway of the γ-acetoxyl organometallic intermediates obtained in the cleavage of cyclopropanes by metal salts, it was determined to seek kinetic evidence for 1,3-acetoxonium ions. The net stereochemical consequences of the two step cleavage-oxidation pathway suggested could be interpreted by combination of steps other than those proposed. To date we have been unsuccessful in our attempts to isolate the

postulated organolead and organothallium derivatives of the cleavage reaction by lead tetraacetate and thallium triacetate. Therefore we turned to the corresponding mercuric acetate adducts.

The adduct II of p-methoxyphenylcyclopropane and mercuric acetate was isolated in 94% yield from the reaction in acetic acid.

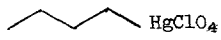
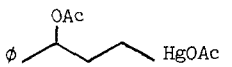
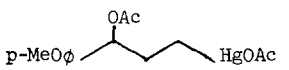


II

The structure of the compound was confirmed by elemental analysis, nmr and reduction with sodium borohydride to 1-(p-anisyl)-propyl acetate. Similarly the adduct of phenylcyclopropane and mercuric acetate was prepared and its structure confirmed by elemental analysis and nmr spectroscopy. For comparative purposes, butyl mercuric acetate and 3-phenylpropylmercuric acetate were prepared by conventional means.

The rates of solvolysis of the three acetates at 135° and two perchlorates at 100° in acetic acid are listed in Table I.

TABLE I

Compound	k(sec^{-1})	T(°C)
	4.8×10^{-5}	102°
	2.4×10^{-5}	101°
	4.7×10^{-8}	135°
	8.6×10^{-7}	135°
	4.4×10^{-4}	135°

That butylmercuric perchlorate solvolyzes at a faster rate than 3-phenylpropylmercuric perchlorate indicates that aryl participation is not important. This conclusion was arrived at by Winstein (4) when he observed that Ar_1-4 ''participations compete very poorly in solvolysis of ω-aryl-1-alkyl arylsulfonates in acetic or formic acid solvents.''

The 3-phenyl-3-acetoxypropylmercuric acetate solvolyzes 18 times faster than does 3-phenylpropyl mercuric acetate. This rate acceleration suggests that 1,3-acetoxyl participation is important in the solvolysis of the primary mercuric acetate derivatives. Furthermore, an additional 510 fold rate increase for 3-(p-anisyl)-3-acetoxypropyl mercuric acetate over the analogous phenyl derivative substantiates the existence of a 1,3-acetoxyl intermediate. Such a rate enhancement corresponds to ρ=-3.6 at 135° if a σ^+ correlation is applicable. Clearly the development of a substantial positive charge at the benzylic carbon atom in the transition state necessitates the formation of a structure in which the acetoxyl group is bridged from the benzyl to primary position. The sole organic product observed in the solvolysis of 3-phenyl-3-acetoxypropylmercuric acetate is cinnamyl acetate.

REFERENCES

1) The authors acknowledge the support of Grant GP-3873 from The National Science Foundation.

2) R. J. Ouellette, A. South, Jr. and D. L. Shaw, J. Am. Chem. Soc., 87, 2602 (1965).

3) L. J. Dolby and M. J. Schwarz, J. Org. Chem., 30, 3581 (1965).

4) R. Heck and S. Winstein, J. Am. Chem. Soc., 79, 3105 (1957).