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# MECHANISMS OF SOLVOLYSIS OF *N,N*-BIS(HALOGENOMETHYLDIMETHYLSILYL)ACETAMIDES

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## Summary

The previously reported unusual course of the reactions of the compounds $MeCON(SiMe_2CH_2X)_2$ (X = Cl or Br) with methanol or water is suggested to involve neighbouring group participation.

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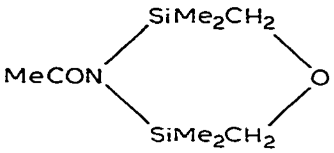
## Introduction

Two of us recently reported that the *N,N*-bis(halogenomethyldimethylsilyl)-acetamides (I) on treatment with water or methanol underwent very ready replacement of halogen rather than the expected cleavage of Si—N bonds, to give the products II and III [1]. We now offer an explanation of this behaviour.

$MeCON(SiMe_2CH_2X)_2$

(I) (X = Cl or Br)



(II)

$MeCON(SiMe_2CH_2OMe)_2$

(III)

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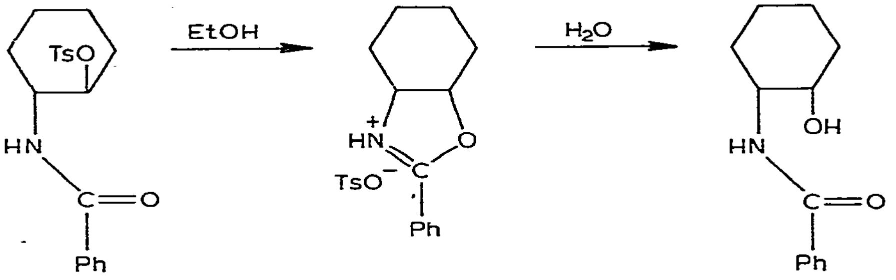
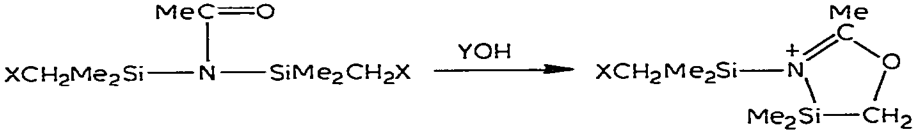
## Discussion

One of the early items of evidence presented by Winstein and his co-workers for the existence of neighbouring group participation concerned the cyclohexyl tosylate IV, which in ethanol was rapidly converted into the oxazolinium salt V, which could be isolated, or hydrolysed to the alcohol VI [2].



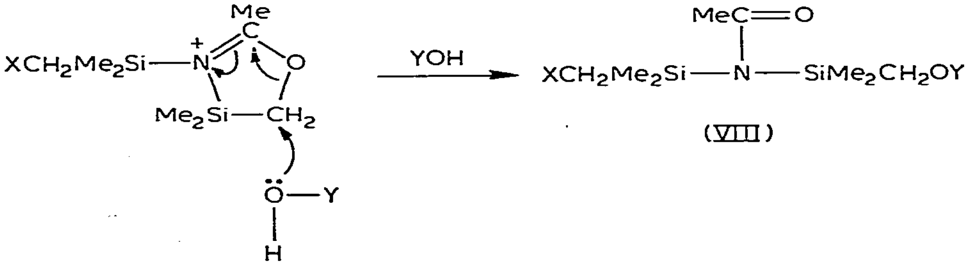
(IV) (V) (VI)

By analogy we suggest that compounds I react with water or methanol (YOH, with Y = H or Me) by the following route:



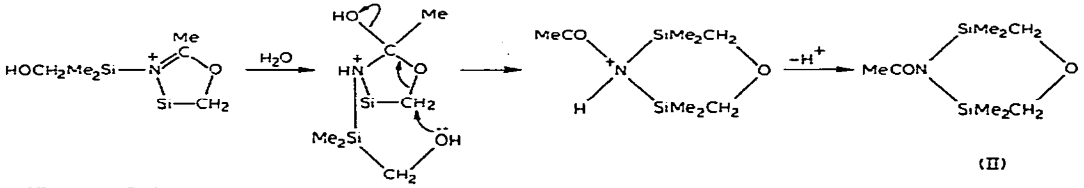
(I) (X = Cl or Br)

(VII)



(VIII)

The remaining halogen in VIII could then be similarly displaced to give the product $MeCON(SiMe_2CH_2OY)_2$. With Y = H, the cyclic ether II could then be formed by loss of a molecule of water. However, there is no obvious reason why this cyclization should occur so readily, and an attractive alternative route to II involves further neighbouring group participation, as follows:

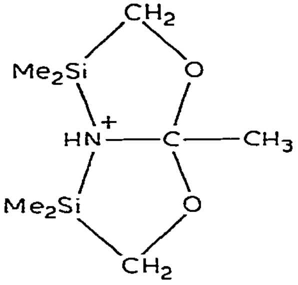


(VIIc. X = OH)

(IX)

(II)

The addition of water to the N=C bond of VIIa is necessary for this process because the geometry of VIIa itself precludes approach of the hydroxyl group of the $SiCH_2OH$ entity to the rear of the $CH_2$—O bond. Intramolecular addition of the OH group to the C=N bond of VIIa would also be expected, to give X; it is possible that X is, indeed, formed reversibly, and disappears as the cyclic ether II is produced.



(X)

The unexpectedly low reactivity of the Si—N bonds of the products II and III is a residual, quite separate, problem, which is receiving attention in the Institute of Polymers, Technical University, Łódź.

## Acknowledgement

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## References

1 J. Kowalski and Z. Lasocki, J. Organometal. Chem., 116 (1976) 75.
2 S. Winstein and R. Boschan, J. Amer. Chem. Soc., 72 (1950) 4669.