Tetrahedron Letters No. 47, pp 4515 - 4516, 1971. Pergamon Press. Printed in Great Britain.

PROPERTIES AND REACTIONS OF 1,3-OXATHIANES - IV: THE DIFFERENCE IN THE CONFORMATIONAL ENERGIES OF AXIAL METHYL GROUPS IN POSITIONS 4 AND 6

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(Received in UK 11 October 1971; accepted for publication 21 October 1971)

Conformational effects in 1,3-dioxans and 1,3-dithianes have been recently largely elucidated.[1-6] That is why we started a systematic study of alkyl-substituted 1,3-oxathianes to compare their conformational features with those of their above-mentioned symmetric analogs.

GELAN and ANTEUNIS[7] investigated the equilibrium between the conformational isomers of trans-4,6-dimethyl-1,3-oxathiane with the aid of coupling constants. They came to the result that the conformation with an axial 4-methyl group is about 1.1 kcal/mol more stable than that with an axial 6-methyl group (Fig. 1; R = H). Nearly the same energy difference is obtainable using the difference between the respective interactions in 1,3-dioxan and 1,3-dithiane (2.9 - 1.7 = 1.2 kcal/mol).[2,6]

However, in a paper presented at the Brussels International Symposium (1969) ANTEUNIS[8] presented an "improved" chemical shift method to evaluate thermodynamic quantities for conformational equilibria. In this connection he argued against the above result and explained that coupling constants lead to an erroneous value. Accordingly, he presented following thermodynamic parameters for the equilibrium discussed above:

$-\Delta H^o$, kcal/mol 0.51; ΔS^o, cal/mol degree 3.7; $-\Delta G^o$, kcal/mol 1.6

In our opinion entropy differences around 4 entropy units are high enough to suggest that the more stable (!) conformation should be in a flexible form. This is a paradox because now also the less stable conformation should inevitably exist in a flexible form and consequently, the entropy difference should be very small.

That is why we undertook the equilibration of cis-2-r-4-trans-6- and trans-2-r-4-trans-6-trimethyl-1,3-oxathianes (Fig. 1; R=CH_3) at various temperatures.

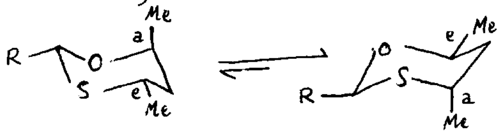

Figure 1. R = H or CH_3.

$-\Delta H^o$ 1143 ± 22 cal/mol

ΔS^o 0.04 ± 0.07 cal/mol degree

The result (Fig. 1) agrees closely with that of GELAN and ANTEUNIS[7] and with the value obtained by comparison with the corresponding 1,3-dioxans and 1,3-dithianes but deviates greatly from the result of ANTEUNIS[8] based on the chemical shifts.

Of course, chemical shift method may also be successful[10-12] but our proposal is that when a chemical shift method is applied to determine conformational energies it might be better to use some independent method to test the derived conclusions. Even in the case of coupling constant calculations we prefer to determine conformational effects by some other method, too.[3,5,9]

A full analysis of the 1,3-oxathiane series will be published in near future but we wished to communicate the above discussion to throw light on the possible disadvantages in the use of proton chemical shifts for evaluation of conformational effects in six-membered rings.

ACKNOWLEDGEMENTS. One of the authors (KP) wishes to express his gratitude to the National Science Foundation for a fellowship.

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