HETEROCYCLES, Vol 3, No 5, 1975

# THE BARRIER TO RING REVERSAL IN SOME 5,5-DISUBSTITUTED 1,2,3-TRITHIANES.

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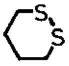
Barriers for ring inversion have been measured in a series of 5,5-disubstituted 1,2,3-trithianes. As expected, these derivatives inverse slower than the parent unsubstituted compound, except for 5-$CH_2R$ (R = Me, i.Pr) substituents.

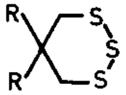
It is known that successive introduction of adjacent sulfur atoms in place of methylene groups in cyclohexane raises the barriers to ring reversal appreciably (TABLE 1).

TABLE 1.

| Compound |  |  |  |
|---|---|---|---|
| $\Delta G^{\neq}$(Kcal.mole$^{-1}$) | 10.5 | 11.6 | 13.2 |
| Ref. | 1 | 2 | 3 |

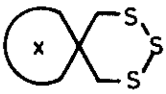
This is not surprising, in view of the high barrier associated with rotation about single S-S bonds (found from thermodynamic measurements) in simple disulfides such as dimethyl disulfide[4] and diethyl disulfide.[5] Also the torsion around the S-S bond in 1,2-dithiane-3,6-dicarboxylic acid is perfectly gauche.[6]

In an attempt to gain more information about the influence of 5-gem substituents on the Gibbs free energy of activation, we synthesised[7] several 5,5-disubstituted-1,2,3-trithianes (Fig. 1).



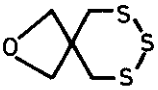
I

a R = Me
b R = Et
c R = i.Bu



II

a x = 5
b x = 6



III

This was the more interesting, because previously reported[3] data for $\Delta G^{\neq}$ on 1,2,3-trithiane itself and the corresponding 5,5-diMe-derivative were obtained only from measurements at the temperature for coalescence ($T_c$), taking simplifications of the observed spin systems in these compounds for granted.

All compounds were identified by u.v.spectroscopy ($\lambda_{max} = 263 - 265$ nm, independent of the substituents at 5-position and independent of the solvent) and mass spectroscopy (significant molecular ion and responses at M-S, M-$HS_2$ and M-$HS_3$).

100 MHz $^1$H-n.m.r.data determined at various temperature (-80 to +120°C) were now obtained, and they were submitted to a complete line shape analysis using the Alexander equations.[8] In our program, which is a modification of a previously reported procedure,[9]

we used a least-squares analysis which in principle permitted us, by an iterative process, to fit the observed spectrum to optimalized values of the two parameters, $\tau$ (life time) and $\Delta\nu$ (shift difference of the spin system under consideration). We used values for the transversal relaxation time ($T_2$) as determined by full linewidth measurements at both the slow and the fast limits of exchange, resulting in almost the same values listed in TABLE 2. Temperatures were measured by the method worked out by Van Geet.[10]

TABLE 2

| Compound (observed signal) | $T_c$ (K) | $\Delta G_c^{\neq}$ (Kcal.mole$^{-1}$) | $\Delta H^{\neq a}$ (Kcal.mole$^{-1}$) | $\Delta S^{\neq a}$ (Cal.mole$^{-1}$.K$^{-1}$) |
|---|---|---|---|---|
| Ia(5-Me) | 296.8 | 15.0 ± 0.1 | 14.0 ± 1.5 | -3.0 ± 4.8 |
| Ib(H-4,6) | 286.8 | 13.8 ± 0.05 | 13.3 ± 0.4 | -1.7 ± 1.5 |
| Ic(H-4,6) | 289.8 | 13.9 ± 0.05 | 14.0 ± 0.5 | -1.0 ± 2 |
| IIa(H-4,6) | 321.2 | $15.5_8$ ± 0.05 | 15.0 ± 0.5 | -1.7 ± 1.5 |
| IIb(H-4,6) | 298.5 | 14.6 ± 0.05 | 13.5 ± 0.5 | -4.0 ± 1.5 |
| III(5-$CH_2$) | 317.3 | 15.9 ± 0.1 | 15.2 ± 0.8 | -2.0 ± 2.0 |

[a] Determined in a range $T_c$ ± 25 K

A raise in barrier for topomerisation is expected for 5,5-gem-substitution. Indeed, a consecutive eclipsing of each ring bond with 5-substituents must occur at some stage during the process of inversion, and the barrier to rotation in 1,1-dimethyl-propane[11] is 1.30 Kcal.mole$^{-1}$ higher than that of propane.[12] It appears however from the table that Ib and Ic have free energies of activation similar to the unsubstituted parent compound, thus implying that the energies of the ground state and of the transition state for ring inversion have been influenced to the same extent. Because the geminal coupling constants between the protons at position 4(6) do not vary significantly in all compounds examined, ring distorsions at carbon-5, induced by the gem-substituents, must be minimal.[13]

ACKNOWLEDGEMENT The "Nationaal Fonds voor Wetenschappelijk Onderzoek" is thanked for a scholarship to one of us (G.G.).

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Received, 5th February, 1975