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REMOTE PARTICIPATION OF A SULFUR ATOM TO THE PROTON EXCHANGE OF 1,3,5-TRITHIANE DERIVATIVES

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The H-D exchange at the 2-position of 2,4,6-trimethyl-1,3,5-trithiane derivatives was found to be accelerated, by a large factor, by converting the sulfur atom at the 5-position to the sulfinyl or the sulfonyl group. The results are interpreted by assuming the remote participation of the sulfur atom. The slow H-D exchange of a 1,3,5-oxadithiane derivative is an additional support for the above assumption.

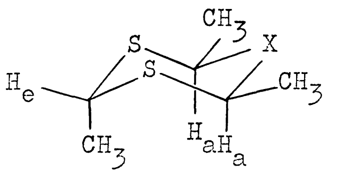
While we were studying the base-catalyzed proton exchange reaction of 1,3,5-trithiane derivatives,1) an interesting phenomenon was revealed : the protons at the 4-position exchanged more quickly when the sulfur at the 1-position was oxidized to sulfoxide or sulfone. Since the enhancement is too large to attribute to the inductive effect of the sulfinyl or sulfonyl group, it should be ascribed to a certain kind of through-space participation. In this communication, we wish to report these findings and an interpretation which has the basis on the participation of a vacant 3-d orbital of the remote sulfur atom.

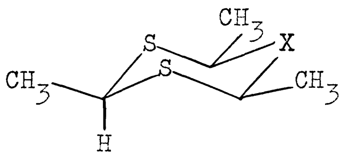
The equatorial proton (H_e) of cis,trans-2,4,6-trimethyl-1,3,5-trithiane (I) underwent H-D exchange in t-butyl alcohol-d in the presence of 0.395 mole/kg of lithium t-butoxide with the exchange half-life of 110 hr at 100°C, whereas the equatorial 4-proton of cis-2,trans-4, cis-6-trimethyl-1,3,5-trithiane r-1-oxide (II)2) was found to exchange with the half-life of 0.60 hr under the similar conditions.3) Therefore the rate of the exchange of the H_e of I was enhanced by 180 times when the remote sulfur atom was converted to the sulfinyl group.

A more remarkable rate enhancement was observed with cis,cis-2,4,6-trimethyl-1,3,5-trithiane (III) series. Thus the rate of the H-D exchange of the ring-proton was enhanced by 120,000 times when III was converted to the sulfoxide IV.[2] The relatively fast exchange rate of the 4-proton of II as compared with that of the 4-proton of IV may be attributed to the fact that the reaction is favored at the equatorial side.[1]

Further rate enhancement was observed when the compound III was converted to cis,cis-2,4,6-trimethyl-1,3,5-trithiane 1,1-dioxide (V). The 4-proton of V exchanged with the half-life of 0.25 hr under the similar conditions with those for the measurements of the exchange rate of IV. The rate of the exchange of the ring-proton is now 10^7 times enhanced when a sulfur atom which is remote from the reaction site is replaced by a sulfonyl group.

EXCHANGE HALF-LIVES





I X = S : H_e : 110 hr^a (2.2×10^4)
88 min^b
H_a : 58 hr^b (550)
4.0 min^c
II X = SO H_e : 0.60 hr^a (4×10^6)

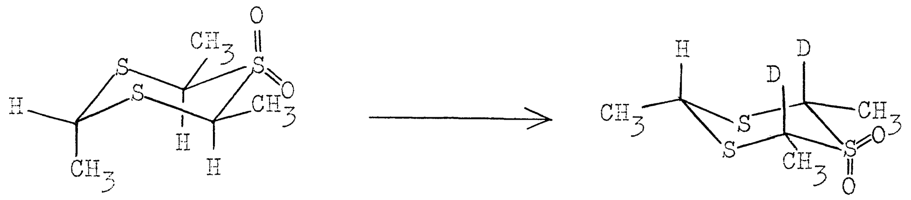
III X = S : 37 hr^c (1)
IV X = SO : 2.0×10 hr^a (1.2×10^5)
V X = SO_2 : 0.25 hr^a (1×10^7)
VII X = O : (< 0.1)

relative rates in parentheses.

a : t-BuOLi 0.395 mole/kg, 100°C
b : t-BuOK 0.172 mole/kg, 65°C
c : t-BuOK 0.974 mole/kg, 100°C

It would be of interest to know the enhancement of the exchange rate of the equatorial proton of cis,trans-isomer VI, since the equatorial proton gives greater exchange rate and the compound VI would give the smallest half-life. However, it was found that the compound VI isomerized instantaneously to the cis,cis-isomer V when it was treated with lithium t-butoxide in t-butyl alcohol-d before exchanging the proton at the 4-position. Therefore the attempt to measure the rate of exchange of the equatorial proton which was remote from the sulfonyl group was unsuccessful.

The mechanism of the isomerization may be the anionic epimerizations at both 2- and 6-carbons. Because the hydrogens of the α-sulfonyl positions are removed as protons with great ease and the carbanion so produced survive for a longer period, there is a good chance of the configurational inversion which leads to the thermodynamically more stable isomer (V) ; during all these courses the exchange at 4-position will proceed to a negligible extent.



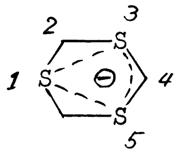
VI

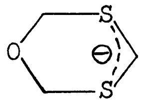
V - d_2

On the other hand, the H-D exchange of 2,4,6-trimethyl-1,3,5-oxadithiane (VII) was found to be rather slow. No deuterium incorporation was observed at any position of this compound after the treatment with 0.487 mole/kg of potassium t-butoxide in t-butyl alcohol-d at 100°C for 375 hr, so far as the NMR spectrum could detect. Under these conditions, the ring-proton of cis,cis-2,4,6-trimethyl-1,3,5-trithiane (III) exchanged with the half-life of 1.0×10^{2} hr. Then the exchange rate apparently decreased by a large factor when the sulfur atom of the remote position of the trithiane ring was replaced by an oxygen atom.

The stability of the carbanions adjacent to the sulfur atoms as compared with the oxygen analogs is usually attributed to the participation of the vacant 3-d orbitals.[4] The electrons of the carbanion carbon are back-donated to the sulfur d-dorbitals, thus causing the delocalization of the negative charge. It is also known from the UV spectral ground that, in 1,3-dithia compounds (mercaptals and mercaptols), there are 3p-3d interactions between the non-bonded sulfur atoms.5)

On these grounds, the above results may best be interpreted by considering the remote sulfur participation of which nature may be described as follows : The anion lone pair electrons at the 4-position delocalize over a 3-d orbital of the adjacent (position 3 and 5) sulfur atom, whereas a $p\pi - d\pi$ interaction exists between 3p electrons of sulfur atoms at 3 and 5-positions and the vacant 3-d orbitals of the sulfur atom at the 1-position. Thus the negative charge is delocalized over the three sulfur atoms. As for the oxadithiane ring, however, the negative charge is not delocalized over the oxygen atom to any significant extent. This difference can be taken as the main cause of the difference in the reactivities between the sulfur and the oxygen analogs





UV spectral results of some 1,3,5-trihetero 6-membered ring compounds in our hands give a support to the above explanation. The details will be described elsewhere.

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1) M. Fukunaga, K. Arai, H. Iwamura, and M. Ōki, Bull. Chem. Soc. Japan, 45, 302 (1972).

2) Configurational assignments of the sulfinyl groups of these compounds were made on the NMR spectral grounds. The results showed that II and IV have the chair conformations with the axial sulfinyl groups. The details will be published elsewhere.

3) The reactions of H-D exchange were followed by the proton NMR spectra. The exchange of the protons at 2,6-positions (alpha to the sulfinyl group) was too fast to be measured under these conditions.

4) S. Oae, W. Tagaki, and A. Ohno, Tetrahedron, 20, 427 (1964).

5) J. Barrett and M. J. Hintch, Spectrochim. Acta, 25A, 407 (1969).

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