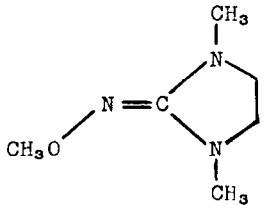
Tetrahedron Letters No.56, pp. 4925-4928, 1970. Pergamon Press. Printed in Great Britain.

THIOÖXIMES - I. BARRIERS TO SYN-ANTI ISOMERISATION IN S-ARYLTHIOÖXIMES

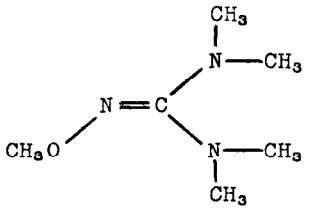
C. Brown[1], B. T. Grayson and R. F. Hudson
University Chemical Laboratory, University of Kent, Canterbury, Kent, England

(Received in UK 29 October 1970; accepted for publication 5 November 1970)

The barrier to syn-anti isomerisation in oximes and oxime ethers has been reported to be large,[2] and is in any case large enough to permit the isolation of geometrical isomers.[3] (However, in a recent publication, Kessler has shown[4] that syn-anti isomerisation in the imidazolidone oxime derivative I proceeded at a rate detectable by NMR with $\Delta G^{\ddagger}$ = 23.2 kcal.mol^{-1}. The acyclic analogue II, however, was configurationally stable up to at least 200°C).



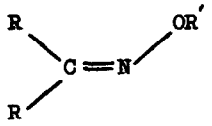
I



II

In the present communication we present NMR spectroscopic evidence for much lower barriers to such isomerisation in the corresponding thioöxime ethers (IV).[5]

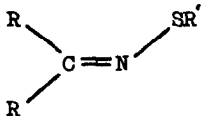
In contrast to IIIa-IIIc which had temperature-independent NMR spectra[6] (up to decomposition at ca. 130-150°), compounds IVa - IVe were found to have temperature-dependent spectra.



III a; R=i-Pr; R′ = 2,4-$(NO_2)_2C_6H_3$

b; R=i-Pr; R′ = 2-$NO_2C_6H_4$

c; R=Me; R′ =2,4-$(NO_2)_2C_6H_3$



IV a; R=4-Me.C_6H_4; R′ = 2,4-$(NO_2)_2C_6H_3$

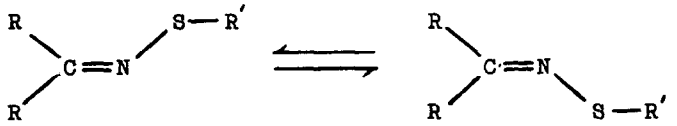
b; R=4-Me.C_6H_4; R′ = 4-Cl.C_6H_4

c; R=Bz; R′ =2-NO_2.C_6H_4

d; R=i-Pr; R′ =2,4-$(NO_2)_2$.C_6H_3

e; R=H; R′ =2-NO_2.C_6H_4

Thus IVa exhibited two equal intensity signals ($\Delta\upsilon$ = 4.0 Hz) for the aromatic methyl groups at room temperature, but as the temperature was raised these signals broadened, coalesced and finally sharpened to a single peak. These changes were completely reversible (T_c=67°), and are consistent with the occurrence of the rapid (degenerate) isomerisation depicted in equation (1). Analogous spectral changes were observed for IVb and for the methylene resonances of IVc. The spectrum of IVd showed two doublets of equal intensity due to the isopropyl methyl groups at low temperatures which collapsed to one doublet on heating. The thioformaldoxime derivative IVe showed a typical AB pattern for the $H_2C{=}N$ protons at low temperatures, and a singlet at high temperatures.



(1)

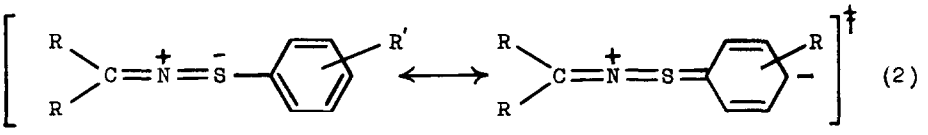
The NMR data and coalescence temperatures for compounds IVa - IVe are given in Table 1, together with the free energies of activation, $\Delta G^{\ddagger}$ derived from the relationship $k_c = 1/2\tau = \pi\Delta\upsilon/\sqrt{2}$ and the Eyring equation.[7] The $\Delta\upsilon$ values given were extrapolated from plots of $\Delta\upsilon$ against temperature. The correction is a minor one (<0.5Hz) for all compounds other than IVd, where a change in $\Delta\upsilon$ from 8Hz at 0°C to 4.6 Hz at T_c (98°C) was noted.[6]

TABLE 1

Compound	IVa[a]	IVb[a]	IVc[b]	IVd[b]	IVe[b]
$\Delta\upsilon$ (Hz)	4.0	4.9	7.5	4.6	24.0
J_{AB} (Hz)	-	-	-	-	12.5
Tc (°C)	67°	72°	101°	98°	ca.0°
$\Delta G^{\ddagger}$ (kcal.mol^{-1})	18.5	18.6	20.0	20.2	13.5[c]

a) $CDCl_3$ solution. b) C_6H_5Cl solution. c) Calculated from the equation[8] $k_c = \pi\sqrt{\Delta\upsilon^2 + 6J_{AB}^2}/\sqrt{2}$.

From the data in Table 1 and those taken from Curtin's paper[2], it can be estimated[9] that thioöximе ethers (IV) undergo syn-anti isomerisation some 10^{11} times faster than the corresponding oxime ethers (III). This is a dramatic difference in reactivity, and it is tempting to invoke d-orbital participation by sulfur, with the formation of various possible linear transition states (equation 2), in an attempt to explain it.



(2)

However, the low sensitivity of the rate of the isomerisation process to substituents R (see IVa, IVb) is not really in accord with such an interpretation, and we are currently examining a series of C- and S- substituted derivatives (IV) with a view to identifying the mechanism of the rearrangement.

Acknowledgment: one of us (B.T.G.) wishes to thank Shell Research Limited, Sittingbourne, Kent, for financial support.

References

1. Author to whom enquiries should be addressed.
2. D. Y. Curtin, E. J. Grubbs and C. G. McCarty, J. Amer. Chem. Soc., 88, 2775 (1966).
3. O. L. Brady and L. Klein, J. Chem. Soc., 874 (1927).

4. H. Kessler and D. Leibfritz, Ann., 737, 53 (1970).

5. The preparation of these compounds will be described in our definitive paper. All compounds in this study were adequately characterised by elemental analysis, mass spectral data, infrared and NMR spectra.

6. Chemical shift changes not associated with syn-anti isomerisation were noted and will be the subject of a later communication.

7. J. W. Emsley, J. Feeney and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. 1, Pergamon, N.Y., 1965, ch. 9.

8. R. J. Kurland, M. B. Rubin and W. B. Wise, J. Chem. Phys., 40, 2426 (1964).

9. Using an activation energy, Ea of ca. 10 kcal.mol^{-1} for IV.