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THE BARRIER TO INTERNAL ROTATION AROUND CARBON-CARBON DOUBLE BONDS IN KETENE MERCAPTALS AND AMINALS

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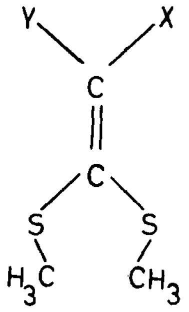
Unusually low barriers to rotation around carbon-carbon double bonds have recently been reported by two groups (1, 2). The publication by Gompper and Schaefer (3) of the preparation of some nitroketene mercaptals and related compounds prompts us to give a preliminary report on the observation of low barriers in these and similar compounds.

The n.m.r. spectrum of 1-nitro-2,2-bis-methylthioethylene (I a) in $CDCl_3$ shows one vinyl proton signal and one single sharp signal for the two S-methyl groups (Table) as mentioned in (3).

TABLE

N.m.r. Spectra in $CDCl_3$ at 34.5°C (τ values)

Compound	CH	SCH_3	SCH_2	NCH_3	NCH_2	OCH_3
I a	2.90	7.44	-	-	-	-
I b	-	7.22; 7.37	-	-	-	6.15
II a	2.41	-	6.45	-	-	-
II b	-	-	6.37	-	-	6.14
III a	3.62	-	-	6.97	6.27	-
III b	-	-	-	6.92	6.21	6.28



I

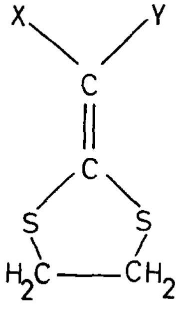
a, X = H, Y = NO_2

b, X = CN, Y = CO_2CH_3

However, when the temperature was lowered, the S-methyl signal became broader, and split into a doublet just below 0°C. At still lower temperatures, the doublet separation increased to a maximum of 1.4 c. p. s. In pyridine solution the same behaviour was observed, but here the splitting increased to 2.3 c. p. s., and the collapse of the doublet occurred at -5°C. From the Eyring equation (4) combined with the relation

k (rate constant) = $\frac{\pi\Delta\nu}{\sqrt{2}}$ (5) which is only approximately valid due to the considerable overlap of the signals, a $\Delta G^{\ddagger}$ value of 14.8 kcal/mole was obtained for the corresponding barrier. In both solvents the low field component of the doublet was lower and broader, which may be due to a long-range coupling with the vinyl proton.

The dimethylmercaptal (I b) (6) showed two separate signals for the S-methyl signals at room temperature. In o-dichlorobenzene solution this doublet remained sharp with a separation of 8.0 c. p. s. up to about 150°C. On increasing the temperature further, the well known pattern of exchange broadening could be observed, and at 185°C the doublet collapsed, which corresponds to a $\Delta G^{\ddagger}$ value of 24.6 kcal/mole. On cooling, the process was reversed, which indicates that no thermal decomposition had occurred.



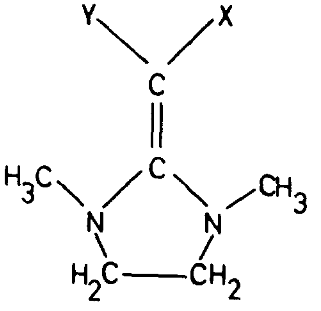
II

a, X = H, Y = NO_2

b, X = CN, Y = CO_2CH_3

The cyclic mercaptals (II a) and (II b) showed only one signal for the methylene protons in a variety of solvents and down to -60°. In (II a) it was quite sharp but somewhat broadened in (II b) (line widths 0.5 and 1.5 c. p. s. respectively). This is probably not due to low barriers but rather a consequence of a small chemical shift between the methylene groups combined with strong coupling.

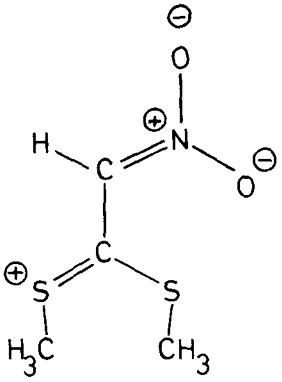
Attempts have also been made to measure the barriers in the cyclic ketene aminals (III a) and (III b), which are easily prepared by reaction of (Ia) and (Ib) with N, N′-dimethylethylenediamine [cf. (7)]. However, in both cases only one signal



III

a, $X = H$, $Y = NO_2$

b, $X = CN$, $Y = CO_2CH_3$



IV

was observed for the N-methyl protons and one for the methylene protons down to -63°C. In these cases an accidental magnetic equivalence of the N-methyl groups is very unlikely. The most probable explanation is a low barrier to rotation around the carbon-carbon double bond.

The low barriers in these compounds can qualitatively be explained by the low bond order of the double bond due to the importance of polar limiting structures such as (IV). However, it has been shown (8) that bond orders and barriers give a poor correlation in amides and thioamides, whereas a better correlation is obtained between barriers and differences in π electron energies in the ground and transition states. In the systems described here the relative stabilities of the transition state must be related to the capacity of the electron accepting part of the molecule to accommodate an extra electron and of the electron donating part to accommodate a positive charge.

It may be worth observing the low field position of the vinyl proton signal in (II a) compared with (I a) and (III a). This indicates less shielding, i.e. less polarization of the double bond, which means that the sulphur atoms are less electron donating in the dithiolane ring than in methylthio groups.

This investigation is being continued with similar systems containing a variety of electron donating and accepting groups. Solvent effects and kinetics of *cis-trans* isomerization will also be examined.

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After this paper was submitted for publication, a paper by Mannschreck and Koelle (9) appeared, which deals with some rather similar systems. The interest was centered on the rotation around the =C-N bond in enamines, however, and in no case a rapid rotation around a double bond was observed.

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