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BARRIERS TO ROTATION IN SUBSTITUTED O-ARYL-HYDROXYLAMINES.

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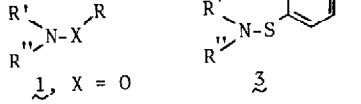
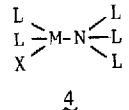
Summary: The effect of substituents on rotational barriers in O-arylhydroxylamines was studied. The results do not support any of the proposed mechanisms for substituent effects in the analogous sulfenamide series.

Barriers to conformational changes in substituted hydroxylamines (1) and sulfenamides (2) have attracted considerable interest in recent years. While in sulfenamides slow rotation about the N-S bond is the rate limiting process[1], it has been shown that both N inversion as well as N-O rotation in hydroxylamines involve substantial free energy barriers of comparable magnitude.[2] Despite extensive research on substituent effects on sulfenamide rotational barriers, the exact mechanism by which polar substituents affect the barriers remains controversial.[3] We have recently proposed a model, based on repulsive interactions between the p-lone pairs on sulfur and nitrogen, to account for the enhancement of torsional barriers in arenesulfenamides (3) upon the introduction of an electron withdrawing substituent X.[4] An earlier mechanism based on conjugation between the nitrogen lone pair and a vacant sulfur d orbital,[3] appears to have been abandoned due to more recent opposing evidence.[4] Recently, Brunck and Weinhold have formulated a general scheme for rotational barriers in ethane like



1, X = O
2, X = S

3



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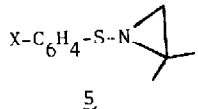

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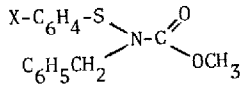

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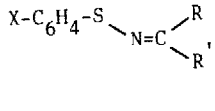

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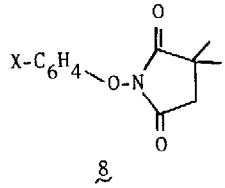

8

molecules (4), where all possible bond-antibond and lone-pair-antibond interactions are considered.[5] The major effect of an electronegative substituent X, according to that study, is to increase the M-X antibonding orbital density in the vicinity of M, and thus enhance stabilizing interactions of vicinal bonds or lone pairs with that M-X antibonding orbital. Whether this effect is also important in 3, where X is removed away from the central bond, is questionable, especially in view of the absence of substituent effects on barriers in 5, 6 and 7.[6] A fourth mechanism has been suggested recently to account for sulfenamide barriers, and has been termed the electro-steric effect.[7]

In view of these many proposed rationales for substituent dependence of sulfenamide rotational barriers, it seemed in order to investigate substituent effects on the analogous O-arylhydroxylamines The present communication describes preliminary results of a study on rotational barriers in para substituted N-aryloxy-2,2-dimethylsuccinimides (8). The compounds were synthesized by the action of the sodium salt of N-hydroxy-2,2-dimethylsuccinimide on the appropriate diaryliodonium salt in ethanol solution, with the exception of X=OCH_3, which yielded a rearranged product.[8]

Free energies of activation for degenerate racemization in series 8 were measured by observing the coalescence of signals from diastereotopic methyl groups as well as methylene protons in the low temperature 270 MHz NMR spectra. That coalescence is due mainly to rotation about the N-O bond, while nitrogen inversion is rapid on the NMR time scale, is ascertained by the structure of 8: the nitrogen atom is flattened by its incorporation into the five membered ring as well as the conjugation to two carbonyl groups, and is therefore expected to be either planar in the ground state, or possess a substantially low activation barrier for inversion.

The results are shown in the Table. The barriers seem to increase when X changes from CH_3 through hydrogen to NO_2. As much as it may be tempting to conclude that the barriers are linearly correlated with Hammett substituent constants, excluding the point for X=Cl, this cannot be the case, as the latter point is not an experimental deviation from the line. The barrier for 8c was measured repeatedly, and must be regarded fairly accurate and significant. Thus, the rotational barriers show no significant correlation with substituent electron withdrawing power.

This conclusion is puzzling, since it does not support any of the above mentioned theories dealing with sulfenamide rotational barriers. Both the four electron interaction[4] as well as the electro-steric effect[7] mechanisms require substantial conjugation between the sulfur p lone pair and the substituent across the aromatic ring. However, the extent of such conjugation in the oxygen analogs must be greater than in arenesulfenamides, as is evident from the greater substi-

Table: 270 MHz DNMR Results.[a]

		CH_3				CH_2			
Compd	X	δ, ppm	$W_{1/2}$, Hz [b]	t_c °C [c]	$\Delta G^{\ddagger}$ [d]	δ, ppm	$W_{1/2}$, Hz [b]	t_c °C [c]	$\Delta G^{\ddagger}$ [d]
8a	CH_3	1.41	22	-86	9.35	2.80	17	-79	9.35
8b	H	1.42	24	-81	9.5	2.83	28	-76	9.5
8c	Cl	1.42	27	-86.5	9.2	2.82	26	-82	9.2
8d	NO_2	1.47	25	-71.5	10.0	2.86	23	-64	10.1

a. Measured in acetone-d_6 containing 10% V/V CD_2Cl_2. b. Width at half height of coalescence spectrum. c. The estimated error range is ±2°. d. In Kcal/mol calculated by the Eyring equation. Estimated error: ±0.1 Kcal/mol. Coalescence rate constants were calculated for methyl signals: $k_c = W_{1/2}\,\pi/\sqrt{2}$; for methylene signals, according to ref.10.

tuent dependence of the first ionisation potentials of substituted anisoles relative to those of thioanisoles.[9] Accordingly, one might have expected to observe a large substituent effect on the barriers in 8, at least in the order of the effect in series 3. The only mechanism that seems to be slightly supported by the present results is the (p-d)π conjugation mechanism:[3] the difference in behavior of series 3 and 8 could be related to the difference between oxygen and sulfur, namely the absence and presence, respectively, of low lying d-orbitals. However, there appears to be substantial other evidence against this mechanism.[4]

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