

other in geometry, which consequently determines the stereochemistry of the olefin produced.

As to the formation of *E* olefins via ylide B, the direct removal of a proton from an *N*-methyl group or removal of the trimethylsilyl group from **2b** or **2f** affords ylide B, which may undergo [2,3] sigmatropic rearrangement leading to *E* olefins via the usual concerted transition state of a doubly suprafacial mode.^{5,1b}

On the other hand, the [2,3] sigmatropic rearrangement of ylide A may take place via transition state I or II to give the *Z* or *E* olefin, respectively (Scheme III). It should be noted that the conformational preference of I over II ($R^1 = H$ and CH_3) does not originate from the vicinal repulsion between R^2CH_2 and R^1 on the vinyl carbon, which was claimed as an important factor for the *Z*-selective Wittig rearrangement ($R^1 = CH_3$ only) by Still et al.^{1a} The present [2,3] sigmatropic rearrangement as well as other examples^{6,7} takes place very rapidly at low temperature, so the rearrangements seem to have a very early (i.e., reactant-like) transition state, and then methylide intermediate A undergoes spontaneous rearrangement as it is formed, before conformational equilibrium to afford the *Z* olefin. A definitive explanation for this exceptional preference of I over II cannot be offered at the present time, but one possible explanation may be that only one direction (path a) may be available for the [1,3] shift of a proton in ylide C because the *cis*-hydrogen of the vinyl group interferes with proton migration in the other direction (path b).

It will require much more experimentation to determine the precise reaction mechanism, including whether it involves inter- or intramolecular proton transfer.⁸

Since the product amines can be converted into the corresponding aldehydes via the Polonovsky reaction,⁹ we think the present method will find application in the field of the synthesis of terpenoids and biologically active substances.

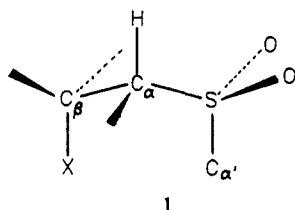
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Geometry Dependence of the Effect of a β -Substituent on the Rate of H–D Exchange: Evidence for a Stereoelectronic Component of the Polar Effect

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It is well-known that the ease of formation of an α -sulfonyl carbanion, $>\bar{C}-SO_2^-$, depends on the orientation of the bond being cleaved to yield the carbanion,¹ the readiest deprotonations, for example, being observed when the C–H bond is as shown in **1**, i.e., aligned with the internal bisector of the O–S–O angle, or, equivalently, antiperiplanar to the S–C $_{\alpha}$ bond. The stereoelec-



- (1) For a recent review of α -sulfonyl carbanions, see: Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277–297.

Table I. Rate Constants for H–D Exchange of α -Hydrogens in Six-Membered Cyclic Sulfones^a

compound ^b	reaction	k_{exch}^c ($M^{-1} s^{-1}$)	
	C3-H _{eq} → C3-D _{eq}	3.2×10^{-2}	
	C3-H _{ax} → C3-D _{ax}	1.6×10^{-4}	
	C10-H _{ax} → C10-D _{ax}	$<3 \times 10^{-8d}$	
	(C3-H ₂ + C5-H ₂) → (C3-D ₂ + C5-D ₂)	2.15×10^{-2} (4.30×10^{-2}) ^e	
		C2-H _{eq} → C2-D _{eq} C2-H _{ax} → C2-D _{ax}	4.5×10^{-4} <i>e</i>
	(C2-H ₂ + C6-H ₂) → (C2-D ₂ , C6-D ₂)	$\sim 10^{-6}$ ($\sim 2 \times 10^{-6}$) ^e	
		C2-H _{eq} → C2-D _{eq} C2-H _{ax} → C2-D _{ax}	1.2×10^{-6f} est. $\sim 10^{-8f}$
		C3-H _{eq} → C3-D _{eq} C5-H _{eq} → C5-D _{eq} (C3-H _{ax} + C5-H _{ax}) → (C3-D _{ax} + C5-D _{ax})	1.6×10^{-2} 2.3×10^{-2} $\sim 2 \times 10^{-4}$
		C2-H ₂ → C2-D ₂	4.8×10^{-3} (9.6×10^{-3}) ^e

^a With NaOD (0.017–0.05 M) in D₂O at 20 °C; determined by ¹H NMR (and ¹³C NMR) spectroscopy. ^b Compounds **2**, **3**, **4**, **5**, and **6** were either commercial materials or obtained as in the sources cited; **7** and **8** were obtained by simple syntheses from known precursors and were characterized by IR, ¹H and ¹³C NMR spectra, and exact mass determinations. ^c The values shown in parentheses are second-order rate constants for H–D exchange on a per-hydrogen basis and were obtained by multiplying the experimental value (k_{exch}) by the statistical factor of two. This factor has its origin in the circumstance that at any particular instant half of the exchanging hydrogens (i.e., those that are axial at that time) are not in a conformation favorable for exchange. The values in parentheses are used in calculating the relative rates discussed in the text. ^d ¹H NMR showed <5% reaction after 6 months in 0.13 M NaOD at 20 °C. ^e Not determined, but NMR spectra show the axial exchange in **4** to be at least 25 times slower than the equatorial. ^f Reaction run in 0.20 M NaOD in D₂O–DMSO (80–20). The relative rates of the equatorial and axial hydrogens were determined in NaOD in D₂O–CD₃OD which showed a 90-fold greater rate for the equatorial exchange. Heating of the same mixture for a further 24 h at 80 °C gave total exchange of the C-2 hydrogens and no sign of any exchange at C-9.

tronic control exerted by the sulfonyl group enables us to find out if any related geometry-dependent factors operate at adjacent carbon centers. In this study we have looked at the effect of the geometry of an alkoxy group β to the sulfonyl function, as in **1** ($X = OR$).² We have found that the orientation of the alkoxy group with respect to the C–H bond significantly affects the ease of α -sulfonyl carbanion formation and suggest that this observation may provide insight into the nature of the polar effect in chemistry.

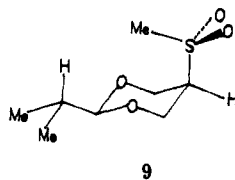
In NaOD in D₂O at 20 °C the equatorial hydrogen on C-3 of **2** exchanges readily, with a first-order dependence on $[OH^-]$.

- (2) Experiments on the detritiation of PhSO₂CHTCH₂X (Stirling, C. J. M.; Thomas, P. J. *J. Chem. Soc., Perkin Trans 2* **1977**, 1909–1913) show the rate to depend strongly on X, with an increase of about 5×10^4 on changing X from CH₃ to OPh; this effect was large enough that we were encouraged in our idea that a geometry-dependent effect might be both present and detectable.

From the similarly determined rate constants for the exchange of the α -hydrogens in the series of six-membered cyclic sulfones shown in Table I, it is evident that α -equatorial hydrogens exchange faster than α -axial, the rate differences in **2**, **4**, **6**, and **7** being, respectively, 200, >25, 90, and ≥ 80 . This result, though surprising in the light of an earlier report⁶ that indicated only a small preference for equatorial exchange, is, in fact, precisely what is expected on the basis of (a) the antiperiplanar orientation of the α -equatorial hydrogens with respect to the S-C α bond and (b) the comparative difficulty for the (normally) α -axial hydrogens to achieve this arrangement (e.g., via the twist-boat form). We conclude that in the exchange reactions for the other sulfones (**3**, **5**, and **8**), which have two identical chair forms, the rate constants reflect the ease of exchange of α -equatorial hydrogens in the different structures.

Comparison of these rates in **4** vs **5** and **6** shows that the presence of a β -synclinal oxygen atom accelerates the reaction by a factor of >200; another syn clinal oxygen on the same carbon, as in **8**, leads to a further 20-fold rate increase. An antiperiplanar oxygen, however, as in **2** and **3** increases the rate more than 10⁴ times relative to **5** and **6**. Alternatively, if we compare **2** and **3** with **4**, changing the oxygen from the synclinal to the antiperiplanar orientation increases the rate by, respectively, 71- and 95-fold.⁸ That this substantial rate difference is not primarily due to simple steric effects or the presence of an extra β -carbon is shown by examining the rates of exchange in **7**; the rate of exchange at C-3 and that at either C-5 or those of the corresponding reactions in **2** and **3** differ by less than a factor of three, showing that neither the steric nor the electronic effect of the methyl group is of significance in this case. We conclude that the important factor in the rapid exchange of the α -equatorial hydrogens in **2** and **3** relative to **4** (and **8**) is the orientation of the hydrogen with respect to the oxygen—specifically, the antiperiplanar geometry in **2** and **3**.

This conclusion suggested that the sulfone **9** (which has been



shown⁹ to have the conformation as drawn) would be expected to be well arranged for exchange of the α -sulfonyl methine hydrogen; we find that the exchange in **9** occurs almost 200 times faster than that in **3** (on a per-hydrogen basis).⁹

To explain our results we suggest that the incipient carbanion in the transition state is stabilized by donation of its electrons into the carbon-oxygen σ^* orbital, i.e., that it is a "kinetic anomeric effect".¹⁰ A related anomeric stabilization of a sulfonyl carbanion

was proposed by Padwa and Wannamaker to explain a strong preference for a synperiplanar arrangement in a methoxy-substituted cyclopropyl carbanion.¹¹

Our observations and those of Padwa and Wannamaker combine to show the existence of a geometry-dependent substituent effect such that an electron pair (incipient or fully formed) is stabilized by either an antiperiplanar or synperiplanar oxygen much more than by a clinal oxygen. These observations are not satisfactorily accounted for by the conventional components of the polar effect, i.e., the inductive and field effects,¹² and we conclude that the polar effect of the oxygen atom in these reactions has a stereoelectronic component as well. Any detailed general analysis of the "polar effect" that is offered in the future should, therefore, contain an explicit consideration of possible stereoelectronic contributions or risk being dismissed as incomplete.¹³

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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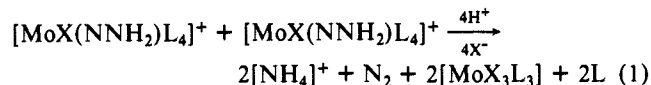
Reactions of a Resin-Bound Dinitrogen Complex of Molybdenum¹

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During reduction of N₂ to ammonia in mono-² and bis-N₂³⁻⁶ complexes of molybdenum, an intermediate hydrazido(2-), NNH₂, complex is formed.^{5,7-10} An accumulation of data supports the suggestion that the hydrazido(2-) complex undergoes net disproportionation as shown in eq 1 (X = Br, Cl; L = organophosphine).^{3,5} Thus one hydrazido(2-) complex loses N₂ and is



a source of electrons for the other hydrazido(2-) complex, which is reduced to afford 2 mol of ammonia (eqs 2 and 3). The

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