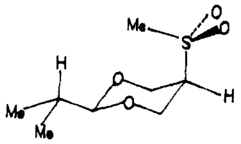
From the similarly determined rate constants for the exchange of the α-hydrogens in the series of six-membered cyclic sulfones shown in Table I, it is evident that α-equatorial hydrogens exchange faster than α-axial, the rate differences in **2**, **4**, **6**, and **7** being, respectively, 200, >25, 90, and ≥80. This result, though surprising in the light of an earlier report[6] 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 10^4 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 shown[9] 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]



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]

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Registry No. 2, 62015-76-3; **3**, 107-61-9; **4**, 99797-76-9; **5**, 4988-33-4; **6**, 71989-44-1; **7**, 26475-39-8; **8**, 125138-13-8.

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[6] Brown, M. D.; Cook, M. J.; Hutchinson, B. J.; Katritsky, A. J. *Tetrahedron* **1971**, *27*, 593–600. These authors report a rate difference of 1.6 for the exchange of the equatorial vs axial hydrogens in *cis*-3,5-diphenyl-*trans*-4-hydroxythian 1,1-dioxide. More recently, however, a 15- to 25-fold greater rate of exchange was reported[7] for the equatorial over the axial hydrogens in 6-methyl-1,3-oxathian 3,3-dioxide.

[7] Fuji, K.; Usami, Y.; Sumi, K.; Ueda, K.; Kajiwara, K. *Chem. Lett.* **1986**, 1655–1658.

[8] A second interesting feature of the Fuji paper[7] in light of the present study is the small net effect on the ease of proton exchange of the α-oxygen as compared with what we find for a β-oxygen (Table I); these authors report that H–D exchange of the equatorial hydrogen on C-4 (in CD_3O^-–CD_3OD) is 1.7 times faster than that on C-2.

[9] Kaloustian, M. K.; Dennis, N.; Mager, S.; Evans, S. A.; Alcudia, F.; Eliel, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 956–965. In 8.0×10^{-4} M NaOD in CD_3OD–D_2O (40:60 v/v), k_{obs} for **9** is 3.9×10^{-4} and for **3**, 1×10^{-6} s^{-1}.

[10] Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer-Verlag: Berlin, 1983; pp 78ff.

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[13] We note a further conclusion from this work. Although it has been suggested in a recent review[14] that phenomena assigned to the kinetic anomeric effect can be more consistently explained on the basis of the principle of least nuclear motion (PLNM), the present results constitute a good case for a kinetic anomeric effect not readily accounted for by PLNM.

[14] Sinnott, M. L. *Adv. Phys. Org. Chem.* **1988**, *24*, 113–204.

Reactions of a Resin-Bound Dinitrogen Complex of Molybdenum[1]

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During reduction of N_2 to ammonia in mono-[2] and bis-N_2[3-6] complexes of molybdenum, an intermediate hydrazido(2–), NNH_2, 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 N_2 and is

$$[MoX(NNH_2)L_4]^+ + [MoX(NNH_2)L_4]^+ \xrightarrow[4X^-]{4H^+} 2[NH_4]^+ + N_2 + 2[MoX_3L_3] + 2L \quad (1)$$

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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[8] George, T. A.; Tisdale, R. C. *Polyhedron* **1989**, *8*, 1756–1757.

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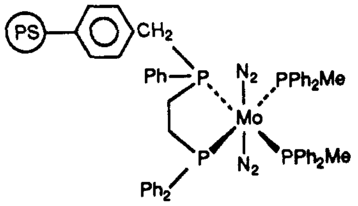
$$\{Mo(NNH_2)\} \rightarrow \{Mo(III)\} + N_2 + 2H^+ + 3e \tag{2}$$

$$3e + \{Mo(NNH_2)\} \xrightarrow{H^+} \{Mo(III)\} + 2[NH_4]^+ \tag{3}$$

molybdenum-containing product isolated in these reactions is $[MoX_3L_3]$. In order to study the electron transfer properties of unsubstituted hydrazido(2−) complexes, it is necessary to prevent or control disproportionation. To prevent interaction between hydrazido(2−) complexes, efforts have been made to site-isolate complexes by anchoring them to a microreticular resin. It is the successful results of this work that we report here.

The $\{Mo(N_2)_2\}$ moiety was attached to a phosphinated polystyrene–divinylbenzene (2%) resin[11] by a phosphine-exchange method similar to that employed by Dubois[12] to attach $\{Mo(N_2)_2\}$ to phosphinated polyacrylamide resins. Since loss of a phosphine ligand is the first step in the conversion of the hydrazido(2−) complex to ammonia, attachment of $\{Mo(N_2)_2\}$ to the resin must be through a chelating ligand. The $P(Ph)CH_2CH_2PPh_2$, diphos, moiety was bonded to polystyrene, PS, by the reaction of $LiP(Ph)CH_2CH_2PPh_2$ with chloromethylated polystyrene, following a procedure reported by Pittman and Hirao.[13] A ^{31}P NMR[15] spectrum of the solvent-swollen resin clearly showed a distinct resonance for each of the two different phosphorus atoms. Elemental analysis of the polymer indicated that the phosphine loading was >85%.[16]

A sample of *trans*-$[Mo(N_2)_2(PMePh_2)_4]$ (**1**)[17] in THF was added to the phosphinated resin, PS-diphos, swollen in THF. After 48 h of stirring, the bright orange resin was isolated.[18] Absorptions due to the symmetric and antisymmetric $\nu(N_2)$ were clearly visible in the difference FTIR spectrum. The ^{31}P NMR spectrum of the solvent-swollen complex clearly showed two broad resonances: one for coordinated PPh_2Me and the other for the unresolved pair of phosphorus atoms of $-P(Ph)CH_2CH_2PPh_2$. The chemical shifts were very similar to those of the phosphorus atoms in *trans*-$[Mo(N_2)_2(dppe)(PPh_2Me)_2]$, where dppe = $Ph_2PCH_2CH_2PPh_2$.[19]



Reaction of *trans*-$[Mo(N_2)_2(PS\text{-}diphos)(PPh_2Me)_2]$ (**2**) with excess fluoroboric acid in THF afforded the hydrazido(2−) complex $[MoF(NNH_2)(PS\text{-}diphos)(PPh_2Me)_2]BF_4$.[20] This is the first report of the successful reaction of N_2 in a resin-supported transition-metal complex. In the FTIR spectrum, ν(NH) absorptions were identical (±4 cm^{-1}) with those in $[MoF(NNH_2)(dppe)(PPh_2Me)_2]BF_4$.[21]

Reaction of *trans*-$[Mo(N_2)_2(dppe)(PPh_2Me)_2]$ with HBr in THF produced 0.68 mol of ammonia per mol of Mo.[5] The reaction of **2** with HBr (20 mol) in THF for 48–72 h yielded *no ammonia*. This result is precisely what is expected if the disproportionation hypothesis outlined above is correct.

Reaction of **2** with HBr in CH_2Cl_2 for 48 h produced no ammonia and 0.24 mol of hydrazine per mol of Mo. The same reaction carried out with *trans*-$[Mo(N_2)_2(dppe)(PPh_2Me)_2]$ produced 0.42 mol of hydrazine and 0.41 mol of ammonia per mol of Mo. Thus, the formation of hydrazine showed that (i) the N_2 ligand of a complex anchored to a resin will undergo chemistry beyond the hydrazido(2−) stage and (ii) hydrazine formation occurs at a single metal site.

In order to further test the hypothesis, a 1:1 mixture of **1** and **2** was treated with HBr in THF. The yield of ammonia from the mixture was 1.01 mol per mol of **1** compared with 0.77 mol per mol of **1** for **1** with acid,[22] a 30% increase in ammonia yield. Furthermore, oxidation by sodium hypochlorite solution of the ammonia produced in the acid reaction of a mixture of **1** and the anchored complex that was labeled with $^{15}N_2$ (>90%) resulted in the recovery of dinitrogen-28, dinitrogen-29 significantly above background measurements, and a trace of dinitrogen-30. Identical results were obtained when the corresponding hydrazido(2−) complexes that had been prepared separately were mixed and reacted with HBr. Thus, the presence of the homogeneous molybdenum N_2 complex led to reduction of the anchored complex with resulting formation of $^{15}NH_3$.

Work is underway to discovery other reagents that will convert N_2 and NNH_2 that are coordinated to anchored metal complexes into ammonia and hydrazine.

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[11] Chloromethylated polystyrene (2% divinylbenzene), 1.06 ± 0.05 mmol of Cl/g of resin, 16% chloromethylated, was purchased from Eastman Kodak Co.

[12] Dubois, D. L. *Inorg. Chem.* **1984**, *23*, 2047–2052.

[13] Pittman, C. U., Jr.; Hirao, A. *J. Org. Chem.* **1978**, *43*, 640–626. For example, the reaction of brominated polystyrene with $LiP(Ph)CH_2CH_2PPh_2$.

[14] This footnote was deleted on revision.

[15] The $^{31}P\{^1H\}$ NMR spectra (C_6D_6, 23 °C) were obtained with a Varian VXR-200 spectrometer operating at 80.894 MHz. Chemical shifts are referenced to PPh_3 (−5.8 ppm; 85% H_3PO_4 = 0.0 ppm). The phosphorus atom assignments are as follows: $-CH_2P_a(Ph)CH_2CH_2P_bPh_2$, P_xPh_2Me.

[16] Anal. Found: C, 86.57; H, 7.29; P, 5.33; Cl, 0.81 (by difference) corresponds to 0.86 mmol of ligand/g of resin. ^{31}P NMR: δ −13.36 (brd, 1, J_{PP} = 23.5 Hz, P_a), −16.19 (brs, 1, P_b). The narrower resonance (doublet) was assigned to the phosphorus atom with lesser restriction to rotation in the solvent-swollen polymer.

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[18] *trans*-$[Mo(N_2)_2(PS\text{-}diphos)(PPh_2Me)_2]$. ^{31}P NMR: δ 63 (b, $P_{a,b}$), 21 (b, P_x). IR: ν(NN) 2022 (w), 1946 (vs) [$^{15}N_2$ 1950 (w), 1880 (vs)] cm^{-1}. Anal. Found: Mo, 4.48; P, 6.25. Mo/P ratio = 1.0/4.2. Calcd: N, 3.04. Found: N, 2.90 (N_2 gas measurement following oxidation by Br_2 in CH_2Cl_2).

[19] George, T. A.; Kovar, R. A. *Inorg. Chem.* **1981**, *20*, 285–287.

[20] $[MoF(NNH_2)(PS\text{-}diphos)(PPh_2Me)_2]BF_4$. IR: ν(NH) 3333 (m), 3253 (s), 3163 (m) cm^{-1}. ^{31}P NMR: δ 43 (b, $P_{a,b}$), 8 (b, P_x).

[21] George, T. A.; Kaul, B. B., unpublished results.

[22] Yields of ammonia are ±3%. Total nitrogen balances for the two reactions are 75 and 77%, respectively.

Total Synthesis of *dl*-Indolizomycin

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The possibility of using mutant microorganisms to produce novel structures is well recognized. An interesting extension of this theme was recently described by Umezawa and colleagues.[1] The Japanese workers achieved a protoplast fusion of two non-antibiotic-producing strains (*Streptomyces teryimanensis* HM16 and *Streptomyces grisline* NPI-1). There were elaborated new clones from which a particular strain (SK2-52) was especially effective in producing antibiotics. It was in this way that the bioengineered antibiotic called indolizomycin (**1**) was isolated. Indolizomycin production in SK2-52 may be the result of enzymic machinery derived from recombinant genes. Alternatively it might reflect newly fashioned mechanisms for expressing "silent" genes already present in one of the parents.

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