

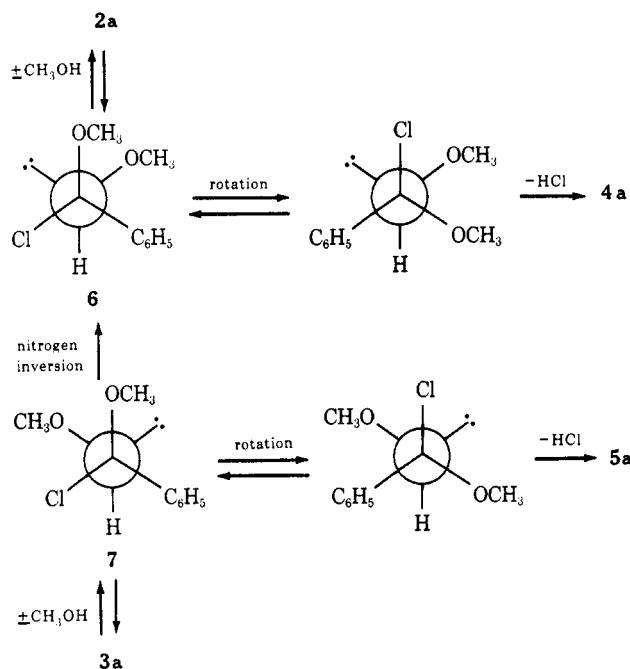
hydroximate whose configurations are known.<sup>4</sup> Comparable results were obtained when the *p*-nitrohydroximoyl chlorides, **2b** and **3b**, were allowed to react with sodium methoxide. Compound **2b** produced **4b** (**4b** : **5b** = 98 : 2) whereas **3b** gave mainly **5b** (**4b** : **5b** = 16 : 84).

Further investigation of the (*Z*)-hydroximoyl chloride (**3a**) reaction revealed that the lower stereoselectivity of this reaction is due in part to a methoxide induced isomerization of **3a** to **2a**. The hydroximates **4a** and **5a** were found to be stable under the reaction conditions; no isomerization of these compounds could be detected by glc over a 48-hr period. When the reaction of **3a** with methoxide was quenched with water after approximately one half-life, it was found by glc analysis that some isomerization of **3a** to **2a** had occurred (ratio of **3a** to **2a** after approximately one half-life = 87 : 13). That this isomerization is catalyzed by methoxide ion was demonstrated by the fact that an 0.08 *M* solution of **3a** in DMSO-methanol did not undergo any detectable isomerization at 44.6° over a 48-hr period.

The rates of the hydroximoyl chloride-sodium methoxide reactions were followed by quenching the reactions with water and titrating. Both **2a** and **3a** follow second-order kinetics through at least 60–70% of the reaction. The rate constant for the reaction of **2a** ( $8.02 \times 10^{-2}$  *M*) with sodium methoxide ( $2.88 \times 10^{-2}$  *M*) was found to be  $1.27 \times 10^{-2}$  l./(mol sec) at 44.6°. At the same temperature, **3a** ( $7.78 \times 10^{-2}$  *M*) reacted with sodium methoxide ( $2.67 \times 10^{-2}$  *M*) at a rate of  $1.44 \times 10^{-2}$  l./(mol sec). In order to determine the effect of the leaving group on the rate of this reaction, *O*-methylbenzohydroximoyl bromide (**2c**, assumed to have the *E* configuration) was synthesized in low yield by the reaction of **1a** with phosphorus tribromide. The second-order rate constant for the reaction of **2c** ( $8.06 \times 10^{-2}$  *M*) with sodium methoxide ( $2.47 \times 10^{-2}$  *M*) is only 1.9 times faster than that of the (*E*)-hydroximoyl chloride (**2a**)-sodium methoxide reaction.

Stereoselective inversion of configuration during nucleophilic substitution at *sp*<sup>2</sup> hybridized carbon has not been reported heretofore.<sup>5</sup> Although additional work is required for a detailed mechanistic proposal, our preliminary results are consistent with the premise that these reactions proceed by a methoxide-catalyzed trans addition of methanol (either concerted or step-

wise) to give a tetrahedral intermediate which undergoes a methoxide induced trans elimination of hydrogen chloride (as illustrated for **2a** and **3a**).<sup>6</sup> In order for this mechanism to be valid, it must be assumed that nitrogen inversion is slower than rotation about the carbon-nitrogen single bond in the tetrahedral intermediate. This assumption seems reasonable since



recent work indicates that nitrogen inversion is slow in *N*-benzyl-*O,N*-dimethylhydroxylamine.<sup>7</sup> It is conceivable that the lower stereoselectivity of the **3a** reaction is due to some inversion at nitrogen in the tetrahedral intermediate **7** to give its diastereoisomer **6**.<sup>8</sup> Inversion at nitrogen could account for the partial stereomutation of **3a** as well as the formation of **4a** during the course of the reaction.

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(6) The relatively small rate increase observed for the reaction of **2c** with sodium methoxide would appear to rule out an *SN*<sub>2</sub> type substitution mechanism.

(7) D. L. Griffith, B. L. Olson and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 1648 (1971), and references cited therein; M. Raban and D. Kost, *J. Org. Chem.*, **37**, 499 (1972).

(8) Since **6** and **7** are diastereoisomers, it is reasonable to assume that the equilibrium between **6** and **7** lies in favor of **6**. It is not clear why **6** is more stable than **7**.

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(5) All stereoselective substitution reactions at vinylic carbon proceed with retention of configuration, G. Modena, *Accounts Chem. Res.*, **4**, 73 (1971). Since submission of this work three reports on inversion during solvolysis of vinyl trifluoromethanesulfonates have appeared: (a) T. C. Clarke, O. R. Kelsey, and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 3626 (1972); (b) T. C. Clarke and R. G. Bergman, *ibid.*, **94**, 3627 (1972); (c) R. H. Summerville and P. v. R. Schleyer, *ibid.*, **94**, 3629 (1972).

## Rate of Intersystem Crossing between <sup>1</sup>A and <sup>5</sup>A States of an Iron(II) Complex in Solution

Sir:

Octahedral complexes of transition metals possessing four to seven d electrons can exist in either high-spin