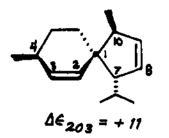

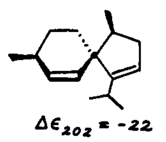

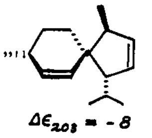

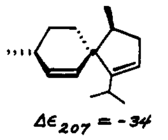

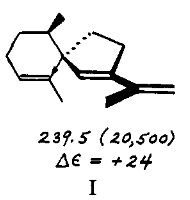

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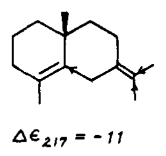
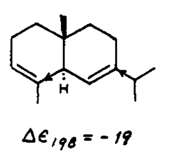


II



III

These limited (by space) examples should serve to illustrate the ABP model and its relationship to the other, apparently conflicting, viewpoints on this topic. An examination of the effects of specific vinylic and allylic substitution in rigid systems is in progress in order to delineate the relationship between ABP and torsional[3] contributions.

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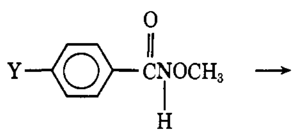
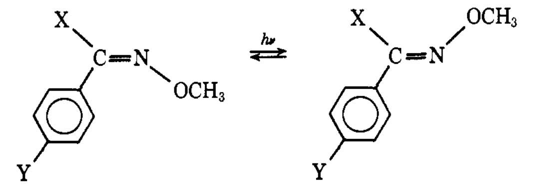
Reaction of *O*-Methylbenzohydroximoyl Chlorides with Sodium Methoxide. Inversion of Configuration at Trigonal Carbon during Nucleophilic Substitution

Sir:

The reaction of phosphorus pentachloride with alkyl benzohydroxamates provides a general preparative method for *O*-alkylbenzohydroximoyl chlorides.[1,2] This previous work[1] indicated that only one geometric isomer of a hydroximoyl chloride is formed in the reaction. In order to study the stereochemistry of the nucleophilic substitution reactions of these compounds, we have prepared and identified the *E* and *Z* isomers of *O*-methylbenzohydroximoyl chloride (**2a** and **3a**) and *O*-methyl-*p*-nitrobenzohydroximoyl chloride (**2b** and **3b**). The reaction of phosphorus pentachloride with methyl benzohydroxamate (**1a**) gave **2a** (71%) as a colorless oil, bp 53–54° (0.1 mm).[3] Ultraviolet irradiation (200-W medium-pressure lamp) of a 0.15 *M* solution of **2a** in hexane for 6 hr produced a photo-



1a, Y = H
b, Y = NO$_2$



2a, X = Cl; Y = H
b, X = Cl; Y = NO$_2$
c, X = Br; Y = H

3a, X = Cl; Y = H
b, X = Cl; Y = NO$_2$

stationary state of the isomers **2a** and **3a** in a 62:38 ratio. The mixture was separated by preparative glc and isomer **3a** was obtained as a colorless oil, bp 43–44° (0.1 mm). The geometric isomers of *O*-methyl-*p*-nitrobenzohydroximoyl chloride (**2b**, mp 121–122° and **3b**, mp 110–112°) were prepared in a similar manner. Stereochemical assignments for the hydroximoyl chlorides were made on the basis of the dipole moment data given in Table I.

Table I. Dipole Moment Data for *E* and *Z* Isomers of *O*-Methylbenzohydroximoyl Chloride and *O*-Methyl-*p*-nitrobenzohydroximoyl Chloride

Hydroximoyl chloride	Conformation	Theor dipole moment, D[a]	Exptl dipole moment, D[b]
2a	*s-trans*	1.13	1.38 (1.41)[c]
2a	*s-cis*	2.46	
3a	*s-trans*	2.00	1.99
3a	*s-cis*	1.65	
2b	*s-trans*	3.55	3.60
2b	*s-cis*	1.76	
3b	*s-trans*	2.98	2.96 (3.00)[c]
3b	*s-cis*	2.78	

[a] Calculated using the following bond (or group) moments and bond angles: CH$_3$—O, 1.06 D; N—O, 0.30 D; C=N, 1.40 D; C—Cl, 1.75 D; NO$_2$, 4.20 D; 110° for N—O—CH$_3$; 120° for C=N—O; 120° for N=C—Cl. [b] The experimental dipole moments were determined in benzene at 25° using the method of E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949); J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955, pp 58–64. [c] Duplicate determination.

We have investigated the stereochemistry of the reaction of sodium methoxide with the hydroximoyl chlorides **2** and **3** in 90% dimethyl sulfoxide (DMSO)–10% methanol. Reaction of a 0.07 *M* solution of **2a** at 45° with sodium methoxide (0.09 *M*) resulted in almost exclusive formation of a compound with inverted configuration, methyl (*Z*)-*O*-methylbenzohydroximate (**4a**, 68% yield). Only about 2% of the product could be attributed to the *E* isomer (**5a**) by glc. Under identical reaction conditions the (*Z*)-hydroximoyl chloride (**3a**) gave predominantly the product with inverted configuration, **5a** (ratio of **4a** to **5a** = 23:77 by glc, 62% yield). In order to establish the configuration of **4a** and **5a**, they were independently synthesized by methylation of the *Z* and *E* isomers of methyl benzo-

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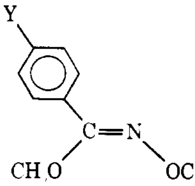
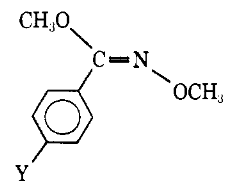
(1) J. E. Johnson, J. R. Springfield, J. S. Hwang, L. J. Hayes, W. C. Cunningham, and D. C. McClaugherty, *J. Org. Chem.*, 36, 284 (1971).

(2) For recent reviews concerning imidoyl chlorides, see (a) H. Ulrich, "The Chemistry of Imidoyl Halides," Plenum Press, New York, N. Y., 1968; (b) R. Bonnett in "The Chemistry of the Carbon-Nitrogen Double Bond," S. Patai, Ed., Interscience, New York, N. Y., 1970, pp 628–642.

(3) All new compounds reported herein gave spectral and elemental analyses in accord with the assigned structures.



4a, Y = H
b, Y = NO_2



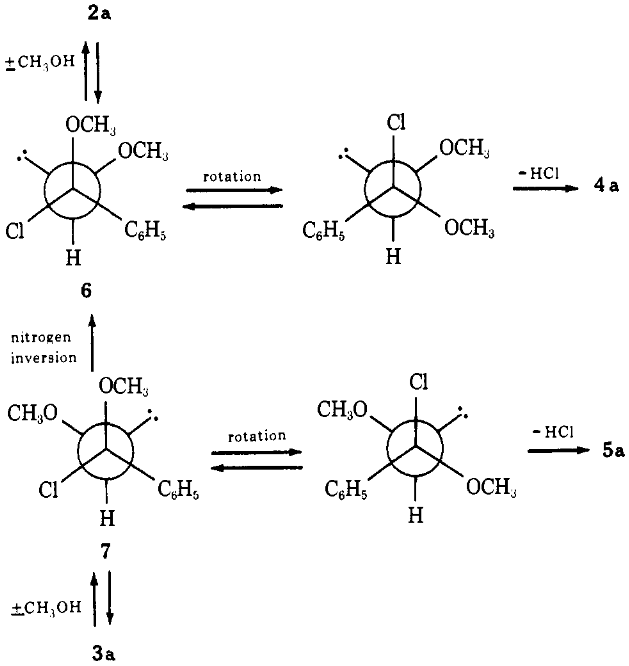
5a, Y = H
b, Y = NO_2

hydroximate whose configurations are known.[4] 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** (8.02×10^{-2} *M*) with sodium methoxide (2.88×10^{-2} *M*) was found to be 1.27×10^{-2} l./(mol sec) at 44.6°. At the same temperature, **3a** (7.78×10^{-2} *M*) reacted with sodium methoxide (2.67×10^{-2} *M*) at a rate of 1.44×10^{-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** (8.06×10^{-2} *M*) with sodium methoxide (2.47×10^{-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^2 hybridized carbon has not been reported heretofore.[5] 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 stepwise) to give a tetrahedral intermediate which undergoes a methoxide induced trans elimination of hydrogen chloride (as illustrated for **2a** and **3a**).[6] 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.[7] 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**.[8] Inversion at nitrogen could account for the partial stereomutation of **3a** as well as the formation of **4a** during the course of the reaction.



Acknowledgments. We are indebted to the Robert A. Welch Foundation for financial support. The authors thank Dr. Timothy Rose, Texas A&M University, for making arrangements for us to use a Kahl dipolmeter.

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(4) (a) A. Werner and J. Suback, *Ber.*, **29**, 1153 (1896); (b) O. Exner, V. Jehlicka, and A. Reiser, *Collect. Czech. Chem. Commun.*, **24**, 3207 (1959); (c) R. Blaser, P. Imfeld, and O. Schindler, *Helv. Chim. Acta*, **52**, 569 (1969).

(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).

(6) The relatively small rate increase observed for the reaction of **2c** with sodium methoxide would appear to rule out an SN2 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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Rate of Intersystem Crossing between ^1A and ^5A 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