

ligand relative to the hydrazido(2-) form where the nitrogen-nitrogen bond length approaches 1.4 Å.⁶

The presently available structural data for azo complexes⁷⁻⁹ all indicate linear bonding. The reactivity of the platinum(II) complex¹ argues for a nonlinear M-N-N bond which, one might anticipate by analogy with the nitrosyl ligand, would also be stabilized by low oxidation state metals in particular stereochemical configurations.¹⁰

(6) G. A. Heath, R. Mason, and K. M. Thomas, *J. Amer. Chem. Soc.*, **96**, 259 (1974).

(7) V. F. Duckworth, P. G. Douglas, R. Mason, and B. L. Shaw, *Chem. Commun.*, 1083 (1970).

(8) V. F. Duckworth, G. J. Gainsford, and R. Mason, manuscript in preparation.

(9) J. A. Ibers and B. L. Haymore, unpublished results cited in ref 2; A. J. Schultz, J. V. McArdle, R. L. Henry, and R. Eisenberg, Proceedings of the American Crystallographic Association, Summer Meeting 1973, Abstract P.5.

(10) D. M. P. Mingos, *Inorg. Chem.*, **12**, 1211 (1973), and references therein.

R. Mason,* K. M. Thomas, J. A. Zubieta

School of Molecular Sciences, University of Sussex
Brighton, England

P. G. Douglas, A. R. Galbraith, B. L. Shaw

School of Chemistry, University of Leeds
Leeds, England

Received July 18, 1973

Stereochemistry of Some Electrophilic Reactions at Iron-Carbon σ Bonds

Sir:

Stereochemical changes occurring at α carbon in reactions of transition metal-alkyl complexes have been the subject of considerable interest.¹⁻⁴ By contrast, the stereochemistry at metal of these reactions has not been extensively explored.^{5,6} Complementary data on changes in configuration at α carbon and at metal are necessary for a complete understanding of mechanisms of transformations at metal-carbon bonds. Herein we report on the stereochemistry at metal of SO₂ insertion into and of the electrophilic cleavage by HI, I₂, and HgI₂ of an iron-carbon σ bond (Scheme I). The SO₂ insertion is highly stereospecific whereas, for the first time, the cleavage processes are shown to involve a reaction intermediate.

The parent methyl complex **1** exists in the form of two diastereomerically related pairs of enantiomers, **1a** and **1b**,⁷ owing to the presence of a chiral metal and an unsymmetrically substituted *h*⁵-cyclopentadienyl ring. **1a** and **1b** were prepared and isolated in varying degrees of isomeric purity (up to 100%) by the stereo-

(1) (a) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971); (b) P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Amer. Chem. Soc.*, in press.

(2) (a) D. Dodd and M. D. Johnson, *Chem. Commun.*, 571 (1971); (b) S. N. Anderson, D. H. Ballard, J. Z. Chrzastowski, D. Dodd, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 685 (1972).

(3) R. W. Johnson and R. G. Pearson, *Chem. Commun.*, 986 (1970).

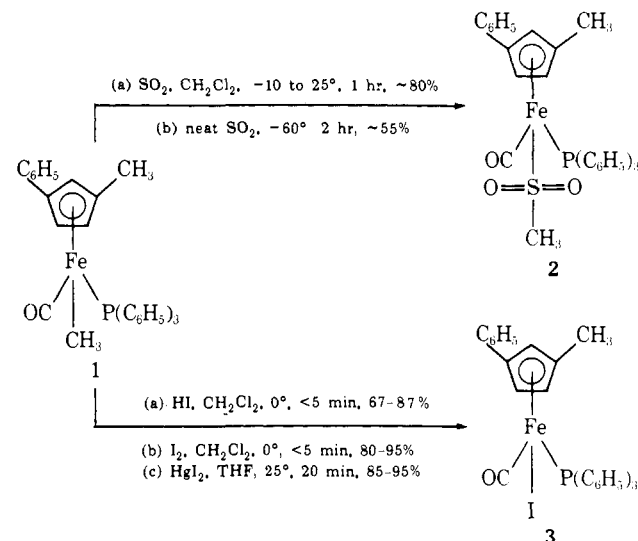
(4) F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, **93**, 5283 (1971).

(5) P. W. Robinson, M. A. Cohen, and A. Wojcicki, *Inorg. Chem.*, **10**, 2081 (1971).

(6) K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967).

(7) **1a** and **1b** are derived, respectively, by the decarbonylation of the more and less soluble diastereomer of the acetyl. **2a** and **3a** are the dominant diastereomers obtained from **1a**, and **2b** and **3b**, from **1b**.

Scheme I



specific photochemical decarbonylation of the two diastereomers of the corresponding acetyl,⁸ followed by fractional crystallization from benzene-pentane. The ¹H nmr spectrum of **1** showed that both the ring (τ 8.22 and 8.53) and the ligated (τ 9.91 d, 9.82 d; $J = 6.4$ Hz) CH₃ groups are diastereotopic.

Reaction between **1a** or **1b** and SO₂ (50-fold excess, 0.4 M) in CH₂Cl₂ yielded **2** (ir (CHCl₃) 1958, (KBr) 1161, 1031 cm⁻¹). The nmr spectra of **2** [diastereotopic CH₃ groups at τ 8.11 and 8.20 (ring) and τ 7.60 and 7.61 (sulfinate)] derived from **1a** and **1b** revealed that each conversion occurred with >95% stereoselectivity at iron. When this same reaction was carried out in liquid SO₂, stereoselectivities of 76 and 82% were observed for the transformation of the two diastereomers of **1** into **2**. On the basis of a recent kinetic study⁹ and the observation of inversion of configuration at α carbon in the reaction of *h*⁵-C₅H₅Fe(CO)₂CHDCHDC-(CH₃)₃ with SO₂,¹ a mechanism has been proposed for the SO₂ insertion which involves the intermediacy of a contact ion pair ([M]⁺SO₂R⁻) and the *O*-sulfinate.⁹ The stereochemical result of this study indicates that such an ion pair must possess high configurational stability. Partial epimerization (~20%) at iron in the reaction conducted in neat SO₂ likely resulted from a high concentration of the *O*-sulfinate which is present in equilibrium with the ion pair.¹⁰ We cannot determine whether the high degree of stereospecificity corresponds to retention or inversion at iron;¹¹ however, the former appears much more likely on mechanistic grounds.

Reaction of **1** with HI, I₂, or HgI₂ proceeded very rapidly to **3** (ir (CHCl₃) 1949 cm⁻¹). Iodine-containing

(8) T. G. Attig, P. Reich-Rohrwig, and A. Wojcicki, *J. Organometal. Chem.*, **51**, C21 (1973).

(9) S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, **95**, 6962 (1973).

(10) (a) S. E. Jacobson, P. Reich-Rohrwig, and A. Wojcicki, *Inorg. Chem.*, **12**, 717 (1973); (b) P. Reich-Rohrwig, private communication, 1971.

(11) Studies have commenced to resolve this problem by X-ray crystallography. We have recently learned that T. C. Flood and D. L. Miles (*J. Amer. Chem. Soc.*, **95**, 6460 (1973)) studied the stereochemistry at iron of the insertion of SO₂ into the Fe-C bond of *h*⁵-C₅H₅Fe(CO)[P-(C₆H₅)₂]CH₂C(O)OC₁₀H₁₉ [C₁₀H₁₉O = (-)-mentholate]. By using nmr and circular dichroism spectroscopy, they showed that the insertion in neat SO₂ occurs with >90% retention of configuration at iron. We thank Professor T. C. Flood for communicating this result to us prior to publication.

electrophilic reagents were selected because of the high configurational stability of the diastereomers of **3**, **3a** and **3b**, and the presence of diastereotopic CH₃ groups (τ 8.05, 7.82).

1 (four parts) enriched in **1a** or **1b** was treated with a deficiency of the cleaving reagent (one part), solvent was removed, and the resultant mixture was chromatographed on alumina to separate unreacted **1** and **3**. Representative results of these experiments are shown in Table I. The following points deserve emphasis.

Table I. Ratios of Diastereomers and Per Cent Stereoselectivity for the Cleavage Reactions of **1**

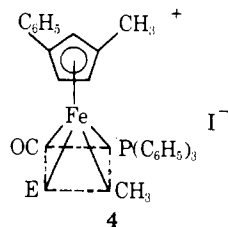
Cleaving reagent	Starting 1a/1b	Recovered 1a/1b (% stereoselectivity)	Isolated 3a/3b (% stereoselectivity)
HI	90:10	73:27 (58)	53:47 (8)
	14:86	27:73 (64)	33:67 (47)
I ₂	100:0	90:10 (80)	69:31 (38)
	8:92	20:80 (71)	22:78 (67)
HgI ₂	100:0	85:15 (70)	50:50 (0)
	8:92	17:83 (79)	34:66 (38)

In all cases, the recovered **1** has undergone partial epimerization, which is highest for the reaction with HI. In a given cleavage process, the extent of epimerization of **1a** did not greatly differ from that of **1b**. By contrast, the formation of **3** always occurred with greater stereospecificity for **1b** than for **1a**; as a function of the cleaving reagent, the degree of stereospecificity followed the order I₂ > HI \approx HgI₂. **1a** and **1b** are configurationally stable under the above reaction conditions and during work-up in the presence or absence of **3**; **3a** and **3b** were shown not to epimerize in the presence of HI, I₂, HgI₂, or CH₃HgI.

The observed epimerization of **1** may be readily accommodated by the reaction scheme



where E = H, I, or HgI. A reasonable intermediate is that derived by oxidative addition of E⁺ to **1**. Such an iron(IV) species, analogous to the known *h*⁵-C₅H₅Fe(CO)(SiCl₃)₂H,¹² would likely adopt a square pyramidal structure, **4** (or another isomer thereof). From the



known fluxional behavior of structurally related complexes of molybdenum(II) of the type *h*⁵-C₅H₅Mo(CO)₂-LX¹³ and *h*⁵-C₅H₅Mo(CO)₂X,¹⁴ one might expect **4** also to exhibit stereochemical nonrigidity. This would give rise to rapid configurational changes at iron, with **4**

(12) (a) W. Jetz and W. A. G. Graham, *Inorg. Chem.*, **10**, 4 (1971); (b) L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *ibid.*, **9**, 447 (1970).

(13) J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **92**, 5852 (1970).

(14) G. Wright and R. J. Mawby, *J. Organometal. Chem.*, **29**, C29 (1971).

having E = H likely epimerizing at the fastest rate, as for *h*⁵-C₅H₅Mo(CO)₂LX when X = H.¹³

Factors which give rise to the preferential formation of **3b** over **3a** are not completely clear at present, although molecular models suggest that one isomer may be sterically less hindered than the other. The higher degree of stereospecificity at iron for the cleavage with I₂ than with HI or HgI₂ may be related to differences in the mechanism of conversion of various **4** to **3**. These differences are suggested by the reported stereochemical changes at α carbon which accompany such reactions.¹⁻⁴ When E = H or HgI, **3** likely arises *via* reductive elimination of CH₄ and CH₃HgI, respectively, and coordination of ionic iodide. However, when E = I, nucleophilic attack of external I⁻ at the CH₃ with extrusion of CH₃I^{2b} may be operative instead of, or in conjunction with, the former type of reductive elimination.

Several mechanistic proposals have been made concerning reactions of coordinatively saturated transition metal alkyls with acids, halogens, and mercury(II) salts.^{1-4,15} The present study is the first to show unequivocally that these processes do not involve direct attack of the electrophile on the alkyl group; instead, addition of the electrophilic species to the metal is occurring.

Acknowledgment. We thank the National Science Foundation for a grant in support of this research.

(15) See, for example, (a) R. W. Johnson and R. G. Pearson, *Inorg. Chem.*, **10**, 2091 (1971); (b) D. Dodd and M. D. Johnson, *J. Chem. Soc. B*, 662 (1971); (c) G. N. Schrauzer, J. H. Weber, T. M. Beckham, and R. K. Y. Ho, *Tetrahedron Lett.*, 275 (1971), and references cited in each.

(16) National Science Foundation Trainee, 1970-1973.

Thomas G. Attig,¹⁶ Andrew Wojcicki*

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received September 13, 1973

Relative Effects of a Methyl and *tert*-Butyl Group on the Rates of Solvolysis of Tertiary *p*-Nitrobenzoates. Evidence for Major Increases in Steric Effects with Increasing Rigidity of the Parent System

Sir:

The replacement of a methyl group by a *tert*-butyl group at the tertiary position of tertiary *p*-nitrobenzoates results in increases in the rates of solvolysis by a factor of 4 for a simple aliphatic system (2-propyl), by approximately 125 for simple alicyclic systems (cyclopentyl and cyclohexyl), and by 40,000 for a bicyclic system (2-norbornyl). It is concluded that steric effects increase markedly from the relatively flexible aliphatic, to the less flexible alicyclic, to the rigid bicyclics.

Some time ago it was suggested that many of the unusual characteristics of the norbornyl system may have their origin in unusually large steric strains arising from the rigidity of this bicyclic structure.¹ It was proposed that strains arising from the presence of a bulky substituent would be small in the relatively flexible aliphatic system, larger in the less flexible alicyclic system, and enormous in the rigid bicyclic

(1) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966).