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The Stereochemistry of Reactions Occurring at Iron–Carbon σ Bonds[1]

Sir:

An interest in the mechanisms of transformations involving carbon–transition metal σ bonds has led us to determine the stereochemistry of the reactions between *threo*-$(CH_3)_3CCHDCHDFe(CO)_2Cp$ (**1**) and molecular bromine, mercuric chloride, and sulfur dioxide, using an nmr procedure described previously.[2,3] This procedure depends on the fact that erythro and threo diastereomers of most substances having the composition $(CH_3)_3CCHDCHDX$ display distinct nmr spectra, reflecting preferred molecular conformations in which the bulky *tert*-butyl and X groups are trans

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(2) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **91**, 4313 (1969).

(3) R. J. Jablonski and E. I. Snyder, *Tetrahedron Lett.*, 1103 (1968); R. G. Weiss and E. I. Snyder, *Chem. Commun.*, 1358 (1968).

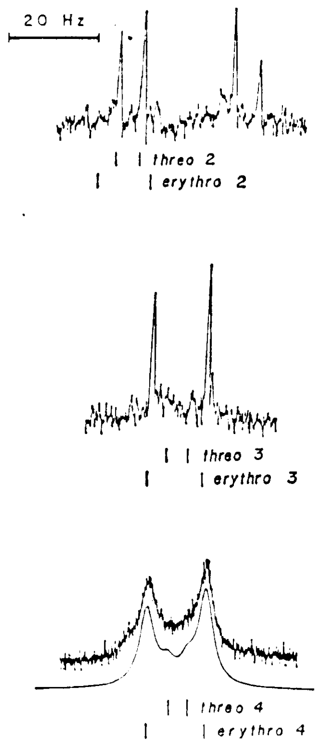
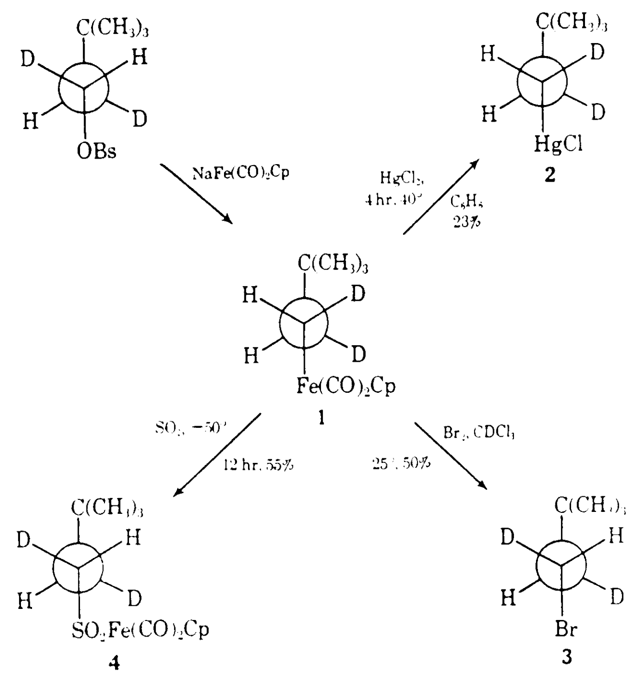


Figure 1. Deuterium-decoupled 100-MHz nmr spectra of the *CHDCHD* protons of 2, the *CHD*Br proton of 3, and the *CHD*SO_2 proton of 4. For comparison, the positions of lines characterizing the threo and erythro diastereomers of 2, 3, and 4 are given below the traces. The calculated spectrum given for 4 is that expected for a mixture of 82% erythro and 18% threo diastereomers.

across the ethylene moiety.[4] Since the resonances due to threo and erythro diastereomers can be identified directly on the basis of the magnitude of their vicinal *CHDCHD* coupling constants,[4] this technique suffers from none of the ambiguities which presently attend efforts to use optical activity to examine the stereochemistry of reactions at carbon–metal bonds. Values of the vicinal coupling constants required for analysis of mixtures of threo- and erythro-**4** were obtained by analysis of the AA′XX′ spectrum of $(CH_3)_3CCH_2$-$CH_2SO_2Fe(CO)_2Cp$ [*Anal.* Calcd for $C_{13}H_{18}O_4FeS$: C, 47.87; H, 5.56; Fe, 17.12; S, 9.83. Found: C, 47.99; H, 5.58; Fe, 17.10; S, 8.92; ir (Nujol) 2057, 2007, 1189, 1178, 1048 cm^{-1}]: J_{threo} = 4.3 Hz; J_{erythro} = 13.0 Hz. Analogous coupling constants for the diastereomers of 3,3-dimethylbutyl-*1,2-d*$_2$ mercuric chloride (**2**) and bromide (**3**) can be inferred from data reported previously.[4]

Reaction between **1** and a suspension of mercuric chloride[5] yielded **2**. Isolation of **2**, followed by examination of its deuterium-decoupled nmr spectrum (Figure 1), established that the conversion of **1** to **2** takes place with >90% retention of configuration at carbon.[6] In contrast, analogous experiments demonstrated that the transformation of **1** to **3** on treatment with bromine occurred with high (>90%)[6] stereoselectivity with *inversion* of configuration. Reaction between **1** and sulfur dioxide yielded **4**.[7] The nmr spectrum of this substance was less easily analyzed than those of **2** or **3**, since its lines were relatively broad. However, comparison of the experimental spectrum with spectra calculated for mixtures containing known proportions of *threo*- and *erythro*-**4** indicated that reaction had occurred with approximately 80% *inversion* of configuration.

The stereochemical outcome of the transformation **1** → **2** is the result expected for frontside electrophilic attack[8] of mercuric chloride on the C–Fe bond. Bromination of carbon–metal bonds has been observed to proceed with inversion of configuration in both main[9]



and transition[10] group compounds, although other stereochemical results have also been established.[8,11] Little is known on which to base a mechanistic proposal for the unexpected stereochemistry characterizing the reaction between sulfur dioxide and **1**; however, the report[12] that reaction between organocobalt compounds and sulfur dioxide appears to be catalyzed by water suggests that carbon monoxide insertion[2] may not provide a useful model for this process. Thus, this and previous[2] studies of the stereochemistry of reactions of **1** indicate that both retention and inversion of configuration at carbon may accompany reactions that formally involve both cleavage of carbon–iron σ bonds by electrophilic reagents ($HgCl_2$, Br_2) and "insertion" into carbon–iron bonds by neutral molecules (CO, SO_2).

Oxidative addition of optically active CH_3CHBr-$CO_2C_2H_5$ (**5**) to $Ir(CO)Cl[P(C_6H_5)_2CH_3]_2$ has recently been proposed to occur with retention of configuration, on the basis of the observation that the **5** obtained on

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(5) A. N. Nesmeyanov, *et al.*, *J. Organometal. Chem.*, 7, 329 (1967).
(6) This estimate of the stereoselectivity of the reaction is a minimum value; none of the erythro diastereomer is observed, but the signal-to-noise ratio characterizing the spectra is such that 10% might have gone undetected.
(7) A. Wojcicki, *J. Organometal. Chem.*, 16, 201 (1969); W. Kitching and C. W. Fong, *Organometal. Chem. Rev. A*, 281 (1970), and references in each.
(8) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968, p 86; D. S. Matteson, *Organometal. Chem. Rev. A*, 4, 263 (1969).
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(12) M. D. Johnson, and G. J. Lewis, *J. Chem. Soc. A*, 2153 (1970).

cleavage of the intermediate alkyliridium(III) complex with bromine had the same configuration as the starting **5**, and on the *assumption* that bromination of this alkyliridium complex occurred with *retention* of configuration at carbon.[13,14] The *inversion* of configuration established for bromination of **1** indicates that this proposal should presently be accepted with reservation. Although the stereochemistry assumed for the bromination leading to **5** may ultimately be demonstrated to be correct, it is clear that either inversion or retention of configuration may characterize brominative cleavage of carbon–metal bonds.

(13) R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970).

(14) Inversion of configuration had been established in oxidative addition of *trans*-1-bromo-2-fluorocyclohexane to $Ir(CO)Cl[P(CH_3)_3]_2$: J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970).

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