Reaction of threo-(CH₃)₃CCHDCHDFe(CO)₅-π-C₅H₅ with Triphenylphosphine

Sir:

The present understanding of the mechanism of the hydroformylation and related carbonylation reactions is based in part on studies of stereochemistry around the metal atom during the steps in which the initially formed alkylmetallic intermediates are converted to acylmetallic compounds. Information concerning the stereochemistry at carbon during typical carbonylation reactions is clearly required for a complete description of the mechanisms of these reactions, but has not been reported. We wish to describe the synthesis of 3,3-dimethylbutyl-1,2-d (3a) and evidence establishing that its reaction with triphenylphosphine to yield π-cyclopentadienylcarbonyltriphosphineiron threo-4,4-dimethylpentanoyl-2,3-d (3b) proceeds with retention of configuration at carbon.

Scheme I. Synthesis of Deuterated Organometallic Compounds

![Scheme I](image)

3.38, δX 1.23, and J = 10.0 Hz (Figure 1). The nmr spectra of erythro and threo diastereomers of 1 are easily distinguishable on the basis of their characteristic vicinal coupling constants: J_{ erythro} = 9.5 and J_{ threo} = 5.8 Hz. The magnitude of the coupling constant observed in the nmr spectrum of 1 confirms the erythro configuration expected from the method of synthesis: the absence of observable peaks in this spectrum attributable to the threo diastereomer indicates that the erythro diastereomer must constitute >95% of the 3,3-dimethylbutan-1-ol-d₂ produced.

Figure 1. Deuterium-decoupled 100-MHz nmr spectra of the -CHDOH proton of 1, the -CHDCHD- protons of 2, and the CHDCHD protons of 3. The peaks marked with an asterisk in the spectrum of 2 are due to impurities. For comparison the positions of the lines characterizing the threo and erythro diastereomers of 1, 2, and 3 are given below the traces; these frequencies were calculated on the basis of coupling constants obtained by analysis of the spectra of the nondeuterated analogs of these compounds.

3a: Only one enantiomer is shown for each compound.

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(5) G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, ibid., 89, 1135 (1967). The coupling constants J_{ erythro} and J_{ threo} are identical with the vicinal coupling constants I and J' obtained on analysis of the AA'XX' spectrum of 3,3-dimethylbutan-1-ol-d₂. The small difference between the magnitude of the observed coupling constant for 1 and J_{ erythro} obtained from the AA'XX' analysis probably reflects a solvent effect on the free-energy difference between the gauche and trans conformers of this alcohol.

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Compound 1 was converted to erythro-3,3-dimethylbutyl-1,2-\textsubscript{d}p-bromobenzensulfonate ($J = 8.6$ Hz), and thence to 2 by reaction with Na[Fe(CO)$_3$C$_6$H$_5$]. The nmr spectrum of the CHDCHD region of 2 consisted of a single AB quartet centered at $\delta 1.38$, with $\Delta \nu = 0.122$ ppm and $J = 4.4$ Hz (Figure 1); the infrared spectrum of 2 in the carbonyl stretching region consisted of bands at 2005 and 1955 cm$^{-1}$. An independent analysis of the nmr spectrum of 2-$\textsubscript{d}6$ established that the threo and erythro diastereomers of 2 are characterized by vicinal coupling constants $J_{\text{threo}} = 13.1$ and $J_{\text{erythro}} = 4.5$ Hz. Thus, transformation of 1 to 2 takes place with inversion of configuration.$^6$ Within the limits of detection of our experiment, no (<5\%) erythro diastereomer is produced in this reaction.

It is worthwhile pointing out that this stereochemical result is of considerable interest in its own right. It provides the first direct evidence that nucleophilic displacement on an alkyl carbon atom by a metalate anion proceeds with inversion of configuration at carbon.$^7$ Further, the observation that no detectable loss in stereochemistry was observed in 2 on standing for >12 hr at 30° provides an indication of the configurational stability to be expected for this class of carbon–transition metal $\sigma$ bonds.

Reaction of 2 with triphenylphosphine in THF followed by unexceptional work-up gave 3 as a yellow solid, mp 143° dec. The deuterium-decoupled nmr spectrum of the compound consists of two, equally intense, AX patterns arising from the two pairs of diastereomers represented by 3a and 3b.$^8$ The –CHD–CO– resonances of 3 occurred at $\delta 2.72$ and 2.46: both patterns were characterized by the same vicinal coupling constant, $J = 4.4$ Hz (Figure 1). The infrared spectrum of 3 in the carbonyl stretching region consisted of bands at 1925 and 1615 cm$^{-1}$. Anal. Calcd for C$_{n}$H$_{m}$O$_r$FeP: C, 71.00; H, 6.34. Found: C, 70.55; H, 6.43. Comparison of the observed coupling constant with those estimated for the threo ($J = 4.2$ Hz) and erythro ($J = 12.5$ Hz) diastereomers of 3 from analysis of the ABXY spectrum of 3-$\textsubscript{d}6$ establishes that conversion of the alkyl–iron bond of 2 to the corresponding carbon–carbon bond of 3 has taken place with complete (>95\%) retention of configuration.

Related studies of the stereochemistry of other reactions occurring at carbon–transition metal $\sigma$ bonds will be reported later.

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6 A similar technique has been used to determine the stereochemistry of solvolysis of 2-phenylethyl tosylate: R. J. Jablonski and E. I. Snyder, Tetrahedron Letters, 1101 (1968); see also R. G. Weiss and E. I. Snyder, Chem. Commun., 1358 (1968).


8 A related proton diastereopism due to chirality at iron has been observed for C$_{n}$H$_{m}$CH$_{2}$Fe(CO)(PPh$_3$)$_3$: J. W. Faller and A. S. Anderson, J. Amer. Chem. Soc., 91, 1550 (1969).


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