*Contribution from the McPherson and Evans Chemical Laboratories,
The Ohio State University, Columbus, Ohio 43210, U.S.A.*

The Stereospecificity of Sulfur Dioxide Insertion[1]

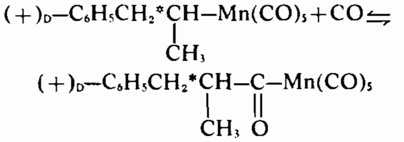
J.J. Alexander[2] and A. Wojcicki

Received March 23, 1971

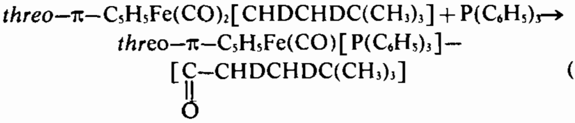
The reaction of the optically active $(-)_{546}$–π–$C_5H_5Fe(CO)_2[C(O)^*CH(CH_3)C_6H_5]$ with $Rh[P(C_6H_5)_3]_3Cl$ yields the optically active alkyl, $(+)_{546}$–π–$C_5H_5Fe(CO)_2[^*CH(CH_3)C_6H_5]$. The latter undergoes sulfur dioxide insertion either in liquid SO_2 at –60° or –10° or in pentane solution at 27° to afford the corresponding sulfinate, $(-)_{546}$–π–$C_5H_5Fe(CO)_2[S(O)_2{}^*CH(CH_3)C_6H_5]$, whose specific rotation, $[\alpha]_{546}$, varies from –186° to –158° depending on the synthetic conditions. Stereospecificity of these reactions with respect to the α carbon of $-CH(CH_3)C_6H_5$ is discussed.

Introduction

Configurational changes which occur at the α carbon atom during insertion reactions of transition metal alkyls have been studied only when the interposing substrate is CO. Calderazzo and Noack[3] demonstrated that the carbonylation and the decarbonylation represented by eq. 1 both proceed with either retention or inversion of configuration. Later, Whitesides and Boschetto[4] showed that the reaction (eq. 2):



$$(+)_D\text{–}C_6H_5CH_2{}^*\underset{\substack{| \\ CH_3}}{C}H\text{–}Mn(CO)_5 + CO \rightleftharpoons (+)_D\text{–}C_6H_5CH_2{}^*\underset{\substack{| \\ CH_3}}{C}H\text{–}\underset{\substack{\| \\ O}}{C}\text{–}Mn(CO)_5 \qquad (1)$$



$$threo\text{–}\pi\text{–}C_5H_5Fe(CO)_2[CHDCHDC(CH_3)_3] + P(C_6H_5)_3 \rightarrow threo\text{–}\pi\text{–}C_5H_5Fe(CO)[P(C_6H_5)_3]\text{–}[\underset{\substack{\| \\ O}}{C}\text{–}CHDCHDC(CH_3)_3] \qquad (2)$$

leads to retention of configuration at the α carbon of the alkyl group. In order to extend the scope of such investigations and to provide a better mechanistic comparison between the CO and SO_2 insertions, we examined stereochemical changes accompanying the sulfonylation. Reported in this paper are the results of our study. A preliminary account of this work appeared earlier in the form of abstracts of lectures.[5,6]

Experimental Section

Materials. The compound $[\pi\text{–}C_5H_5Fe(CO)_2]_2$ was prepared by the procedure of King.[7] $Rh[P(C_6H_5)_3]_3Cl$,[8] $C_6H_5CH(CH_3)CO_2H$,[9] and $C_6H_5CH(CH_3)COCl$[9] were synthesized using literature methods. Hydratropic acid was resolved with quinine by the method of Levene, *et al.*,[10] and converted to the acyl chloride. The optically active $C_6H_5{}^*CH(CH_3)COCl$ had $[\alpha]_{546}{}^{27} = -95°$ (0.40 g/100 ml, ether). The ORD curve for this compound leads to a value of $[\alpha]_D{}^{27} = -80°$ which is somewhat larger than that reported in the literature[10] for the «completely resolved» acyl chloride. We take this to mean that our sample of $C_6H_5{}^*CH(CH_3)COCl$ is virtually completely optically pure $(-)_{546}$–(R)–$C_6H_5{}^*CH(CH_3)COCl$.

Sulfur dioxide was supplied by Matheson and was passed through a $CaCl_2$–P_4O_{10} column before use. Tetrahydrofuran (THF) was distilled immediately prior to use from CaH_2 under a nitrogen atmosphere. Ventron alumina (acid-washed) was employed in all chromatographic separations. All other chemicals except pentane were of reagent grade and were used as received.

Measurements and Analyses. Infrared spectra were measured on a Perkin-Elmer Model 337 instrument using NaCl cells of 0.1 mm thickness. A Varian Associates Model A-60 nuclear magnetic resonance spectrometer was employed for measuring ^1H resonance spectra. Tetramethylsilane (TMS) was the internal standard, unless otherwise noted.

Specific rotations at the Hg green line were measured on a Rudolph Model 200 polarimeter using a 1 dcm tube. All values of $[\alpha]_{546}$ reported in this paper are averages of at least 4 such measurements. ORD curves were determined using a Jasco ORD/CD Model 5 recording spectropolarimeter. Reported values of $[\alpha]_D$ are taken from these curves.

Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and

---

(1) Sulfur Dioxide Insertion. XVI. For part XV of this series see J.E. Thomasson, P.W. Robinson, D.A. Ross, and A. Wojcicki, *Inorg. Chem.*, *10*, 2130 (1971).

(2) Postdoctoral Fellow of The Ohio State University Graduate School. Present address: Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, U.S.A.

(3) F. Calderazzo and K. Noack, *Coordination Chem. Rev.*, *1*, 118 (1966).

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

(5) A. Wojcicki, J.J. Alexander, M. Graziani, J.E. Thomasson, and F.A. Hartman, Proceedings of the First International Inorganica Chimica Acta Symposium on New Aspects of the Chemistry of Metal Carbonyls and Derivatives, Venice, Italy, Sept. 2-4, 1968, Paper C6.

(6) J.J. Alexander and A. Wojcicki in « Progress in Coordination Chemistry » (Proceedings of the 11th International Conference on Coordination Chemistry, Haifa and Jerusalem, Israel, Sept. 1968), M. Cais, Ed., Elsevier, New York, N.Y., 1968, pp. 383-384.

(7) R.B. King, « Organometallic Syntheses », Vol. 1, Academic Press, New York, N.Y., 1965, p. 114.

(8) J.A. Osborn and G. Wilkinson, *Inorg. Syntheses*, *10*, 68 (1967).

(9) E.L. Eliel and J.P. Freeman, *J. Amer. Chem. Soc.*, *74*, 923 (1952).

(10) P.A. Levene, L.A. Mikeska, and K. Passoth, *J. Biol. Chem.*, *88*, 27 (1930).

by Mr. P.J. Kovi of these laboratories using a Coleman Model 29 analyzer. Molecular weights were determined in chloroform with a Mechrolab Model 301-A vapor pressure osmometer by Dr. M.A. Jennings.

Preparation of π*–*$C_5H_5Fe(CO)_2[C(O)CH(CH_3)C_6H_5]$. 2.50 g (7.06 mmoles) of $[\pi\text{–}C_5H_5Fe(CO)_2]_2$ in THF was converted to $Na[\pi\text{–}C_5H_5Fe(CO)_2]$ by stirring under dry nitrogen with excess 2% sodium amalgam. After 1 hr the amalgam was removed and a solution of 2.15 g (12.8 mmoles) of $C_6H_5CH(CH_3)COCl$ in 40 ml of THF was added dropwise. After stirring for 7 hr the solvent was removed under reduced pressure. The residue was extracted with 200 ml of pentane in several portions and the combined extract was filtered through alumina. The volume of the filtrate was reduced in a stream of nitrogen. Cooling to –78° yielded 1.50 g of an orange-brown powder. Chromatography on grade III alumina, followed by concentration in a stream of N_2 and cooling to –78°, afforded yellow crystals which were collected on a cold frit and washed with cold pentane. The yield was 1.25 g (32%).

Anal. Calcd for $C_{16}H_{14}FeO_3$: C, 61.9; H, 4.50; mol. wt., 310. Found: C, 62.1; H, 4.60; mol. wt., 322. The compound melts at 57-59°. It gradually turns brown over a period of several weeks even when stored under N_2 in the freezer.

^1H nmr spectrum: resonances at τ 8.68 (doublet, J = 7 Hz, CH_3), 5.65 (quartet, J = 7 Hz, CH), 5.28 (singlet, C_5H_5), and 2.64 (singlet, C_6H_5) in $CDCl_3$ solution.

Infrared spectrum: ν_{CO} (terminal) at 2015 (vs) and 1960 (vs) cm^{-1} and ν_{CO} (bridging) at 1645 (m) and 1623 (m) cm^{-1} in CH_2Cl_2 solution.

The optically active $(-)_{546}$–π–$C_5H_5Fe(CO)_2[C(O)^*CH(CH_3)C_6H_5]$ was prepared similarly by using $(-)_{546}$–$C_6H_5{}^*CH(CH_3)COCl$. The yellow crystals were collected on a cooled frit. On warming to room temperature, the compound melted to a yellow-brown oil which was identified by its infrared spectrum. The measured $[\alpha]^{27}_{546}$ was $-64.3 \pm 0.4°$ ($CHCl_3$) solution). The optically active oil decomposed after several days; solutions in organic solvents decomposed within hours.

Preparation of π*–*$C_5H_5Fe(CO)_2[CH(CH_3)C_6H_5]$. 4.17 g (13.5 mmoles) of π–$C_5H_5Fe(CO)_2[C(O)CH(CH_3)C_6H_5]$ and 9.25 g (10.0 mmoles) of $Rh[P(C_6H_5)_3]_3Cl$ were stirred in 100 ml of benzene for 5 hr.[11] After filtering off yellow $Rh[P(C_6H_5)_3]_2(CO)Cl$, the solvent was removed at reduced pressure. The black residue was extracted with CH_2Cl_2 and the volume of the extract reduced in a stream of N_2. Chromatography on grade I alumina eluting with pentane afforded a single yellow band. On concentration in a stream of N_2 and cooling to –78° of the eluate, yellow crystals were obtained which were collected on a frit and washed with cold pentane. The yield was 2.10 g (55%).

Anal. Calcd for $C_{15}H_{14}FeO_2$: C, 63.8; H, 4.93; mol. wt., 282. Found: C, 63.3; H, 4.82; mol. wt., 256. The compound melts at 50-51°. It is reasonably stable over a period of several weeks when stored in the freezer but gradually darkens to a brown solid.

^1H nmr spectrum: signals at τ 8.42 (doublet, J = 7 Hz, CH_3), 6.09 (quartet, J = 7 Hz, CH), 5.63 (singlet, C_5H_5), and 2.98 (broad peak, C_6H_5) in $CDCl_3$ solution.

Infrared spectrum: ν_{CO} at 2005 (vs) and 1948 (vs) cm^{-1} in CH_2Cl_2 solution.

The optically active $(+)_{546}$–π–$C_5H_5Fe(CO)_2[{}^*CH(CH_3)C_6H_5]$ was prepared similarly from $(-)_{546}$–π–$C_5H_5Fe(CO)_2[C(O)^*CH(CH_3)C_6H_5]$. The yellow-orange crystals were collected on a cooled frit; they melted to a yellow-brown oil at room temperature. The compound was identified by its infrared spectrum. The measured $[\alpha]^{27}_{546}$ was $+78.4 \pm 1.0°$ ($CHCl_3$ solution).

Preparation of π*–*$C_5H_5Fe(CO)_2[S(O)_2CH(CH_3)C_6H_5]$. Sulfur dioxide was condensed onto 1.0 g (3.5 mmoles) of π–$C_5H_5Fe(CO)_2[CH(CH_3)C_6H_5]$ and the mixture was allowed to reflux for about 4 hr. Excess SO_2 was then removed, the residue was dissolved in $CHCl_3$, and the solution was chromatographed (grade III alumina) eluting with chloroform. The eluate was concentrated in a stream of nitrogen; addition of pentane and cooling to –78° affforded yellow crystals which were collected on a frit and washed with cold pentane. The yield was 0.81 g (66%).

Anal. Calcd for $C_{15}H_{14}FeO_4S$: C, 52.0; H, 4.05; mol. wt., 346. Found: C, 51.9; H, 4.24; mol. wt., 340. The solid melts with decomposition at 180-182°; it is stable in air for long periods. Its solutions in organic solvents show no sign of decomposition over a period of several hours.

^1H nmr spectrum: signals at τ 8.70 (doublet, J = 6.5 Hz, CH_3) and 6.4 (broad peak, CH) in $C_6H_5CH(CF_3)OH$ solution and τ 5.11 (singlet, C_5H_5) and 3.0 (broad peak, C_6H_5) in DMSO solution (external TMS).

Infrared spectrum: ν_{CO} at 2064 (vs) and 2015 (vs) cm^{-1} and ν_{SO_2} at 1203 (s) and 1052 (s) cm^{-1} in CH_2Cl_2 solution.

The optically active $(-)_{546}$–π–$C_5H_5Fe(CO)_2[S(O)_2{}^*CH(CH_3)C_6H_5]$ was synthesized by each of the following three procedures.

(a) *In Liquid* SO_2 *at Reflux*. The procedure was similar to that described above, except that the optically active $(+)_{546}$–π–$C_5H_5Fe(CO)_2[{}^*CH(CH_3)C_6H_5]$ was employed. The product melted at 172–173°; its $[\alpha]^{27}_{546}$ was $-176 \pm 3°$ ($CHCl_3$ solution).

(b) *In Liquid* SO_2 *at –60°*. The optically active alkyl was treated with SO_2 as in part (a), but at –60°. Solvent was removed while maintaining the reaction vessel at –60°. The yield was 25%. The isolated sulfinate had $[\alpha]^{27}_{546} = -186° \pm 2°$ ($CHCl_3$ solution).

(c) *In Pentane Solution at 27°*. Sulfur dioxide was bubbled through a pentane solution of the optically active alkyl for *ca.* 4 days. The solvent was then removed at reduced pressure and the residue was chromatographed as described above. The yield of the sulfinate with $[\alpha]^{27}_{546} = -158 \pm 2°$ ($CHCl_3$ solution) was approximately 60%.

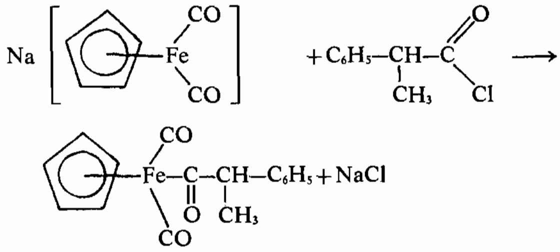
Shorter reaction times decrease the yield (*e.g.*, after 20 hr., only 12% yield) but do not alter optical purity of the product.

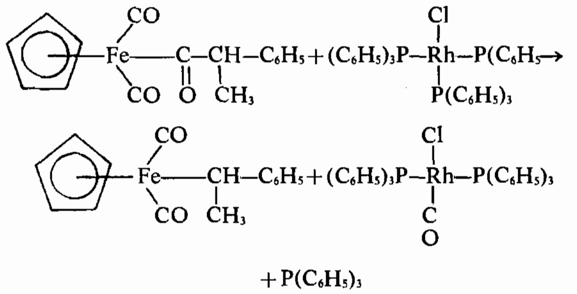
---

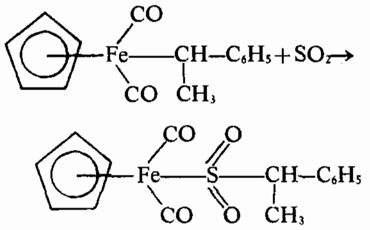
(11) J.J. Alexander and A. Wojcicki, *J. Organometal. Chem.*, *15*, P23 (1968).

Results and Discussion

The reactions carried out as part of this investigation are represented by eq. 3-5. Particular attention focusses on the sulfonylation (eq. 5), since elucidation of stereospecificity of this process was the chief objective of our study.


(3)


(4)


(5)

By starting the above sequence of reactions with optically active $(-)_{546}$–$C_6H_5{*}CH(CH_3)COCl$, one obtains the desired organometallic compounds—the acyl, alkyl, and sulfinate—which are also optically active. These optically active complexes melt at lower temperatures (the alkyl and acyl complexes are oils at room temperature) than their respective inactive forms, which are yellow, crystalline solids at 27°. The latter are therefore racemic compounds.[12]

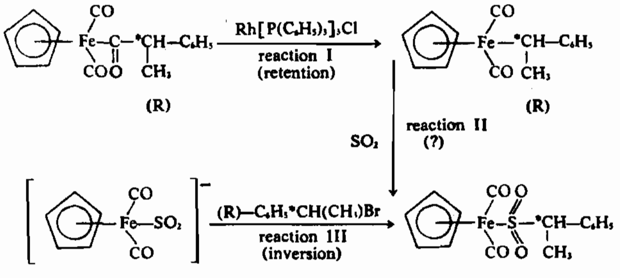
There are two principal points of interest which we shall consider. The first concerns the degree of stereospecificity of reaction 5. The second is related to the nature of stereochemical change during the same reaction at the α carbon of the alkyl group, *i.e.*, retention or inversion of configuration. We shall discuss them in this same order.

Since the acyl chloride, $(-)_{546}$–$C_6H_5{*}CH(CH_3)COCl$, was essentially 100% optically pure, reaction 3 gives the iron acyl, $(-)_{546}$–π–$C_5H_5Fe(CO)_2[C(O){*}CH(CH_3)C_6H_5]$, of comparable optical purity, as no transformation occurs at the α carbon. Stereospecificity of decarbonylation of metal acyl complexes by $Rh[P(C_6H_5)_3]_3Cl$ (eq. 4) has not been studied. However, a related process, that of carbonylation of π–$C_5H_5Fe(CO)_2[CHDCHDC(CH_3)_3]$ with $P(C_6H_5)_3$,[4] represented by eq. 2, has been shown to proceed with at least 95% retention of configuration. If we assume—and this is an entirely reasonable assumption—that reaction 4 is also almost completely stereospecific, then the isolated $(+)_{546}$–π–$C_5H_5Fe(CO)_2[{*}CH(CH_3)C_6H_5]$ should be the virtually pure dextrorotatory enantiomer. This compound is stable with respect to racemization. For example, stirring a solution of the optically active alkyl in benzene for 2 days at 27° results in no change in the value of $[\alpha]_{546}$.

Three somewhat different experimental conditions were employed in the synthesis of the sulfinate from the optically active alkyl (eq. 5). The variations entailed using (1) liquid SO_2 at −60° as the solvent, (2) liquid SO_2 at −10° as the solvent, and (3) solutions of SO_2 in pentane at 27°. The sulfinate obtained from these preparations exhibited $[\alpha]_{546} = -186°$, −176°, and −158°, respectively. In the solid it showed no sign of racemization on storage at 0° for 1 week. These results would be consistent with an assumption that the lowest energy and hence predominant path for the sulfonylation is stereospecific. However, at higher temperatures some racemization occurs which may possibly be a consequence of another, competing pathway for SO_2 insertion.

We tried to determine the extent of racemization accompanying reaction 5 by examining the ^1H nmr spectrum of $(-)_{546}$–π–$C_5H_5Fe(CO)_2[S(O)_2{*}CH(CH_3)C_6H_5]$ in the chiral $(+)_{546}$–π–$C_6H_5{*}CH(CF_3)OH$. This solvent has been effectively employed for determination of enantiomeric purity of various organic compounds, including the sulfoxides.[13] However, no splitting of either the C_5H_5 or CH_3 signals could be observeded for the sulfinate even at 220 MHz.[14]

It is not possible to say anything concrete about the nature of configurational change at the α carbon in reaction 5 solely from the results of this study. In an attempt to resolve the above dilemma, we designed a reasonable alternative stereospecific synthesis for the sulfinate. The procedure—an adaptation of the reaction discovered by Downs[15]—was to comprise the preparation of $[\pi$–$C_5H_5Fe(CO)_2SO_2]^-$ from $[\pi$–$C_5H_5Fe(CO)_2]^-$ and SO_2, and its subsequent interaction with optically active $C_6H_5{*}CH(CH_3)Br$ to give π–$C_5H_5Fe(CO)_2[S(O)_2{*}CH(CH_3)C_6H_5]$. This reaction (III) is shown below as part of an overall scheme correlating transformations of optically active relevant compounds.



Scheme I

---

[12] E.L. Eliel, « Stereochemistry of Carbon Compounds », McGraw-Hill Co., New York, N.Y., 1962, p. 45.

[13] W.H. Pirkle and S.D. Beare, *J. Amer. Chem. Soc.*, 90, 6250 (1968).

[14] We are indebted to Dr. N.A. Beach and G. Kreishman of the California Institute of Technology for these measurements.

[15] R.L. Downs and A. Wojcicki, to be submitted for publication.

We were to assume that reaction I proceeds with retention of configuration to yield the (R)-alkyl. A justification of this supposition was presented above (*vide supra*). Further, by analogy with nucleophilic displacement at an alkyl carbon atom by $[\pi\text{–}C_5H_5Fe(CO)_2]^-$,[4] we were to formulate reaction III as taking place with inversion at carbon to afford the (S)-sulfinate. Comparison of signs of $[\alpha]_{546}$ for samples of the sulfinate obtained *via* reactions II and III would then reveal the nature of configurational change at the α carbon accompanying the sulfonylation.

Reaction III was carried out in this laboratory by Dr. Reich-Rohrwig.[16] It yielded a small amount of the desired sulfinate which, unfortunately, showed no optical activity. Thus, still no conclusion can be reached regarding retention or inversion of configuration at carbon during SO_2 insertion. It is noteworthy, however, that the sulfonylation in liquid SO_2 and in pentane solution gives the sulfinate with the same sign (and approximately the same angle) of rotation. Consequently, it appears that the predominant mechanism is the same under both conditions.

In the course of preparation of this manuscript we were informed by Professor Whitesides[17] that the reaction between *threo*–π–$C_5H_5Fe(CO)_2[CHDCHDC(CH_3)_3]$ and liquid SO_2 at –50° proceeds with approximately 80% inversion of configuration. There is no obvious mechanistic rationale of this unexpected result at present.

Acknowledgments. This investigation has been supported by grants from the Petroleum Research Fund (2117-A3), administered by the American Chemical Society, and from the National Science Foundation (GP-8135 and GP-22544). We are also grateful to Miss S.R. Su for her assistance with some of the experiments described herein.

---

[16] P. Reich-Rohrwig, unpublished work. We thank Dr. Reich-Rohrwig for his collaboration.

[17] We thank Professor Whitesides for disclosing this information prior to publication. G.M. Whitesides and D.J. Boschetto, *J. Amer. Chem. Soc.*, 93, 1529 (1971).