Stereochromy of Reactions at Carbon–Transition Metal σ Bonds. (CH3)2CCHDCHDFe(CO)5C,H1

Paul L. Bock, David J. Boschetto, James R. Rasmussen, James P. Demers, and George M. Whitesides*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received September 24, 1973

Abstract: Convenient, stereoselective syntheses of three- and erythro-3,3-dimethylbutan-1-ol-1,2-d, (1) are described. Reaction of the p-bromobenasulfonate esters of 1 with CH3Fe(CO)5MgBr, -Li, or -Na yields \( \pi \)-cyclopentadienylidicarbonyliron \( \epsilon \)erythro- and \( \epsilon \)three-3,3-dimethyl butyl-1,2-d, (erythro- and \( \epsilon \)three-2) with >95% inversion of configuration at carbon. Bromination of 2 in pentane, chloroform, carbon disulfide, and dimethylformamide, and iodination in carbon disulfide, all take place with >90% inversion of configuration at carbon. Reaction of 2 with triphenylphosphine, tert-butyl isocyanide, bromine (in methanol), oxygen, cerium(IV) ion, or chlorine (in chloroform) leads to derivatives of 4,4-dimethylpentanoic-2,3-d; acid with >90% retention of configuration at carbon. Reaction of 2 with sulfur dioxide in a variety of solvents yields the product of sulfur dioxide insertion, (CH3)2CCHDCHDOSOFe(CO)5Cp, with >95% inversion of configuration at carbon. Insertion of dimethyl acetylenedicarboxylate into the carbon–iron bond of 2 takes place with >80% retention of configuration at carbon. Thermal decomposition of 2 produces a range of isotopically substituted derivatives of 3,3-dimethyl-1-butene. The mechanistic significance of the results is discussed.

The most valuable single type of information to have in characterizing the mechanism of a reaction that makes or breaks bonds at a tetrahedral carbon atom is the stereochromy of the transformation at that carbon. With this information it is possible to judge whether a reaction involves intermediate free carbon radicals or ions or occurs by Sn2 or S2 transition states. It is experimentally difficult to obtain stereochemical information about reactions involving transition metal alkyls. Traditional experimental procedures based on the preparation and reaction of enantiomeric organometallic compounds suffer from serious shortcomings. Enantiomerically pure organolithium and magnesium reagents are not generally available, and nucleophilic displacements by metalate anions and decarbonylation reagents are not generally available, and nucleophilic starting materials and products in organometallic reactions are complicated by side reactions and stereochemistry have not been established. 

The usefulness of this alkyl group rests in the fact that it can exist in solution as a rapidly interconverting mixture of one trans and two gauche conformers. The vicinal coupling constant characterizing the CHDCHD fragment is a weighted average of the couplings in each conformation. For most groups X, the trans conformation is sufficiently favored energetically that the vicinal coupling constants for erythro and threo diastereomers are easily distinguishable experimentally. Analysis of the AA'XX' or (AA'BB') spectra of the CH3X2

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References

(1) Supported by the National Science Foundation, Grants GP-14247 and GP-28586X, and by the National Institutes of Health, Grant GM 16020.
(4) M.I.T. UROP Participant.
(6) Cobaloxime anion, and to a lesser extent other strongly nucleophilic reagents are not generally available, and nucleophilic reagents are not generally available, and nucleophilic starting materials and products in organometallic reactions are complicated by side reactions and stereochemistry have not been established.
(7) Carbonylation and decarbonylation may prove to be one such reaction: vide infra.
(16) G. M. Whitesides, J. F. Sevenair, and R. W. Goetz, J. Amer. Chem. Soc., 89, 1135 (1967). The uncertainties listed for \( \Delta E \) in the third column of Table IV of this paper are in error; each should be ca. 10% of the value of \( \Delta E \); the first entry in this column should read \( \Delta E = 2.33 \pm 0.28 \text{ kcal mol} \).
whether the product belongs to the erythro or threo series using the same technique immediately establishes the stereochemistry at carbon that characterizes the reaction.  

This technique has a number of practical advantages over other available methods for examining the stereochemistry of reactions of transition metal alkyls: first, the organometallic compounds involved are primary alkyls, and relatively stable thermally; second, E2 elimination seems to be a less important side reaction for SN2 displacement at C-1 of the 3,3-dimethylbutyl group than for similar reactions at secondary centers; third, since there is no significant steric difference between threo- and erythro-(CH3)3CCHDCHDX, it is only necessary to examine one diastereomer; finally, since many impurities do not hinder the identification of the diastereomeric composition of the sample, the standard of purity required for accurate analysis of these substances is less rigorous than that required for, e.g., measurement of optical rotation.

Certain restrictions characteristic of this use of the 3,3-dimethylbutyl system deserve mention. First, organometallic derivatives of this alkyl moiety must be synthesized by nucleophilic displacements using metallating reagents rather than by other less direct routes such as decarbonylation or transmetallation. Second, 3,3-dimethylbutylcyclopentadienyl magnesium and lithium reagents are not configurationally stable. The rate of SN2 displacement at C-1 of this alkyl group is relatively slow. Second, since nmr spectroscopy is the only practical method of distinguishing between diastereomeric derivatives in this series, the organometallic substances being examined must be diamagnetic. Finally, conclusions derived from studies of 3,3-dimethylbutylmetal compounds cannot necessarily be generalized to other types of alkylmetal systems, since the mechanisms of organometallic reactions seem particularly sensitive to changes in the structures of the alkyl moieties involved.

These restrictions notwithstanding, the study of 3,3-dimethylbutyl-1,2-d2-metal compounds offers the most convenient method presently available for studying the stereochemistry of reactions of transition metal...
alkyls. In this paper we detail procedures for the synthesis of the deuterated starting materials and the results of studies of a number of reactions of one transition metal compound, cyclopentadienyldicarbonyliron 3,3-dimethylbutyl-1,2-d$_2$ (2).

**Results**

**Synthesis of erythro- and threo-(CH$_3$)$_3$CCHDCHDOAc, -CH$_2$CHDCHDOH (1), and -CH$_2$CHDCHDFe(CO)$_2$Cp (2).**

![Diagram of Scheme I](image)

Scheme I. Synthesis of threo- and erythro-3,3-Dimethylbutan-1-ol-1,2-d$_2$ (Only One Enantiomer of Each Compound is Shown)

(29) The synthesis of erythro-1 used in the early stages of the project was based on *trans*-ethylene-1,2-d$_2$ oxide; the synthesis of this substance requires the manipulation of large volumes of acetylene-1,2-d$_2$ and ethylene-1,2-d$_2$ and has been discarded in favor of the more convenient synthesis reported here. Details of the earlier procedure are contained in the Ph.D. Thesis of D. J. Boschetto, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1971.

retention at carbon is observed in certain instances when the nucleophilic reagent is (CH_3)_2SnLi. We find that attack of CpFe(CO)_n^+ on brosylates derived from 1 takes place with >95% inversion of configuration at carbon for M^+ = Na^+, Li^+, and MgBr^+ 36-38 and that reaction of CpFe(CO)_nLi with 3,3-dimethylbutyl-1,2-d-bromide also proceeds with inversion. Thus, there is no suggestion in this system of the mechanistic duality that apparently exists in analogous reactions using trimethyltin lithium. Typical spectra for the erythro- and threo-2 are shown in Figure 1. The spectrum of the erythro diasteriomer provides an example of the line broadening that has occasionally proved troublesome in these studies; this broadening presumably reflects paramagnetic impurities present in the solution that are not removed by the purifications employed for 2.

The observation that nucleophilic displacement by CpFe(CO)_n^+ on the brosylate derived from threo-1 yields erythro-2 establishes two useful facts: first, that this displacement has the stereochemical characteristics expected of an unexceptional SN2 displacement, and second, that the carbon–iron σ bond of 2 is configurationally stable over periods of time sufficiently long for it to be a useful substrate for mechanistic studies. 39,40

Reactions of erythro-2 with Halogens. Reaction of erythro-2 with molecular bromine in pentane and carbon disulfide occurs rapidly at 0°, yielding threo-(CH_3)_2-CCHDCHDBr (3) with greater than 95% inversion of configuration at carbon (Figure 2); reaction in dimethylformamide (DMF) yields a 9:1 mixture of threo- and erythro-3; reaction in methanol yields no 3 but carbonyl containing products (vide infra). Reaction of threo-2 with bromine in chloroform-d had previously been shown to yield erythro-3 with greater than 95% inversion of stereocchemistry. 21 The partial loss of stereocchemistry observed in DMF may be an artifact of the work-up procedure; bromide ion catalyzed epimerization of 3 might be sufficiently rapid in DMF under the conditions used in these experiments to influence the apparent stereocchemistry of the reaction. Cleavage of the carbon–iron bond of 2 with bromine thus proceeds with inversion of configuration, in a reaction whose stereocchemistry shows no significant dependence on solvent polarity. 14,47

(36) The sodium salt is produced by reduction of [CpFe(CO)_n^+ with sodium amalgam, the lithium salt by reduction with lithium (1°, sodium) wire, and the magnesium bromide salt by reaction with magnesium and 1,2-dibromoethane. 2


(38) The alkylation of CpFe(CO)_n^+ by (-)-(+)-sec-butyl bromide has been inferred to proceed with 75% inversion of configuration at carbon cf. ref 14d.


(40) We have seen no evidence of epimerization of 2 on standing as a solid for longer than 3 weeks at -20° or in solution in CCl_4 or CDCl_4 at room temperature for 12 hr.


(44) It has been suggested that these reactions should be called ligand transfer processes (cf. ref 85) and F. Bonolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1968, p 578.
Although these reactions were carried out in the ortho-acetyliron compound are both included in this scheme, phosphine and the decarbonylation of the resulting product with the expected retention of stereochemistry. Less expectedly, reaction of erythro-2 with a number of oxidizing agents (bromine, ceric ammonium nitrate (CAN), oxygen, all in methanol, and chlorine in chloroform) also lead to carbonyl inserted products, all characterized by >95% retention of configuration at carbon (Figure 3). 

**Sulfur Dioxide Insertion.** The mechanism of insertion of sulfur dioxide into carbon-iron σ bonds remains a puzzle, despite extensive investigation. The reaction is characterized by large, negative, entropies of activation and by rate acceleration from electron-releasing substituents on the alkyl group attached to the metal; O-sulfinato complexes have been implicated as intermediates, and the reaction occurs with high stereoselectivity (and presumably with retention of configuration) at iron. These data are compatible with a mechanism for sulfur dioxide insertion resembling that for carbon monoxide insertion. However, the stereochemistry at carbon for these two reactions is opposite. We have examined carefully the S-sulfinato complex obtained by reaction of erythro-2 with sulfur dioxide in a variety of solvents and find in each instance that the reaction proceeds with greater than 95% inversion of configuration at carbon (Figure 4); by contrast, carbon monoxide insertion proceeds stereospecifically with retention of configuration at carbon (vide supra).

**Addition of erythro-2 to Dimethyl Acetylenedicarboxylate. Elimination of tert-Butylethylene on Thermal Decomposition of erythro-2.** The addition of transition metal alkyls to carbon-carbon multiple bonds, and the generation of carbon-carbon unsaturation by metal hydride elimination from transition metal alkyls, are both reaction types of central importance in catalysis. Organoiron compound 2 does not add to simple olefins or to most of the reactive carbon–carbon unsaturations commonly used in organometallic chemistry (tetracyanoethylene, tetrfluoroethylene, hexafluorobut-2-yn, or diphenylacetylene). However, when erythro-2 was heated with dimethyl acetylenedicarboxylate in THF for 24 hr at 50–60°C a new compound was produced which could be isolated in 60% yield as a black oil. This compound was assigned the structure 5 based on spectroscopic data summarized in the Experimental Section.

For convenience, the reaction of 2 with triphenylphosphine and the decarbonylation of the resulting acyliron compound are both included in this scheme, although these reactions were carried out in the opposite diastereomeric series. Reaction of erythro-2 with tert-butyl isocyanide led to the carbonyl insertion product with the expected retention of stereochemistry.
Although the stereochemistry around the carbon–carbon double bond cannot be assigned with any assurance, examination of the nmr spectrum of the 3,3-dimethylbutyl-\(d_1\) moiety of this compound indicates that the transfer of this alkyl group to the acetylenic bond has occurred with \(\geq 80\%\) retention of configuration (Figure 5). The low precision of this estimate reflects the poor quality of the spectrum; we were unable to eliminate the broadening of the lines, even after extensive purification. To increase our confidence in this conclusion, the same experiment was carried through starting with \textit{threo}-2. The spectrum of the resulting adduct was also broad (Figure 5) but again gave no indication of inversion of configuration in the product.

An effort to determine the stereochemistry of the process leading to generation of 3,3-dimethylbut-1-ene on thermal decomposition of 1 was not successful; the yield of olefins was low (\textit{ca. 15\%}), and, although the signals of the various possible isotopic substitution patterns could be clearly resolved (Figure 6), the mixture of products obtained strongly suggested that the rates of both intra- and intermolecular scrambling processes were rapid under the conditions used.\(^{54}\)

**Discussion**

The retention of configuration at carbon observed for reactions resulting in carboxylation of the 3,3-dimethylbutyl-\(d_1\) moiety of 2 is the result anticipated on the basis of previous studies of related reactions.\(^{10,21,42}\) This reaction promises to be very useful in future studies of the stereochemistry of reactions involving transition metal organometallic compounds: a wide variety of organometallic substances can be carboxylated, and with only one possible exception,\(^{55}\) all carboxylations and de-carboxylations whose stereochemistry has been determined.


\(^{55}\) F. Calderazzo and K. Neack\(^{14}\) have reported that the conversion of optically active \textit{i} to \textit{ii} preserves the sign of rotation, while conversion of optically active \textit{iii} to \textit{iv} results in change in sign.\(^{26}\) Without knowing the relative configuration of \textit{i} and \textit{ii}, and of \textit{iii} and \textit{iv}, it is impossible to interpret these signs of rotation in any convincing way. Further, conversion of \textit{i} to \textit{ii} was low, and the rotation result is open to some suspicion. Nonetheless, the fact that two, at least superficially similar, transformations take place with opposite effects on the signs of rotation suggests that one might take place with inversion of configuration at carbon.

The stick spectra under the experimental spectrum represent the positions of the various deuterated olefins, based on coupling constants of 1.6 Hz (geminal), 10.6 Hz (cis), and 17.1 Hz (trans); where indicated, Z and E designate the configuration of the substance around the oleinic bond: a, 1,1-d$_2$; b, 3,3-dimethylbut-1-ene-1,1-d$_2$; c, 1,2-d$_2$; d, 1,2-d$_2$; e, 1-d$_2$; f, 2-d$_2$; g, 3-d$_2$. The chemical shifts used for these spectra varied slightly between compounds as a result of isotope effects, but (approximately) $\delta_1 = 5.81$, $\delta_2 = 4.80$, and $\delta_3 = 4.88$.

Retained have been found to take place with retention of stereochemistry at carbon. Thus, carbonylation and decarbonylation may prove to be the stereochemical equivalent of the SN2 reaction in aliphatic organic chemistry, in the sense of providing reactions of dependable stereochemical course that can be relied on in chemical correlations of configuration in the organometallic series. The mechanism(s) of the oxidative carbonylations is not presently known. Conversion of tetracarbonylalkyliron anions, $\text{RFe(CO)}_4^-$, to acyl compounds is Lewis acid catalyzed; certain of the reactions reported in Scheme II might also be. However, those of these reactions run in the presence of oxidizing agents more probably involve electron transfer as an important step. It is not immediately evident why oxidation should encourage acyl formation, but the phenomenon occurs both in the several examples summarized in Scheme II and elsewhere.\(^{(57)}\)

The halogenation reactions studied here that result in carbon-halogen bond formation all occur cleanly with inversion of configuration at carbon. Inversion of configuration has also been inferred to be the major stereochemical result of halogenation of several organolithium,\(^{(19,58)}\) boron,\(^{(59)}\) cobalt,\(^{(11,60)}\) and silicon,\(^{(12)}\) germanium,\(^{(42)}\) tin,\(^{(42)}\) and lead\(^{(42)}\) compounds. Retention has been observed for palladium(II),\(^{(17)}\) manganese,\(^{(14)}\) and mercury\(^{(11)}\) alkyls. It is not yet possible to construct convincing rationalizations for all of these stereochemical results. The retention of configuration observed for palladium(II) probably reflects an oxidative addition of halogen followed by reductive elimination of alkyl halide and would be expected to characterize halogenations of similar, coordinatively unsaturated, \(d^7\) alkyls. The mechanism describing the bromination of 2 is less obvious, but the stereochemistry-determining transition state probably resembles either that proposed by Jensen for tetraallyltin reagents (6), and probably important for bromination of boronate ions,\(^{(39)}\) or the substance formally obtained by oxidative addition of bromonium ion to iron (7). Since the compound resulting from oxidative addition of a full equivalent of molecular bromine to 2 would both contain a formal iron(IV) species and violate the 18-electron rule,\(^{(51)}\) a halogenation mechanism analogous to that discussed for palladium seems unlikely for 2. The partial oxidative addition represented by 7 would serve to convert the $\text{CpFe(CO)}_2$ moiety into a $\text{[CpFe(CO)Br]}_2$ group.\(^{(58)}\)

\begin{align*}
\end{align*}
tion of the lithium, cobalt, and manganese organo-
that apparently characterize the oxidation of 2 dtr
ation seem unlikely, because the carbonylation prcp-
the latter would be expected to be an excellent leaVing
group. The several plausible radical chain pathways
resulting from coordination of the acetylene to iron ap-
pears no more attractive than does 8, but if this re-
action actually involves electrophilic attack on the
carbon–iron bond without prior coordination, it is not
evident that it should not also follow whatever dictates
that lead to backside attack in reaction with sulfur
dioxide. However, it is pertinent that cleavage of the
carbon–iron bond of 2 with mercuric chloride, normally
an electrophilic reagent, occurs cleanly with retention
of configuration at carbon.²¹

In summary, reactions at the carbon–iron bond of 2
appear to involve at least three types of processes: alkyl
shift, with retention of configuration at carbon, to
coordinated carbon monoxide induced by an attacking
nucleophile and/or by oxidation of the iron; attack
on a noncoordinated electrophile with inversion of con-
figuration; and transfer to an electrophile with re-
tention of configuration. Too few data are presently
available to resolve these processes into detailed mech-
nisms capable of predicting the stereochemical course
of new reactions, but the high stereoselectivity charac-
terizing reactions of 2, and the configurational
stability of its carbon–metal bond, establish that stereo-
chemical studies should prove as useful in the elabora-
tion of the mechanisms of reactions of organonitrogenic
derivatives of transition metals as they have of organic
compounds.

Experimental Section

General Methods. All reactions involving organometallic
compounds were carried out under nitrogen. Prepurified nitrogen
was passed through a 12-in. tube containing Drierite. All solvents
were reagent grade; THF was distilled from a dark purple solution
of benzophenone dianion before use; ether was distilled from
lithium aluminum hydride; other solvents were dried over molec-
ular sieves and degassed by bubbling a vigorous stream of nitrogen
through them. Methyl- and o-butyllithium were supplied by Foonie
Mineral Corp. or Ventron Corp. Cyclopentadienyldicarbonyliron
dimer was obtained from Strem Chemicals Inc. and was recrystalliz-
ted before use by dissolving in the minimum amount of acetone at
room temperature, adding ¹, that volume of water, and cooling in a
refrigerator maintained at –20. Technical grade deuterium
was obtained from the Matheson Co., Inc., Platinum black
catalyst was supplied by Engelhard Ind. Stainless steel cannulas
were obtained on special order from Pepper and Sons Co., New
York, N. Y. 10010. Melting points and boiling points are un-
corrected. Infrared spectra were taken in sodium chloride cells on a
Perkin-Elmer Model 237 grating spectrophotometer. Routine
nmr spectra were recorded on a Varian T-60 spectrometer; chemi-


(63) Flood and Miles have provided evidence that sulfur dioxide in-
insertion into a carbon–iron bond proceeds with high stereo-
selectivity at iron. If an ion pair is an intermediate in this reaction, the obser-
vation that stereochemistry at iron is (presumed to be) retained suggests
that stereochemical studies at metallic centers will be less useful for
identifying ionic intermediates than are analogous studies at carbon
centers.

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Boron trifluoride gas\(^{65}\) was introduced with a syringe needle through the No-Air stopper and was allowed to bubble through the rapidly stirred solution. The flask and contents were weighed occasionally, and after a total of 180 g of boron trifluoride had dissolved, the contents of the flask were transferred by forced siphon through a stainless steel cannula into a 54-ml, three-necked flask equipped with a mechanical stirrer, Dry ice condenser, and an addition funnel. The temperature, containing 560 ml of concentrated sulfuric acid. The No-Air stopper was replaced with a dripping funnel,\(^{66}\) the flask was immersed in an ice bath, and rapid stirring was initiated. A solution of 458 g (6.18 mol) of tert-butyl alcohol in 884 g (9.11 mol) of 1.1-dichloroethane was added slowly from the dripping funnel to the stirred sulfuric acid over 6.5 hr. Evolution of hydrochloric acid began immediately; the evolved gas was vented through a short hypodermic syringe needle through the No-Air stopper. After 64 hr and when the temperature was 60°C, material was allowed to distill at room temperature and was taken up in 200 ml of pentane. The pentane solution was washed with three 100-ml portions of saturated aqueous sodium bicarbonate solution and once with 100 ml of water and dried (MgSO\(_4\)). A solution of 210 g (2.10 mol) of isobutyl chloride in 500 ml of three-necked flask equipped with a magnetic stirring bar and a No-Air stopper was charged with 500 ml of concentrated sulfuric acid, tared, and cooled by immersion in an ice bath. Boron trifluoride gas\(^{\text{64}}\) was introduced with a syringe needle through the No-Air stopper and was allowed to bubble through the rapidly stirred solution. The flask and contents were weighed occasionally, and after a total of 180 g of boron trifluoride had dissolved, the contents of the flask were transferred by forced siphon through a stainless steel cannula into a 54-ml, three-necked flask equipped with a mechanical stirrer, Dry ice condenser, and an addition funnel. The temperature, containing 560 ml of concentrated sulfuric acid. The No-Air stopper was replaced with a dripping funnel,\(^{66}\) the flask was immersed in an ice bath, and rapid stirring was initiated. A solution of 458 g (6.18 mol) of tert-butyl alcohol in 884 g (9.11 mol) of 1.1-dichloroethane was added slowly from the dripping funnel to the stirred sulfuric acid over 6.5 hr. Evolution of hydrochloric acid began immediately; the evolved gas was vented through a short hypodermic syringe needle through the No-Air stopper. After 64 hr and when the temperature was 60°C, material was allowed to distill at room temperature and was taken up in 200 ml of pentane. The pentane solution was washed with three 100-ml portions of saturated aqueous sodium bicarbonate solution and once with 100 ml of water and dried (MgSO\(_4\)).

3,3-Dimethylbutyl acid was prepared using a modification of a literature procedure.\(^{66}\) A 1-L round-bottomed flask equipped with a magnetic stirring bar and a No-Air stopper was charged with 500 ml of concentrated sulfuric acid, tared, and cooled by immersion in an ice bath. Boron trifluoride gas\(^^{64}\) was introduced with a syringe needle through the No-Air stopper and was allowed to bubble through the rapidly stirred solution. The flask and contents were weighed occasionally, and after a total of 180 g of boron trifluoride had dissolved, the contents of the flask were transferred by forced siphon through a stainless steel cannula into a 54-ml, three-necked flask equipped with a mechanical stirrer, Dry ice condenser, and an addition funnel. The temperature, containing 560 ml of concentrated sulfuric acid. The No-Air stopper was replaced with a dripping funnel,\(^{66}\) the flask was immersed in an ice bath, and rapid stirring was initiated. A solution of 458 g (6.18 mol) of tert-butyl alcohol in 884 g (9.11 mol) of 1.1-dichloroethane was added slowly from the dripping funnel to the stirred sulfuric acid over 6.5 hr. Evolution of hydrochloric acid began immediately; the evolved gas was vented through a short hypodermic syringe needle through the No-Air stopper. After 64 hr and when the temperature was 60°C, material was allowed to distill at room temperature and was taken up in 200 ml of pentane. The pentane solution was washed with three 100-ml portions of saturated aqueous sodium bicarbonate solution and once with 100 ml of water and dried (MgSO\(_4\)). A solution of 606 g (1.00 mol) of 1.65 M n-tetraethylammonium in 2822
ether, transferred by cannula into the dropping funnel, was added over a 45-min period to the rapidly stirred dihydronaphthalene solution. Evolution of methane began immediately and continued for several minutes after the addition was complete. The resulting solution was a clear dark green. The dropping funnel was rinsed with 10 ml of dry degassed ether and charged with 92.2 g (4.92 mmol of 3,3-dimethylbutanal. The aldehyde was slowly added with continued stirring to the cold solution of lithium dihydride; addition was complete in 30 min.6 The mechanical stirrer and dropping funnel were replaced with No-Air stoppers. The reaction mixture was set aside in a Dry Ice bath. After the resulting solution had been allowed to stir for 0.5 hr, the dropl-ring funnel was charged with a solution of 3.50 g of sodium hydroxide in 50 ml of water and 15 ml of dry degassed ether. The ether extracts were washed twice with 5-ml portions of water and dried (MgSO4). The ether was removed by distillation through a 10-cm Vigreux column, and the higher boiling material was distilled through a MiniLab microdistillation apparatus, yielding 1.86 g (1.84 mmol, 68%), based on trans-1-acetoxy-3,3-dimethylbut-1-ene of three-3,3-dimethylbutan-1-ol-1,2-d, bp 140-144 (lit.5 bp 140-145); ir (CHCl3) 3450, 1650, 1340, 1040, 940 cm-1; deuterium-decoupled nmr (CHCl3) δ 3.39 (d, J = 5.8 Hz), 3.40 (t), 1.46 (d, J = 5.8 Hz), 0.92 (s, 9). erystoro-1-Acetoxy-3,3-dimethylbutan-1,2-d, erythro-1 was prepared via cis-1-acetoxy-3,3-dimethylbutan-1,2-d following the method described for the synthesis of three-2. The product had the same glpc retention time as an authentic sample of 3,3-dimethylbutan-1-ol and had: deuterium-decoupled nmr (CHCl3) δ 3.91 (d, J = 8.9 Hz), 1.92 (s), 1.39 (d, J = 8.9 Hz), 0.93 (s, 9). cyclopentadienylricarbonyl iron erythro-3,3-Dimethylbutyl-1,2-d (9). A using a literature procedure,27 magnesium powder (40 mesh, 0.68 g, 28 mg-atoms), 2.84 g (80 mmol) of r-cyclopenta
dienylricarbonyl dimer, 0.69 ml (1.50 g, 8.0 mmol) of 1,2-dibromoethane, and 100 ml of dried, degassed THF were placed in a flame-dried 250-ml flask equipped with a magnetic stirring bar and a nitrogen inlet. This reaction mixture was allowed to stir at room temperature for 19 hr. A 30-ml centrifuge tube was equipped with a magnetic stirring bar and a No-Air stopper and was flame dried. Anhydrous ether (10 ml) and 1.58 g (11.5 mmol) of erythro-1 were introduced through thestopper using a syringe, and the mixture was cooled and stirred in an ice bath. To this solution was added 7.0 ml (16.0 mmol) of a 2.28 M solution of n-butyllithium in hexane. A white precipitate formed during the slow addition of the lithium reagent. After the addition was complete, the reaction mixture was allowed to stir for 15 min, and 8.8 g (15.2 mmol) of p-bromobenzensulfonyl chloride was cautiously added. The solution was allowed to warm to room temperature and to continue stirring for 1 hr. The solution was centrifuged and the supernatant liquid was removed and stored under nitrogen. The remaining white precipitate was washed through on 25-nil portions of degassed ether, and the solutions of brosylate and washings were added by forced siphon through a stainless steel cannula to the previously prepared solution of iron amnon. The resulting solution was allowed to stir under nitrogen at room temperature for 3 hr. The reaction solvent was removed by distillation at 0.1 mm of pressure, and the solid residue was extracted with five 25-nil portions of degassed pentane. The extracts were concentrated to a 10-nil volume and chromatographed under nitrogen on a 2 x 20-cm column of Merck acid-washed alumina, using degassed pentane as the eluent. One yellow band eluted: removal of the pentane at room temperature and 0.1 mm of pressure left 2.64 g (10.0 mmol, 66%, based on erythro-1) of a yellow solid: mp 33-34 °C (CHCl3) 2980, 2010, 1740, 1465, 1365, 1240, 1045 cm-1: deuterium-decoupled nmr (CDCl3) δ 4.02 (d, J = 6.1 Hz), 1.95 (s, 3), 1.50 (d, J = 6.1 Hz), 0.93 (s, 9). The crude acetate was hydrolyzed without further purification. three-3,3-Dimethylbutan-1-ol-1,2-d. To 3.75 g of crude three-1 was added 15 ml of 20% AgNO3 (w/v) in water, and the reaction mixture was allowed to stir at reflux overnight. Glpc analysis indicated that all the acete had been hydrolyzed. The reaction mixture was extracted with five 5-nil portions of ether, and the ether extracts were washed twice with 5-nil portions of water and dried (MgSO4). The ether was removed by distillation through a 10-cm Vigreux column, and the higher boiling material was distilled through a MiniLab microdistillation apparatus, yielding 1.86 g (1.84 mmol, 68%), based on trans-1-acetoxy-3,3-dimethylbut-1-ene of three-3,3-dimethylbutan-1-ol-1,2-d, bp 140-144 (lit.5 bp 140-145); ir (CHCl3) 3450, 1665, 1340, 1040, 940 cm-1; deuterium-decoupled nmr (CHCl3) δ 3.39 (d, J = 5.8 Hz), 3.40 (t), 1.46 (d, J = 5.8 Hz), 0.92 (s, 9). erystoro-1-Acetoxy-3,3-dimethylbutan-1,2-d, erythro-1 was prepared via cis-1-acetoxy-3,3-dimethylbutan-1,2-d following the method described for the synthesis of three-2. The product had the same glpc retention time as an authentic sample of 3,3-dimethylbutan-1-ol and had: deuterium-decoupled nmr (CHCl3) δ 3.91 (d, J = 8.9 Hz), 1.92 (s), 1.39 (d, J = 8.9 Hz), 0.93 (s, 9). cyclopentadienylricarbonyl iron erythro-3,3-Dimethylbutyl-1,2-d (9). A using a literature procedure,27 magnesium powder (40 mesh, 0.68 g, 28 mg-atoms), 2.84 g (80 mmol) of r-cyclopenta
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ffask was equipped with a magnetic stirring bar, a syringe needle methanol as the solvent. Glpc analysis of the crude product mixtures indicated the presence of 1-bromo-3,3-dimethylbutane-dz which showed isotopic composition (70 eV) : 1 .O '% do, 3 .9 % db 93 .4% dz, 1 .7 7t" dt, and 0.0 7(, of e ry t lt ro- and th reo-l-bromo-3,3-dimethylbutane-1,2-dz (330 mg, 43%) of a yellow solid whose ir spectrum was indistinguishable from that reported above: deuterium-decoupled nmr (CHC1) n.0 .92 (s, 9), 1 .62 (d, 1, J : 11.0 Hz), 2 .78 (d, 1, J : 4.4 Hz). The lines were broad and small amounts (10%) of the erythro diastereomer probably would not have been detected.

1-Bromo-3,3-dimethylbutane-1,2-dz for Mass Spectral Analysis. A 25-ml round-bottomed flask equipped with a magnetic stirring bar and a No-Air stopper was flame dried, and 10-ml of dry (molecular sieves), degassed dimethylformamide, 1.28 g (4.9 mmol) of triphenylphosphine, and 0.50 c @.9 mmol) of erythro-l were introduced. Bromine (0.27 ml, 0.88 g, 4.9 mmol) was added in drops over a 2 min period a solution of 100 mg (0.38 mmol) of 2 in 0.20 ml of dry, degassed CHCl3. The reaction mixture immediately turned brown. The reaction mixture was allowed to warm to room temperature and all volatile contents was distilled at 30° and 0.02 Torr into a collector held at -78°. Collection of product by glpc afforded a sample of 1-bromo-3,3-dimethylbutane-1,2-dz which showed isotopic composition (70 eV) : 1 .O '% do, 3 .9 % db 93 .4% dz, 1 .7 7t" dt, and 0.0 7(, of e ry t lt ro- and th reo-l-bromo-3,3-dimethylbutane-1,2-dz (330 mg, 43%) of a yellow solid whose ir spectrum was indistinguishable from that reported above: deuterium-decoupled nmr (CHC1) n.0 .92 (s, 9), 1 .62 (d, 1, J : 11.0 Hz), 2 .78 (d, 1, J : 4.4 Hz). The lines were broad and small amounts (10%) of the erythro diastereomer probably would not have been detected.

Reaction of 2 with Bromine. Bromine vapor (0.15 ml 2.7 mmol) was swept with a stream of nitrogen through a rapidly stirred solution of 450 mg (1.7 mmol) of the alkyl bromide compound 2 in 0.5 ml of solvent (pentane, carbon disulfide, or dimethylformamide) under a nitrogen atmosphere at 0°. After 15 min all of the bromine had been bubbled through the reaction mixture, and the components of this mixture were distilled at room temperature (60° for the reaction mixture employing DMF) and 0.005 Torr into a trap cooled with a liquid nitrogen bath. Glpc analysis of the product mixtures indicated the presence of 1-bromo-3,3-dimethylbutane-1,2-dz: deuterium-decoupled nmr (pentane) 5 .32 (d, 1, J : 5.3 Hz), 1 .78 (d, 1, J : 5.1 Hz), 0.92 (s, 9); the carbon disulfide 5 .32 (d, 1, J : 5.1 Hz), 1 .78 (d, 1, J : 5.1 Hz), 0.92 (s, 9); in dimethylformamide 5 .17 (d, 1, J : 5.1 Hz), 0.91 (s, 9); the doublet at 3.24 was obscured by dimethylformamide absorptions.

Methyl erythro-4,4-Dimethylpentanoate-2,3-dz-l. The bromination of 2 was carried out as described above, using anhydrous methanol as the solvent. Glpc analysis of the crude product mixture showed only a minor amount (~5% of the major product) of the alkyl bromide 4, the majority of the product being identified as methyl-4,4-dimethylpentanoate-2,3-dz. A solution of 100 mg of the mixture in 2 ml of THF was added to 0.52 g (20 mmol) of triphenylphosphine in a 25-ml flask equipped with a water-cooled condenser and a magnetic stirring bar. The mixture was heated to 65° for 19 hr. An ir spectrum of an aliquot of the reaction mixture indicated carbynyl stretching at 1920 and 1615 cm⁻¹. The solvent was removed under reduced pressure and the red-orange residue was dissolved in 2 ml of chloroform and chromatographed on a 2 x 20 cm column of Activity III neutral alumina (Woelm). Two yellow bands separated. The first was collected with 50 ml of cyclopentane eluant and had an ir spectrum with carbynyl stretching at 2005 and 1955 cm⁻¹. The second yellow fraction collected with 50 ml of chloroform and was eluted with a 2 x 25-cm column of neutral alumina packed in pentane. Elution with the same solvent indicated a major product.

Reaction of 2 with Chlorine. A 25-ml round-bottomed flask was flushed with chlorine gas, and the chlorine (25 ml, 1.1 mmol) was then condensed into a liquid nitrogen cooled trap on a vacuum line. The chlorine was allowed to bulb-to-bulb distill into a 5-ml flask held at -195° and containing 0.5 ml of dry (molecular sieves), degassed CHCl3, and a magnetic stirring bar. The flask was stoppered with a No-Air stopper and transferred to a bath held at -20°. To this rapidly stirred chlorine solution was added in drops over a 2 min period a solution of 100 mg (0.38 mmol) of 2 in 0.20 ml of dry, degassed CHCl3. The reaction mixture immediately turned brown. The reaction mixture was allowed to warm to room temperature and all volatile contents was distilled at 25° (0.005 mm). Glpc analysis of the crude product mixture indicated one major product, erythro-4,4-dimethylpentanoyl-2,3-dz-chloride, identified on the basis of its ir and nmr spectra: 22 ir (CHCl3) 2930, 1790, 1510, 1360, 1280, 955 cm⁻¹; deuterium-decoupled nmr 6 0.94 (s, 9), 1.62 (d, 1, J : 11.0 Hz), 2.78 (d, 1, J : 11.0 Hz).

1-Cyclopentadienyl(triphenylphosphine)carbonyl iron threo-3,3-Dimethylbutyl-1,2-dz. A solution of 100 mg of the mixture of 1-cyclopentadienyl(triphenylphosphine)carbonyl iron threo-3,3-dimethylbutyl-1,2-dz in 5 ml of dry pentane was added dropwise to a stirred solution of iron acyl having mp 143° dec. Spectral data: ir (CHC13) 2930, 1790, 1510, 1360, 1280, 955 cm⁻¹; deuterium-decoupled nmr (CDCl3) 6 0.70 (9H, s), 1.78 (1H, d, J : 4.4 Hz, 1H, d, J : 4.4 Hz), 2.46 (0.5 H, d, J : 4.4 Hz), 2.72 (0.5 H, d, J : 4.4 Hz), 4.04 (0.5 H, d, J : 1.0 Hz), 7.33 (15H, m).

The nmr spectrum of the nondeuterated analog prepared in the same manner consisted of an ABXY pattern for the CHDCHD moiety, two equally intense ABX spectra with zr : 0.85 ppm, zH : 1.18 ppm, vx : 2.57 ppm, vy : -12.5 Hz, vz : +12.5 Hz. Anal. Calcd for C22H20FeP: C, 71.00; H, 6.34. Found: C, 70.55; H, 6.43.
The experimental spectrum, and the theoretical spectrum generated using these parameters, are reproduced in Figure 6.

\( \text{7} \)tert-butyl isocyanide

In Neat \( \text{SO}_2 \). A solution of 180 mg (0.68 mmol) of the alkyliron compound 3 in 50 ml of liquid sulfur dioxide was stirred under nitrogen at reflux for 16 hr. The \( \text{SO}_2 \) was allowed to evaporate, and the resulting orange residue was chromatographed twice under nitrogen on a 2 x 20 cm column of Merck acid-washed alumina, using degassed ether as eluent. Only one mobile yellow band appeared on the column under these conditions. The yellow band was collected under nitrogen, the solvent was removed, and 250 mg (0.72 mmol, 81%) of yellow crystals were collected: mp 63-66°; ir (CHCl₃) 2950, 2150, 1940, and 1630 cm⁻¹; deuterium-decoupled nmr (CHCl₃) 6 0.73 (s, 9), 1.24 (d, J = 11.9 Hz), 1.34 (s, 9), 2.64 (d, J = 11.9 Hz), 4.48 (s, 5).

A sample of \( \text{SO}_2 \) prepared in a manner analogous to the above preparation yielded yellow crystals giving elemental analysis below.

Anal. Calcd for \( \text{C}_8\text{H}_9\text{O}_2\text{FeN} \): C, 56.21; H, 6.21.

Yields in the various solvents were 45% (\( \text{SO}_2 \)), 54% (pentane), 83% (CHCl₃), 62% (CH₂OH), and 94% (DMF).

Reaction of 2 with Dimethyl Acetylenedicarboxylate. Dry, degassed tetrahydrofuran (5 ml) and 0.70 g (4.9 mmol) of dimethyl acetylenedicarboxylate were placed in a flame-dried 10-ml flask equipped with a magnetic stirring bar, a No-Air, stopper, and a nitrogen inlet. The flask and contents were degassed by bubbling a stream of nitrogen through the flask and contents. Alkyliron compound \( \text{trz} \)-2 (264 mg, 1.0 mmol) was introduced, and degassing was continued for 10 min. The nitrogen inlet was removed, the flask was stoppered, and the flask was heated at 50-60° with stirring for 24 hr. All volatile material was distilled at 60 and 0.05 Torr into a trap cooled with a liquid nitrogen bath. The residue was extracted with 5 ml of degassed reagent grade chloroform, and the extracts were chromatographed under nitrogen on a 2 x 20 cm column of Merck acid-washed alumina using degassed pentane to elute unreacted 3 followed by degassed acetone to elute the greenish band of product. The acetone was evaporated from the crude product, leaving 244 mg (0.60 mmol, 60%) of a dark brown viscous oil. This material was rechromatographed using acetone as eluent, and the product was assigned structure 5 on the basis of its ir and nmr spectrum: ir (CHCl₃) 2960, 2870, 1995, 1970, 1670, 1525, 1340, 1360, 1180; deuterium-decoupled nmr (CDCl₃) 6 4.64 (s, 5), 3.87 (s, 3), 3.71 (s, 3), 2.83 (d, J = 10.5 + 0.5 Hz), 1.32 (d, J = 10.5 + 0.5 Hz), 0.83 (s, 9). An analogous procedure was used to convert \( \text{trz} \)-2 to product having \( J = 4.9 \) Hz.

A sample of \( \text{SO}_2 \) prepared in an analogous manner yielded a dark brown oil whose AA'XX' spectrum yields vicinal coupling constants \( J = 12.0 \) Hz, \( J' = 4.9 \) Hz.

Thermal Decomposition of 2. A 12.5 spherical joint was sealed at the jointless end and 530 mg (2.0 mmol) of 2-\( \text{SO}_2 \) was introduced. The tube and contents were attached to a vacuum line and degassed by twice evacuating and refliling with nitrogen. Cyclohexane, 0.5 ml, dried over molecular sieves and degassed in a stream of nitrogen, was added to the tube, and the tube and contents were degassed by four freeze-thaw cycles. The reaction tube was sealed and heated at 150° for 24 hr during which time the contents turned dark brown and became quite viscous. The contents of the tube were distilled at 0.02 mm of pressure and 100° into a trap cooled by a liquid nitrogen bath. 1-Hecone was added as an internal standard, and the crude reaction mixture was analyzed by gc. Four major products, two having low boiling points and two having high boiling points, were produced in the approximate ratio of 1:1:2:1. The two low boiling substances were identified by coinjection of genuine samples as 3,3-dimethylbutane and 3,3-dimethylbutene, and they were produced in 11 and 15% yields, respectively. The experiment was repeated using labeled \( \text{trz} \)-2. The 3,3-dimethylbutene was collected by gc and analyzed by deuterium-decoupled nmr. The resulting spectrum is shown in Figure 6.

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