Novel Regio- and Stereoselective Olefin Syntheses: Hydride Abstraction from Organoiron Compounds

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Treatment of the compounds η^5-$C_5H_5Fe(CO)_2CHR^1CH_2R^2$ (R = H, alkyl, aryl) with $Ph_3C^+BF_4^-$ results in abstraction of a β-hydrogen atom to give triphenylmethane and the cationic olefin complexes, $[\eta^5$-$C_5H_5Fe(CO)_2(CHR^1CHR^2)]^+BF_4^-$; liberation of the olefins can be effected by treatment with sodium iodide in acetone. The reactions have synthetic utility because (a) 1- and 2-alkyliron compounds generally give only the terminal olefin and (b) 3-alkyliron compounds give only (*Z*)-2-olefins. The thermodynamically more stable *E* internal olefins are not formed. Optimum reaction conditions and compatibility of various functional groups with the reaction conditions are also discussed.

The synthetic utility of olefin-forming elimination reactions depends largely on the degree to which one is able to predict reasonably the positional and, for internal olefins, geometrical orientation of the double bond. Although methods currently available for the preparation of alkenes via β elimination of a halide or other leaving group offer varying degrees of selectivity with respect to orientation in the product,[1] there are actually few satisfactory methods for conversion of, say, a primary halide into the corresponding 1-alkene or a secondary halide to a *Z* internal olefin. Instead, product distributions of most elimination reactions are in many cases strongly influenced by the relative thermodynamic stabilities of the olefins being generated, i.e., *E* internal olefins > *Z* internal olefins > terminal olefins.[1,2]

Thus HMPA treatment of cyclohexylmethyl bromide gives both endocyclic and exocyclic olefin,[3] while alkoxide treatment of 1-chloro-1-methylcyclohexane gives, in one instance, only methylene cyclohexane,[4] while other conditions lead to additional internal olefin.[5] Elimination from 1-halooctane gives, depending on the base used, 1- and 2-octene mixtures as well as substitution product, a problem especially prevalent with base elimination of tosylates.[6] The effects of various alkoxide/alcohol mixtures in producing 1- and (*E*)/(*Z*)-2-pentenes from 2-pentyl tosylates and *E*/*Z* mixtures from 3-pentyl tosylates have also been investigated.[7] Other less direct methods for the formation of terminal olefins include formation of selenoxides from the tosylate, halide, or unsaturated ketone, followed by elimination,[8] the reaction of alkyl lithium reagents with tosyl hydrazones,[9] a reaction often accompanied by isomerization or rearrangement, and the Wittig reaction, long known as a preparative method for the conversion of ketones or aldehydes into olefins.[10]

We have recently described a synthetically useful organometallic analogue of the β-elimination reaction.[11] Treatment of an alkyliron complex of the type η^5-$C_5H_5Fe(CO)_2CHR^1CH_2R^2$ (**1**) with triphenylmethyl fluoroborate (**2**) results in abstraction of a hydrogen from the carbon atom β to the metal atom, giving triphenylmethane and a cationic iron olefin complex, $[\eta^5$-$C_5H_5Fe(CO)_2(CHR^1CHR^2)]^+$ (**3**), i.e.,

$$\underset{\mathbf{1}}{\eta^5\text{-}C_5H_5Fe(CO)_2CHR^1CH_2R^2} + \underset{\mathbf{2}}{Ph_3C^+BF_4^-} \rightarrow \underset{\mathbf{3}}{[\eta^5\text{-}C_5H_5Fe(CO)_2(\text{olefin})]BF_4^-} + Ph_3CH \quad (1)$$

where R = H, alkyl, or aryl.

This type of reaction of organometallic complexes with **2** has been known for compounds of iron for some time.[12] Other examples include similar reactions of alkyl compounds of mercury,[13,14] tin,[14] germanium,[14] lithium,[15] magnesium,[15] and zirconium.[16] These reactions proceed with concurrent dehydrometalation and exhibit varying degrees of selectivity. In contrast, the transfer of hydride ion from the organoiron species **1** leaves the olefin coordinated to the metal, as in **3**.

On the basis of stereochemical evidence and a kinetic isotope effect, we have previously suggested[11a] that abstraction of a β-hydride, as in (1), involves direct interaction between the bulky triphenylmethyl carbenium ion and the hydrogen undergoing attack. In addition, it seemed that the latter has to be in an antiperiplanar configuration with respect to the iron–carbon bond, the alkyliron compound thus assuming a conformation which is relatively unstable for steric reasons.[17]

We expected, therefore, that regio- and stereoselectivity in the abstraction reaction should be governed largely by steric considerations, leading to the hypothesis that abstraction from, for instance, a secondary alkyliron complex of the type η^5-$C_5H_5Fe(CO)_2CH(Me)CH_2R$ (R = alkyl, aryl) should occur from the relatively unhindered methyl group rather than from the methylene group. Such a result would be of synthetic value, because it would lead to the

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(9) (a) Shapiro, R. H. *Org. React.* **1976**, *23*, 405. (b) Kolonko, K. J.; Shapiro, R. H. *J. Org. Chem.* **1978**, *43*, 1404.
(10) House, E. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: New York, 1972, pp 682–709.
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(16) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333.
(17) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 4292.

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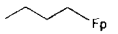
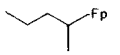
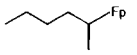
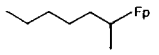
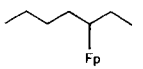
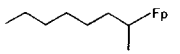
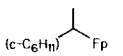
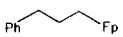
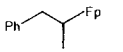
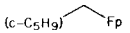
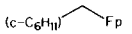
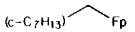
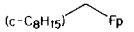
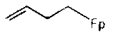
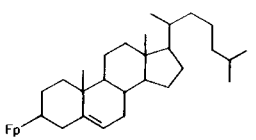
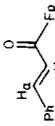
Table I. Alkyliron Complexes: Preparative Details and Physical Data

Fp(alkyl)	compd no.	leaving group in RX	yield, %	mp, °C	ν_{CO}, cm^{-1} [a]	^1H NMR data (δ relative to Me_4Si)[b,c]
	1a	Br	96	oil	2010, 1955	4.68 (s, Cp), 1.44 (m, CH_2), 0.88 (m, CH_3)
	1b[55]	Br	30	oil	2006, 1952	4.60 (s, Cp), 2.32 (m, CH), 1.92–1.98 (m, CH_2, CH_3)
	1c	Br	30	oil	2004, 1952	4.62 (s, Cp), 2.38 (m, CH), 1.9–0.7 (m, CH_2, CH_3)
	1d	OTs	17	oil	2005, 1949	4.69 (s, Cp), 2.38 (m, CH), 1.63 (m, CH_2), 0.95 (t, CH_3)
	1e	OTs	65	oil	2005, 1948	4.65 (s, Cp), 2.8–2.3 (m, CH), 1.9–0.7 (m, CH_2CH_3)
	1f	Br	40	oil	2006, 1954	4.68 (s, Cp), 2.8–2.36 (m, CH), 1.9–0.8 (m, CH_2, CH_3)
	1g[56]	OTs	30	oil	2005, 1945	4.67 (s, Cp), 2.7–2.2 (m, CH), 2.0–0.7 (m, CH_2, CH_3)
	1h	OTs	49	oil	2007, 1954	4.61 (s, Cp), 2.60 (m, CH), 2.0–1.1 (m, CH_2, CH_3), 1.1–0.8 (m, CH_3)
	1i	OTs	34	oil	2004, 1952	4.68 (s, Cp), 2.83 (m, CH), 2.1–0.9 (m, CH_2), 1.30 (d, CH_3)
	1j[56]	Br	54	44	2010, 1955	7.22 (br s, Ph), 4.65 (s, Cp), 2.68 (m, $PhCH_2$), 2.1–1.3 (m, CH_2, CH_2)
	1k[42]	OTs	47	oil	2008, 1957	7.18 (m, Ph), 4.68 (s, Cp), 3.26–2.50 (m, FeCH, $PhCH_2$), 1.20 (d, CH_3)
	1l	OTS	78	0	2009, 1958	4.69 (s, Cp), 2.1–0.7 (m, CH, CH_2)
	1m[57]	OTs	90	48–50	2010, 1958	4.68 (s, Cp), 2.0–0.8 (m, CH, CH_2)
	1n	OTs	65	oil	2008, 1958	4.70 (s, Cp), 1.5 (m, CH, CH_2)
	1o	OTs	88	20–23	2010, 1955	4.70 (s, Cp), 2.1–0.8 (m, CH, CH_2)
	1p[58]	Br	77	oil	2008, 1960	6.2–5.48 (m, =CH), 5.2–4.4 (m 7 H, Cp and $=CH_2$), 4.70 (s, Cp), 2.15 (m, allylic CH_2), 1.45 (m, $FeCH_2$)
	1q	OTs	40	glass	2005, 1952	5.35–5.1 (m, =CH), 4.68 (s, Cp), 3.51 (m, FeCH), 2.3–0.7 (m, ring, side chain H's)

	1r[59]	Cl	25		2025, 1960[d]	7.4 (m, Ph), 7.02 (d, J_{trans} = 15 Hz, H_a), 6.64 (d, J_{trans} = 15 Hz, H_b), 4.90 (s, Cp)
	1s[60]	from 1r	18		2022, 1977	7.2 (m, Ph), 7.70 (d, J_{trans} = 16 Hz, H_a), 6.60 (d, J_{trans} = 16 Hz, H_b), 4.83 (s, Cp)
	1t[18,36]	I	50	oil	2005, 1955	5.95 (ddt, J = 16, 10, 8 Hz, =CH), 4.98–4.32 (m, $=CH_2$), 4.59 (s, Cp), 2.10 (d, J = 8 Hz, $FeCH_2$)
	1u	Cl	49	50°	2022, 1954[e]	4.80 (s, Cp), 2.3–1.2 (m, CH_2), 1.00 (s, CH_3)
	1v	from 1u	40	oil	1995, 1940	4.63 (s, Cp), 2.1–1.0 (m, CH_2), 1.52 (s, CH_3)

[a] Petroleum ether (30–60 °C) solution. [b] $CDCl_3$ solution. [c] s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, br = broad. [d] Acyl ν_{CO} = 1635 cm^{-1}. [e] Acyl ν_{CO} = 1654 cm^{-1}.

product of Hofmann-type elimination. As shown in a preliminary communication,[11b] the Hofmann elimination products are generally obtained and can be liberated from the iron quantitatively and without isomerization by treatment with sodium iodide.[11b,18]

We now wish to report in detail the method previously described, elaborate on some of the relevant chemistry, including the initial metalation steps, and comment further on a rationale for the observed orientation in the olefinic products. The moiety η^5-$C_5H_5Fe(CO)_2$ will hereafter be designated Fp.

Results and Discussion

Syntheses of the Compounds Fp(alkyl) (1). Of the several methods available for preparation of compounds of the type 1,[19,20] the most convenient in the present context is the alkylation of the anion 4 (available upon reductive cleavage of the dimer, $[Fp]_2$, as in (2))[21] with an

$$[Fp]_2 \xrightarrow[THF]{Na\text{-}Hg} \underset{4}{[Fp^-]Na^+} \xrightarrow{RX} RFp + NaX \qquad (2)$$

appropriately substituted alkyl halide or tosylate (RX).[18,20] The products, Fp(alkyl), are easily handled after column chromatography as somewhat air-sensitive oils or crystalline compounds. They are readily characterized by the presence of two carbonyl stretching bands in the infrared spectra (~2000 and ~1950 cm^{-1})[22] and a cyclopentadienyl (η^5-C_5H_5) signal in the ^1H NMR spectra (ca. δ 4.7, singlet). The alkyl compounds prepared are listed and described in Table I. Although, as noted, many of the compounds are not new, we include IR and ^1H NMR data for all for purposes of comparison and, in some cases, because the data have not previously been reported. Table II lists the results of a series of preparative experiments, run under controlled, strictly comparable circumstances, in order to determine optimum reaction conditions (see the Experimental Section).

The order of the thermal stabilities of the alkyl complexes is generally acyl > primary > secondary > tertiary.[20] Solutions in chlorinated hydrocarbon solvents are generally less stable than solutions in ethers or saturated hydrocarbons, and the complexes are usually more stable as crystalline solids than as oils. The mode of thermal decomposition of these compounds is thought to involve migration of a β-hydrogen atom to give free olefin and the hydride, FpH.[23]

In the case of primary alkyl compounds, at least, stereochemical studies have shown that alkylation involves inversion of configuration at the α-carbon atom,[24,25] and the reactions are believed to involve S_N2 mechanisms. It is interesting to note, therefore, that the yields of the alkylation reaction, as shown in Table II, are generally consistent with this mechanism. Thus yields are much higher for primary alkyl halides and tosylates than for secondary,[26] and the relatively bulky 2-methyl-3-pentyl and

(18) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosen, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.
(19) Coates, G. E.; Green, M. L. H.; Wade, K. "Organometallic Compounds", 3rd ed.; Chapman and Hall: London, 1968; Vol. 2, p 234.
(20) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417.
(21) Eisch, J. J.; King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, p 161.
(22) Giering, W. P.; Rosenblum, M. *J. Organomet. Chem.* **1970**, *25*, C71.
(23) Baird, M. C. *J. Organomet. Chem.* **1974**, *64*, 289.
(24) Boschetto, D. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1969**, *91*, 4313.
(25) Slack, D. A.; Baird, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5539.

Table II. Fp Anion Alkylation Reactivity (0.5% Amalgam, 1.2 equiv of Fp^-)

	RX	counterion in Fp^-	solvent	% yield Fp(alkyl)	side products (Cp ≡ η^5-C_5H_5)
a	phenethyl tosylate	Na	THF	75	
b	phenethyl bromide	Na	THF	72	
c	phenethyl chloride	Na	THF	72	
d	phenethyl chloride	K	THF	71	
e	phenethyl mesylate	Na	THF	73	
f	phenethyl triflate	Na	THF	15	$FeCp_2$ + $Hg[Fp]_2$
g	2-heptyl bromide	K	THF	26	$Hg[Fp]_2$
h	2-heptyl bromide	K	hexane	0	
i	2-hexyl mesylate	Na	THF	19	$Hg[Fp]_2$
j	2-hexyl tosylate	Na	50/50 THF/DMF	30	$Hg[Fp]_2$
k	2-hexyl tosylate	Na	20/80 DMF/THF	45	
l	chloroethyl tosylate	Na	20/80 DMF/THF	0	$FeCp_2$ + $Hg[Fp]_2$
m	ethoxyethyl tosylate	Na	THF	<2	
n	allyl chloride	Na	THF	50	
o	allyl iodide	Na	THF	0	FpI, $Hg[Fp]_2$, $[Fp]_2$
p	ethyl 3-bromopropionate	Na	THF	22	
q	*p*-nitrophenethyl tosylate	Na	THF	<10	$FeCp_2$
r	(−)-menthyl tosylate	Na	THF	0	
s	2-methyl-3-pentyl tosylate	Na	THF	0	
t	2-methyl-3-pentyl triflate	Na	THF	0	Cp_2Fe, olefin
u	1-chloro-1-methylcyclohexane	Na	THF	0	$[Fp]_2$, FpH
v	β-bromostyrene	Na	THF	0	$FeCp_2$

(−)-menthyl tosylates are inert to substitution.

It was anticipated that changes in the solvent and the counterion of Fp^- might have some effect on reactivity, as has been observed for similar reactions of $Fe(CO)_4^{2-}$.[27] Solvent effects are clearly important, as no reaction with 2-heptyl bromide was observed in *n*-hexane, but little difference is observed between the sodium and potassium salts.

While little difference in yields of primary alkyl compounds was found with a variety of leaving groups (Br, Cl, OTs, OMs), a surprisingly low yield was observed with triflate (OTf) (see Table II). Some ferrocene and $Hg[Fp]_2$[30] were obtained in the latter case.

The failure of triflates to substitute may result from the high basicity expected for the metal anion 4.[31] It has been demonstrated elsewhere[12,32] that 4 induces elimination of Cl^- from *tert*-butyl chloride to yield the hydride, FpH, and free isobutylene. Similarly, in the present study we have noted the formation of FpH in the reaction of 4 with 1-chloro-1-methylcyclohexane (Table II).

A number of studies have been carried out to investigate compatibility of 4 with various functional groups. As Table II shows, *p*-nitrophenethyl tosylate gave no alkyliron product, suggesting that it may have undergone attack by 4 at the nitro group. The tolerance of the anion 4 for aldehyde and ester groups has been shown by others[18] and is demonstrated here for the latter by the reaction of ethyl 3-bromopropionate (Table II).

The failure of the compounds chloroethyl and ethoxyethyl tosylate (Table II) to react with 4 should perhaps not be surprising. It has been mentioned elsewhere[33] that while the inductive effect presented by an OR or halide group would be expected to result in a mild rate enhancement of substitution, a rate retardation is actually observed. King and Bisnette[34] have reported an ~14% yield of $FpCH_2CH_2SMe$ from $ClCH_2CH_2SMe$ and 4, and this may be explained in terms of an anchimeric effect of the SMe.[33]

The considerable variation in yield (usually relatively low) and side product composition observed with secondary substrates is of interest. Inspection of the data in Table II shows that tosylate is the preferred leaving group for secondary alkyls; the overall yields can be further optimized by the use of at least 2 equiv of anion 4. The appearance of $Hg[Fp]_2$ accompanied most low-yield secondary alkyl reactions.

These variations in reactivity may also indicate a change in mechanism on passing from primary to secondary alkyl substrates. Indeed one-electron transfer processes have been invoked on occasion, and recent results by San Filippo[35] indicate possible free-radical participation in reactions of cyclopropyl carbinyl halides with the iron anion 4 and with $(CH_3)_3Sn^-$. The observed production of FpI in the reaction of allyl iodide with 4 may be a further indication of radical processes in competition with an S_N2 (or S_N2'[36]) mechanism. In contrast, the reaction of allyl chloride with 4 is rapid and exothermic, giving the expected product.

Not surprisingly, perhaps, we find that a vinyl compound, β-bromostyrene, is quite inert to 4.[37] The preferred route to vinyl- (and tertiary alkyl-) iron compounds is via treatment of 4 with the corresponding carboxylic acid halides,[38] as in (3), to give the acyliron species **5**, i.e.,

$$4 + RCOCl \rightarrow \underset{\mathbf{5}}{FpCOR} \qquad (3)$$

where R = vinyl and tertiary alkyl.

The latter can be readily decarbonylated to give the desired products (see Experimental Section).

Preparation of the Olefin–Iron Complexes (3). Treatment of the alkyliron compounds with 2 in anhydrous

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(29) Nitay, M.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *136*, C23.

(30) Fischer, R. D.; Vogler, A.; Noack, K. *J. Organomet. Chem.* **1967**, *7*, 135.

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(32) Green, M. L. H.; Nagy, P. L. I. *Proc. Chem. Soc., London* **1962**, 74.

(33) Okamoto, T.; Kita, T.; Araki, K.; Shingu, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1913.

(34) King, R. B.; Bisnette, M. B. *J. Am. Chem. Soc.* **1964**, *86*, 1267.

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(36) Mérour, J.-Y.; Cadiot, P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1970**, *271*, 83.

(37) Green, M. L. H.; Ishaq, M.; Mole, T. *Z. Naturforsch., B* **1965**, *20*, 598.

(38) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1918.

methylene chloride gives the olefin complexes **3** as stable yellow flocculent precipitates or crystalline compounds which can be recrystallized from methylene chloride–ether at −78 °C. The complexes are virtually insoluble in diethyl ether and hydrocarbon solvents. Solvents previously reported to be suitable for use in the abstraction reaction[12,32] (i.e., THF and CH_3CN) have been found by us to be generally unsatisfactory because of reactivity of THF with **2**[39] and the coordinating ability of acetonitrile. Solutions of many of the olefin–iron complexes in CH_3CN have been observed to undergo substitution to give free olefin and the cationic acetonitrile complex $[\eta^5\text{-}C_5H_5Fe(CO)_2MeCN]^+$.[40] The rate of this substitution reaction varies, being extremely rapid with complexes of the bulkier olefin ligands but slow for complexes in which the olefin ligand is relatively small ((ethylene)Fp^+ is quite stable in CH_3CN).

The isomer purities of the olefin complexes were determined by ^1H NMR spectroscopy (Table III), as well as by GLC analyses of the olefin(s) generated on demetalation by sodium iodide in acetone (see the Experimental Section). The yields of free olefin obtained on demetalation have been shown to be essentially quantitative (GLC and ^1H NMR spectroscopy).

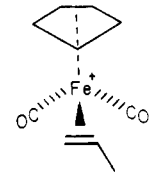
Table III lists the results of the β-hydride abstraction reactions. As can be seen, relatively high yields of terminal olefins are obtained *without isomerization* from primary alkyliron substrates (**1a** → **3a**, **1j** → **3j**, **1l** → **3l**, **1m** → **3m**, **1n** → **3n**, **1t** → **3t**). The formation of the complex of 3-phenylpropene (**3j**) rather than that of its more stable, conjugated isomer, β-methylstyrene, from **1j** is noteworthy, as is the formation of the exocyclic olefin complexes **3l**, **3m**, and **3n**. Elimination reactions from other cycloalkylmethyl substrates often give mixtures of endocyclic olefin isomers.[1] Abstraction reactions of the cycloalkylmethyliron compounds were slow, probably for steric reasons, and the cyclooctylmethyl analogue was inert.

Abstraction could also not be effected from the ester $FpCH_2CH_2CO_2Et$ (**1w**). It is to be expected that the β-hydrogens would be deactivated toward electrophilic attack by the electron-withdrawing ester group,[41] and it is possible that slow attack did occur at the ester group itself.[42] Attack by **2** at oxygen has been reported for the compound $FpCH_2CH_2OMe$.[43] As reported elsewhere,[44] the σ-allyl compound **1t**, $FpCH_2CH{=}CH_2$, is attacked by **2** at the double bond, giving a complex of 4,4,4-triphenylbutene (**3t**).

Abstraction reactions of secondary alkyliron compounds proceeded relatively slowly and in generally rather lower yields. In these cases, more than one product is possible, and the results in many cases point to a degree of balance between steric factors, which would favor attack at the methyl group of a 2-alkyliron compound, and electronic factors, which might disfavor attack at a methyl group, methylene C–H bond strengths being lower than methyl C–H bond strengths.[45] While most 2-alkyl compounds (**1c**, **1e**, **1f**, **1h**, and **1i**) gave only the terminal olefin products, illustrating the dominance of steric factors, the 2-butyl compound (**1b**) gave a 2:1 ratio of the complexes of (*Z*)-2-butene (**3b**) and 1-butene (**3a**). Of all the 2-alkyl compounds investigated, this is the one in which the β-hydrogen atoms on an internal carbon atom are the least shielded by other substituents and the one in which internal hydrogen atoms might compete with the methyl hydrogens for the attention of **2**. Also, if the abstraction reaction can be considered as proceeding via an incipient carbonium ion,[12,32] the transition state of the internal olefin complex might be stabilized by inductive contributions from the adjacent methyl group to a greater extent in this case than would be true with the terminal olefin complex. While the 3-pentyl complex **1d** presents no alternatives with respect to positional orientation of the double bond in the product, the 3-heptyl complex **1g** provides further illustration of steric effects on abstraction, giving only the complex of 2-heptene **3g**.

Electronic factors may also be less important than steric factors in the abstraction from **1k** (benzylic vs. methyl hydrogens), although the reactions, and hence the conclusions, are not clear-cut. While electronic factors would favor the breaking of the weaker benzylic C–H bonds, steric factors should favor attack at the methyl group. Unfortunately, because of slow abstraction from and the low thermal stability of **1k**, some (*E*)-β-methylstyrene was formed by thermal decomposition,[46] and a good sample of olefin complex could not be obtained. Since, as will be shown below, abstraction of a benzylic hydrogen would be expected to give (*Z*)- rather than (*E*)-β-methylstyrene, abstraction probably occurs primarily from the methyl group. In contrast, the product of abstraction from **1q**, a result obtained elsewhere,[47] may reflect to some extent the weakness of allylic C–H bonds relative to secondary C–H bonds.[45]

As indicated in Table III, the internal olefins formed were normally the *Z* isomers, results generally consistent with both the expected greater stabilities of complexes of the *Z* isomers[48] and with the peculiar steric and conformational requirements of an olefin coordinated to the Fp^+ moiety. The stable conformation of, for instance, the propylene complex is that in which the C=C axis lies parallel to the Cp plane,[49] with the methyl group pointing away from the Cp ring for steric reasons.



Thus it is reasonable on steric grounds to expect that internal olefins would prefer to form in such a way as to minimize steric interactions with the cyclopentadienyl hydrogens, leading to predominant formation of the *Z* rather than of the thermodynamically more stable *E* olefins.

A most interesting result, though as yet unexplained and still under investigation, is the reaction of the vinyl complex **1s** with **2** to give, in good yield, the styrene complex **3s**. This is clearly not a typical hydride abstraction reaction, and it is not known at this time if the reaction is

(39) Kabir-ud-Din; Plesch, P. H. *J. Chem. Soc., Perkin Trans. 2* **1978**, 937.
(40) Treichel, P. M.; Shubkin, R. L.; Barnett, K. W.; Reichard, D. *Inorg. Chem.* **1966**, *5*, 1177.
(41) As is probably also the case with $FpCH_2CH_2CN$ and $FpCF_2CF_2H$.[12,32]
(42) See, for instance: Cutler, A.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* **1974**, *77*, 381. Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426.
(43) Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93.
(44) Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V.; Sanders, A. *J. Organomet. Chem.* **1974**, *65*, C57.
(45) Carey, F. A.; Sundberg, R. J. "Advanced Organic Chemistry"; Plenum: New York, 1977; Part A, pp 524–526.
(46) See: Reger, D. L.; Culbertson, E. C. *Inorg. Chem.* **1977**, *16*, 3104.
(47) Rosenblum, M., private communication.
(48) Henrici-Olivé, G.; Olivé, S. "Coordination and Catalysis"; Verlag Chemie: New York, 1977; p 114.
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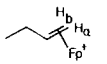
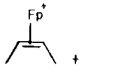
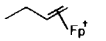
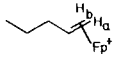
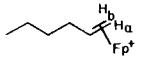
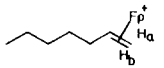
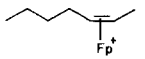
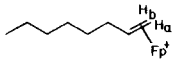
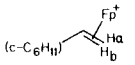
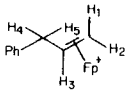
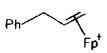
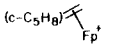
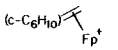
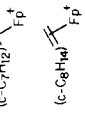
Table III. Olefin-Iron Complexes: Preparative Details and Physical Data

[Fp(olefin)]$^+BF_4^-$	compd no.	precursor	yield, %	ν_{CO}, cm^{-1} [a]	^1H NMR data (δ rel to Me_4Si) [b,c]
	3a[18]	1a	56	2080, 2040	5.61 (s, Cp), 5.6-4.7 (m, =CH), 3.92 (d, J_{cis} = 8 Hz, H_a), 3.49 (d, J_{trans} = 14 Hz, H_b), 2.7-1.4 (m, CH_2), 1.26 (t, CH_3)
	3b	1b	82	2080, 2040	5.67 (s, Cp), 5.15 (m, =CH), 1.82 (d, J = 5.5 Hz, CH_3)[d]
	3a[18]				
	3c[61]	1c	74	2080, 2040	5.68 (s, Cp), 5.5-4.7 (m, =CH), 3.97 (d, J_{cis} = 8 Hz, H_a), 3.50 (d, J_{trans} = 14 Hz, H_b), 2.6-0.7 (m, CH_2, CH_3), 1.0 (t, CH_3)
	3d	1d	55	2080, 2040	5.62 (s, Cp), 5.08 (m, =CH), 1.82 (d, CH_3), 1.20 (t, CH_3), 2.67-0.9 (m, CH_2)
		e	10	2072, 2035	5.66 (s, Cp), 4.74 (m, =CH), 2.82-1.05 (m, CH_2, CH_3)
	3e	1e	60	2080, 2040	5.63 (s, Cp), 3.95 (d, J_{cis} = 8 Hz, H_a), 3.50 (d, J_{trans} = 14 Hz, H_b), 5.6-4.7 (m, =CH), 2.70-0.75 (m, CH_2, CH_3)
	3f[62]	1f	82	2080, 2040	5.62 (s, Cp), 5.45-4.72 (m, =CH), 3.93 (d, J_{cis} = 8 Hz, H_a), 3.45 (d, J_{trans} = 14 Hz, H_b), 2.72-0.75 (m, CH_2, CH_3)
	3g	1g	57	2075, 2035	5.61 (s, Cp), 5.06 (m, =CH), 2.5-0.75 (m, CH_2, CH_3)
	3h[62]	1h	88	2080, 2040	5.68 (s, Cp), 5.5-4.7 (m, =CH), 3.93 (d, J_{cis} = 8 Hz, H_a), 3.50 (d, J_{trans} = 14 Hz, H_b), 2.68-0.7 (m, CH_2, CH_3)
	3i[63]	1i	92	2080, 2040	5.63 (s, Cp), 5.48-4.8 (m, =CH), 3.80 (d, J_{cis} = 9 Hz, H_a), 3.42 (d, J_{trans} = 15 Hz, H_b), 2.42-1.10 (m, ring hydrogens)
	3j[57]	1j	79	2077, 2039	7.4 (br s, Ph), 5.70 (s, Cp), 5.33 (m, H_3), 4.01 (d, J_{cis} = 8 Hz, H_2), 3.76 (d, J_{trans} = 14 Hz, H_1), 3.90 (dd, J = 4, 13 Hz, H_4 or H_5), 2.82 (dd, J = 10, 13 Hz, H_4 or H_5)
	3k	1k	f	2078, 2038	7.40 (m, Ph), 6.5-6.0 (m, =CH), 2.1 (d, J = 6 Hz, CH_3)
	3j[57]	1k	f	see above	see above
	3l	1l	75	2065, 2025	5.64 (s, Cp), 4.01 (s, $=CH_2$), 2.88-1.62 (m, ring CH_2)
	3m	1m	50	2070, 2027	5.60 (s, Cp), 3.88 (s, $=CH_2$), 3.0-1.2 (m, ring CH_2)

	**3n**	**1n**	77	2067, 2027	5.62 (s, Cp), 4.05 (s, $=CH_2$), 2.93–1.54 (m, ring CH_2)
	3o	**1o**	0		
	3p[18]	**1p**	87	2075, 2040	5.65 (s, Cp), 6.15–5.25 (m, $H_{3,4,5,6}$), 4.05–3.61 (m, $H_{1,2}$)
	3q	**1q**	57	2065, 2025	5.58 (s, Cp), 5.75–5.2 (m, $H_{3,4}$), 6.65–6.23 (m, H_6), 2.8–0.7 (m, remaining H's)
	3s[64]	**1s**	88	2072, 2038	7.42 (m, Ph), 6.13 (dd, J_{cis} = 8 Hz, J_{trans} = 15 Hz, H_1), 5.86 (s, Cp), 4.10 (dd, J_{cis} = 8 Hz, J_{gem} = 1 Hz, H_2), 4.28 (dd, J_{trans} = 15 Hz, J_{gem} = 1 Hz, H_3)
	3t[51]	**1t**	87	2078, 2038	7.32 (m, Ph), 5.60 (s, Cp), 5.40 (m, H_a), 3.50 (d, J_{cis} = 8 Hz, H_b), 2.84 (d, J_{trans} = 14 Hz, H_c), 2.18 (m, CH_2)
	3m	**1v**	trace	see above	see above

[a] In CH_2Cl_2 solution. [b] In CD_3NO_2 solution. [c] s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, br = broad. [d] Data for the (*Z*)-2-butene complex (3b). [e] Prepared from[76] $[Fp(THF)]^+BF_4^-$ and (*E*)-2-pentene for the purpose of comparison. [f] The alkyl precursor, 1k, is very labile thermally, and a mixture of products was obtained following the abstraction and demetalation steps. The (*E*)-propenylbenzene may be a product of thermal decomposition of 1k.

general for substituted vinyl Fp complexes. Attempted abstraction from the tertiary alkyl complex, **1v**, also failed, perhaps because of steric hindrance, although the reactants were consumed. Certainly other pathways are available for reactions of **2** with "nontypical" Fp(alkyl) complexes.[50-52]

The results and interpretations presented here are largely consistent with those of previous investigators for alkyl compounds of the main group metals.[53] It has been suggested that σ–π conjugation associated with the metal–carbon bond in compounds containing a metal–CH_2 moiety (metal = Si, Ge, Sn, Pb, and Hg) should result in stabilization of an adjacent carbonium ion center. Interestingly, as mentioned in the introduction, abstraction of a β-hydride by **2** does occur with alkyl compounds of these metals and apparently requires an antiperiplanar arrangement of the metal atom and the β-hydrogen atom.[53]

Finally, and of possibly only marginal relevance to the work discussed here, recent calculations reported by Reetz and Stephan[54] seem to indicate that the hydrogen atoms trans antiperiplanar to the metal atoms in ethyllithium and 2-butyllithium carry the greatest electron density in relation to the other hydrogens. These alkyllithium compounds are essentially carbanionic species, and hence one would hesitate to extend predictions of similar behavior to the compounds referred to in this paper. However, the calculations do suggest possible electronic factors not considered previously.

Experimental Section

All procedures involving the metal complexes were carried out in a nitrogen atmosphere. All reagents were used as received with the exception of tosyl chloride (Aldrich), which was recrystallized from benzene/petroleum ether prior to use, and triphenylmethanol (Aldrich), which was recrystallized from 95% ethanol. All solvents were dried and distilled immediately before use. IR spectra were obtained on Beckman IR4240 or Beckman Acculab-6 spectrophotometers, and ^1H NMR spectra were obtained on a Varian EM360 spectrometer. ^{13}C NMR spectra were run at 15.09 MHz on a Bruker HX60 spectrometer with proton noise decoupling, operating in the pulse Fourier Transform mode with deuterium lock. Mass spectra were obtained on a JEOL JMS-01SC double focusing instrument at 75 eV with 10 000 resolving power. Gas–liquid chromatography was carried out using a Hewlett-Packard F & M Scientific 700 gas chromatograph with a UCON 50HB-280X on 20% Chromosorb W column (6 ft × $^1/_8$ in.) with a He flow rate of 40 mL/min. Chemical analyses were performed by Microanalysis Laboratories, Ltd., Toronto.

Materials. Starting materials listed in Tables I[55-64] and II

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include purchased compounds (i.e., all halides, from Aldrich Chemical Co.) and compounds prepared in this laboratory following published procedures (tosylates,[65] mesylates,[66] and triflates[67]), in most cases from available alcohols (Aldrich) and in others (i.e., for **1l** and **1m**) from alcohols obtained by reduction of the appropriate carboxylic acid.[68] Complexes **1s** and **1v** were obtained by photodecarbonylation (Pyrex vessel, Hanovia medium pressure Hg-vapor lamp) of the acyl iron species **1r** and **1u** (described herein), using for **1r** cinnamoyl chloride (Aldrich) and for **1u** 1-methylcyclohexane carboxylic acid chloride[69] prepared from the Koch-Haaf synthesized acid[70] (from 2-methylcyclohexanol (Aldrich)). Triphenylmethyl tetrafluoroborate (**2**) was prepared according to the method of Dauben[71] and stored under nitrogen at 0 °C. Although **2** is quite stable, carefully stored but aged samples generally gave lower yields of the olefin complexes. The dimer $[Fp]_2$ was obtained from Strem Chemical Co.

Preparation of NaFp (4). One equivalent of the dimer, $[Fp]_2$, was added to a 30% excess of freshly prepared ~1% sodium amalgam in THF. The mixture was stirred mechanically for ~2 h, and excess amalgam was drained from the reaction through a stopcock at the bottom of the vessel. The THF solution of the anion was then transferred under a positive N_2 pressure to a second flask to be subsequently reacted with the desired alkylating agent.

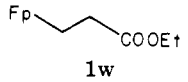
The number of equivalents of anion prepared was determined by the nature of each individual alkylating agent and in fact varied from 1 equiv for a primary tosylate to ~2 equiv for a secondary halide or tosylate.

Preparation of the 1a–q and 1t Complexes of Fp(alkyl) (Table I). In each case, the alkyl reagent RX was added dropwise in the THF solution to a stirred THF solution of the anion, usually at room temperature, with the exception of allyl chloride, which was added at −5 °C. The reactions were allowed to proceed for 5–18 h, depending on the nature of RX, and then concentrated in vacuo. The residue was extracted with petroleum ether (30–60 °C) (or, for more polar complexes, 20% ether–petroleum ether), and the extracts were chromatographed on an alumina (80–200 mesh) column, eluting with petroleum ether to isolate the yellow band (Fp(alkyl)), and leave the more polar dimer side product behind as a reddish band on the column. Solvent was removed in vacuo, and the yellow-amber oil (or crystalline solid) was stored at 0 °C under N_2.

The above procedure was essentially used for the study listed in Table II but varied where necessary according to the conditions outlined in the table.

Preparation of the Fp(alkyl) Complex of Ethyl 3-Bromopropionate (1w). The anion **4** (1 equiv) was allowed to react with ethyl 3-bromopropionate (2.0 g, 0.011 mol) (obtained by esterification of the acid according to published procedure:[72] bp 135 °C (50 mm); IR (film) ν_{max} 1738 cm^{-1}; NMR ($CDCl_3$) δ 4.20 (q, 2 H, OCH_2), 3.60 (t, 2 H, $BrCH_2$), 2.92 (t, 2 H, $CH_2C(O)$), 1.30 (t, 3 H, CH_3)).

Normal workup for the iron alkyls gave 1.2 g (22%) of a yellow oil after 5 h. Spectral data were in accord with the desired Fp(alkyl) structure (**1w**): IR (petroleum ether) ν_{CO} 2018, 1962



1w

cm^{-1}, $\nu_{C=O}$ 1738 cm^{-1}; NMR ($CDCl_3$) δ 4.78 (s, 5 H, Cp), 4.09 (q, 2 H, $-OCH_2-$), 2.42 (t, 2 H, CH_2 C(O)), 1.60 (t, 2 H, CH_2Fe), 1.25 (t, 3 H, CH_3); mass spectrum in Table IV.

Preparation of Acyl Complexes (1r and 1u). The procedure was identical with that outlined above for Fp(alkyl) complexes.

Table IV. Molecular Ion Determinations for Fp(alkyl) Complexes

	m/z (rel intensity)	
Fp(alkyl)	M^+ calcd for	M^+ obsd
1a	234.034	234.035 (10)
1b	234.034	234.035 (6)
1c	248.050	248.052 (8)
1d	248.050	248.064 (0.9)
	M^+ − CO 220.055	220.059 (17)
1e	262.065	262.064 (5)
	M − CO 234.070	234.069 (20)
1f	276.081	276.082 (6)
	M − CO 248.086	248.088 (21)
1g	*a*	276 (4)
	M − CO 248.086	248.088 (25)
1h	290.096	290.087 (4)
1i	288.081	288.085 (3)
	M − CO 260.085	260.086 (13)
1j	*a*	296 (2)
	M − 2CO 240.060	240.057 (100)
1k	296.050	296.059 (2)
1l	260.050	260.047 (1)
1m	274.065	274.066 (1)
	M − CO 246.070	246.072 (11)
1n	*a*	288 (0.4)
	M − CO 260.086	260.085 (9)
1o	*a*	302 (2)
	M − CO 274.101	274.093 (15)
1p	232.018	232.014 (6)
1u	M − C(O) 274.065	274.066 (5)
1v	274	274 ± 1 (2)
	M − CO 246	246 ± 1 (6)
1w	*a*	*b*
	M − CO 250.029	250.010 (14)
	M − 2CO 222.034	222.029 (81)

[a] Indicates M^+ of too low intensity to peak match. [b] Not observed.

A variation in the order of elution on the alumina column was required for **1r**, as mentioned by King.[59] Both complexes were very stable crystalline solids.

Decarbonylation of 1r[59] and 1u. Photodecarbonylation of **1u** was carried out on 200-mg samples in 100 mL of petroleum ether (30–60 °C) for ~45 min with the lamp ~3 in. from the wall of the Pyrex vessel. Removal of solvent in vacuo followed by alumina column chromatography furnished the tertiary complex **1v** in ~40% yield (corrected for recovered starting material). Longer reaction times resulted in extensive decomposition of the product.

Similar decarbonylation of the complex **1r** in THF solution gave an ~20% yield of the vinyl complex **1s**.

N.B. Trimethylamine oxide[73] (1.1 equiv) treatment of **1r** gave **1s** in 32% yield.

Many of the alkyl- and acyliron complexes listed in Table I are rather unstable. Therefore, as some could clearly not be sent by post for chemical analyses, all of those which were volatile were characterized instead by high resolution mass spectral analysis (Table IV), in most cases by measurement of the molecular ion or M − CO ion. For the most part, the fragmentation patterns observed are consistent with previously reported data for these types of complexes.[74] The steroid complex **1q** underwent rapid decomposition in the mass spectrometer. A satisfactory analysis has been obtained for **1q** and is listed as follows. Calcd for $C_{34}H_{50}O_2Fe$: C, 74.72; H, 9.21. Found: C, 74.3[..]; H, 9.41.

Hydride Abstractions. General Procedure. To a stirred CH_2Cl_2 solution of alkyliron complex cooled in an ice bath was added dropwise a CH_2Cl_2 solution of 1.2 equiv of **2**. After addition of the cation was complete, the reaction was allowed to reach room temperature and continue to completion as determined by IR monitoring of the ν_{CO} region of the spectrum. The reaction solution was then cooled to at least 0 °C and treated with diethyl ether to precipitate the product. This was collected by vacuum

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filtration, washed with several small portions of ether, and dried in vacuo. The yellow olefin complexes could then be recrystallized from CH_2Cl_2–ether with ~10% acetone at −78 °C.

Demetalation of Olefin Complexes. An acetone solution of the olefin complex was treated with 2 equiv of NaI at room temperature, usually for ~1 h; with many of the complexes, the reaction was complete in much less time. For complexes **3a–h**, the reactions were carried out in a known volume of acetone in an ampule fitted with a serum cap. After 1 h, samples were withdrawn by syringe and injected into the gas chromatograph; the results were compared against known standards. The column was calibrated in order to determine relative yields. All reactions were found to be essentially quantitative (94–100% yield), and isomer purity as determined in the complexed olefins by ^1H and ^{31}C NMR spectroscopy was confirmed. For the remaining complexes, reactions in acetone-d_6 were examined by ^1H NMR spectroscopy and found to give quantitative conversion to the free olefin by comparison of relative integrated intensities of hydrocarbon peaks compared with the η^5-C_5H_5 (δ 5.03) signal for FpI formed.

For the $\Delta^{3,5}$-cholestadiene complex **3q**, treatment of the olefin complex with NaI–acetone followed by chromatography on silica gel (eluting with petroleum ether) gave a white solid (73%) which, when recrystallized from 95% EtOH, showed the following properties: mp 79.5–80.5 °C; ^1H NMR ($CDCl_3$) δ 6.05–5.2 (3 envelope m, 3 H, olefinic H), 2.5–0.6 (m, 41 H, ring H's and side chain H's and CH_3's as signals at δ 0.96, 0.90, 0.81, 0.70); UV (95% EtOH) λ (ϵ) 238 (17 600), 232 (15 800), and 248 nm (12 400); all are consistent with the structure for $\Delta^{3,5}$-cholestadiene.[75]

Preparation of the (*E*)-2-Pentene Complex (see Table III). The (*E*)-2-pentene complex was prepared by the method of Reger and Coleman.[76] Thus $Fp^+(THF)BF_4^-$ (2 equiv) (prepared from FpI and $Ag^+BF_4^-$ in THF) was stirred with (*E*)-2-pentene in CH_2Cl_2 for 10 h. Precipitation and recrystallization from CH_2Cl_2–ether at −78 °C furnished the (*E*)-2-pentene complex as a light yellow solid. Spectral properties are listed in Table III. The data were used to verify the isomeric purity of the (*Z*)-2-pentene complex **3d**.

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Registry No. **1a**, 69661-74-1; **1b**, 69661-73-0; **1c**, 69661-75-2; **1d**, 71988-05-1; **1e**, 69683-87-0; **1f**, 59980-61-9; **1g**, 71988-06-2; **1h**, 71988-07-3; **1i**, 71988-08-4; **1j**, 60003-79-4; **1k**, 59980-62-0; **1l**, 71988-09-5; **1m**, 42769-10-8; **1n**, 71988-10-8; **1o**, 72016-69-4; **1p**, 34807-88-0; **1q**, 71988-11-9; **1r**, 72028-88-7; **1s**, 72028-89-8; **1t**, 38960-10-0; **1u**, 71988-12-0; **1v**, 71988-13-1; **1w**, 71988-14-2; **2**, 34690-18-1; **3a**, 56336-61-9; **3b**, 56323-75-2; **3c**, 64942-00-3; (*Z*)-**3d**, 71988-16-4; (*E*)-**3d**, 72028-91-2; **3e**, 69661-77-4; **3f**, 59980-54-0; **3g**, 71988-18-6; **3h**, 60791-19-7; **3i**, 59744-57-9; **3j**, 59980-55-1; **3k**, 71988-20-0; **3l**, 71988-22-2; **3m**, 69661-80-9; **3n**, 71988-24-4; **3p**, 60349-23-7; **3q**, 72030-19-4; **3s**, 59744-57-9; **3t**, 37668-15-8; **4**, 12152-20-4; phenethyl tosylate, 4455-09-8; phenethyl bromide, 103-63-9; phenethyl chloride, 622-24-2; phenethyl mesylate, 20020-27-3; phenethyl triflate, 61795-01-5; 2-heptyl bromide, 1974-04-5; 2-hexyl mesylate, 4551-08-0; 2-hexyl tosylate, 4563-91-1; chloroethyl tosylate, 80-41-1; ethoxyethyl tosylate, 17178-11-9; allyl chloride, 107-05-1; allyl iodide, 556-56-9; ethyl 3-bromopropionate, 539-74-2; *p*-nitrophenethyl tosylate, 6948-72-7; (−)-menthyl tosylate, 7212-65-9; 2-methyl-3-pentyl tosylate, 1516-13-8; 2-methyl-3-pentyl triflate, 71988-87-9; 1-chloro-1-methylcyclohexane, 931-78-2; β-bromostyrene, 103-64-0; $[Fp]_2$, 12154-95-9.

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Stereoselectivity in the Epoxide Hydrase Catalyzed Hydrolysis of the Stereoisomeric 4-*tert*-Butyl-1,2-epoxycyclohexanes

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The steric course of the rabbit liver microsome promoted hydrolysis of the racemic cis and trans forms of the title epoxide was investigated. The (+) and (−) forms of *c*-4-*tert*-butylcyclohexane-*r*-1,*t*-2-diol were the only hydrolysis products, indicating that the enzyme reaction takes place exclusively by diaxial opening of the oxirane ring. The absolute configuration and maximum rotation of this diol were determined by correlation with (1*S*,3*R*)-*cis*-3-*tert*-butylcyclohexanol. Of the four stereoisomers of the epoxide, the (1*S*,2*R*,4*S*) form was by far the best substrate and the (1*R*,2*S*,4*S*) form the worst. At low conversion, high enantiomeric excesses of the (−)-diol and the (+)-diol were obtained, respectively, from the (±)-trans and the (±)-cis epoxide; optical purities decreased with increasing conversion. The results are discussed in terms of the helicity of the cyclohexane ring and of the orientation of the *tert*-butyl group with respect to the oxirane ring.

The microsomal epoxide hydrase is an important enzyme involved in the metabolism of xenobiotic compounds, playing a fundamental role in the detoxification of the often highly carcinogenic and mutagenic epoxides that are formed by the action of monooxygenases on alkenes and arenes.[1] Although the sensitivity of the hydrase to substrate structure is rather low, as can be expected from its role in attacking compounds that are foreign to the biological system within which it acts, several cases have been reported of a high stereoselectivity that enables it to discriminate between diastereoisomers and enantiomers of some compounds. Practically nothing being known so far on the detailed structure of the hydrase and little on that of its active site and reaction mechanism, the investigation of the structural and steric requirements for substrate reactivity can provide helpful, though indirect, hints on the geometry of the active site. Whereas a wide range of different epoxides has been investigated with regard to the influence of structural variations on their ability to act as substrates for the hydrase, often with rather unpredictable

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