Table I. Epr Parameters for $[(CH_3)_3C]_2\dot{C}CH_2MR_n$ and Related Radicals at 20° and Calculated Spin Densities at M (a Values in G)

	Radical[a]	g	$a^{H\beta}$	$a^{^{13}C\gamma}{}_{(CH_3)_3C}$[b]	$a^{H\gamma}{}_{(CH_3)_3C}$	$a^{^{13}C\alpha}$	a^M	a^R	ρ_σ
3a	$B_2\dot{C}CH_2CF_3$	2.0026	12.16	11.53	0.45	45.45	30.08	0.90	0.108
3b	$B_2\dot{C}CH_2CCl_3$	2.0034	10.68	10.44	0.42	45.57	34.0	2.1	0.122
3c	$B_2\dot{C}CH_2SiMe_3$	2.0025	15.76	10.23	0.36	46.35	35.02		0.116
3d	$B_2\dot{C}CH_2SiBu_3{}^n$	2.0024	15.78	10.10	c	47.38	30.87		0.102
3e	$B_2\dot{C}CH_2SiCl_3$	2.0030	14.58	c	0.43	c	77.24	2.2	0.255
	$B_2\dot{C}H$[d,e]	2.0027		12.25[f]	0.68	42.98[f]			0.084[g]
	$B_3C\cdot$[d]	2.0025		10.99[f]	0.51[f]	51.10[f]			0.079[g]

[a] B = $(CH_3)_3C$ group. [b] $a^{^{13}C\beta}$ must be $\leq a^{^{13}C\gamma}{}_{(CH_3)_3C}$ for all three β carbons since it could not be detected in most of the above radicals. [c] Not resolved. [d] Data from ref 17 unless noted. [e] $a^{H\alpha}$ = 21.89. [f] Measured for this work. [g] Value for $B_2\dot{C}CH_2CH_3$. Calculation of ρ_σ is based on the assumption that $a^{^{13}C\gamma}{}_{(CH_3)_3C}$ for $B_2\dot{C}H$ and $B_3\dot{C}$ would be half as large as a^M for $B_2\dot{C}CH_2CH_3$ in conformation 1 since the *tert*-butyl groups in these two radicals rotate freely.

established the conformation of **3** we wish to concentrate on the proportion of unpaired electron density, ρ_σ, which is delocalized into the C_β–M bond by hyperconjugation. This may be calculated from a^M using the equation[4,7]

$$\rho_\sigma = 4a^M/a_0{}^M$$

where $a_0{}^M$ is the coupling constant for M with unit unpaired electron density in its valence shell s atomic orbital.[19] Taking $a_0{}^{^{13}C}$ = 1110 G and $a_0{}^{^{29}Si}$ = 1207 G yields the ρ_σ values[20] listed in Table I.

The ρ_σ values for particular M tend to increase with increasing electronegativity of R (compare estimated value for R_nM = CH_3[21] with **3a** and **3b**, and also **3c** and **3d** with **3e**). However, the significant factor is that when the groups CF_3 and CCl_3 are constrained by the di-*tert*-butyl moiety so that conformation **1** applies, their ρ_σ values and hence the extent of their hyperconjugative interactions are essentially the same as for the Me_3Si and $Bu^n{}_3Si$ groups. Since, in the simple ethylene adducts only the silicon centered groups adopt conformation **1**[22] while the carbon centered groups adopt conformation **2**,[23] it must be concluded that hyperconjugation *alone* is not sufficient to hold β-trialkylsilylethyl radicals in conformation **1** and that some additional factor, *e.g.*, p–d homoconjugation,[10] provides the force required to stabilize this conformation.

We are not unaware that additional conclusions concerning **3** can be drawn from the epr parameters in Table I. However, for the present we would merely point out that the $a^{^{13}C\alpha}$ values support Symons' conclusion[27] that an $a^{^{13}C\alpha} \approx$ 46 G for *tert*-butyl should not be cited as evidence for the nonplanarity of *tert*-butyl.[28] That is, it seems highly unlikely that the radicals we report, which contain extremely bulky ligands, could be anything but planar. Values of $a^{^{13}C\alpha}$ increase from 38.34 G for CH_3,[29] to 39.07 G for $CH_3\dot{C}H_2$,[29] to 41.3 G for cyclohexyl,[29] to 43 G for $[(CH_3)_3C]_2CH$, and to *ca.* 46 G for tertiary carbon radicals.

Acknowledgment. We are extremely grateful to Professor T. T. Tidwell for a generous sample of 1,1-di-*tert*-butylethylene.

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[19] Although approximate sp^3 hybridization of M is hereby assumed, fairly large changes in the s:p ratio would not substantially affect our conclusions.

[20] Calculated (ignoring difference in g factor) from data listed by J. E. Werz and J. R. Bolton in "Electron Spin Resonance," McGraw-Hill, New York, N. Y., 1972.

[21] See footnote g of Table I. We were unsuccessful in attempts to add CH_3 to di-*tert*-butylethylene.

[22] For $Et_3SiCH_2\dot{C}H_2$ at −112° $a^{H\beta}$ = 17.67 G, $a^{^{29}Si}$ = 37.4 G,[2,7] and for $Cl_3SiCH_2\dot{C}H_2$ $a^{H\beta}$ = 17.22 G.[10]

[23] For $Cl_3CCH_2\dot{C}H_2$ between −20 and −160° $a^{H\beta}$ = 22.3 G,[10] for $CF_3CH_2\dot{C}H_2$ $a^{H\beta}$ = 26.30 G[24,25] at −120°.

[24] D. Griller, unpublished results.

[25] Values of $a^{F\beta}$ for $CF_3\dot{C}F_2$ and $CF_3CF_2\dot{C}F_2$ (11.2 and 15 G, respectively[26]) imply that the latter radical also prefers conformation **2**.

[26] R. V. Lloyd and M. T. Rogers, *J. Amer. Chem. Soc.*, **95**, 1512 (1973).

[27] M. C. R. Symons, *Mol. Phys.*, **24**, 461 (1972); *Tetrahedron Lett.*, 207 (1973).

[28] D. E. Wood, L. F. Williams, R. F. Sprecker, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 6241 (1972).

[29] R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

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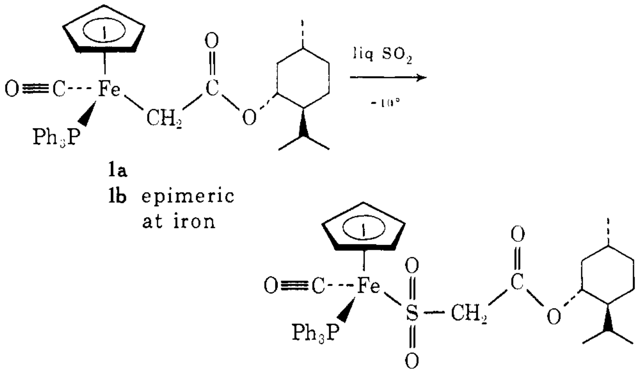
Stereochemistry at Iron of the Insertion of SO_2 into the Iron–Carbon σ Bond

Sir:

Considerable interest centers around the mechanisms of reaction of the metal–carbon σ bond because of their relevance to catalytic systems.[1] We report herein the synthesis and resolution of the iron–carbon σ-bonded compound **1** and describe the first example of the use of such a molecule to establish the stereochemistry at the metal resulting from reaction of the iron–carbon bond. The insertion reaction of **1** with liquid sulfur dioxide has been found to proceed with a high degree of stereospecificity at iron.



1a
1b epimeric at iron

2a
2b epimeric at iron

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[1] M. L. H. Green, "Organometallic Compounds," Vol. 2, Methuen, London, 1968, Chapters 7 and 9; C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967.

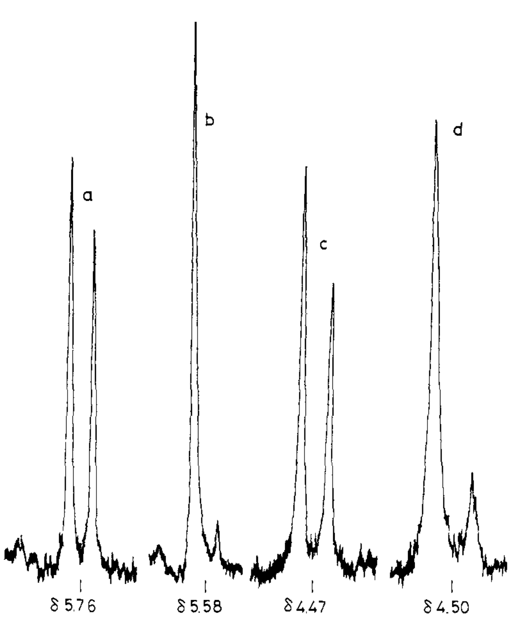

Figure 1. $Eu(FOD)_3$-d_{27} shifted nmr spectra of the diastereotopic Cp resonances: a, **1a** and **b**; b, **1a**, $[\alpha]^{25}_{578}$ +330°; c, **2a** and **b**; d, **2a**, $[\alpha]^{25}_{578}$ +206°. Typically, spectra were run *ca.* 15%, w/v, in $CDCl_3$ with *ca.* 0.9 wt equiv of shift reagent for **1**, and *ca.* 0.6 wt equiv for **2**.

Diastereomers **1a** and **b** were prepared by the addition of $CpFe(CO)_2Na$ to (−)-menthol bromoacetate, followed by incorporation of triphenylphosphine under photolytic conditions. Crystallization of the red-orange oil from pentane afforded crystals (**1a**) which after four recrystallizations exhibited a rotation of $[\alpha]^{25}_{578}$ +330° and mp 129–130°.[2] Diastereomer **1b** was similarly purified, $[\alpha]^{25}_{578}$ −309°, mp 115–116.5°. The degree of resolution was readily assessed by nmr spectroscopy with the use of the lanthanide shift reagent $Eu(FOD)_3$-d_{27}. Normally the Cp group is essentially a singlet ($J_{P-H} \sim 1$ Hz) at δ 4.26 ppm, but upon addition of the lanthanide complex, the Cp resonance of **1a** is shifted further downfield than is the same resonance of **1b** (Figure 1). For example, it could be determined by simple integration that **1a**, $[\alpha]^{25}_{578}$ +330° contained only 4% of **1b**.

Diastereomer **1a**, $[\alpha]^{25}_{578}$ +295°, underwent reaction with liquid SO_2 at reflux over several hours forming the SO_2 insertion product **2a**, $[\alpha]^{25}_{578}$ +206°, in 54% yield. Similarly **1b**, $[\alpha]^{25}_{578}$ −304°, afforded **2b**, $[\alpha]^{25}_{578}$ −270°, in 53% yield: ir (film) 1970 and 1710 (*cf.* for **1**, 1930 and 1650 cm^{-1}), 1265, 1180, 1090, and 1040 cm^{-1} among others. Fortuitously, the diastereomeric purity of **2** was easily assayed also through the use of $Eu(FOD)_3$-d_{27} and nmr. In this case, the Cp resonance of **2a** is not substantially affected upon addition of the shift reagent, while for **2b** it is moved *upfield.* For example, the Cp resonance of **2a**, [α] +206°, while initially a singlet at δ 4.58 ppm, in the presence of 60 weight % of the shift reagent exhibits two peaks at δ 4.63 and 4.38 ppm with relative intensities of 89:11, respectively. Given that the [α] +295° of **1a** indicates *ca.* 82% optical purity, the SO_2 insertion can be said to proceed with stereospecificity well in excess of 90%.

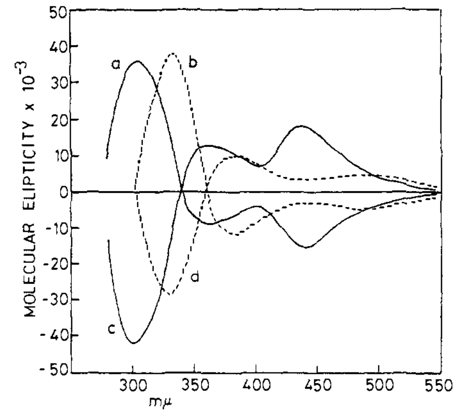

Figure 2. Circular dichroism spectra of compounds **1** and **2**, with their respective $[\alpha]^{25}_{578}$ values: a, **1b**, −260°; b, **2b**, −270°; c, **1a**, +330°; d, **2a**, +206°.

The relative configuration of starting material and product may be tentatively assigned by the use of circular dichroism spectroscopy. Figure 2 reveals that the CD spectrum of **1a** is the mirror image of **1b** and similarly that of **2a** is the mirror image of **2b** establishing that in these regions the transitions are entirely those of the metal and are independent of the (−)-menthyl group. Furthermore, CD spectra of compounds $CpFe(CO)(PPh_3)X$ appear to be highly insensitive to the nature of X. Data have been published for compounds wherein $-X$ is $-CO_2C_{10}H_{19}$-(menthyl) (**3**),[3] $-COCH_3$ (**4**),[3] and $-C(=N^+HCH$-$PhCH_3)CH_3{}^-BF_4$ (**5**).[4] In each case, the spectra of molecules with opposite configuration at iron are mirror images and, furthermore, the curves for all the compounds are very similar, spectrum a in Figure 2 being quite representative. The implication of these observations is that the absolute configuration for this closely related series of compounds is the same for all species with similar CD spectra.[3,5] We believe this argument implies that the *SO_2 insertion reaction occurs with retention of configuration at iron.*[6]

The absolute stereochemistry of the diastereomers of **1** and **2** may be predicted by relating their CD spectra to that of **5**[4] for which the absolute stereochemistry has been determined by X-ray crystallography.[7] The stereoisomer of **5** with a positive maximum at 350 nm in its spectrum has the configuration which we have accordingly assigned to **1b** and **2b**. Thus the absolute stereochemistries of **1a** and **2a** are tentatively as shown in the accompanying structures.[6]

Whitesides has observed *inversion at carbon* for the SO_2 insertion,[8] and Wojcicki recently reported the detection by nmr of what is probably an Fe–O sulfinate ester intermediate, Fe–OS(O)R (**6**).[9] An O to S

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(2) All new compounds have satisfactory elemental analyses and consistent ir and nmr spectra.

(3) H. Brunner and E. Schmidt, *J. Organometal. Chem.*, **36**, C18 (1972).

(4) A. Davison and D. L. Reger, *J. Amer. Chem. Soc.*, **94**, 9237 (1972).

(5) H. Brunner and M. Lappus, *Angew. Chem., Int. Ed. Engl.*, **11**, 923 (1972).

(6) These CD correlations have not been unequivocally established for any of the above mentioned compounds; their validity and generality must ultimately be proved by X-ray structure determinations. Such X-ray studies are under way for compounds **1a** and **2a**.

(7) V. W. Day and A. Davison, personal communication.

(8) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971).

(9) S. E. Jacobson, P. R. Rohrwig, and A. Wojcicki, *Inorg. Chem.*, **12**, 717 (1973).

migration of iron with retention of configuration at the metal is easily envisaged, but formation of sulfinate **6** with both retention at iron and inversion at carbon is more difficult to explain. A dissociative process cannot be ruled out as yet since there are no data available bearing on the configurational stability of the corresponding coordinatively unsaturated iron cation. Further work will clearly be necessary before a detailed mechanism for this intriguing reaction is entirely elucidated.

Brunner has observed Walden inversion at molybdenum in isocyanide exchange of CpMo(CO)(NO)(CNR) compounds,[5] and inversion of configuration at iron in the conversion of **3** to **4** by reaction of **3** with methyllithium.[3] To our knowledge, however, ours is the first example of the demonstration of the stereochemistry at iron of a reaction of an iron–sp^3 carbon bond. This stereochemical tool should prove to be important as a general mechanistic probe, and we are continuing our investigations of other reactions of the iron–carbon bond.

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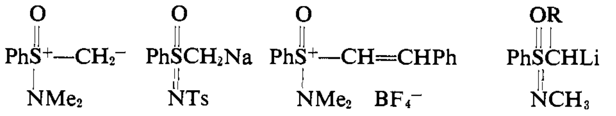
Olefin Synthesis by Reductive Elimination of β-Hydroxysulfoximines. Methylenation of Carbonyl Compounds[1]

Sir:

Sometime ago we began a systematic investigation of new reagents based on the sulfoximine group. It appeared to us that the structural features of sulfoximines afforded unique opportunities to tailor compounds for specific synthetic functions. Ylide **1**[2] and anion **2**[3] were the first members of a new family of nucleophilic alkylidene transfer reagents useful in the synthesis of oxiranes, aziridines, and cyclopropanes. Chiral members in these series have been shown to provide high asymmetric induction in their reactions.[4] Salts of type **3** have been shown to be excellent reagents for the electrophilic ethylene transfer to dibasic nucleophiles and have been used for the production of aziridines, cyclopropanes, and dihydrofurans.[5] A resolved version of reagent **4** has been employed in the synthesis of optically pure cyclopropanes[6] and alcohols.[7] We have now discovered a simple new method for the conversion of aldehydes and ketones to olefins which we



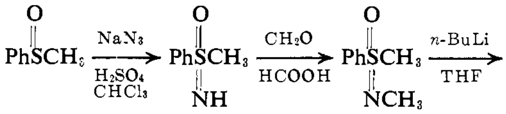
$$\mathrm{Ph\overset{O}{\underset{NMe_2}{\overset{\|}{S}^{+}}}{-}CH_2^{-}} \qquad \mathrm{Ph\overset{O}{\underset{NTs}{S}}CH_2Na} \qquad \mathrm{Ph\overset{O}{\underset{NMe_2}{S}^{+}}{-}CH{=}CHPh\ \ BF_4^{-}} \qquad \mathrm{Ph\overset{O}{\underset{NCH_3}{S}}\overset{R}{C}HLi}$$

1 **2** **3**

4, R = H
5, R = CH_3
6, R = $CH_3(CH_2)_2$

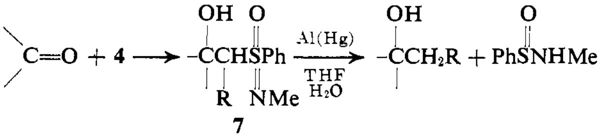
find to be a useful complement to the Wittig reaction[8] and other recent methylenation procedures.[9]

N-Methylphenylsulfonimidoylmethyllithium (**4**) (eq 1) readily adds to aldehydes and ketones to yield β-hydroxysulfoximines.



$$\mathrm{Ph\overset{O}{S}CH_3} \xrightarrow[\mathrm{H_2SO_4,\ CHCl_3}]{\mathrm{NaN_3}} \mathrm{Ph\overset{O}{\underset{NH}{S}}CH_3} \xrightarrow[\mathrm{HCOOH}]{\mathrm{CH_2O}} \mathrm{Ph\overset{O}{\underset{NCH_3}{S}}CH_3} \xrightarrow[\mathrm{THF}]{n\text{-BuLi}} \mathbf{4} \qquad (1)$$

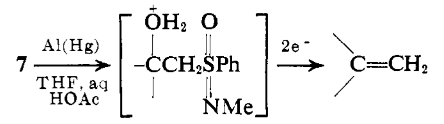
We have shown that aluminum amalgam[10] in aqueous THF is capable of reductively cleaving the carbon–sulfur bond in these adducts to produce alcohols (eq 2). We envisioned designing an



$$>\!C{=}O + \mathbf{4} \longrightarrow -\overset{OH}{C}\underset{R}{C}H\overset{O}{\underset{NMe}{S}}Ph \xrightarrow[\mathrm{THF,\ H_2O}]{\mathrm{Al(Hg)}} -\overset{OH}{C}CH_2R + Ph\overset{O}{S}NHMe \qquad (2)$$

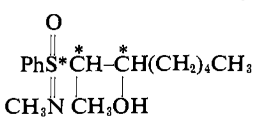
7

olefin synthesis based on a reductive elimination of *O*-acyl or other "leaving group" derivatives of **7**.[9] However, we found that a remarkably simple modification of the conditions used in the reduction step of eq 2 resulted in olefin formation at the expense of the alcohol. When acetic acid was added to the aqueous THF in the Al(Hg)[10] reduction step, reductive elimination occurred.[11] The exact role of the acid is unclear; one possibility is that the acid protonates the hydroxy group, converting it to a better leaving group (eq 3). The fact that both the formation of adduct **7** and the reductive elimination are carried out in THF makes it unnecessary to isolate the adduct **7**; the entire procedure can be completed in a single vessel (see entry 2 and 7, Table I).



$$\mathbf{7} \xrightarrow[\mathrm{THF,\ aq\ HOAc}]{\mathrm{Al(Hg)}} \left[-\overset{\overset{+}{O}H_2}{C}CH_2\overset{O}{\underset{NMe}{S}}Ph \right] \xrightarrow{2e^-} >\!C{=}CH_2 \qquad (3)$$

The intermediate adducts **7** in most cases are mixtures of diastereomers; this is of no consequence in methylenation reactions (entries 1 through 11, Table I). In adducts such as that formed in entry 13 (**8**), there are



$$\mathrm{Ph\overset{O}{\underset{CH_3N}{S}}{}^{*}\underset{CH_3}{\overset{*}{C}}H{-}\underset{OH}{\overset{*}{C}}H(CH_2)_4CH_3}$$

8

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[1] Part XLVII in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 19623).

[2] C. R. Johnson, M. Haake, and C. W. Schroeck, *J. Amer. Chem. Soc.*, **92**, 6594 (1970).

[3] C. R. Johnson and G. F. Katekar, *ibid.*, **92**, 5753 (1970).

[4] C. R. Johnson and C. W. Schroeck, *ibid.*, **90**, 6852 (1968).

[5] C. R. Johnson and J. P. Lockard, *Tetrahedron Lett.*, 4589 (1971).

[6] C. R. Johnson and C. W. Schroeck, *J. Amer. Chem. Soc.*, **93**, 5303 (1971).

[7] C. W. Schroeck and C. R. Johnson, *ibid.*, **93**, 5305 (1971).

[8] A. Maercker, *Org. React.*, **14**, 270 (1965).

[9] R. L. Sowerby and R. M. Coates, *J. Amer. Chem. Soc.*, **94**, 4758 (1972), and pertinent references cited therein. Sowerby and Coates have described an olefin synthesis based on the reductive (Li–liq NH_3) elimination of β-acyloxy sulfides.

[10] Granular aluminum was stirred with 2% aqueous mercuric chloride followed by washing with water, ethanol, and ether.

[11] Adducts of type **7** are structurally related to the β-hydroxysulfinamides which have been found to thermally decompose to olefins, sulfur dioxide, and amines: E. J. Corey and T. Durst, *ibid.*, **88**, 5656 (1966). Conceptionally, our adducts **7** could thermally decompose to yield olefins and sulfonamides. At this time we have not found conditions conducive to such reactions; most likely the higher oxidation state of the sulfur in the sulfoximine does not readily accommodate the formation of the necessary cyclic intermediate. Under thermal stress adducts **7** tend to revert to ketones and the starting sulfoximines.