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.

Acknowledgments. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Dr. P. J. Stephens for the use of his Cary 61 CD spectrometer and Dr. K. L. Servis and Mr. D. J. Bowler for assistance in obtaining the nmr spectra.

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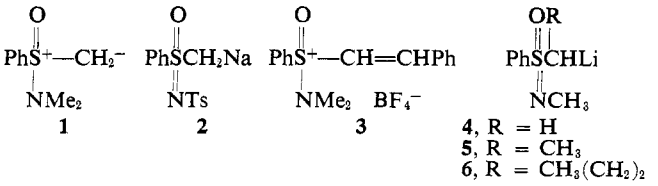
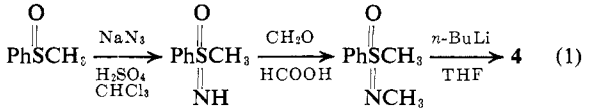
Olefin Synthesis by Reductive Elimination of β-Hydroxysulfoximines. Methylenation of Carbonyl Compounds[1]

Sir:

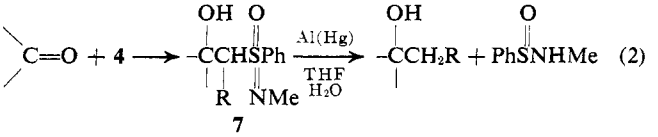
Sometime ago we began a systematic investigation of new reagents based on the sulfoximine group. It appeared to us that the structural features of sulfoximines afforded unique opportunities to tailor compounds for specific synthetic functions. Ylide **1**[2] and anion **2**[3] were the first members 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 find to be a useful complement to the Wittig reaction[8] and other recent methylenation procedures.[9]



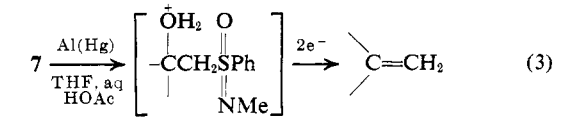
N-Methylphenylsulfonimidoylmethyllithium (**4**) (eq 1) readily adds to aldehydes and ketones to yield β-



hydroxysulfoximines. 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

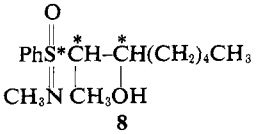


olefin synthesis based on a reductive elimination of *O*-acyl or other "leaving group" derivatives of **7**.[9] However, we found that a remarkably simple modification of the conditions used in the reduction step of eq 2 resulted in olefin formation at the expense of the alcohol. When acetic acid was 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



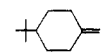
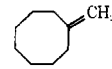
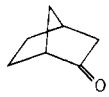
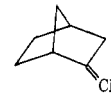
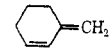
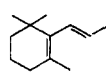
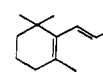
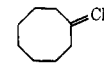
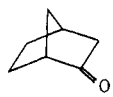
that both the formation of adduct **7** and the reductive elimination are carried out in THF makes it unnecessary to isolate the adduct **7**; the entire procedure can be completed in a single vessel (see entry 2 and 7, Table I).

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



(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.

Table I. Conversion of Carbonyl Compounds to Olefins

Entry	Carbonyl compound	Sulfoximine	Yield of adduct, %	Olefin	Yield, %
1	$CH_3(CH_2)_{14}C(=O)CH_3$	4	90	$CH_3(CH_2)_{14}C(=CH_2)CH_3$	90
2	$CH_3(CH_2)_{14}C(=O)CH_3$	4	*a*	$CH_3(CH_2)_{14}C(=CH_2)CH_3$	85
3	$CH_3(CH_2)_6CHO$	4	50	$CH_3(CH_2)_6CH=CH_2$	60
4	$CH_3(CH_2)_8CHO$	4	80	$CH_3(CH_2)_8CH=CH_2$	70
5	PhCHO	4	90	$PhCH=CH_2$	60
6	$CH_3(CH_2)_3C(=O)(CH_2)_5CH_3$	4	90	$CH_3(CH_2)_3C(=CH_2)(CH_2)_3CH_3$	80
7		4	*a*		73
8		4	75		85
9		4	50		82
10		4	89		50
11		4	85		93
12	$CH_3(CH_2)_8CHO$	5	60	$CH_3(CH_2)_5CH=CHCH_3$ cis–trans mixture	60
13	$CH_3(CH_2)_4CHO$	5	75	$CH_3(CH_2)_4CH=CHCH_3$ 60% trans 40% cis	100
14	$CH_3(CH_2)_2CHO$	6	78	$CH_3(CH_2)_2CH=CH(CH_2)_2CH_3$ 64% trans 36% cis	78
15		5	85		70
16		5	75	 78%-22% mixture	65

[a] Not isolated.

three asymmetric centers and hence the possibility that the adduct as produced is a mixture of four diastereomers. This provides for the intriguing and potentially useful possibility that the individual diastereomers, upon separation and reduction, could provide pure samples of cis or trans olefins. At this juncture we have not achieved this goal. We have, in several cases (entires 14 and 16), separated and purified what we believe to be single diastereomers. However, upon reduction the purified diastereomers resulted in cis/trans mixtures, albeit enriched in a single isomer (as compared with the direct reduction of the original diastereomeric mixture). Our efforts along these lines are continuing.

The sulfoximines (**4**, **5**, **6**), dissolved in THF (30 mmol/100 ml), were treated at 0° with 1 equiv of *n*-butyllithium. The carbonyl compounds, dissolved in THF, were added to the reagent, and the reaction mixture was maintained at 0° for 1 hr, then allowed to warm to room temperature over 1 additional hr (with conjugated substrates, the reaction mixtures were maintained constantly at 0° for 2–4 hr).[12] Acetic acid (30–45 equiv) diluted with an equal volume of water was added to the reaction mixture followed by addition of 10–15 g-atom equiv of aluminum amalgam. The reactions, run at room temperature, were monitored by thin-layer chromatography; typically, reductive elimination was complete in 4 hr. The olefins were isolated and purified by extraction with pentane and washing the pentane extract with 20% aqueous sodium hydroxide[13] followed by distillation or chromatography. The yields reported in Table I are for isolated and purified materials.

(12) When the β-hydroxysulfoximines were isolated, the reaction mixtures were quenched at this point with 10% aqueous ammonium chloride; the adducts were extracted into methylene chloride, washed with water, dried, and purified, if desired, by chromatography on silica gel. The crude or purified adducts were dissolved in THF and reduced as described without isolation.

(13) To remove thiophenol produced by reduction of *N*-methylbenzenesulfinamide.

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Thermal Isomerization of But-1-en-3-yl(dimethylamino)ethylborane. The Reluctant 1,3-Sigmatropic Shift of Boron in an Unusually Stable Allylborane

Sir:

The high reactivity of allylboranes with a host of diverse nucleophiles under generally mild conditions has been widely exploited in organic synthesis.[1] There

(1) For a recent review, see B. M. Mikhailov, *Organometal. Chem. Rev., Sect. A*, **8**, 1 (1972).