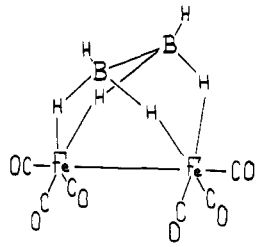
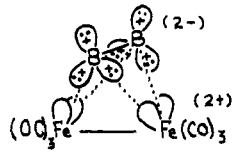


Figure 1. The proposed structure of $B_2H_6Fe_2(CO)_6$.

obsd 279.9094 amu). The parent ion in the mass spectrum fragments by the sequential loss of six CO molecules and the envelopes of the parent ion and first two fragment ions are inconsistent with a molecule containing more than two boron atoms. The Fe_2^+ ion is also present in the fragmentation pattern. The gas phase infrared spectrum exhibits bands in the CO region at 2070 (s), 2058 (sh), and 2003 (s) cm^{-1}. The IR spectrum of a film of the compound also contains a band at 2530 (w) cm^{-1} which is attributed to ν_{BH}. No bands were observed in the BHB bridging region. The 100-MHz ^1H FT NMR spectrum in CD_2Cl_2 exhibits a broad resonance (300 Hz, fwhm, relative area 1) at δ 0.2 and a broad resonance (250 Hz, fwhm, relative area 2) at -10.3. On ^{11}B decoupling both resonances sharpen considerably (40 Hz, fwhm) and retain the same relative areas. The 25.2-MHz ^{11}B FT NMR spectrum consists of a broad resonance at -24 ppm (200 Hz, fwhm).[9] The resonance is a doublet ($J \approx 90$ Hz) each component of which appears to be an incompletely resolved multiplet.

The compound is formulated as $B_2H_6Fe_2(CO)_6$ and the NMR and IR spectra are consistent with the structure shown in Figure 1. The broad ^1H resonance at $\delta -10.3$ is assigned to the four BHFe protons while the resonance at 0.2 is assigned to the two terminal protons.[10] For this structure the ^{11}B NMR spectrum is expected to consist of a doublet of triplets. The observed spectrum is consistent with this prediction; however, the B-H-Fe coupling is not resolved. The IR spectrum in the carbonyl region is not unlike that reported for $S_2Fe_2(CO)_6$[11] and, thus, is also consistent with the proposed structure.

In terms of the electron counting rules,[5] the framework is nido having 12 skeletal electrons (2 from each $Fe(CO)_3$, 2 from each BH, and 1 from each BHFe) in a four-atom cage. As such it is the analogue of B_4H_8, an unstable borane that has been detected[12] but not isolated. Alternatively, the compound can be viewed as the eight-electron donor $B_2H_6^{2-}$ bound to the $Fe_2(CO)_6^{2+}$ dimer as a structure in which the 18-electron rule is satisfied. The high negative charge on the borane implied



by this formulation is consistent with the small BH terminal coupling constant suggested by the ^{11}B spectrum.[13]

The new compound is isoelectronic with $C_2H_2Co_2(CO)_6$, the parent of the known $C_2R_2Co_2(CO)_6$.[14] As such it is a new member of the growing class of bridged X_2 dimetal carbonyl compounds.[15,16] It is also the third example of a B_nM_n cage[17] and another bridge between metal clusters and boranes, e.g., $H_4Ru_4(CO)_{12}$ and B_4H_8. As the compound is volatile, the UV photoelectron spectrum is presently being obtained. This study, as well as the results of other ongoing chemical investigations, should reveal more of the nature of this compound.

Acknowledgments. The support of the National Science Foundation through Grant CHE75-10938 is gratefully acknowledged as are helpful discussions with Dr. Jay Labinger. We thank Mr. Donald Schifferl for assistance with the NMR studies.

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(6) For example, the ferraborane $B_4H_8Fe(CO)_3$ has been shown to provide a synthetic route to both four- and six-carbon carboranes: T. P. Fehlner, *J. Am. Chem. Soc.*, **99**, 8355 (1977).
(7) The mass spectrometric identification of this compound and $B_3H_7Fe_2(CO)_6$ has been reported earlier: J. A. Ulman and T. P. Fehlner, the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Sept 1976, INORG 84. A compound identified mass spectrometrically as either $B_2H_4Co_2Cp_2$ or $B_2H_6Co_2Cp_2$ has also been reported: R. N. Grimes, *Ann. N.Y. Acad. Sci.*, **239**, 180 (1974).
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A Simple Synthesis of Sulfur Substituted Cyclopropanes. Effect of Solvent and Gegenion upon Mechanism and Product Composition

Sir:

In connection with another project, we had occasion to prepare sulfides of general structure **1**. We reasoned that, based upon the well known propensity for methyl 4-bromocrotonate to undergo S_N2 displacement reactions,[1,2] mercaptide induced displacement of bromide from the bromocrotonate would suffice.[3] We were therefore somewhat surprised to find that the product isolated in good yield (65–85%) from the reaction of methyl 4-bromocrotonate with lithium *sec*-butyl- or *tert*-butylmercaptide did not show any vinyl hydrogens in the ^1H NMR. Combustion and complete spectral analysis[4] showed that the *trans*-cyclopropane **2** was the product.[5]

We were intrigued by the potential mechanistic and synthetic implications of this observation. Why did we not observe the formation of the expected product **1**? Could we vary the

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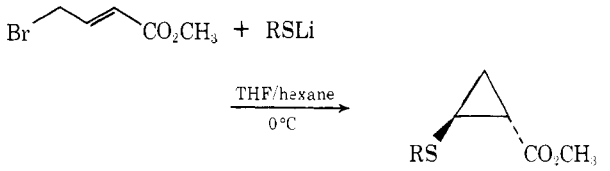
Table I. Summary of Solvent and Gegenion Studies[a,b]

Product, %	CH_2Cl_2			Et_2O			THF			PhH			Pentane			DMF		
	Li	Na	K	Li	Na	K	Li	Na	K	Li	Na	K	Li	Na	K	Li	Na	K
2 (R = *tert*-butyl)	73	0	0	70	5	2	65	8	4	81	2	0	74	2	0	0	0	0
t-BuSCH$_2$CH=CH-CO$_2$CH$_3$	20	96	95	29	95	96	35	89	89	19	92	97	26	93	99	80	82	90
t-BuSCH=CHCH$_2$-CO$_2$CH$_3$	4	0	0	0	0	0	0	0	0	0	3	0	0	2	0	20	19	9

[a] The mercaptide is added to the methyl 4-bromocrotonate in these runs. [b] VPC yields. Careful checks have shown complete mass balance.

$$RSCH_2CH{=}CHCO_2CH_3$$

1



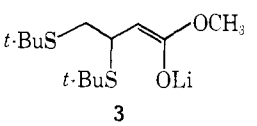
2, R = *sec*-butyl or *tert*-butyl

conditions of the reaction in such a way as to selectively favor the formation of **1** rather than cyclopropane **2**? Finally, heteroatom substituted cyclopropanes have been shown to be very useful synthetic intermediates and have been the subject of much effort in recent years.[6] We were therefore obviously intrigued by the fact that these compounds were available to us in a single good-yield reaction starting from very simple commercially available substrates. This paper reports the results, both mechanistic and synthetic in nature, of our studies to date.

The course of the reaction was found to be critically dependent upon solvent and the mercaptide gegenion. Thus, in methylene chloride, THF, diethyl ether, benzene, and pentane with lithium as the gegenion the yields of cyclopropane remained essentially constant and within the range of 70-80%. A careful examination of the reaction mixtures revealed that the remainder of the material could be accounted for in terms of the initially desired γ adduct **1**. When the same reaction was conducted in DMF or HMPA, *no* cyclopropane product was formed. Instead, only **1** (R = *tert*-butyl) and its corresponding β,γ-unsaturated isomer were produced.

The effect of changing the gegenion is even more striking. For example, the amount of cyclopropane produced in CH_2Cl_2, THF, Et_2O, PhH, and pentane drops from 70-80% when lithium is the gegenion to 0-8% with sodium and 0-4% with potassium. Furthermore, the amount of the γ adduct **1** (R = *tert*-butyl) increases dramatically as the amount of cyclopropane decreases when the gegenion is changed from lithium to sodium to potassium. For example, in each of the solvents listed, the yield of γ adduct is no less than 89% and is as high as 99% when potassium is the gegenion. The results of solvent and gegenion variation are summarized in Table I.

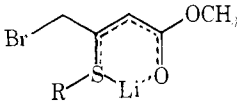
A priori, it would appear that the cyclopropane products could result from Michael attack upon an initially formed γ adduct, **1**, to produce an intermediate enolate **3** which could



3

then displace mercaptide and form **2**. This was shown not to be the case by demonstrating that authentic **1** (R = *tert*-butyl) is not converted to **2** under the reaction condition most likely to generate **2** (viz., Li, THF, or THF/hexane).

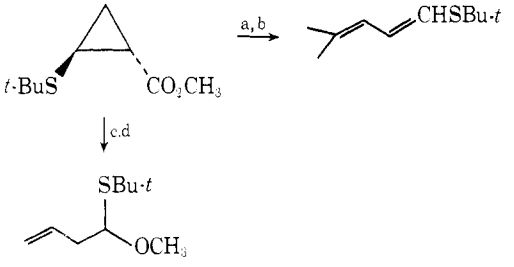
We interpret the results summarized in Table I in the following way. In the most simplistic terms, Michael addition of mercaptide to methyl 4-bromocrotonate leads to an intermediate enolate which in turn displaces bromide in the cyclopropane forming step. Consideration of the solvent and gegenion effects suggests that solvation and coordination effects are important in determining the course of the reaction. We suggest that, when lithium is the gegenion and in the solvents CH_2Cl_2, THF, Et_2O, PhH, and pentane, the lithium metal is coordinated both with sulfur and with the ester carbonyl oxygen thereby holding the attacking sulfur atom in close proximity to the β-carbon atom—the observed site of predominant attack. When the solvent is changed to DMF and



HMPA, these solvents solvate the metal and effectively remove its effect upon the course of the reaction. The mercaptide is then free to attack at either the β or the γ positions—γ attack is observed. The effect of gegenion change can be accounted for by simply realizing that, in progressing from Li to Na to K, the metals become progressively less effective in their ability to coordinate with oxygen, thereby allowing more access to the γ-carbon atom.

One other point bears comment. That is, in DMF and HMPA, there are dramatic color changes which take place during the course of the reaction. This fact suggests the possibility that an electron-transfer reaction occurs from mercaptide to the γ-bromocrotonate; mercaptides have been shown to do so in a number of well-documented cases.[7] To test this hypothesis, we attempted to quench the process with both 2-nitroso-2-methylpropane and 2,6-di-*tert*-butyl-4-methylphenol. No quenching was observed even when a twofold excess of radical trapping agent was used. We therefore do not have any absolute proof that even a small portion of the observed reaction pathway follows an electron-transfer pathway in polar aprotic solvents, though we cannot exclude the possibility.[8]

Finally, we have used these sulfur substituted cyclopropyl esters to effect a number of useful transformations. The corresponding more difficultly synthesized oxygen analogues are of course known to behave similarly.[6d,e] We are, however, studying other reactions which are possible with the sulfur compounds but not with the oxygen substituted cases and will report our results in future papers.



[a] $2CH_3Li$, Et_2O. [b] CH_3SO_2Cl, Et_3N, CH_2Cl_2; −20 °C to room temperature. [c] $LiAlH_4$, Et_2O. (d) CH_3SO_2Cl, Et_3N, CH_2Cl_2; −40 °C, then CH_3OH, −40 °C to room temperature.

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(2) There are a few scattered reports of cyclopropane formation from the reaction of methyl 4-bromocrotonate with nucleophiles. Specifically, Rambaud[2a] has reported that the addition of sodium methoxide (and ethoxide) to the crotonate leads to a low yield of methyl-2-methoxycyclopropane. This result was also reported by Owen and Sultanbawa.[2b] However, Dreiding and Pratt[2c] later showed that the material previously presumed to be the cyclopropane was instead dimethyl 2,4,6-octatrienedioate. It appears that the only bona fide example is due to English[2d] wherein inverse addition of phenylmagnesium bromide to methyl 4-bromocrotonate afforded a 13% yield of the cyclopropane product. (a) R. Rambaud, *C. R. Hebd. Seances Acad. Sci.*, **200**, 2089 (1935); R. Rambaud, *Bull. Soc. Chim. Fr.*, **5**, 1595 (1949). (b) L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3098 (1949). (c) A. Dreiding and R. Pratt, *J. Am. Chem. Soc.*, **75**, 4580 (1953). (d) R. Ratney and J. English, Jr., *J. Org. Chem.*, **25**, 2213 (1960).

(3) We routinely use mercaptides to effect displacement of bromide from methyl 2-bromomethylacrylate for the synthesis of the corresponding acyclic sulfides.

(4) New compounds were characterized using IR, ^{1}H NMR, mass spectral analysis, combustion analysis, and occasionally ^{13}C NMR.

(5) The idea of forming cyclopropanes via Michael addition followed by elimination is not new. However, in each of the routes which has been used previously, the leaving group is attached to the incoming attacking carbon atom. Thus the leaving group (heteroatom) is lost rendering heteroatom substituted cyclopropanes much less readily accessible. In our route, the heteroatom (sulfur) is the attacking group and remains attached to the resulting cyclopropane. See H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, New York, N.Y., 1972, pp 614, 689, 719–721, and references cited therein.

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(8) It is, of course, still possible that an electron-transfer process may still be occurring. Our results simply require that the radicals collapse before diffusion from the solvent cage and subsequent trapping.

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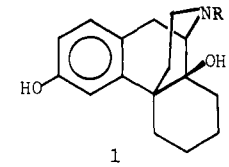
A Stereoselective Total Synthesis of 14-Hydroxymorphinans. Grewe Approach

Sir:

The 3,14-dihydroxymorphinans have been synthesized by modification of thebaine[1] and by total synthesis.[2] Since a number of these compounds have shown interesting biological properties, in particular, clinically effective analgesia[2,3] (butorphanol, **1a**) and strong narcotic antagonism[2] (oxilorphan, **1b**), a new synthesis in which optical resolution could be accomplished at an earlier step was desirable. Thus a modification of the classical Grewe synthesis of morphinans[4,5] to the synthesis of 14-hydroxymorphinans, using a common intermediate 1-*p*-methoxybenzyloctahydroisoquinoline (**2a**) (Scheme I) attracted our attention.[6]



1

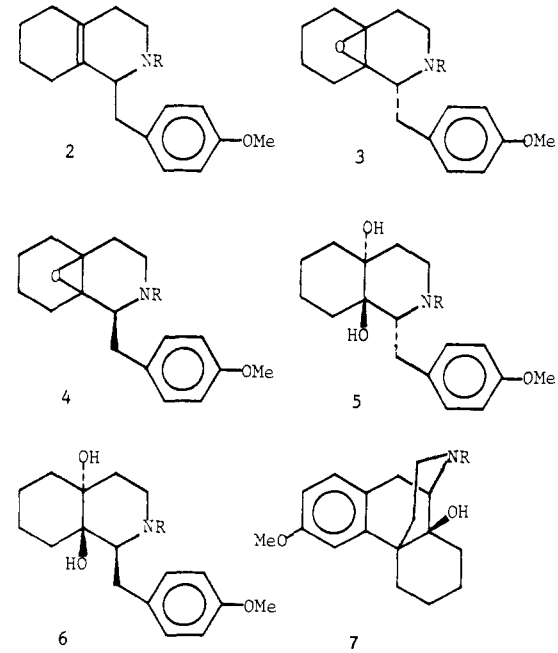
a) butorphanol R = CH_2-cyclobutyl

b) oxilorphan R = CH_2-cyclopropyl

We now report on the first successful synthesis of 14-hydroxymorphinans via a Grewe synthesis, using **2a** as starting material. An initial attempt was to epoxidize amide **2b** (mp 75–78 °C),[7] to the corresponding trans epoxide (**3b**), which would be expected to undergo a direct one-step acid-catalyzed epoxide opening-cyclization, to give **7b.** However, a mixture of epoxides was obtained in which **4b** was the major product, and thus an efficient direct cyclization was precluded. The mixture was separated by column chromatography to give **4b** (mp 84–86 °C from petroleum ether) and **3b** (mp 102–105 °C) in 9:1 ratio. Treatment of **4b** with sodium borohydride in ethanol under reflux for 1 h gave **4a,** an oil, in quantitative yield, whereas **3b** required treatment for 20 h under the same reaction conditions to give **3a** (mp 69–70 °C). Acid-catalyzed hydrolysis of **4a** gave stereoselectively the product of C-10 opening, the diol **6a** (mp 159–160 °C), while the same treatment of **3a** resulted in a 7:3 mixture of **5a** (mp 156–157 °C) and **6a,** respectively. In contrast to these results, acid-catalyzed opening of epoxide **3b** gave exclusively the product of C-10 opening, the trans diol **5b** (mp 103–105 °C), whereas **4b** gave a mixture of 46% **5b** and 54% **6b** (mp 84–85 °C).

The structure and stereochemistry of the diols was indicated by the fact that both **5a** and **5b** upon treatment with phosphoric acid (5 days, 65 °C) gave 14-hydroxymorphinan (**7a**), albeit in yields (4–6%) and with decomposition of starting materials. However, under the same reaction conditions, **6a** and **6b** were completely destroyed. The structural assignments of **5a** and **6a** were confirmed by an x-ray crystallographic study,[8] which

Scheme I



a) R = H, b) R = $COCF_3$, c) R = CO-cyclopropyl,

d) R = CH_2-cyclopropyl, e) R = CH_3

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