Table I.

$$\underset{\mathbf{2}}{\mathrm{OMo(NNCR'R'')(S_2CNR_2)_2}} + \mathrm{Ph_3P{=}CR_1R_2} \rightarrow \mathrm{R'R''C{=}CR_1R_2} + \mathrm{N_2} + \mathbf{1} + \mathrm{PPh_3}$$

metalloazine				yields[a] of $R''R'C{=}CR_1R_2$ (%, Z/E)		
2	R′	R″	R	$R_1 = R_2 = H$	$R_1 = H$; $R_2 = n$-Bu	$R_1 = H$; $R_2 = Ph$
a	H	Ph	Et	70	90 (1.25)	99 (0.4)
b	Me	Ph	Et	65	10 (0.5)	55 (1.2)
c	H	Pr	Et	40	50[b]	70 (0.6)
d	H	*i*-Pr	Et	40	99 (0.3)	80 (0.1)
e	H	*t*-Bu	Et	99	25 (1.5)[c]	70 (1.0)[c]
f	H	4-cyclohexenyl	Et	35	99 (0.14)	99 (0.1)
g	Ph	Ph	Et	40[d]	54	0[c]
h	Ph	Ph	Me	70	70	0[c]

[a] All reactions were run at room temperature for 24 h with 2 equiv of ylide unless otherwise stated. THF or toluene were used as solvents. Yields were determined by GC and all products were confirmed by GC/MS analysis. [b] Only one isomer observed. [c] Reaction was heated at 60 °C. [d] See footnote 18.

for reaction with the aldehyde. In contrast, reaction of the ylide with 1:1 mixtures of **2a** and ketone (acetophenone) or **2a** and ester (methyl benzoate) resulted exclusively in products derived from the metalloazine.

The olefin synthesis described above directly parallels conventional "Wittig" chemistry with one important difference: In conventional "Wittig" chemistry, when a carbonyl group is converted to an olefin, the "redox couple" is balanced by conversion of a phosphine to a phosphine oxide. Apart from recovery of triphenylphosphine oxide as a problem of practical consequence, the inability to easily recycle it to triphenylphosphine is a major negative attribute of the "Wittig" sequence. In the "Wittig analogous" reaction described herein, a carbonyl group starting material is sequentially converted to an olefin through its hydrazone and diazoalkane derivatives. Thus, ultimately, *only hydrazine is oxidized to dinitrogen* to balance the reduction of the carbonyl group to the olefin, and both the organometallic and the triphenylphosphine are readily recovered from the reaction, to be recycled.

Acknowledgment. We acknowledge support for this work given by the NSF and NIH.

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(2) Effectively this would provide long-chain analogues of the Tebbe Reagent; see: Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270.

(3) Smegal, J. A.; Schwartz, J., unpublished results.

(4) For example, see: Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800–812 and references cited therein.

(5) Kaufman, G. M.; Smith, J. A.; VanderStouw, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1965**, *87*, 935.

(6) A small excess of phenyldiazomethane was used to ensure complete conversion of $OMo(S_2CNR_2)_2$ to $OMo(NNCHPh)(S_2CNR_2)_2$ (which does, however, react slowly with $PhC(H)N_2$ to give *cis*- and *trans*-stilbene, N_2, and **1**).

(7) For **2g** empirical formula $C_{23}H_{30}N_4OS_4Mo$: C, H, N, O, S, Mo; $\nu_{Mo{=}O} = 883$ (s), 916 (sh) cm^{-1}; for **2a**, $\nu_{Mo{=}O} = 893$ (s), 914 (sh) cm^{-1}.

(8) In preliminary studies we found that $Cp_2Mo(PPh)_3$[9] (**3**) could also be converted to a metalloazine as follows. A toluene solution of **3** (0.2 g, 0.88 mmol in 10 mL of toluene) was cooled to −30 °C and a toluene solution containing 1.5 equiv of phenyldiazomethane[5] (1.32 mmol in 4 mL of toluene) was added to give a yellow-brown solution. Concentration of the reaction mixture, addition of pentane, and cooling resulted in the formation of red-brown solid **4**. The absence of N_2 formation during the reaction of **3** with the diazo compound and the formation of the corresponding hydrazone upon hydrolysis of **4** indicates the presence of the entire diazoalkane unit in **4**, formulated as $Cp_2Mo^{IV}(NNCHPh)$ (^1H NMR (C_6D_6) δ 4.85 (s, Cps 10 H), 6.0 (s, N_2CHPh, 1 H), 7.6, 7.0 (m, Ph, 5 H)). Although a definitive assignment of the bonding mode of the diazo moiety to Mo cannot be determined from the NMR data, the chemical shift of the iminic hydrogen in **4** is consistent with an end-on binding mode by analogy with another Mo^{IV} complex, $[MoF(NNCHPh)(dppe)_2]BF_4$ [^1H NMR ($CDCl_2$) δ 5.6 (s, NNC*H*Ph, 1 H)], for which end-on binding of the diazo unit was determined through X-ray crystallographic analysis of a tungsten analogue.[10–13]

(9) Geoffroy, G.; Bradley, M. G. *Inorg. Chem.* **1978**, *17*, 2410–2414.

(10) Hidai, M.; Mizobe, Y.; Sato, M.; Kodama, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5740–5748.

(11) Chatt, J.; Head, R. A.; Hitchcock, P. B.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1977**, *133*, C1. A structure was determined by X-ray crystallography of a representative example, $[WBr(NNCMe_2)(dppe)_2]Br$, of a series of compounds of this type including $[MoF(NNCHPh)(dppe)_2]BF_4$, all of which were synthesized by the same method.

(12) For a unique Mo analogue, see: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Ratesmann, A. L. *Inorg. Chem.* **1984**, *23*, 2303–2311. (b) Herrmann, W. A. *J. Organomet. Chem.* **1975**, *84*, C25.

(13) The assertion of a high formal oxidation state requires the assignment of the diazo unit as a $(NNCR_2)^{2-}$ ligand, an assignment that is substantiated by noting M–N and N–N distances in analogous molybdenum and tungsten diazo adduct structures which have been determined crystallographyically.[12,14]

(14) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 7295–7301.

(15) A series of W and Mo carbonyl complexes of possibly analogous structure, though of different reactivity, has been prepared. Hillhouse, G. L.; Haymore, B. L. *J. Am. Chem. Soc.* **1982**, *104*, 1537.

(16) A dimeric structure containing bridging diazo units for **2** and **4** cannot be ruled out at this time.

(17) An excess of phosphorane was used to ensure complete reaction of the metalloazine. Although $OMo(S_2CNR_2)_2$ is regenerated in the procedure shown, olefin synthesis by reaction between the diazo compound and the phosphorane cannot be catalyzed by **1** since these reagents react rapidly to yield a mixture of byproducts (but not the desired olefin).

(18) The α-nitrogen of the diazo adduct unit can also show susceptibility to nucleophilic attack as evidenced by the formation of $Ph_2CNNCH(CH_2)_3CH_3$ in 70% yield by reaction between sterically crowded **2g** and $Ph_3PCH(CH_2)_3CH_3$. No reaction occurred between **2g** and Ph_3PCHPh. In an attempt to enhance susceptibility of **2g** to nucleophilic attack, an $AlCl_3$ adduct (presumably by coordination to the oxo group[19]) was formed. This adduct reacted with Ph_3PCH_2 to give 1,1-diphenylethylene in 40% yield.

(19) Osborn, J. A.; Kress, J.; Wesolek, M. *J. Chem. Soc., Chem. Commun.* **1982**, 514.

(20) All geometric isomers of **2** are, therefore, reactive.

(21) Metalloazine **4** also reacts with ylides to yield olefins, dinitrogen, and $Cp_2Mo(PPh)_3$. For example, **4** reacts with CH_2PPh_3 to give styrene (60%).

Metal-Mediated Cycloaddition Reactions of 1,1,2,2-Tetrafluoro-1,2-disilacyclobutene with Cyclohexadiene. Correlation between the Stereochemistry of Intermediates and Reaction Pathways

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Received June 10, 1985

Photochemical preparation of silyl–transition-metal compounds and the chemistry of Si–M bonds under photochemical conditions have been a subject of recent interest.[1-4] We recently reported the metal-mediated cycloaddition reactions of 1,1,2,2-tetrafluoro-1,2-disilacyclobutene with 1,3-butadiene derivatives.[5] The reactions proceed via a very unusual 1,1-addition pathway which involves either H- or F-migration depending on the nature of the metal used.[5] Since all butadiene derivatives used in the work involved substituents on carbon 2 and/or carbon 3, it is desirable to investigate the steric effect of the substituents on the target carbons, namely, carbon 1 and carbon 4. One of the prominent examples is cyclohexadiene.

Cycloaddition reaction of 1,1,2,2-tetrafluoro-1,2-disilacyclobutene **1** with cyclohexadiene proceeded smoothly at 100 °C and

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(1) Jetz, W.; Graham, A. G. *Inorg. Chem.* **1971**, *10*, 4.

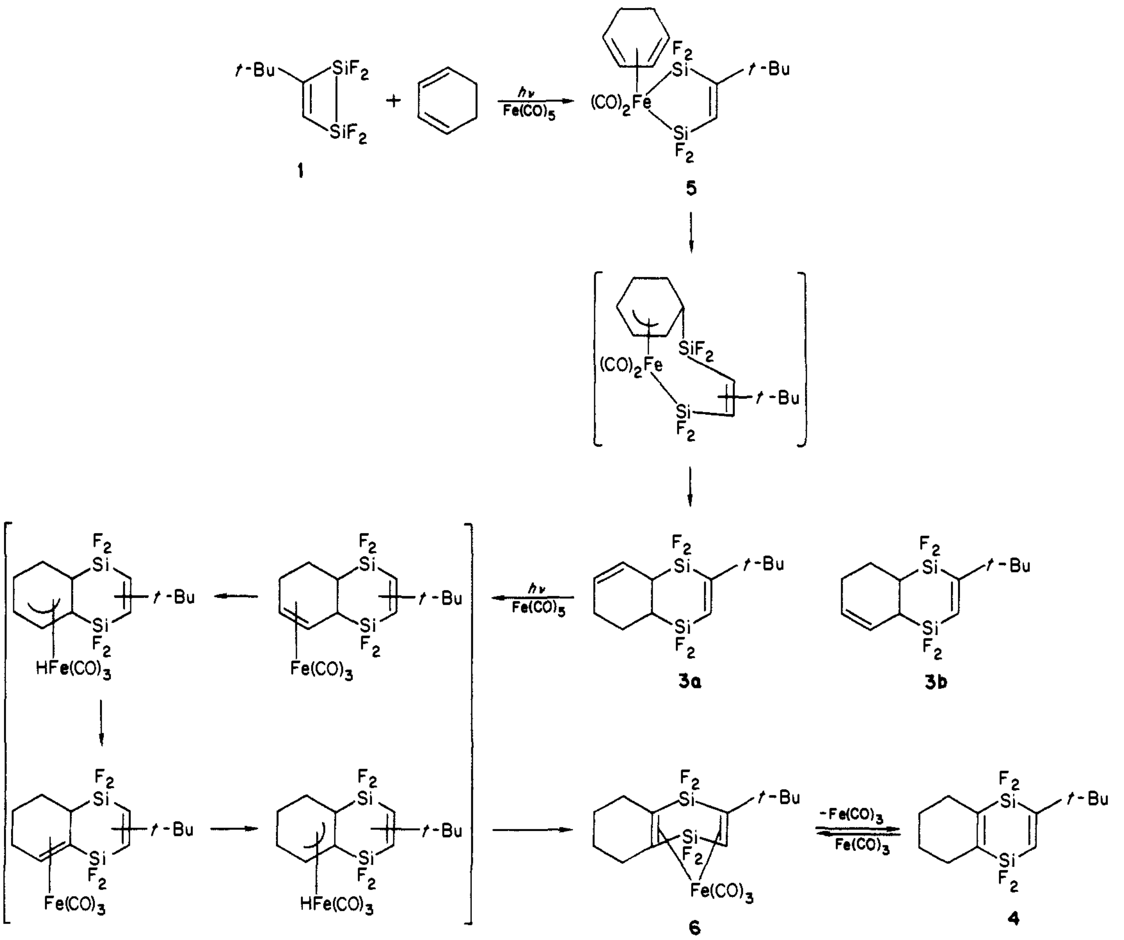
(2) Mitchener, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 975.

(3) Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345.

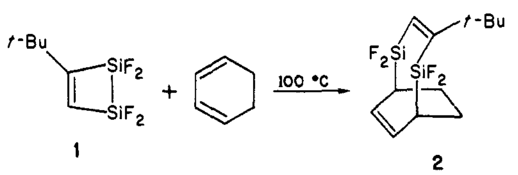
(4) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 551.

(5) Lee, C. Y.; Lin, C. H.; Liu, C. S. *Organometallics*, submitted for publication.

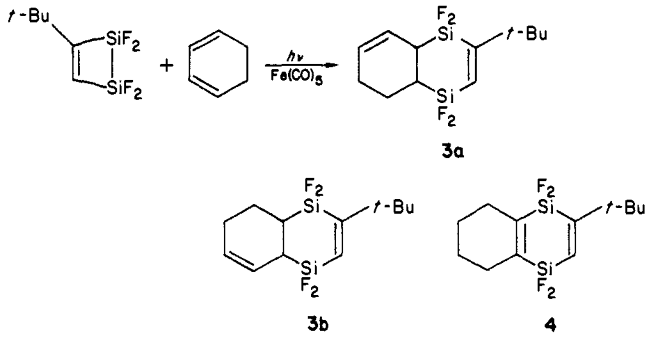
Scheme I



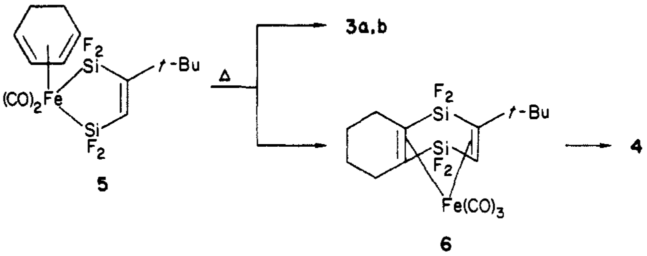
the only product found was the product from 1,4-addition, compound **2**.[6]



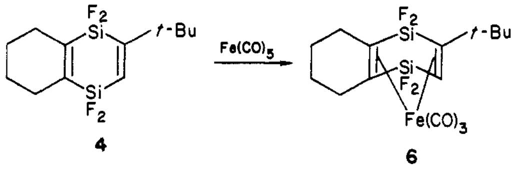
When a *n*-pentane solution of equimolar **1** and cyclohexadiene (~10 mmol) was reacted with Fe(CO)$_5$ photochemically (in a quartz tube with medium-pressure Hg lamp), compounds **3a**,**b** and **4** were obtained as the products.[6]



When the reaction was carried out at 0 °C photochemically, a reaction intermediate was isolated. This intermediate has been fully characterized as compound **5** by mass spectrometry, ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy in solution, and X-ray diffraction in a single crystal. At 100 °C, compound **5** decomposed to products **3a**,**b** and **4**. During the process of thermal decomposition of **5**, one more intermediate, **6**, was isolated,[6] which led to the formation of **4** quantitatively at elevated temperature.



When the products **3a**,**b** and **4** were treated with Fe(CO)$_5$ separately under the same reaction conditions as those of thermal decomposition of **5**, there was no observation of interconversion among the three. The only reaction observed was the reconversion of **4** to **6**. In fact, pure **6** was conveniently obtained by this means.



However, when **3a**/**3b** were treated with Fe(CO)$_5$ under UV irradiation, conversion to **4** was observed. Since the major coordinatively unsaturated species under the condition of thermal decomposition is Fe(CO)$_4$, it appears that more reactive species such as Fe(CO)$_3$ are required for the isomerization of **3a**/**3b**. This could arise via photodissociation of a CO ligand from an olefin–

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[6] All isolated intermediates and products, namely, compounds **2**, **3a**,**b**, and **4**–**7** were fully characterized by mass spectrometry and ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy.

[7] Detailed X-ray diffraction data of compounds **5** and **7** will be published elsewhere.

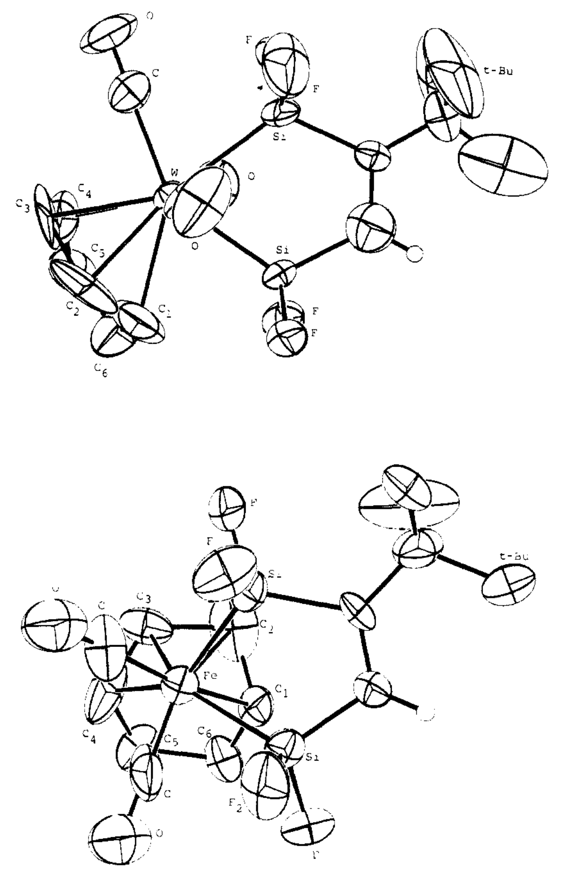
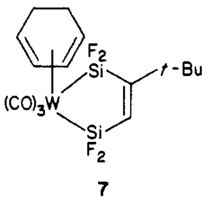


Figure 1. Molecular structure of $(C_6H_{10}Si_2F_4)Fe(C_6H_8)(CO)_2$ and $(C_6H_{10}Si_2F_4)W(C_6H_8)(CO)_3$.

$Fe(CO)_4$ complex formed initially.[4] One plausible reaction mechanism which would account for all the intermediates and products observed experimentally can be proposed in Scheme I.

It is interesting to note that when $W(CO)_6$ was used instead of $Fe(CO)_5$, only one product, **3a**, was obtained. The intermediate in the reaction of $W(CO)_6$ was also isolated and characterized as compound **7**.[6]



7

Since both compound **5** and compound **7** can be obtained as single crystals, X-ray diffraction experiments were carried out.[7] The structures are shown in Figure 1. In the case of **5**, the iron–disilacycle five-membered ring is puckered in such a way that two silicon atoms are located within 2.80–3.20 Å to carbon 1 of the cyclohexadiene ring. This steric relationship, in turn, facilitates bond formation between either of the Si atoms and the cyclohexadiene ring. On the other hand, the structure of **7** shows that the tungsten–disilacycle ring is flat and oriented nearly perpendicular to the cyclohexadiene ring so that only one silicon atom is in the vicinity (~3.0 Å) of carbon 1, whereas the other silicon atom (near the *tert*-butyl group) is located very far away (>5 Å) from any of the four diene carbons of the cyclohexadiene ring. The structural difference between intermediates **5** and **7** seems to offer an explanation for the fact that **5** led to both isomers whereas **7** lead to only one. The fact that **7** led to only **3a** on thermal decomposition is entirely in agreement with the reaction mechanism proposed above.

Acknowledgment. We thank the Chinese National Science Council for financial support to this work. C.H.L. thanks the Nuclear Energy Research Institute for a research fellowship. Mass and NMR data for **2**, **3a**,**b**, **4**, **5**, and **6** (8 pages). Ordering information is given on any current masthead page.

Supplementary Material Available: Mass and NMR data for **2**, **3a**,**b**, **4**, **5**, and **6** (8 pages). Ordering information is given on any current masthead page.

Aldehydes, Alcohols, and Enol Acetates via Reductive Homologation of Esters

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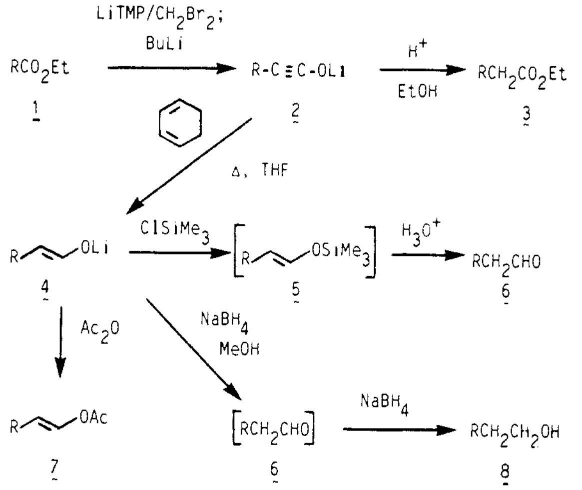
Recently we published a new method for the homologation of esters via alkynolate anion intermediates (i.e., **1** → **2** → **3**).[1] Herein we report that these electron-rich alkynolate anions, on refluxing with 1,3- and 1,4-cyclohexadienes in THF under strongly basic conditions, undergo an unprecedented reduction to afford aldehyde enolate anions **4**. These enolates (**4**) have been trapped as the corresponding enol acetates **7** after quenching with acetic anhydride (see Table I). Only trans-enol acetates were obtained, except for the alkynyl case in which **22** was formed as a nearly 1:1 ratio of cis and trans isomers. The reaction was successful for esters **1** having attached R groups which were primary, secondary, aryl, and alkynyl; it failed in the tertiary (R = CMe_2CH_2Ph) and conjugated alkene (R = CH=CHPh) cases, however, which afforded no alkynolate reduction and a complex mixture of products, respectively.



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† Smith Kline & French Postdoctoral Research Scientist.

(1) Kowalski, C. J.; Haque, M. S.; Fields, K. W. *J. Am. Chem. Soc.* **1985**, *107*, 1429.

(2) Yields (based on starting esters) reported in Table I are for isolated, purified product, except for the GC yield provided for aldehyde **19**. Starting esters were purchased from commercial sources except for **28b**, which was prepared in 74% yield from **28a** using the original homologation procedure.[1]

(3) Spectroscopic data (IR, NMR, and MS) and combustion analyses for new compounds are provided in the supplementary material.

(4) Occolowitz, J. L. *Aust. J. Chem.* **1967**, *20*, 2387.

(5) Hands, A. R.; Mercer, A. J. H. *J. Chem. Soc. C* **1968**, 2448.

(6) Twice the amounts of lithium tetramethylpiperidine, *n*-butyllithium, and CH_2Br_2 called for in the general procedure[14] were used in forming the alkynolate anion.

(7) Taguchi, T.; Takigawa, T.; Towara, Y.; Morikawa, T.; Kobayashi, Y. *Tetrahedron Lett.* **1984**, 5689.

(8) MacInnes, I.; Nonhebel, D. C.; Orszulik, S. T.; Suckling, C. J. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2777.

(9) Kikukawa, K.; Naritomi, M.; He, G.; Wada, F.; Matsuda, T. *J. Org. Chem.* **1985**, *50*, 299.

(10) Merrill, R. E.; Allen, J. L. *Tetrahedron Lett.* **1977**, 1019.

(11) Fetizon, M.; Lazare, C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 842.

(12) Svirskaya, P. I.; Leznoff, C. C. *J. Chem. Eng. Data* **1979**, *24*, 152.