derivative as well as other dialdehydes is currently under investigation.[8]

Treatment of **1a** with 1-bromo-2-chloroethane under the usual cycloalkylation conditions resulted in an 85% yield of **8** which was reduced and subsequently cleaved to cyclopropanecarboxaldehyde in 65% over-all yield.

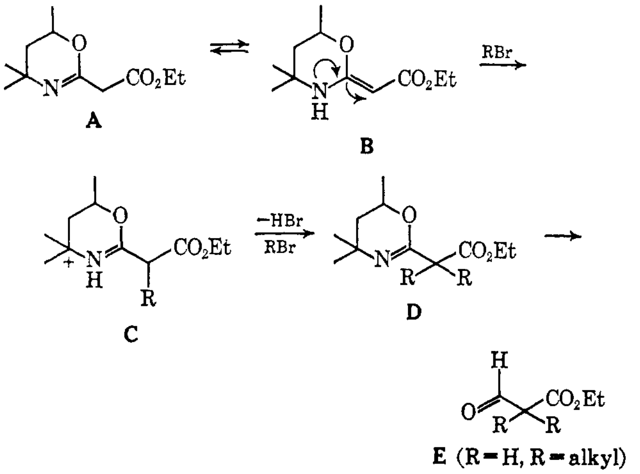
As a further extension of the successive alkylation of dihydro-1,3-oxazines, the anions **2** were alkylated using methyl iodide followed by a second equivalent of base and then a second equivalent of halide. In this manner the dimethyloxazines **11** and **12** were obtained in 76 and 85% yields, respectively.[9] Hydride (or deuteride) reduction of both products proceeded in 90–95% yields and cleavage in oxalic acid solution afforded the dimethyl derivatives **13** (53% over-all, semicarbazone mp 177–178°; (lit.[10] mp 178–179°) and **14** (66% over-all, 2,4-DNP mp 99–100°).[11]

Additional studies are in progress to assess fully the potential of this synthetic method for obtaining a wide variety of aldehydes including those possessing additional functional groups.

**Acknowledgments.** The authors wish to acknowledge partial financial assistance from the National Institutes of Health (RG-06248-09).

(8) The reaction of **2** and dibromoethane was found to also give a high yield of **9** after the omission of the second equivalent of butyllithium. The formation of **10** in this manner now provides us with a highly useful intermediate, generated *in situ*, which should react with other organometallic reagents (RLi, RMgX) affording a route to otherwise inaccessible dihydro-1,3-oxazines and, ultimately, aldehydes. This behavior will be the subject of a future paper.

(9) Current studies in this laboratory have revealed that the oxazine ester **1c** which exists as a tautomeric mixture (A ⇆ B) can efficiently be alkylated with alkyl bromides in refluxing acetonitrile to the monoalkyl oxazine C. The latter can, after neutralization, undergo further alkylation to the dialkyloxazine D. Hence, the oxazine ester behaves as an enamine which exhibits the expected C-alkylation. This technique should likewise be useful in preparing mono- and dialkyl ester aldehydes E.



(10) N. H. Cromwell and H. H. Eby, *J. Am. Chem. Soc.*, **74**, 4201 (1952).

(11) The structures of all intermediates and final products were consistent (as were all the other examples in Table I) with their infrared, nmr, and mass spectra. All new compounds gave satisfactory analyses.

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## Allenic–Propargylic and Allylic Rearrangements Accompanying Sulfur Dioxide Insertion into Carbon–Tin Bonds

*Sir:*

The chemistry of allenic[1] and allylic derivatives[2] of group IVb elements and the details of sulfur dioxide insertion into carbon–metal bonds[3–6] are subjects of current interest, and in this communication we wish to describe results pertinent to both areas.

The allenic tin compound I (from "propargyl Grignard reagent"[7] and $(CH_3)_3SnCl$) reacts very rapidly with gaseous $SO_2$ to yield a colorless air-stable product, mp 83–84°, analyzing well[8] for a monoinsertion product, formulated as II on the basis of spectral data (given in Table I).

$$\underset{\text{I}}{(CH_3)_3SnCH{=}C{=}CH_2} \xrightarrow{SO_2} \underset{\text{II}}{(CH_3)_3SnSO_2CH_2C{\equiv}CH}$$

Thus insertion is accompanied by rearrangement of the allenic to the propargyl moiety. The dimethyltin compound III undergoes diinsertion to yield IV.

$$\underset{\text{III}}{(CH_3)_2Sn(CH{=}C{=}CH_2)_2} \xrightarrow{SO_2} \underset{\text{IV}}{(CH_3)_2Sn(SO_2{-}CH_2{-}C{\equiv}CH)_2}$$

The propargyltin compound V (from triphenyltin iodide and "propargyl Grignard reagent") rapidly inserts $SO_2$ to yield the rearranged allene VI.

$$\underset{\text{V}}{(C_6H_5)_3SnCH_2C{\equiv}CH} \xrightarrow{SO_2} \underset{\text{VI}}{(C_6H_5)_3SnSO_2CH{=}C{=}CH_2}$$

In a predominantly $CDCl_3$–$CD_3COOD$ solvent V slowly isomerizes[9] to yield the allene isomer VII which reacts with $SO_2$ to produce the rearranged acetylene VIII.

$$\underset{\text{VII}}{(C_6H_5)_3SnCH{=}C{=}CH_2} \xrightarrow{SO_2} \underset{\text{VIII}}{(C_6H_5)_3SnSO_2CH_2C{\equiv}CH}$$

---

(1) H. G. Kuivila and J. C. Cochran, *J. Amer. Chem. Soc.*, **89**, 7152 (1967).

(2) H. G. Kuivila and J. A. Verdone, *Tetrahedron Letters*, 119 (1964).

(3) J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, **88**, 4862 (1966), and subsequent papers.

(4) N. A. D. Carey and H. C. Clark, *Can. J. Chem.*, **46**, 643 (1968).

(5) G. B. Deacon and P. W. Felder, *J. Amer. Chem. Soc.*, **90**, 493 (1968). $\nu_{S-O}$ in metal S-sulfinates ordinarily arise (when M–S $\pi$ bonding is unimportant) in the regions 1200–1100 and 1000–1050 cm$^{-1}$, while in $Cu(H_2O)_4(p\text{-}OS(O)C_6H_4CH_3)_2$, known[5] to contain CuOS(O) bonds, $\nu_{S-O}$ arises at 979 and 954 cm$^{-1}$ (D. A. Langs and C. R. Hare, *Chem. Commun.*, 853 (1967)). Chemical and ir evidence favors the O-sulfinate structure for $(C_6H_5)_3SnOSOC_6H_5$ (F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, **7**, 1508 (1968)) prepared from triphenyltin hydride and benzenesulfinic acid (M. Pang and E. I. Becker, *J. Org. Chem.*, **29**, 1948 (1964)). It is not yet clear that $SO_2$ insertion into tetraphenyltin yields the same product as that prepared by Pang and Becker above.

(6) W. Kitching and B. F. Hegarty, Abstracts of Papers, Symposium on Organometallic Chemistry, Melbourne, May 1968.

(7) The actual structure of this Grignard reagent is not certain, although one report (B. J. Benaim, *Compt. Rend.*, 262, 937 (1966)) suggests that the propargyl structure is retained. Formation of allenic products then can be rationalized on the basis of rearrangement mechanisms, which would be more facile for more electrophilic reactions; *e.g.*, compare contrasting behavior of $(CH_3)_3SnCl$ and $(C_6H_5)_3SnI$ reported here. The actual nature of "propargyl Grignard reagent" will be discussed elsewhere.

(8) All products reported here had satisfactory elemental analyses and nmr and ir spectral data. Nmr spectra integrated satisfactorily.

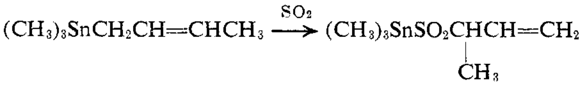
(9) Substitution of triphenyltin for a trimethyltin group appears to slow down considerably (factor of $10^2$) electrophilic cleavage reactions of allylic and allenic tin compounds.[1,2]

Table I. Nmr Data for Organotin Compounds and Insertion Products[a]

| Starting compound | Chemical shift, $\tau$ | Insertion product | Chemical shift, $\tau$ |
|---|---|---|---|
| $(CH_3)_3SnCH{=}C{=}CH_2$ | 9.80 (9) (s); 5.80 (2) (d); 4.49 (1) (t) | $(CH_3)_3SnSO_2CH_2C{\equiv}CH$ | 9.38 (9) (s); 7.69 (1) (t); 6.88 (2) (d) |
| $(C_6H_5)_3SnCH_2C{\equiv}CH$ | 2.55 (15) (m); 7.88 (2) (d); 8.17 (1) (t) | $(C_6H_5)_3SnSO_2CH{=}C{=}CH_2$ | 2.34 (15) (m); 5.18 (2) (d); 4.43 (1) (t) |
| $(C_6H_5)_3SnCH{=}C{=}CH_2$ | 2.18 (15); 5.72 (2) (d); 4.64 (1) (t) | $(C_6H_5)_3SnSO_2CH_2C{\equiv}CH$ | Insoluble but $\nu_{C\equiv CH}$ at 3280 cm$^{-1}$ |
| $(CH_3)_2Sn(CH{=}C{=}CH_2)_2$ | 9.68 (6) (s); 5.78 (4) (d); 4.93 (2) (t) | $(CH_3)_2Sn(SO_2CH_2C{\equiv}CH)_2$ | 9.09 (6) (s); 6.92 (4) (d); 7.74 (2) (t) |
| $(CH_3)_3SnCH_2CH{=}CH_2$ | 9.89 (9) (s); 8.23 (2) (d); 4.5 (3) (m) | $(CH_3)_3Sn(SO_2)CH_2CH{=}CH_2$ | 9.43 (9) (s); 6.92 (2) (d); 4.45 (3) (m) |
| $(CH_3)_3SnCH_2C(CH_3){=}CH_2$ | 9.99 (9) (s); 8.21 (2) (s); 8.32 (3) (d); 5.54 (2) (br s) | $(CH_3)_3Sn(SO_2)CH_2C(CH_3){=}CH_2$ | 9.44 (9) (s); 8.05 (3) (br s); 6.82 (2) (s); 5.08 (2) (m) |
| $(CH_3)_3SnCH_2CH{=}CHCH_3$ | 9.96 (9) (s); 8.31 (5) (m); 4.58 (2) (m) | $(CH_3)_3SnSO_2CH(CH_3)CH{=}CH_2$ | 9.44 (9) (s); 8.82 (3) (d); 7.21 (1) (q); 4.50 (3) (m) |
| $(CH_3)_3SnC_6H_4$-$p$-$CH_3$ | 9.75 (9) (s); 7.73 (3) (s); 2.76 (4) (m) | $(CH_3)_3SnSO_2C_6H_4$-$p$-$CH_3$ | 9.45 (9) (s); 7.60 (3) (s); 1.98 (4) (m) |
| $(CH_3)_3SnCH_2C_6H_4$-$p$-$CH_3$ | 9.99 (9) (s); 7.76 (3) (s); 7.76 (2) (s); 3.07 (4) (m) | $(CH_3)_3SnSO_2CH_2C_6H_4$-$p$-$CH_3$ | 9.63 (9) (s); 7.65 (3) (s); 6.47 (2) (s); 2.85 (4) (m) |
| $(CH_3)_3SnCH_2C_6H_4$-$p$-F | 10.0 (9) (s); 7.77 (2) (s); 3.15 (4) (m) | $(CH_3)_3SnSO_2CH_2C_6H_4$-$p$-F | 9.64 (9) (s); 6.49 (2) (s); 2.90 (4) (m) |
| $(CH_3)_3SnCH_2C_6H_5$ | 10.0 (9) (s); 7.70 (2) (s); 2.92 (5) (m) | $(CH_3)_3SnSO_2CH_2C_6H_5$ | 9.64 (9) (s); 6.48 (2) (s); 2.87 (5) (m) |
| $(CH_3)_4Sn$ | 9.94 | $(CH_3)_3SnSO_2CH_3$ | 9.42 (9) (s); 7.70 (3) (s) |

[a] s = singlet, d = doublet, q = quintet, m = multiplet, br = broad. $CDCl_3$ with internal TMS. In the allenic structures $J_{^1H-^1H} \sim$ 7–8 Hz, while in the acetylenes $J_{^1H-^1H} \sim$ 3 Hz. In the ir $\nu_{C=C=C}$ arose in the region of 1930–1950 cm$^{-1}$ and $\nu_{C\equiv CH}$ in the region of 3270 cm$^{-1}$. $^{119}Sn$ and $^{117}Sn-^1H$ coupling generally could be observed and in $(CH_3)_3SnR$ $J_{^{119}Sn-CH_3} \sim$ 54 Hz, which increased to 70 Hz in $(CH_3)_3SnSO_2R$. Coupling to R protons could be observed also in $(CH_3)_3SnR$, but not in $(CH_3)_3SnSO_2R$, confirming the position of insertion.

Crotyltrimethyltin[2,10] (IX) (mixture of *cis* and *trans* isomers) reacts rapidly with $SO_2$[11] and the pmr spectrum of the product (Table I) confirms that allylic rearrangement has occurred since the spectrum is that expected for the $\alpha$-methallyl structure X.[12]



$$(CH_3)_3SnCH_2CH{=}CHCH_3 \xrightarrow{SO_2} (CH_3)_3SnSO_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH{=}CH_2$$

IX X

Allyl-, $\beta$-methallyl-, benzyl-, $p$-fluorobenzyl-, $p$-methylbenzyl-, and $p$-tolyltrimethyltins and tetramethyltin react readily to yield monoinsertion products (Table I). In all cases cited it was possible to observe directly (by nmr) the reaction mixtures after partial reaction, and there was no indication that isomerization before or after insertion was a complication. We conclude that rearrangement is a consequence of the reaction mechanism for insertion.

Infrared spectra in the S–O stretching regions (both as Nujol mulls and $CHCl_3$ solutions) showed characteristically strong bands in the 950–990-cm$^{-1}$ region; these may be assigned to $\nu_{S-O}$ and to $\nu_{S=O}$ lowered by 50–100 cm$^{-1}$ by intermolecular coordination. These S–O stretching frequencies strongly suggest O-sulfinate structures,[5] and there was no evidence for linkage isomerism.

In all of the insertion products containing the $(CH_3)_3Sn$ group, $J_{^{119}Sn-CH_3}$ = 70 Hz and corresponds to a planar $(CH_3)_3Sn$ moiety.[13] $\nu_{Sn-C}$(asym)[14] uniformly arose in the region of 545–550 cm$^{-1}$, but the region of $\nu_{Sn-C}$(sym), which is ir inactive for a planar $C_3Sn$ system, is overlaid by what is probably $\nu_{Sn-O}$. Molecular weight data showed the products to be associated, with $i \sim$ 3–4, and we consider the most likely structures to be either linear or cyclic (trimeric) structures with bridging $SO_2$ groups and planar $(CH_3)_3Sn$ groups (*e.g.*, *cf.* trimethyltin acetate).[15] Such structures account for methylene proton equivalence in the appropriate cases.[3,16] A sulfone structure appears less likely to

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(10) Professor D. Seyferth kindly provided some preparative and spectral details for this compound.

(11) It is clear that $SO_2$ does discriminate between the *cis* and *trans* isomers (relative intensities change after partial reaction), but as yet we do not know which reacts faster. We were concerned at this stage in demonstrating the allylic rearrangement, but actual rates will be reported later.

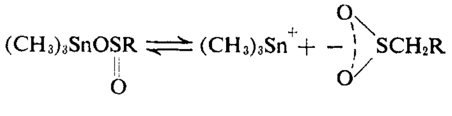
(12) Allylic rearrangement also accompanies protic cleavage of crotyltrimethyltin, since only 1-butene is produced.[2]

(13) J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, **83**, 3903 (1961).

(14) V. G. Kumar Das and W. Kitching, *J. Organometal Chem.*, **13**, 523 (1968).

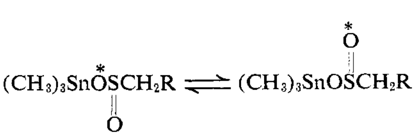
(15) P. B. Simons and W. A. G. Graham, *ibid.*, **8**, 479 (1967).

(16) Another phenomenon, which could lead to proton equivalence, involved dissociation to yield the symmetrical anion



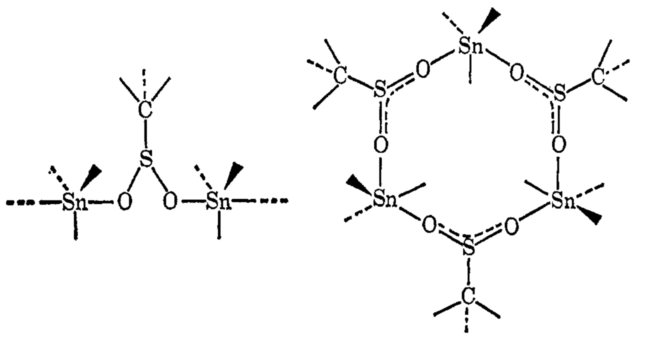
$$(CH_3)_3SnO\underset{\displaystyle O}{\underset{\|}{S}}R \rightleftharpoons (CH_3)_3Sn^+ + {}^-\left[\begin{array}{c}O\\ \vdots\\ O\end{array}\right]SCH_2R$$

This may be unlikely since the solution and solid ir spectra were identical, and also strongly coordinating solvents (*e.g.*, $H_2O$, DMSO) normally are required to stabilize alkyltin cations.[13,14] However this explanation may suffice to explain the equivalence in $C_6H_5CH_2HgOSOCH_2C_6H_5$. Rearrangement in the sense below also needs consideration as a mechanism for proton equilibration. Care must be exercised in employing



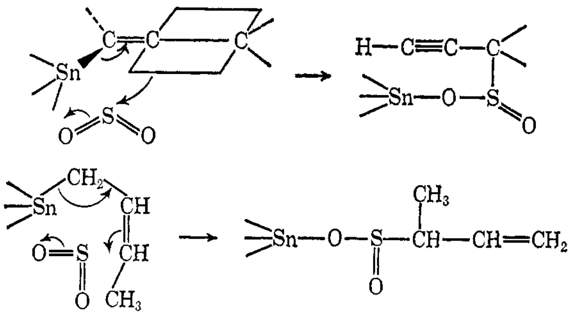
$$(CH_3)_3Sn\overset{*}{O}\underset{\displaystyle O}{\underset{\|}{S}}CH_2R \rightleftharpoons (CH_3)_3SnO\overset{\overset{*}{O}}{\overset{\|}{S}}CH_2R$$

the "methylene proton inequivalence" argument for distinguishing O- and S-sulfinates.



engage in intermolecular coordination.[17]

As regards mechanism, the following appear to account well for the high rate of reaction,[18] the complete rearrangements, and O-sulfinate structures. They may be considered variants of the $S_E'$ processes now commonly encountered in electrophilic cleavages of allylic and related organometallics.[18]



We regard $SO_2$ insertion into carbon–tin, -lead,[19] and -mercury[6,20] bonds as examples of electrophilic cleavage, and details of these processes are being studied[21] by rate and stereochemical measurements.

**Acknowledgments.** The authors are grateful to Professors D. Seyferth and H. Kuivila for details concerning the preparation and spectra of some allylic tin compounds. Dr. G. Deacon of Monash University, Melbourne, kindly contributed information on the ir spectra of sulfinates.

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(17) The intermolecular coordination depicted may be considered a sulfoxide type of coordination to tin, and this may lower $\nu_{S-O}$ by 50–100 $cm^{-1}$. Sulfoxide complexes of organotin species are well known.[14]

(18) W. Kitching, *Rev. Pure Appl. Chem.*, in press.

(19) C. W. Fong, unpublished results.

(20) Allylmercuric acetate (which has the σ-allyl structure) also rapidly reacts with $SO_2$ to yield an insertion product considered[6] to have the structure $CH_2{=}CHCH_2SOOHgOAc$. This product, which is unstable in other than $SO_2$ solution, may be formed by an $S_Ei$ process. Crotylmercuric acetate reacts very rapidly also, but yields an unstable, difficult to characterize product.

(21) Professor Kuivila kindly informed us that he had observed a reaction between crotyltrimethyltin and $SO_2$, but the product or the reaction was not characterized.

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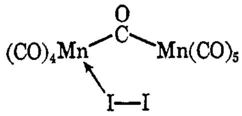
## Cleavage of Tetracarbonyldi-π-cyclopentadienyldiiron and Its Monosubstituted Derivatives with Halogens

*Sir:*

A standard method of synthesis of neutral halogenometal carbonyl derivatives involves the fission of the metal–metal bond in dinuclear metal carbonyls or π-cyclopentadienylmetal carbonyls by halogens.[1] Thus treatment of $Mn_2(CO)_{10}$, $\{\pi\text{-}C_5H_5Mo(CO)_3\}_2$, and $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ with iodine affords $Mn(CO)_5I$, $\pi\text{-}C_5H_5Mo(CO)_3I$, and $\pi\text{-}C_5H_5Fe(CO)_2I$, respectively.[2] The iodination of $Mn_2(CO)_{10}$ in solution has been studied kinetically, and a mechanism based upon the fission of $Mn_2(CO)_{10}$ to $Mn(CO)_5$ radical pairs has been postulated.[3] These radical pairs react further with the iodine to yield $Mn(CO)_5I$. Although the above mechanism was favored, an alternative involving the bridged intermediate



was also suggested.[3]

Infrared spectroscopic studies have shown the presence of two isomers of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ in solution. One isomer contains both terminal and bridging carbonyl groups, while the other contains terminal carbonyls only.[4] The existence of the latter isomer, albeit a small percentage, suggests the possibility of iodination of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ occurring by a mechanism similar to that for $Mn_2(CO)_{10}$.

We have studied the halogenation of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ and have found that under certain experimental conditions products other than $\pi\text{-}C_5H_5Fe(CO)_2X$ (X = Cl, Br, or I) are formed. Treatment of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ with bromine or iodine in $CH_2Cl_2$ afforded the expected neutral compound $\pi\text{-}C_5H_5Fe(CO)_2X$ (X = Br or I) only. However, the analogous reaction involving chlorine gave a second product in low yield which was shown by infrared spectroscopy to be $[\pi\text{-}C_5H_5Fe(CO)_3]Cl$.

By utilizing nonpolar solvents in the above halogenation reactions, it is expected that the yield of the ionic derivative relative to the neutral compound would be increased. The reaction of $\{\pi\text{-}C_5H_5Fe(CO)_2\}_2$ with iodine in benzene has indeed been found to yield, as well as $\pi\text{-}C_5H_5Fe(CO)_2I$, an ionic compound which separates from solution as the triiodide. However, this has been characterized as $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2I]I_3$ containing a bridging iodine group (*cf.* $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2I]BF_4$ previously synthesized from $\pi\text{-}C_5H_5Fe(CO)_2I$[5]).

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(1) R. B. King, "Organometallic Syntheses," Vol. 1, "Transition Metal Compounds," Academic Press, New York, N. Y., 1965.

(2) E. O. Brimm, M. A. Lynch, and W. J. Sesny, *J. Amer. Chem. Soc.*, **76**, 3831 (1954); E. W. Abel, A. Singh, and G. Wilkinson, *J. Chem. Soc.*, 1321 (1960); T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

(3) L. I. B. Haines and A. J. Poe, *Nature*, **215**, 699 (1967); L. I. B. Haines, D. Hopgood, and A. J. Poe, *J. Chem. Soc., A*, 421 (1968).

(4) F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967); R. D. Fischer, A. Vogler, and K. Noack, *J. Organometal. Chem.*, **7**, 135 (1967).

(5) E. O. Fischer and E. Moser, *Z. Anorg. Allgem. Chem.*, **342**, 156 (1966).