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The Preparation of Organolithium Compounds by the Transmetalation Reaction. VII. *cis*- and *trans*-Propenyllithium: The Stereochemistry of the Transmetalation Reaction. Isopropenyllithium[1]

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It has been established, using n.m.r. spectroscopy, that the formation of *cis*- and *trans*-propenyllithium by the transmetalation reaction occurs with retention of the geometric configuration of the propenyl group in the organotin precursor used. The reactions of these lithium reagents with trimethylchlorosilane, carbon dioxide, and benzaldehyde also are stereospecific. Further examples are described which show that the transmetalation reaction involves an equilibrium situation. The preparation and n.m.r. spectrum of isopropenyllithium are described.

Previous papers in this series have dealt mainly with the use of the transmetalation reaction occurring between organotin compounds and organolithium reagents as a source of new organolithium species.

$$\geqslant\text{Sn–R} + \text{R'Li} \longrightarrow \geqslant\text{Sn–R'} + \text{RLi}$$

Among the organolithium reagents thus prepared were vinyllithium,[3] allyllithium and methallyllithium,[4] perfluorovinyllithium,[5] and cyclopropyllithium.[1a] Some factors which influence the transmetalation reaction were discussed in another paper.[6]

Of further interest to us in these studies was the question of the stereochemistry of the transmetalation reaction. In particular, since the transmetalation reaction is of particular value in the synthesis of vinylic lithium reagents, the question of retention of geometric configuration *vs.* isomerization of substituted vinylic groups attached to tin during the course of their transfer to lithium was of some importance to us. Accordingly, *cis*- and *trans*-propenyltrimethyltin, as well as tetra-*cis*-propenyltin and tetra-*trans*-propenyltin, were prepared, and their configurational stability in the absence of a source of ultraviolet radiation was noted.[1b] The reactions of these tin compounds with organolithium reagents in diethyl ether and in pentane then were studied.

The formation of *cis*- and *trans*-propenyllithium by the direct reaction and the stability of the geometric configuration of these reagents had been studied previously by Braude and Coles,[7] by Curtin and Crump,[8] and by Nesmeyanov, Borisov, and Novikova.[9] In all of these investigations the configurational stability of the propenyllithium compounds was studied using chemical techniques. From the observed reaction sequences

$$\textit{cis}\text{-CH}_3\text{CH}{=}\text{CHX} \xrightarrow[(1)]{\text{Li}} \text{Li reagent} \xrightarrow[(2)]{} \textit{cis}\text{-CH}_3\text{CH}{=}\text{CH— derivative}$$

$$\textit{trans}\text{-CH}_3\text{CH}{=}\text{CHX} \xrightarrow[(1)]{\text{Li}} \text{Li reagent} \xrightarrow[(2)]{} \textit{trans}\text{-CH}_3\text{CH}{=}\text{CH— derivative}$$

it was inferred that reaction 1, the formation of the lithium reagents, proceeded with no change in geometric configuration of the propenyl group and that the lithium reagents were configurationally stable in solution. This required the reasonable, but unproved assumption that no change occurs in the propenyl group configuration in the reaction of the propenyllithium reagents with the organic substrates used in the characterization reactions. Nesmeyanov and Borisov[9] applied their "Method of Odd and Even Cycles" to this problem, but, as has been mentioned by others,[8,10] this approach does not give the unambiguous answers claimed for it.

The most convincing experimental evidence concerning the stereochemistry of formation of the *cis*- and *trans*-propenyllithium reagents and their configurational stability in solution would be given not by a study of their reactions, but rather by physical measurements capable of distinguishing between *cis*- and *trans*-propenyllithium as present in solution with this aim in mind, Allinger and Hermann[10] examined the infrared spectra of the lithium compounds prepared in diethyl ether solution from *cis*- and *trans*-1-chloropropene, respectively. In assigning structures to the *cis*- and *trans*-propenyllithium isomers, these authors assumed bands at 1035 and 1045 cm.$^{-1}$, respectively, to be due to the C–Li stretching vibrations. A further band at 1030 cm.$^{-1}$, present only in the infrared spectrum of the presumed *trans* isomer, was believed to be indicative of the *trans* configuration. The results of this study thus seemed to confirm the conclusions of the previous investigators. This infrared spectral study, however, does not appear to be definitive. Other workers[11] have shown that absorption in the infrared spectra of organolithium compounds in the region around 1050 cm.$^{-1}$ is not due to the C–Li bond, and that the only bands which involve the motion of the lithium atom occur between 350 and 570 cm.$^{-1}$. In the case of ethyllithium, absorption near 1050 cm.$^{-1}$ appears to be due to oxidation products of the lithium reagent.[12]

An unambiguous answer to this question was mandatory for the purposes of the present study. We have used nuclear magnetic resonance spectroscopy to investigate this long-standing question and have obtained results which confirm the assumptions of the previous workers.

cis-Propenyllithium was prepared by the reaction of *cis*-1-bromopropene with metallic lithium in ether. Its n.m.r. spectrum is described in the Experimental part[13]; of importance to the present discussion is the observed value of the coupling constant between the olefinic protons, 17.4 c.p.s. *trans*-Propenyllithium was prepared

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[1] (a) Part VI: D. Seyferth and H. M. Cohen, *Inorg. Chem.*, **2**, 625 (1963); (b) also part XIX of the series, "Vinyl Derivatives of Metals"; for part XVIII see D. Seyferth and L. G. Vaughan, *J. Organometal. Chem.*, **1**, 138 (1963); (c) presented in part at the International Colloquium on Organometallic Compounds sponsored by the Centre National de la Recherche Scientifique, Paris, September 24–28, 1962.

[2] (a) Alfred P. Sloan Research Fellow; (b) National Science Foundation Cooperative Graduate Fellow, 1961–1963; National Science Foundation Summer Graduate Fellow, 1963.

[3] D. Seyferth and M. A. Weiner, *J. Am. Chem. Soc.*, **83**, 3583 (1961).

[4] D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **26**, 4797 (1961).

[5] D. Seyferth, D. E. Welch, and G. Raab, *J. Am. Chem. Soc.*, **84**, 4266 (1962).

[6] D. Seyferth and M. A. Weiner, *ibid.*, **84**, 361 (1962).

[7] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078, 2085 (1951).

[8] D. Y. Curtin and J. W. Crump, *J. Am. Chem. Soc.*, **80**, 1922 (1958).

[9] (a) A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957); (b) A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1216 (1959).

[10] N. L. Allinger and R. B. Hermann, *J. Org. Chem.*, **26**, 1040 (1961).

[11] R. West and W. Glaze, *J. Am. Chem. Soc.*, **83**, 3580 (1961).

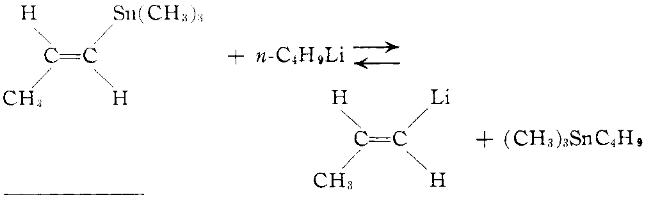
[12] T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *ibid.*, **84**, 1371 (1962).

[13] The n.m.r. spectrum is recorded in a preliminary communication concerning this work: D. Seyferth and L. G. Vaughan, *J. Organometal. Chem.*, **1**, 201 (1963).

in a similar manner from *trans*-1-chloropropene. Its n.m.r. spectrum also is described in the Experimental section.[13] J_{H-H} was observed to be 22.2 c.p.s. The basis for these assignments of configuration is provided by the numerous studies[14-20] which have shown that coupling between *trans* protons in olefinic systems is greater than *cis* coupling. Thus the coupling constants observed, 17.4 and 22.2 c.p.s., could with some confidence be assigned to the *cis*- and *trans*-propenyllithium structures, respectively. These values are both sufficiently far outside the range of *cis* and *trans* coupling constants reported for wholly organic olefins of known configuration so as to raise a question concerning the correctness of using in the present case the geometric configuration–coupling constant correlation cited above. In the case of simple vinyl compounds the correlation of vinylic proton coupling constants with electronegativity of the atom or group to which the vinyl group is attached has been demonstrated.[16,17,21] Of interest and significance to the present discussion is that both *cis* and *trans* coupling constants increase with decreasing electronegativity of the atom or group attached to the vinyl group. Thus J_{cis} increases from 4.65 c.p.s. in vinyl fluoride to 19.3 c.p.s. in vinyllithium; for the same compounds J_{trans} increases from 12.75 to 23.9 c.p.s. (Table I in ref. 17 gives J_{cis} and J_{trans} values found in vinyl compounds ($CH_2{=}CHZ$) for a whole range of electronegativities, χ_Z). Thus values as high as J_{cis} = 17.4 c.p.s. and J_{trans} = 22.2 c.p.s. for the propenyllithiums are not surprising; in fact, they are expected to be that high. It may be noted that the similarities of J_{cis} and J_{trans} of propenylsilicon and -tin compounds with the analogous vinylsilicon and -tin compounds have been pointed out by us.[1b] The evidence thus suggests that the geometric configuration–coupling constant correlation should be applicable to the propenyllithium case.

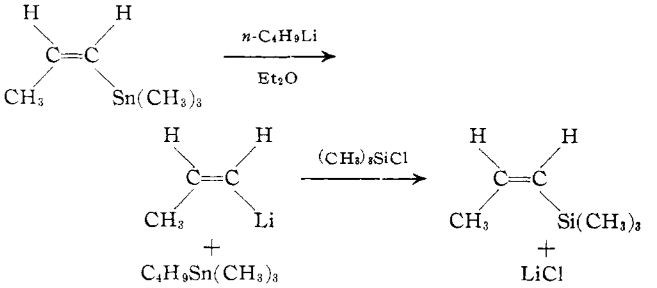
The availability of a physical technique capable of distinguishing between *cis*- and *trans*-propenyllithium then permitted the study of the transmetalation reactions leading to the propenyllithium reagents.

cis-Propenyllithium was prepared by reaction of *cis*-propenyltrimethyltin with two molar equivalents of methyllithium in ether. The n.m.r. spectrum of the reagent prepared in this manner was identical with that of *cis*-propenyllithium prepared *via* the direction reaction. When only one molar equivalent of methyllithium per equivalent of *cis*-propenyltrimethyltin was used, the n.m.r. spectrum of the solution showed considerably diminished absorption due to the *cis*-propenyllithium reagent, and also moderately intense signals due to *cis*-propenyltrimethyltin were observed. The position of equilibrium in the reaction



lies considerably further to the right, since treatment of *trans*-propenyltrimethyltin with one equivalent of *n*-butyllithium in ether gave a solution whose n.m.r. spectrum showed the presence of *trans*-propenyllithium (chemical shifts and coupling constants identical with those observed for *trans*-propenyllithium as obtained by the direct reaction), but not of *trans*-propenyltrimethyltin. Similarly, an ether solution prepared from solid *trans*-propenyllithium (obtained from the reaction of tetra-*trans*-propenyltin with 2.3 equivalents of *n*-butyllithium in pentane, followed by partial evaporation of the pentane) gave an n.m.r. spectrum identical with that of authentic *trans*-propenyllithium. Thus, the preparation of *cis*- and *trans*-propenyllithium by the transmetalation reaction was shown to involve retention of the geometric configuration of the propenyl groups in the organotin precursor.

Preliminary characterization experiments were carried out on a microscale, starting with *cis*- and *trans*-propenyltrimethyltin. For the *cis* isomer the results are summarized by the equations

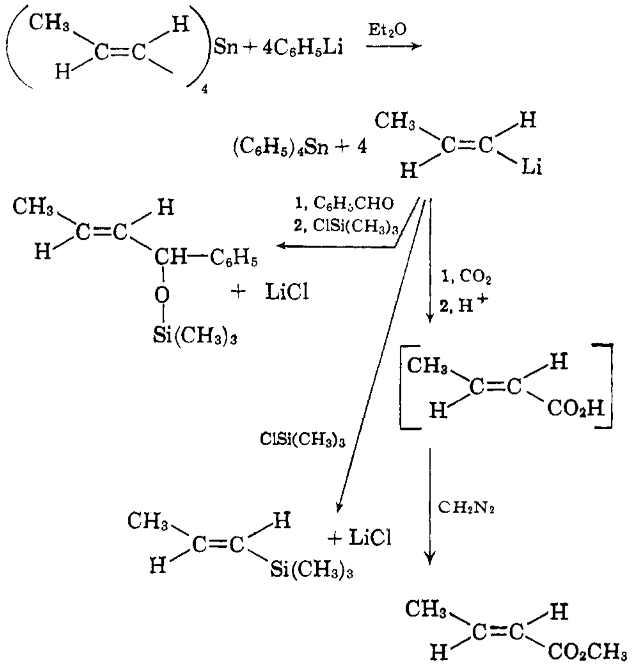


With the *trans* isomer similar over-all retention of geometric configuration was observed. A more detailed study was made using tetra-*cis*- and tetra-*trans*-propenyltin as propenyl group sources.

$(CH_3CH{=}CH)_4Sn + 4C_6H_5Li \longrightarrow$
cis and *trans*
$4CH_3CH{=}CHLi + (C_6H_5)_4Sn$
cis and *trans*

The characterization reactions carried out on the derived lithium reagents are outlined in Chart I for the *trans* isomer. Similar reactions were carried out with the *cis* isomer. In all cases, complete retention of con-

CHART I



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(14) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry," Pergamon Press, London, 1959, p. 57.

(15) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 54.

(16) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

(17) T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962).

(18) D. W. Moore and J. A. Happe, *J. Phys. Chem.*, **65**, 224 (1961).

(19) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

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(21) (a) C. N. Banwell, N. Sheppard, and J. J. Turner, *Spectrochim. Acta*, **16**, 794 (1960); (b) C. S. Johnson, Jr., M. A. Weiner, J. S. Waugh, and D. Seyferth, *J. Am. Chem. Soc.*, **83**, 1306 (1961).

figuration was found, in confirmation of the assumption made by the previous authors cited that reactions of *cis*- and *trans*-propenyllithium occurred without change of geometric configuration. In the case of the reactions of *trans*-propenyllithium, none of the derivatives prepared showed the presence of any *cis* contaminants. However, the products obtained from *cis*-propenyllithium as prepared from tetra-*cis*-propenyltin contained *ca.* 4–5% of *trans* contaminant. It seems probable that the *trans* isomer obtained in these reactions arises from a small amount of the *trans*-propenyl group in the starting tetrapropenyltin rather than from a nonstereospecific transmetalation mechanism. The infrared spectra of all samples of tetra-*cis*-propenyltin showed weak absorption at 985 cm.$^{-1}$, indicating at least several per cent of the *trans* isomer was present. The exact percentage could not be determined accurately by any instrumental method.

The product of the condensation of the propenyllithium reagents with benzaldehyde was converted to the trimethylsiloxy derivative rather than to the corresponding alcohol, because the latter was found to undergo complete dehydration when passed through a short Dow Corning 710 silicone oil column at 130° to give *trans*-1-phenylbutadiene.

Two major differences were noted in the transmetalation reactions involving tetra-*cis*-propenyltin compared with those of tetra-*trans*-propenyltin: (1) markedly lower yields (50–56%) of tetraphenyltin in the *cis* case (*vs.* 70–80% yields when the tetra-*trans*-propenyltin was used); (2) the presence of substantial amounts of products arising from unreacted phenyllithium in the *cis* case. These observations suggested that the position of equilibrium in the transmetalation reaction lay considerably further on the side of the reactants in the *cis* case than in the *trans* case. (Here also the results obtained with *cis*- and *trans*-propenyltrimethyltin are to be noted.) This question was examined further by studying the reverse reaction, namely, the reaction in ether of four equivalents of the respective propenyllithium reagent with one equivalent of tetraphenyltin. The organolithium species present at equilibrium were characterized by reaction with trimethylchlorosilane. The results obtained are given in Table I. As can be seen, agreement between the results of the forward and reverse reactions is good. The yield values obtained are, however, not considered to be accurate enough for calculation of equilibrium constants for these reactions, and a more detailed study concerning these and related systems is in progress, which hopefully will give accurate values of equilibrium constants for Li–Sn transmetalation reactions.

TABLE I

TRANSMETALATION EQUILIBRIA, TETRAPROPENYLTIN ISOMERS

Reaction: $(cis\text{-}CH_3CH{=}CH)_4Sn + 4C_6H_5Li \rightleftarrows (C_6H_5)_4Sn +$
$4\ cis\text{-}CH_3CH{=}CHLi$

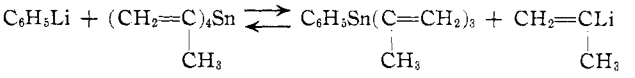
Reaction	% $(C_6H_5)_4Sn$	% *cis*- $CH_3CH{=}CHLi$[a]	% C_6H_5Li[a]
Forward	50–56	49	29
Reverse	51	46	25

Reaction: $(trans\text{-}CH_3CH{=}CH)_4Sn + 4C_6H_5Li \rightleftarrows (C_6H_5)_4Sn +$
$4\ trans\text{-}CH_3CH{=}CHLi$

	% $(C_6H_5)_4Sn$	% *trans*- $CH_3CH{=}CHLi$[a]	% C_6H_5Li[a]
Forward	70–81	61	Not detd.
Reverse	79	69	20

[a] Yield of trimethylsilyl derivative.

A more striking example of the existence of this type of equilibrium was obtained with tetraisopropenyltin. When four equivalents of phenyllithium was added to an ether solution of this compound, no tetraphenyltin precipitated and only a low equilibrium yield of isopropenyllithium was present. Again, the reverse reaction, that of four molar equivalents of isopropenyllithium with one equivalent of tetraphenyltin, was studied. In both cases the organolithium species present were characterized by adding trimethylchlorosilane. In the forward reaction this procedure gave the products: isopropenyltrimethylsilane (14%), trimethylphenylsilane (67%), phenyltriisopropenyltin (identified, but not isolated in sufficient purity), tetraisopropenyltin (19% recovery). During the reverse reaction the initially insoluble tetraphenyltin dissolved completely on addition of the isopropenyllithium solution, and subsequent addition of trimethylchlorosilane led to the following products on work-up: isopropenyltrimethylsilane (16%), trimethylphenylsilane (70%), phenyltriisopropenyltin (29%), tetraisopropenyltin (20% recovery). These results are in good agreement with those obtained in the forward reaction, and the equilibrium situation thus is described best by the equation



$$C_6H_5Li + (CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}})_4Sn \rightleftarrows C_6H_5Sn(\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2)_3 + CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}Li$$

These results demonstrate that the low yield of isopropenyllithium is due to an unfavorable equilibrium, not to steric inhibition of the forward transmetalation reaction by the α-methyl groups in tetraisopropenyltin. The observed results for reactions of phenyllithium with all three propenyltin isomers are in complete agreement with the suggested hypothesis[6] that the driving force in transmetalation reactions is the relative difference in base strengths of the reactant and product organolithium reagents. For vinylic lithium reagents the relative base strength then would be: $CH_2{=}CHLi < trans\text{-}CH_3CH{=}CHLi < cis\text{-}CH_3CH{=}CHLi < CH_2{=}C(CH_3)Li$. The inductive effect of the β-methyl group explains the stronger base strengths of *cis*- and *trans*-propenyllithium relative to vinyllithium. The greatly enhanced base strength of isopropenyllithium is then due to the stronger inductive effect of the α-methyl group. In the aliphatic series, it is well established that base strengths increase in the order primary < secondary < tertiary organolithium reagent.[22,23]

During an attempt to prepare isopropenyllithium by transmetalation between isopropenyltrimethyltin and methyllithium (1:1 stoichiometry) for an n.m.r. study, the n.m.r. spectrum of the resulting solution indicated that an approximately 50:50 mixture of isopropenyllithium and isopropenyltrimethyltin was present, an observation in line with the results obtained with tetraisopropenyltin. The n.m.r. spectrum of isopropenyllithium was obtained using a solution of this reagent as prepared by the direct reaction and is described in the Experimental part.

Our studies concerned with the transmetalation reaction are continuing.

Experimental

Methods.—All reactions and manipulations involving organolithium reagents were performed under an atmosphere of argon or prepurified nitrogen. Carefully purified solvents were used throughout these studies. Analyses were performed by Dr. S. M. Nagy (M.I.T.) and by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were recorded using a Baird Model B or a Perkin–Elmer Model 21 infrared spectrophotometer, n.m.r. spectra using a Varian Associates A60 n.m.r. spectrometer. Chemical shifts are given in p.p.m. downfield from tetramethylsilane. The columns used for gas chromatographic analyses and separations were 265 cm. in length (1 cm. i.d.

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[22] H. Gilman, A. H. Haubein, and H. Hartzfeld, *J. Org. Chem.*, **19**, 1034 (1954).

[23] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 70.

Pyrex tubing). For certain high-boiling compounds the use of 90-cm. columns proved advantageous.

N.m.r. Spectrum of *cis*-Propenyllithium (from *cis*-1-Bromopropene and Lithium Metal).—In a 100-ml. Morton flask, equipped with a high speed stirrer and protected by an argon atmosphere, was placed 50 ml. of ether and 1.40 g. (0.20 g.-atom) of sliced lithium wire (low sodium content). After the solution was cooled to 0°, 12.1 g. (0.10 mole) of *cis*-1-bromopropene was added over a 1-hr. period. At the end of this period, the lithium had reacted completely. A 0.5-ml. sample was then withdrawn with a pipet and placed in an n.m.r. tube. The spectrum of this sample showed one proton as a doublet (J 17.4 c.p.s.) at 6.30 p.p.m., the second proton as two quartets (J 6.0 c.p.s.) at 7.23 and 7.52 p.p.m., and the methyl group as a doublet (J 6.0 c.p.s.) at 1.88 p.p.m. Addition of an excess of trimethylchlorosilane to this sample gave *cis*-propenyltrimethylsilane, identified by a comparison of its retention time (silver nitrate column, jacket temperature 40°, 14 p.s.i. He) with that of an authentic sample. About 2% of the *trans* isomer was also detected.

N.m.r. Spectrum of *trans*-Propenyllithium (from *trans*-1-Chloropropene and Lithium Metal).—In a 100-ml. Morton flask, equipped with a high speed stirrer and protected by an argon atmosphere, was placed 75 ml. of ether and 5.7 g. (0.815 g. atom) of sliced lithium wire (1.1% sodium content). Over a 1-hr. period, 18.7 g. (0.245 mole) of *trans*-1-chloropropene was added. The stirring was continued for an additional 0.5 hr.. The precipitated sodium chloride was allowed to settle, and a 0.5-ml. sample was then withdrawn and placed in an n.m.r. tube. The spectrum of this sample showed one proton as a doublet (J 22.2 c.p.s.) with its midpoint at 6.70 p.p.m. The second proton appeared as two quartets (J 4.2 c.p.s.) at 6.42 and 6.05 p.p.m. The methyl group appeared as a doublet (J 4.2 c.p.s.) at 1.78 p.p.m. Addition of 25.0 g. (0.23 mole) of trimethylchlorosilane to the original solution gave 12.0 g. (46% yield) of *trans*-propenyltrimethylsilane, b.p. 85–88°, $n^{25}\text{D}$ 1.4041. The retention time of this sample (silver nitrate column, jacket temperature 40°, 14 p.s.i. He) was identical with that of an authentic sample, and none of the *cis* isomer could be detected.

N.m.r. Spectrum of Isopropenyllithium (from 2-Bromopropene and Lithium Metal).—The procedure followed was identical with that used in the preparation of *cis*-propenyllithium, 13.1 g. (0.108 mole) of 2-bromopropene being added to 1.90 g. (0.27 g.-atom) of lithium in 40 ml. of ether. The spectrum of the solution showed each of the two olefinic protons as two quartets at 6.21 and 5.71 p.p.m., with $J_{\text{H-H}}$ 5.4 c.p.s. and $J_{\text{CH}_3\text{-H}}$ 1.5 c.p.s. (methyl group coupled equally to both protons). The methyl group appeared as a triplet (J 1.5 c.p.s.) at 2.11 p.p.m.

N.m.r. Spectrum of *cis*-Propenyllithium (Transmetalation Procedure).—In a 10-ml. flask, flushed with argon and equipped with a rubber stopper, was placed 295 mg. (1.44 mmoles) of *cis*-propenyltrimethyltin, followed by the addition of 0.82 ml. of 1.75 N methyllithium (1.44 mmoles). The flask was swirled for 15 min. to ensure complete mixing and reaction, and a 0.25-cc. sample was then withdrawn with a syringe and placed in an n.m.r. tube. The spectrum showed strong signals from *cis*-propenyllithium at 6.28 p.p.m. (doublet, J 17.4 c.p.s.), and two quartets (J 6.0 c.p.s.) at 7.22 and 7.51 p.p.m. In addition, signals arising from unreacted *cis*-propenyltrimethyltin were also observed: sextet (J 6.6 c.p.s.) at 6.5 p.p.m. and a doublet (J 14.2 c.p.s.) at 5.8 p.p.m.[1b]

A second sample was then prepared in an identical manner from 233 mg. (1.14 mmoles) of *cis*-propenyltrimethyltin and 1.3 ml. of 1.75 N methyllithium (2.28 mmoles, 100% excess). In this sample, with a large excess of methyllithium present, the signals due to *cis*-propenyllithium showed an increase in strength, while those due to *cis*-propenyltrimethyltin had practically disappeared.

N.m.r. Spectrum of *trans*-Propenyllithium (Transmetalation Procedure).—The procedure followed was identical with that used in the preparation of *cis*-propenyllithium by the transmetalation route, 0.62 ml. of 1.51 N butyllithium (0.93 mmole) being added to 190 mg. (0.93 mmole) of *trans*-propenyltrimethyltin. The spectrum of the resulting solution showed a doublet (J 22.2 c.p.s.) at 6.68 p.p.m., a quartet (J 4.2 c.p.s.) at 6.42 p.p.m., and three peaks (J 4.2 c.p.s.) at 6.05 p.p.m.

N.m.r. Spectrum of Isopropenyllithium (Transmetalation Procedure).—The procedure used was identical with that used in the preparation of *cis*-propenyllithium by the transmetalation route, 1.0 ml. of 1.7 N methyllithium (1.70 mmoles) being added to 333 mg. (1.62 mmoles) of isopropenyltrimethyltin. The spectrum of the resulting solution showed a peak at 6.21 p.p.m. from isopropenyllithium, a large peak at *ca.* 5.65 p.p.m., arising from overlapping of peaks due to one proton of isopropenyllithium and one proton of isopropenyltrimethyltin, and a peak at 5.07 p.p.m. from isopropenyltrimethyltin. The integrated areas of the peaks at 6.21 and 5.07 p.p.m. were approximately equal, indicating a 50–50 mixture of isopropenyllithium and unreacted isopropenyltrimethyltin in the solution.

Preparation of Solid *trans*-Propenyllithium.—To a solution of 1.45 g. (5.1 mmoles) of tetra-*trans*-propenyltin in 5 ml. of pentane was added 13.8 ml. of 0.87 N *n*-butyllithium (12.0 mmoles) in pentane. The mixture was stirred for 15 min., and became turbid after 10 min. Argon then was vigorously blown through the flask, and after 5 min. a precipitate began to form. The argon blast was continued for 20 min., reducing the volume of the solution by approximately 5 ml. The liquid was then drawn off through a sintered glass filter in the bottom of the flask, and the solid was washed with two 20-ml. portions of pentane. After the addition of 2 ml. of ether, the solid was observed to dissolve partially. The ether solution was filtered through the sintered glass filter, and a 0.5-ml. sample was transferred by means of a pipet into an n.m.r. tube. The spectrum of this solution showed a doublet (J 22.2 c.p.s.) with its midpoint at 6.60 p.p.m., a quartet (J 4.2 c.p.s.) at 6.42 p.p.m., and a quartet (J 4.2 c.p.s.) at 6.05 p.p.m. When the ether solution was treated with an excess of trimethylchlorosilane, *trans*-propenyltrimethylsilane was formed exclusively. The silane was identified by a comparison of its retention time (silver nitrate column, jacket temperature 40°, 14 p.s.i. He) with that of an authentic sample.

An attempt to prepare solid *cis*-propenyllithium by the same method was of questionable success. A solid slowly precipitated as the pentane solution was evaporated almost to dryness, but failed to dissolve in a large excess of ether. The solid was observed to react violently with acetone.

Analysis of N.m.r. Spectra of *cis*- and *trans*-Propenyllithium. (A) ***cis*-Propenyllithium.**—The spectrum of *cis*-propenyllithium can be immediately identified as an ABX_3 type spectrum. The two quartets at 7.52 and 7.23 p.p.m. were assigned to the β-proton on the basis of the CH_3–H_β coupling constant (6.0 c.p.s.). Geminal coupling of this type is known to produce coupling constants in the order of 4–10 c.p.s.[14] The doublet peaks were assigned to the α-proton, and the slight splitting of these peaks (J *ca.* 1.2 c.p.s.) is consistent with an expected[14] coupling constant of 1–2 c.p.s. between H_α and a β-methyl group.

The ratio of the olefinic coupling constant to chemical shift was sufficiently small in this isomer ($J_{AB}/\delta_B - \delta_A = 0.27$) so that the midpoints of the two quartets could be taken for the position of the β-proton and the midpoint of the doublet taken as the position of the α-proton. An approximate calculation similar to that outlined below for the *trans* isomer indicated that the actual proton positions were no greater than 0.02 p.p.m. away from these midpoints.

(**B**) *trans*-**Propenyllithium.**—The spectrum of *trans*-propenyllithium can also be recognized as an ABX_3 type spectrum, although a more extreme example is encountered here than in the case of *cis*-propenyllithium. A small, unsplit peak at 6.89 p.p.m. and a large, unsplit peak at 6.52 p.p.m. are obviously the doublet due to the α-proton. Two additional sets of three peaks each are visible at 6.4 and 6.0 p.p.m. and were presumed to be parts of the expected quartets from the β-proton. The coupling constant (J 4.2 c.p.s.) is in the expected range for coupling between the β-proton and the methyl group, as discussed in the case of the *cis* isomer. At this point, a decision had to be made in deciding whether the fourth peak, not visible, occurred on the upfield or downfield side of the three visible peaks. It seems most likely that this peak occurs on the downfield side, and in the case of the signals at 6.4 p.p.m. is obscured by the upfield half of the α-proton doublet. A small shoulder can be observed on this peak at 6.53 p.p.m.

To calculate the actual positions of the α- and β-protons, the ABX_3 system was first reduced to an AB system. This was done by assuming that the midpoints of the β-proton quartets could be taken as the position of an unsplit (by the methyl group) β-proton doublet. It has been established[14] that for systems where $J_{AB}/\delta_B - \delta_A$ is very small (<0.1), the midpoint of a splitting pattern is identical with the actual proton position; in the case at hand (for H_β and the methyl group) $J_{AB}/\delta_B - \delta_A = 0.016$. The system was then treated as an AB system by the method outlined by Jackman,[14] and it was established that $\delta_\alpha = 6.60$ p.p.m. and $\delta_\beta = 6.33$ p.p.m.[24]

Preparation of *trans*-Propenyltrimethylsilane by the Transmetalation Reaction.—In a 500-ml. flask equipped with a stirrer, reflux condenser, addition funnel, and with a withdrawal stopcock on the bottom was placed 3.54 g. (12.5 mmoles) of tetra-*trans*-propenyltin and 47.5 ml. of 1.07 N phenyllithium (50.0 mmoles) was added. A precipitate of tetraphenyltin appeared immediately. The mixture was stirred vigorously for 2 hr., then filtered through a sintered glass filter into a 200-ml. three-necked flask. This flask, equipped with a reflux condenser and magnetic stirring bar, was previously flushed with argon. The reaction flask then was washed with two 20-ml. portions of ether. To the filtrate was added dropwise a solution of 5.4 g. (50.0 mmoles) of freshly distilled trimethylchlorosilane in 10 ml. of ether. After this addition was completed the mixture was stirred at room temperature overnight. The solution then was filtered to remove the precipitated lithium chloride, and the ether was distilled. Fractional distillation of the residue gave 3.45 g. (61% yield) of

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(24) See L. G. Vaughan, Ph.D. Thesis, M.I.T., 1963, for details of these calculations.

propenyltrimethylsilane, b.p. 84–87°, $n^{25}_{\rm D}$ 1.4070. The gas chromatographic retention time (silver nitrate column, jacket temperature 46°, 14 p.s.i. He) of this product was identical with that of an authentic sample of *trans*-propenyltrimethylsilane,[1b] and none of the *cis* isomer could be detected. The infrared spectra of the two samples were identical. The residue from the distillation (2.0 g.) was estimated by gas chromatography (Dow Corning 710 silicone oil short column, jacket temperature 110°, 15 p.s.i. He) to contain 1.0 g. (14% yield) of trimethylphenylsilane.

A sample of the crude precipitated tetraphenyltin (3.70 g., 70% yield) was recrystallized twice from THF and had m.p. 228–229°. A mixture melting point with an authentic sample showed no depression.

Preparation of *trans*-Methyl Crotonate by the Transmetalation Reaction.—Tetra-*trans*-propenyltin (16.2 mmoles) was treated with 65 mmoles of 1.07 *N* phenyllithium solution as described above. The mixture was stirred vigorously for 1 hr., then filtered through a sintered glass filter and into a well stirred slurry of crushed solid Dry Ice in 300 ml. of ether. The reaction flask was then washed with two 20-ml. portions of ether. After the addition was complete, ths slurry was allowed to warm to room temperature overnight. The solution was then acidified with 10 ml. of 12 *N* HCl, and the ether layer withdrawn. The aqueous layer was washed five times with 50-ml. portions of ether. Since the combined ether fractions had a deep yellow color, they were washed with 50 ml. of a 10% sodium bicarbonate solution. The aqueous solution was acidified with 12 *N* HCl and then extracted five times with 60-ml. portions of ether. The acid was esterified by treating it with an ether solution of diazomethane until the yellow color of diazomethane remained. The ether was then removed by fractional distillation, and fractional distillation of the residue gave 1.8 g. (28% yield) of methyl crotonate, b.p. 117–120°, $n^{20}_{\rm D}$ 1.4248. A comparison of the gas chromatographic retention time (cyanoethylsilicone column, jacket temperature 80°, 14.5 p.s.i. He) of this compound with that of authentic *trans*-methyl crotonate showed the two to be identical. None of the *cis* isomer could be detected. The infrared and n.m.r. spectra of the two samples were also identical.

Authentic *trans*-methyl crotonate was prepared by esterification of *trans*-crotonic acid. Its physical constants[25] and n.m.r. spectrum[26,27] were in good agreement with those reported in the literature.

A sample of the crude precipitated tetraphenyltin (5.6 g., 81% yield) was recrystallized twice from THF and had m.p. 228–229°. A mixture melting point with an authentic sample showed no depression.

Preparation of Authentic *trans*-1-Phenyl-1-trimethylsiloxy-2-butene. (a) ***trans*-Phenylpropenylcarbinol.**—To 125 ml. of 1.56 *N* (0.196 mole) phenyllithium was added dropwise a solution of 13.4 g. (0.192 mole) of *trans*-crotonaldehyde in 25 ml. of ether (vigorous refluxing) over a 0.5-hr. period. The mixture was then hydrolyzed with 8 ml. of water. The ether layer was dried and the ether removed by rotary evaporation. Fractional distillation of the residue gave 19.5 g. (69% yield) of *trans*-phenylpropenylcarbinol, b.p. 72–74° (0.3 mm.), $n^{20}_{\rm D}$ 1.5379 (lit.[8] b.p. 79° (0.95 mm.), $n^{20}_{\rm D}$ 1.5380). In the n.m.r. spectrum of this alcohol, the five phenyl protons occurred as a sharp peak at 7.21 p.p.m. The two olefinic protons occurred as an unresolved multiplet at 5.53 p.p.m. The benzylic proton occurred as a broad multiplet at 4.91 p.p.m., while the hydroxyl proton gave a sharp singlet at 3.88 p.p.m. The methyl group occurred as a doublet (J 4.8 c.p.s.) at 1.62 p.p.m.

The *p*-nitrobenzoate derivative was prepared by the addition of 4.1 g. (27.5 mmoles) of the alcohol to 5.1 g. (27.5 mmoles) of *p*-nitrobenzoyl chloride in pyridine, followed by refluxing for 2 hr. After one recrystallization from ethanol and two from methanol, the *p*-nitrobenzoate had m.p. 99.5–101° (lit.[28] m.p. 99°).

(b) ***trans*-1-Phenyl-1-trimethylsiloxy-2-butene.**—In a 100-ml. flask, equipped with a reflux condenser and a side-arm thermometer, was placed 4.5 g. (30 mmoles) of *trans*-phenylpropenylcarbinol and 3.8 g. (24 mmoles) of hexamethyldisilazane. The mixture was heated for 6 hr., during which time the temperature in the flask rose from 125 to 145°. No attempt was made to fractionally distil the product, but rather analytical samples were collected by gas chromatography. The compound had a retention time of 22 min. on a Dow Corning 710 silicone oil short column, with jacket temperature at 125°, preheater temperature at 140°, and 17 p.s.i. of helium. The product had $n^{25}_{\rm D}$ 1.4877, and the infrared spectrum (pure liquid film) had bands at 3000 (m), 2940 (m), 1600 (w), 1495 (m), 1450 (m), 1250 (s), 1200 (m), 1095 (s), 1050 (s), 965 (s), 885 (s), 840 (s), 750 (s), 700 (s) cm.$^{-1}$.

The n.m.r. spectrum of this alkoxysilane was in agreement with the expected structure. The five phenyl protons occurred as a sharp peak at 7.15 p.p.m., while the two olefinic protons occurred as a complex multiplet at 5.5 p.p.m. The benzylic proton occurred as a multiplet (quartet?) at 5.0 p.p.m., and the methyl group as a doublet (J 4.8 c.p.s.) at 1.59 p.p.m. The nine trimethylsilyl protons occurred as a sharp singlet at 0.0 p.p.m. Unfortunately, the complex AB character of the olefinic protons made it impossible to obtain a *trans* coupling constant for these two protons.

Anal. Calcd. for $C_{13}H_{20}SiO$: C, 70.84; H, 9.15. Found: C, 71.18; H, 8.95.

Preparation of *trans*-1-Phenyl-1-trimethylsiloxy-2-butene by the Transmetalation Reaction.—*trans*-Propenyllithium was prepared in the usual way from 11.7 mmoles of tetra-*trans*-propenyltin and 46.5 mmoles of 1.07 *N* phenyllithium in ether. The reagent mixture was filtered through a sintered glass filter into a 200-ml., three-necked flask. This flask, equipped with a reflux condenser and magnetic stirring bar, had been previously flushed with argon. The reagent flask was then washed with two 20-ml. portions of ether. To the filtrate was then added dropwise a solution of 4.75 g. (45 mmoles) of freshly distilled benzaldehyde in 20 ml. of ether. After this addition was completed, the mixture was stirred at room temperature overnight. A solution of 4.90 g. (45 mmoles) of freshly distilled trimethylchlorosilane in 20 ml. of ether was then added dropwise to the solution. No evidence of immediate reaction could be detected, but lithium chloride slowly precipitated as the solution was stirred for the next 24 hr. The solution was then filtered to remove the lithium chloride and the ether was distilled off. Fractional distillation of the residue gave 5.8 g. (59% yield) of *trans*-1-phenyl-1-trimethylsiloxy-2-butene, b.p. 54–57° (0.2 mm.), $n^{25}_{\rm D}$ 1.4869. The gas chromatographic retention time (Dow Corning 710 silicone oil short column, jacket temperature 125°, preheater temperature 140°, 17 p.s.i. He) of this product was identical with that of an authentic sample, and the two infrared spectra were identical.

A sample of the crude precipitated tetraphenyltin (3.5 g., 71% yield), recrystallized twice from THF, had m.p. 228–229°. A mixture melting point with an authentic sample showed no depression.

Preparation of *cis*-Propenyltrimethylsilane by the Transmetalation Reaction.—The general procedure was identical with that used in the case of the *trans* isomer. After the addition of 81.5 ml. of 0.86 *N* phenyllithium (70.0 mmoles) to 4.78 g. (16.9 mmoles) of tetra-*cis*-propenyltin, the mixture was stirred at room temperature for 4 hr. It was then refluxed for an additional 1.5 hr. After removal of the precipitated tetraphenyltin by filtration, a solution of 7.85 g. (67.5 mmoles) of trimethylchlorosilane in 10 ml. of ether was added dropwise, and the solution stirred overnight. The mixture was hydrolyzed with saturated ammonium chloride solution, and the ether solution dried over magnesium sulfate. The ether was removed by distillation, and fractional distillation of the residue furnished 3.75 g. (49% yield) of propenyltrimethylsilane, b.p. 86–89°. Gas chromatographic analysis (silver nitrate column, jacket temperature 40°, 14 p.s.i. He) revealed the isomer ratio to be 95% *cis* and 5% *trans*. The retention time of the major component was identical with that of an authentic sample. The two infrared spectra also were identical.

Further fractional distillation of the residue furnished 3.0 g. (29% yield) of material, b.p. 35° (0.5 mm.), $n^{22}_{\rm D}$ 1.4920. This compound was identified as trimethylphenylsilane after the identity of its refractive index, infrared spectrum, and retention time (Dow Corning 710 silicone oil column, jacket temperature 105°, 15 p.s.i. He) with those of an authentic sample was established.

A sample of the crude precipitated tetraphenyltin (3.9 g., 55% yield) was recrystallized twice from THF and had m.p. 227.5–229°. A mixture melting point with an authentic sample showed no depression.

Preparation of Authentic *cis*-Methyl Crotonate.—*cis*-Propenyllithium was prepared[1b] from 46 g. (0.38 mole) of *cis*-propenyl bromide and 7.0 g. (1.0 g.-atom) of lithium shot. The ether solution of propenyllithium was poured slowly onto a stirred slurry of Dry Ice and ether in a dewar flask and then allowed to warm to room temperature over a 48-hr. period. The salts were dissolved in 200 ml. of water, acidified with 25 ml. of concentrated HCl, then extracted with five 200-ml. portions of ether. After the ether was removed by evaporation, the residue was recrystallized from petroleum ether to give 12.0 g. (37% yield) of *cis*-crotonic acid, m.p. 10–13° (lit.[29] m.p. 13.5–13.8°). The acid was not purified further, but 6.0 g. (0.07 mole) was treated with a slight excess of diazomethane. After fractional distillation of the ether, fractional distillation of the residue gave 5.2 g. (75% yield) of the methyl ester, b.p. 107–109°. As gas chromatographic analysis revealed a small amount of the *trans* isomer present in the product (silver nitrate column, jacket temperature

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79°, 15 p.s.i. He), analytical samples ($n^{29.5}\mathrm{D}$ 1.4185) for infrared and n.m.r. spectra were collected by gas chromatography (lit.[30] b.p. 102–104° (754 mm.), $n^{20}\mathrm{D}$ 1.4225). In the n.m.r. spectrum of this ester, one olefinic proton occurred as two overlapping quartets (J 7.2 c.p.s.) centered at 6.33 and 6.16 p.p.m. The second olefinic proton occurred as a doublet (J 12.0 c.p.s.) at 5.67 p.p.m. The methoxyl group appeared as a sharp singlet at 3.61 p.p.m., while the allylic methyl group occurred as a doublet (J 7.2 c.p.s.) at 2.09 p.p.m. This spectrum was in complete agreement with published data for this isomer.[26]

***threo*-α,β-Dibromobutyric Acid.**—Of considerable interest and importance in connection with this preparation was the preparation of a solid dibromide derivative of *cis*-crotonic acid (prepared by the same method) reported by Russian workers.[9b] This dibromide was said to melt at 86.5–87°. As Braude[7] reported that the dibromide (crude) from *trans*-crotonic acid had m.p. 84°, it seemed possible that the two dibromides were identical. Accordingly, the preparation of both dibromides was undertaken.

From *trans*-crotonic acid, a dibromide (presumably the *erythro*) was obtained with m.p. 87–88.5°, in good agreement with the results of Braude. However, when *cis*-crotonic acid was brominated, a dibromide (presumably the *threo*) of m.p. 60–61.5° was obtained. As iodine is known to cause a complete *cis* to *trans* isomerization of *cis*-methyl crotonate,[31] it seems likely that the bromination conditions (not specified) used by the Russian workers caused a similar isomerization of *cis*-crotonic acid.

To a 0.5-g. sample of the crude *cis*-crotonic acid in chloroform was added bromine in the dark until a slight excess of bromine was present in the solution. The chloroform was then partially removed and on cooling a solid precipitated. After two recrystallizations, first from carbon disulfide, then from chloroform, the solid (0.55 g., 49% yield) had m.p. 60–61.5°. A mixture melting point with a sample of *erythro*-α,β-dibromobutyric acid (m.p. 87–88.5°, prepared by treating *trans*-crotonic acid with a slight excess of bromine; lit.[7] m.p. 84°) showed a 15° depression (melting began at 45°). The infrared spectrum of this acid (5% in carbon tetrachloride) showed bands at 3000 (m) (broad), 1715 (s), 1425 (m), 1380 (m), 1275 (m), 1245 (m), 1200 (w), 1170 (m), 1060 (w), 1010 (w) cm.$^{-1}$.

Anal. Calcd. for $C_4H_6Br_2O_2$: C, 19.54; H, 2.46. Found: C, 19.49; H, 2.50.

Preparation of *cis*-Methyl Crotonate by the Transmetalation Reaction.—The general procedure was identical with that used in the case of the *trans* isomer. After 76.5 ml. of 0.86 *N* phenyllithium (66.0 mmoles) was added to 4.65 g. (16.4 mmoles) of tetra-*cis*-propenyltin, the mixture was stirred at room temperature for 3 hr. It was then filtered through a sintered glass filter to remove the precipitated tetraphenyltin and into a well-stirred slurry of 250 g. of crushed Dry Ice in 300 ml. of ether. The usual work-up, followed by methylation of the crude acid in ether with diazomethane gave 1.7 g. (26% yield) of methyl crotonate, b.p. 47–50° (125 mm.), $n^{29.6}\mathrm{D}$ 1.4189. The isomer ratio was revealed by gas chromatographic analysis (silver nitrate column, jacket temperature 79°, 15 p.s.i. He) to be 96% *cis* and 4% *trans*. The retention time of the major component was identical with that of an authentic sample of *cis*-methyl crotonate, and the infrared and n.m.r. spectra of the two samples were identical.

Further fractional distillation of the residue gave a product, b.p. 125–130° (15 mm.). A comparison of the infrared spectrum of this product with that of authentic methyl benzoate revealed the two to be identical. A total of 1.2 g. (15% yield) of methyl benzoate was thus obtained.

A sample of the crude precipitated tetraphenyltin (3.5 g., 50% yield) was recrystallized twice from THF and had m.p. 228–229°. A mixture melting point with an authentic sample showed no depression.

Preparation of *cis*-1-Phenyl-1-trimethylsiloxy-2-butene by the Transmetalation Reaction.—The general procedure was similar to that used in the preparation of the *trans* isomer. After 3.95 g. (14.0 mmoles) of tetra-*cis*-propenyltin was treated with 50.0 ml. of 1.12 *N* phenyllithium (56 mmoles), the mixture was stirred for 3 hr. The solution was then filtered through a sintered glass filter to remove the precipitated tetraphenyltin, and the reaction flask was washed with 20 ml. of ether. To the filtrate was then added dropwise a solution of 5.95 g. (56 mmoles) of freshly distilled benzaldehyde in 10 ml. of ether. After this addition was complete, the solution was stirred for 1 hr. A solution of 6.3 g. (58 mmoles) of trimethylchlorosilane in 10 ml. of ether was then added, and the solution refluxed for 96 hr. The mixture was then filtered to remove the precipitated lithium chloride, followed by removal of the ether by rotary evaporation. Fractional distillation of the residue gave 7.5 g. (61% yield) of *cis*-1-phenyl-1-trimethylsiloxy-2-butene, b.p. 60–63° (0.1 mm.), $n^{25}\mathrm{D}$ 1.4890. The infrared spectrum (pure liquid film) of this product had bands at 3010 (m), 2980 (s), 1600 (m), 1495 (m), 1445 (s), 1395 (m), 1250 (s), 1195 (m), 1080 (m), 1060 (s), 1000 (m), 880 (s), 840 (s), 700 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{20}SiO$: C, 70.84; H, 9.15. Found: C, 70.92; H, 9.07.

Gas chromatographic analysis (Dow Corning 710 silicone oil short column, jacket temperature 153°, preheater temperature 150°, 17 p.s.i. He) revealed this product to contain less than 5% of the *trans* isomer. Further distillation gave 2.8 g. (20% yield) of trimethylsiloxydiphenylmethane, b.p. 86–90° (0.1 mm.), $n^{25}\mathrm{D}$ 1.5271. The infrared spectrum, n.m.r. spectrum, and gas chromatographic retention time (same conditions as above) of this compound were identical with an authentic sample prepared as described below.

A sample of the crude precipitated tetraphenyltin (3.30 g., 56% yield) was recrystallized twice from THF and had m.p. 228–229.5°. A mixture melting point with an authentic sample showed no depression.

Preparation of Authentic *cis*-1-Phenyl-1-trimethylsiloxy-2-butene (Hydrogenation Procedure). (a) Phenylpropynylcarbinol.—In a 500-ml. flask was placed 300 ml. of ether which was then saturated with methylacetylene. While methylacetylene continued to bubble into the solution, 140 ml. of 1.56 *N* phenyllithium (0.22 mole) was added dropwise. A solution of freshly distilled benzaldehyde (23.0 g., 0.22 mole) in 20 ml. of ether was then added dropwise to the solution. After a 2-hr. reflux period, the solution was hydrolyzed with 10 ml. of water. The ether layer was then dried over magnesium sulfate and the ether removed by rotary evaporation. Fractional distillation of the residue gave 25.2 g. (79% yield) of product, b.p. 85–88° (0.3 mm.), $n^{20}\mathrm{D}$ 1.5562 (lit.[8] b.p. 78–78.5° (0.4 mm.), $n^{20}\mathrm{D}$ 1.5545).

The *p*-nitrobenzoate derivative was obtained by the addition of 2.9 g. (0.02 mole) of the alcohol to 3.5 g. (0.019 mole) of *p*-nitrobenzoyl chloride in 5 ml. of pyridine, followed by refluxing for 2-hr. After two recrystallizations from ethanol, the *p*-nitrobenzoate had m.p. 103.5–105° (lit.[7] m.p. 107°).

(b) 1-Phenyl-1-trimethylsiloxy-2-butyne.—In a 100-ml. flask, equipped with a reflux condenser and a side-arm thermometer was placed 5.2 g. (36 mmoles) of phenylpropynylcarbinol and 4.3 g. (27 mmoles) of hexamethyldisilazane. The mixture was heated for 6 hr., during which time the temperature in the flask rose from 120 to 145°. No attempt was made to fractionally distil the product, but rather an analytical sample was collected by gas chromatography. The compound had a retention time of 18 min. on a Dow Corning 710 silicone oil short column, with jacket temperature 160°, preheater temperature 205°, and 13 p.s.i. He. The collected sample had $n^{25}\mathrm{D}$ 1.5006 and showed infrared bands (pure liquid film) at 2940 (w), 1495 (w), 1455 (m), 1250 (s), 1140 (m), 1050 (m), 880 (s), 845 (s), 700 (m) cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{18}SiO$: C, 71.49; H, 8.31. Found: C, 71.85; H, 8.18.

(c) *cis*-1-Phenyl-1-trimethylsiloxy-2-butene.—To a solution of 6.6 g. (30 mmoles) of 1-phenyl-1-trimethylsiloxy-2-butyne in 100 ml. of ethyl acetate was added 80 mg. of 10% palladium-on-charcoal catalyst and 50 mg. of freshly distilled pyridine, a catalyst system known to produce *cis*-olefins in high yield and purity.[32] The mixture was hydrogenated for 31 hr. at room temperature and atmosphere pressure, during which time 620 cc. of hydrogen (84% of theoretical) was absorbed. The mixture was then filtered to remove catalyst, and the ethyl acetate was removed by rotary evaporation. Fractional distillation of the residue gave 5.0 g. (74% yield) of product, b.p. 62–63° (0.1 mm.). An analytical sample collected by gas chromatography (retention time of 18 min. on a Dow Corning 710 silicone oil short column, jacket temperature 132°, preheater temperature 220°, 17 p.s.i. He) had $n^{25}\mathrm{D}$ 1.4881, and an identical retention time, infrared spectrum, and n.m.r. spectrum with the sample prepared by the transmetalation reaction.

The n.m.r. spectrum of this assumed *cis*-alkoxysilane was in good agreement with the expected structure. The five phenyl protons occurred at 7.25 p.p.m. A complex multiplet, with integrated area equivalent to three protons, occurred at 5.5 p.p.m. This signal was obviously due to the two olefinic protons plus the one benzylic proton. The methyl group appeared as a multiplet at 1.7 p.p.m., while the nine trimethylsilyl protons occurred as a sharp singlet at 0.0 p.p.m. The complex nature of the signal at 5.5 p.p.m. made it impossible to obtain a *cis* coupling constant.

Of particular interest in this preparation is the slow rate at which this trimethylsiloxy-substituted acetylene underwent catalytic hydrogenation. In contrast, the corresponding acetylenic alcohol absorbed the theoretical amount of hydrogen in a 12-min. period.[8] The slow rate observed in the case of the trimethylsilyl derivative is undoubtedly due to steric interference with hydrogenation by the trimethylsilyl group.

Preparation of Authentic Trimethylsiloxydiphenylmethane.—Over a 45-min. period, 21.0 g. (0.2 mole) of freshly distilled

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(30) J. L. H. Allan, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1862 (1955).

(31) F. Dalton, P. S. Ellington, and G. D. Meakins, *ibid.*, 3681 (1960).

(32) D. M. Lemal, P. D. Pacht, and R. B. Woodward, *Tetrahedron*, **18**, 1275 (1962).

benzaldehyde was added to 200 ml. of 1.0 *N* phenyllithium solution. When this addition was complete, 45.0 g. (0.41 mole) of trimethylchlorosilane in 15 ml. of ether was added to the solution and the mixture was refluxed for 24 hr. After the mixture was filtered to remove the precipitated lithium chloride, the ether and excess trimethylchlorosilane were distilled off. Fractional distillation of the residue gave 32.7 g. (64% yield) of product, b.p. 92–95° (0.2 mm.), $n^{25}\mathrm{D}$ 1.5272. The infrared spectrum (5% in carbon tetrachloride) had bands at 3000 (w), 2920 (w), 1495 (m), 1455 (m), 1250 (s), 1190 (m), 1090 (m), 1065 (s), 1030 (m), 920 (m), 885 (s), 840 (s), 700 (s) cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{20}SiO$: C, 74.94; H, 7.86. Found: C, 74.98; H, 7.76.

Preparation of *trans*-1-Phenyl-3-trimethylsiloxy-1-butene.—In view of the difficulty with which *cis*-1-phenyl-1-trimethylsiloxy-2-butene was formed, and the inability of n.m.r. to provide rigorous proof of the *cis* configuration (due to the extreme AB olefinic system in both the *cis* and *trans* isomers), it was felt desirable to eliminate the possibility that this compound might in reality be the allylic rearrangement product *trans*-1-phenyl-3-trimethylsiloxy-1-butene. A rearrangement of this type is known to occur readily with the corresponding alcohols in the presence of traces of acid.[7]

Over a 1-hr. period, a solution of 30.1 g. (0.23 mole) of freshly distilled *trans*-cinnamaldehyde in 30 ml. of ether was added to 250 ml. of 1.0 *N* methyllithium solution. When the addition was complete, 45 g. (0.41 mole) of trimethylchlorosilane was added to the solution and the mixture was then refluxed for 16 hr. The mixture was then filtered to remove the precipitated lithium chloride, and the ether was removed by rotary evaporation. Fractional distillation of the residue gave 42.8 g. (85% yield) of product, b.p. 70–73° (0.1 mm.), $n^{25}\mathrm{D}$ 1.5014. The ultraviolet spectrum of the compound (*n*-heptane) indicated a β-substituted styryl chromophore: λ_{sh} 216 (ϵ 12,500); $\lambda_{\max}$ 253 (ϵ 16,400), 284 (ϵ 1530), 292 (ϵ 1053). The infrared spectrum (pure liquid film) had bands at 3000 (w), 2940 (m), 1600 (w), 1495 (m), 1450 (m), 1370 (m), 1250 (s), 1150 (m), 1075 (s), 1000 (m), 965 (m), 905 (m), 840 (s), 750 (m), 695 (m) cm.$^{-1}$.

The n.m.r. spectrum was completely different from that of either of the 1-phenyl-1-trimethylsiloxy-2-butenes. The five phenyl protons occurred at 7.22 p.p.m., while the α-proton occurred as a doublet (*J* 16.2 c.p.s.) at 6.43 p.p.m. The β-proton occurred as two doublets (*J* 6.0 c.p.s.) at 6.17 and 5.90 p.p.m. The allylic proton occurred as a quintet (*J* 6.0 c.p.s.) at 4.34 c.p.s., while the methyl group appeared as a doublet (*J* 6.0 c.p.s.) at 1.18 p.p.m. The trimethylsilyl group appeared as a sharp singlet at 0.0 p.p.m.

Anal. Calcd. for $C_{13}H_{20}SiO$: C, 70.84; H, 9.15. Found: C, 70.69; H, 9.37.

Preparation of Tetraisopropenyltin.—In a 1-l., three-necked flask, equipped with a stirrer and reflux condenser and protected by an argon atmosphere, was placed 500 ml. of ether and 7.5 g. (1.07 g.-atoms) of sliced lithium wire (containing 1% sodium). Over a 1-hr. period, 67.2 g. (0.555 mole) of 2-bromopropene was added to the mixture. When this addition was complete, 50.0 g. (0.114 mole) of tin tetrabromide in 25 ml. of ether was added over a 1-hr. period. The mixture was then refluxed for 2 hr. and allowed to stand at room temperature overnight. Hydrolysis was carried out with saturated ammonium chloride solution, and the ether layer was dried over magnesium sulfate. After the solution was treated with ammonia for an hour to remove any unreacted tin bromides, the ether was removed by rotary evaporation. Fractional distillation of the residue gave 23.3 g. (72% yield) of tetraisopropenyltin, b.p. 47–50° (0.1 mm.), $n^{25}\mathrm{D}$ 1.5010. The infrared spectrum (pure liquid) showed bands at 3020 (m), 2910 (s), 2840 (m), 1600 (w), 1450 (s), 1375 (m), 1185 (m), 1000 (m), 915 (s) cm.$^{-1}$. The n.m.r. spectrum of this compound showed one olefinic proton as a multiplet at 5.91 p.p.m., the second olefinic proton as a multiplet at 5.31 p.p.m., and the methyl group as a triplet (*J ca.* 1.0 c.p.s.) at 2.05 p.p.m. Satellite signals arising from splitting of the methyl group by the Sn^{117} and Sn^{119} isotopes occurred at 1.61 and 2.46 p.p.m. (*J* 51 c.p.s.).

Anal. Calcd. for $C_{12}H_{20}Sn$: C, 50.93; H, 7.12. Found: C, 50.79; H, 7.04.

Preparation of Isopropenyltrimethylsilane by the Transmetalation Reaction.—The general procedure was identical with that used in the preparation of *trans*-propenyltrimethylsilane by the transmetalation reaction. After 120 ml. of 0.86 *N* phenyllithium (0.103 mole) was added to 7.3 g. (0.0258 mole) of tetraisopropenyltin, the mixture was stirred at room temperature for 4 hr. As no tetraphenyltin had yet precipitated, the mixture was refluxed for 2 hr., then cooled to −70° for 16 hr. No precipitate had formed, so the solution was allowed to warm to room temperature and was filtered through a sintered glass filter into a 300-ml. flask. A solution of 11.2 g. (0.103 mole) of trimethylchlorosilane in 20 ml. of ether was then added dropwise and the mixture stirred at room temperature overnight. It was then hydrolyzed with saturated ammonium chloride solution, dried over magnesium sulfate, and the ether fractionally distilled off. Fractional distillation of the residue gave first a product, b.p. 77–80°. This product (1.6 g., 14% yield) was identified as isopropenyltrimethylsilane after the identity of its infrared spectrum with that of an authentic sample[1b] was established. The second fraction (b.p. 125–130° (135 mm.), 10.3 g., 67% yield, $n^{22}\mathrm{D}$ 1.4860) was identified as trimethylphenylsilane. Its infrared spectrum and retention time (Dow Corning 710 silicone oil short column, jacket temperature 110°, 15 p.s.i. He) were identical with those of an authentic sample. The third fraction, b.p. 53–54° (0.2 mm.), $n^{25}\mathrm{D}$ 1.5010, was identified as unreacted tetraisopropenyltin (1.4 g., 19% recovery). The fourth fraction, b.p. 62–65° (0.05 mm.), $n^{25}\mathrm{D}$ 1.5489, was identified as phenyltriisopropenyltin after its infrared spectrum and retention time (Dow Corning 710 silicone oil short column, jacket temperature 155°, preheater temperature 175°, 17 p.s.i. He) were found to be identical with those of an authentic sample.

Reverse Transmetalation Reaction between *trans*-Propenyllithium and Tetraphenyltin.—In a 500-ml. flask, equipped with a stirrer, reflux condenser, addition funnel, and with a withdrawal stopcock on the bottom, was placed 14.2 g. (33.1 mmoles) of tetraphenyltin. After the system was thoroughly flushed with argon, 200 ml. of a 0.66 *N* solution of *trans*-propenyllithium (132 mmoles) was added and the mixture stirred for 2 hr. The mixture was then filtered through a sintered glass filter into a 300-ml., three-necked flask equipped with a reflux condenser, magnetic stirrer, and previously flushed with argon. The reaction flask was then washed with 40 ml. of ether. The recovered tetraphenyltin amounted to 11.2 g. (79% recovery). To the filtrate was then added 15.6 g. (132 mmoles) of trimethylchlorosilane. After the mixture was stirred overnight, it was filtered to remove the precipitated lithium chloride. Fractional distillation of the solution through a Widmer column gave 9.4 g. (63% yield) of *trans*-propenyltrimethylsilane, b.p. 86–89°. The compound had an identical retention time (silver nitrate column, jacket temperature 40°, 14 p.s.i. He) as an authentic sample of *trans*-propenyltrimethylsilane. Further vacuum distillation gave 4.09 g. (20% yield) of trimethylphenylsilane, b.p. 60–62° (5 mm.), $n^{25}\mathrm{D}$ 1.4876. The retention time (Dow Corning 710 silicone oil short column, jacket temperature 100°, 14 p.s.i. He) of this sample was identical with that of an authentic sample, and the two infrared spectra were identical.

Reverse Transmetalation Reaction between *cis*-Propenyllithium and Tetraphenyltin.—The general procedure was identical with that given above for the case of the *trans* isomer. After the addition of 160 ml. of 0.875 *N* *cis*-propenyllithium solution (140 mmoles) to 15.0 g. (35 mmoles) of tetraphenyltin in 40 ml. of ether, the mixture was stirred for 4 hr. After filtration to remove the remaining tetraphenyltin, the reaction flask was washed with 40 ml. of ether. A total of 7.6 g. of tetraphenyltin was recovered (51% recovery). To the filtrate then was added 15.2 g. (140 mmoles) of trimethylchlorosilane, and the mixture was stirred overnight. Fractional distillation of the solution through a Widmer column gave 7.3 g. (46% yield) of *cis*-propenyltrimethylsilane, b.p. 87–90°, $n^{25}\mathrm{D}$ 1.4107. The compound had an identical retention time (silver nitrate column, jacket temperature 40°, 14 p.s.i. He) as an authentic sample. Further vacuum distillation gave 5.3 g. (25% yield) of trimethylphenylsilane, b.p. 63–66° (6 mm.), $n^{25}\mathrm{D}$ 1.4875. The retention time of this sample (Dow Corning 710 silicone oil short column, jacket temperature 110°, 15 p.s.i. He) was the same as that of an authentic sample.

Reverse Transmetalation Reaction between Isopropenyllithium and Tetraphenyltin.—The general procedure was identical with that used in the case of the *trans* isomer. After the addition of 412 ml. of a 0.88 *N* solution of isopropenyllithium (0.362 mole) to 38.6 g. (0.0905 mole) of tetraphenyltin, the mixture was stirred for 5 hr. During this period, the tetraphenyltin dissolved completely. To the mixture was then added 48.0 g. (0.44 mole) of trimethylchlorosilane, after which the mixture was stirred overnight. The solution was then filtered to remove the precipitated lithium chloride. Fractional distillation then gave 6.45 g. of isopropenyltrimethylsilane, b.p. 78–82°. The retention time of this silane (Dow Corning 710 silicone oil column, jacket temperature 50°, 14 p.s.i. He) was identical with that of an authentic sample. Fractional distillation under reduced pressure gave 38.0 g. (70% yield) of trimethylphenylsilane, b.p. 68–70° (8 mm.), $n^{25}\mathrm{D}$ 1.4875. The infrared spectrum of this compound and its retention time (Dow Corning 710 silicone oil column, jacket temperature 110°, 15 p.s.i. He) were identical with those of an authentic sample. Further distillation gave 5.2 g. tetraisopropenyltin, b.p. 49–53° (0.1 mm.), $n^{25}\mathrm{D}$ 1.4999, and 8.4 g. of a fraction, b.p. 70–72° (0.1 mm.). This final fraction was identified as phenyltriisopropenyltin on the basis of its elemental analysis, infrared spectrum, and n.m.r. spectrum. The infrared spectrum (pure liquid) showed bands at 3020 (m), 2915 (s), 2850 (m), 1600 (w), 1485 (m), 1450 (s), 1375 (m), 1335 (w), 1300 (w), 1250 (w), 1185 (m), 1075 (m), 1025 (w), 1000 (m), 920 (s), 850 (w), 725 (s), 700 (s) cm.$^{-1}$. The n.m.r. spectrum showed the five phenyl protons as a multiplet at 7.45 p.p.m. One set of three identical olefinic protons occurred as a multiplet at 5.96

p.p.m., while the other set of three occurred as a multiplet at 5.34 p.p.m. The methyl group occurred as a triplet (*J* 2.0 c.p.s.) at 2.11 p.p.m.

Anal. Calcd. for $C_{15}H_{20}Sn$: C, 56.47; H, 6.32. Found: C, 56.43; H, 6.57.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, W. LAFAYETTE, IND.]

Factors Governing Orientation in Metalation Reactions. III. The Metalation of Alkylferrocenes[1]

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A systematic study of the metalation of methyl-, ethyl-, isopropyl-, and *t*-butylferrocene by *n*-amylsodium and *n*-amylpotassium has been made. The monometalation products in these reactions consisted of a mixture of 3- and 1′-metalloalkylferrocenes in an approximate ratio of 1:2.6. A statistical distribution would be 1:2.5. Despite a 1:1 molar ratio of alkylferrocene to metalating agent, dimetalation was predominant in these reactions. It was established by n.m.r. spectroscopy that the major dimetalation product in each case was the 3,1′-dimetalloalkylferrocene. The suggestion is made that the dianion is more thermodynamically stable than the monoanion, which would account for its preferential formation. Even in metalations of ferrocene and alkylferrocenes with *n*-butyllithium (1:1 molar ratio), which were knowingly carried out in a homogeneous fashion, there was produced about a 3:2 mixture of mono- to dimetalation products. There was no observable tendency for the metal atom in any of these metalations to revert from the ring to the side chain in contradistinction to results with alkylbenzenes. Apparently the ring carbanions are more stable than the corresponding α-carbanions in the ferrocene system.

In the first two papers in this series,[2] a detailed study was made of the metalation of ethyl- and isopropylbenzene by *n*-amylsodium and *n*-amylpotassium. It was found that, in the early stages of reaction, the aromatic ring wasm etalated principally in the *meta* and *para* positions to the alkyl group. As reaction progressed, the ring isomers were converted, *via* a transmetalation process, to the more thermodynamically stable α-isomers.

It has been known for some time that ferrocene,[3] as well as its alkyl derivatives,[4] can be metalated in a similar fashion to benzene. No systematic study of orientation has been made, however, in the alkylferrocene series. One of the difficulties inherent in such a study is the quantitative separation of many closely related isomer structures, which, in the case of ferrocene compounds, often possess very similar solubilities. Another difficulty is the problem of identifying the ferrocene isomers once they have been separated from the mixture. Up to this time, principal reliance for structure determination in substituted ferrocenes has been placed on infrared spectroscopy.[5] However useful this tool has been, it has very definite limitations, and, in some instances, structural assignments have been based solely on subtle spectral differences.[6]

With our recent discovery[7] of the usefulness of n.m.r. spectroscopy in the determination of ferrocene structures, one of the principal difficulties connected with metalation studies in the ferrocene series has been removed. Likewise, as is reported in this paper, we have found that vapor phase chromatography can be applied very profitably to a variety of ferrocene compounds. Thus, the perennial problems of separation which have plagued chemists working in this area have now been alleviated considerably.

It was the purpose of this present work to make a systematic study of the metalation of alkylferrocenes with *n*-amylsodium and *n*-amylpotassium, and to contrast these results with those reported for the alkylbenzenes.[2] We were particularly interested in the directive effects of the alkyl groups on the ferrocene nucleus toward metalation and whether there was any tendency for side chain reversion of the metal atom with time as was the case with the alkylbenzenes.[2]

Results.—Methyl-, ethyl-, isopropyl-, and *t*-butylferrocene were metalated with *n*-amylsodium in decane in duplicate runs. Methyl- and ethylferrocene were also metalated by *n*-amylpotassium under identical conditions. In the case of the *n*-amylsodium metalations, a 1:1 mole ratio of metalating agent to alkylferrocene was employed throughout.[8] The reaction time (30–40 hr.), quantity of solvent, and temperature were held constant in all runs.

Initially, all metalation products were carbonated and esterified with diazomethane to convert the products to methyl esters. It was hoped that these could be analyzed by vapor phase chromatography. This analytical procedure had proved quite successful in our earlier metalation work.[2] It became apparent immediately that the dimetalation products which were forming in considerable quantities (despite a 1:1 mole ratio of reactants) could be nicely separated and analyzed by this technique. Unfortunately, the monoesters thus produced resisted separation by v.p.c. despite our use of eight different column packings. An attempt was made to reduce the methyl esters with lithium aluminum hydride–aluminum chloride to a mixture of completely alkylated ferrocenes. The hope was that a v.p.c. separation of the dialkylferrocenes (arising from the monometalated products) could be effected. As

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(8) It was established through carbonation and esterification with diazomethane that a 70% yield of *n*-amylsodium from *n*-amyl chloride could be obtained. We used this value in each case as a basis for calculating the amount of *n*-amylsodium necessary to attain the 1:1 mole ratio.