

CATALYTIC ASYMMETRIC HYDROSILYLATION OF OLEFINS

III *. CHIRAL PHOSPHINE-PALLADIUM(II) COMPLEXES AS HYDROSILYLATION CATALYSTS **

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Summary

A palladium(II) complex of menthyl(diphenylphosphine) (MDPP) or epimeric neomenthyl(diphenylphosphine) (NMDPP) was used as an effective catalyst for the asymmetric hydrosilylation of styrene and some cyclic conjugated dienes, such as cyclopentadiene; the reaction giving optically active 1-phenylethylsilane and 2-cycloalkenylsilane derivatives, respectively.

MDPP and NMDPP, as ligands which have configurations opposite to each other only at the chiral C(3) center adjacent to the diphenylphosphino group, gave enantiomeric (*S*)-(–)- and (*R*)-(+)-1-phenylethyltrichlorosilane, respectively, in the hydrosilylation of styrene with trichlorosilane. However, this is not the case for 2-cycloalkenylsilane formation.

Intervention of a π -allylic palladium is suggested to account for the observed enantioselectivity as well as regioselectivity in the palladium complex-catalyzed addition of trichlorosilane to these olefins.

Introduction

In the two previous papers [2,3], asymmetric homogeneous hydrosilylation of prochiral olefins using certain chiral phosphine-platinum(II) and -nickel(II) or -rhodium(I) complexes was described. In these reactions (*R*)-(+)-benzylmethylphenylphosphine was the most useful chiral phosphine ligand to exert asymmetric induction.

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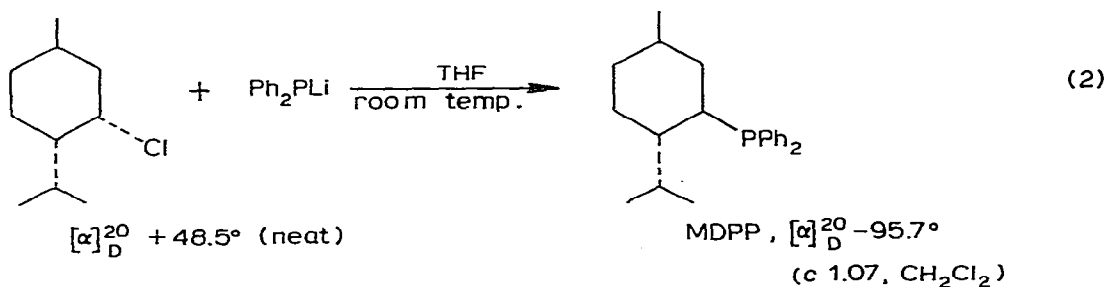
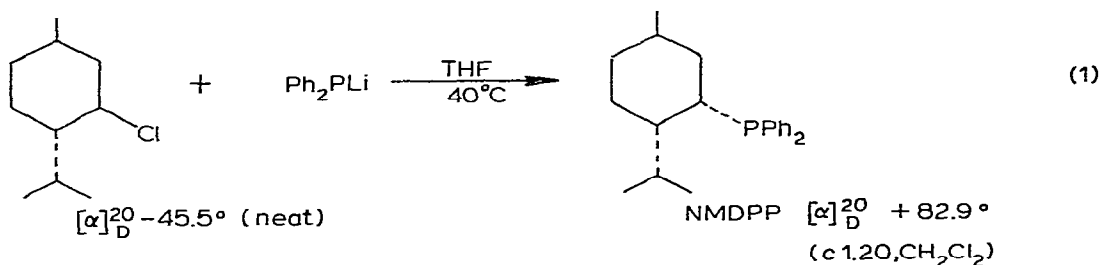
Recently, various types of phosphine-palladium complexes have been reported to be active catalyst precursors for the addition of hydrosilanes specifically to 1,3-dienes [4,5]. In connection with an exploratory asymmetric hydrosilylation of prochiral olefins using chiral phosphine complexes of the nickel triad as catalysts, the chiral palladium complex-catalyzed hydrosilylation was undertaken.

Morrison and coworkers [6] have reported that a chiral rhodium complex containing neomenthylidiphosphine ligands, instead of using tertiary phosphines which are asymmetric at phosphorus, is very effective as an asymmetric homogeneous hydrogenation catalyst. The fact that a complex with ligands that are dissymmetric remote from phosphorus does fulfill the necessary conditions for asymmetric catalysis prompted us to investigate asymmetric hydrosilylation using complexes of this type of chiral phosphines, since dichlorobis[(*R*)-benzylmethylphenylphosphine]palladium(II) proved to be useless for the asymmetric synthesis in hydrosilylation of olefins.

We describe here that a palladium(II) complex of menthylidiphosphine (MDPP) or epimeric neomenthylidiphosphine (NMDPP) is specifically useful for inducing asymmetry in the hydrosilylation of styrene and some cyclic conjugated dienes. Significantly different features of palladium-catalyzed asymmetric hydrosilylation compared with those of platinum- or nickel-catalyzed reaction are also discussed.

Results and discussion

Neomenthylidiphosphine (NMDPP) was prepared, using the method outlined in the literature [6], by a reaction of lithium diphenylphosphide in



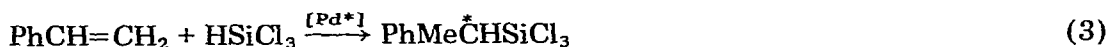
tetrahydrofuran (THF) with menthyl chloride (86% epimeric purity based on a maximum rotation reported [7]). Similarly, menthildiphenylphosphine (MDPP) was prepared in relatively low yield using neomenthyl chloride (89% epimeric purity [8]). Although the reaction of neomenthyl chloride was so exothermic as to occur more readily than that with menthyl chloride (eqs. 1 and 2), facile elimination to yield menthenes seemed to be an important side-reaction. Morrison and Masler [9] also have reported details of synthetic procedures for NMDPP and MDPP. It should be mentioned that reactions of lithium diphenylphosphide as a nucleophile with either menthyl chloride or neomenthyl chloride proceed with inversion of configuration at C(3). In contrast, the reaction of lithium dimethylphosphide revealed little stereospecificity [10]. Recently, menthildiphenylphosphine (MDPP) has been prepared by the reaction of diphenylchlorophosphine with menthylmagnesium chloride, which is found to be configurationally stable [11].

Asymmetric hydrosilylation of styrene and cyclic conjugated dienes

Although the dichlorobisphosphinepalladium(II) complex of MDPP was isolated in low yield, palladium complexes prepared in situ by mixing dichlorobis(benzonitrile)palladium(II) with two equivalents of NMDPP or MDPP were conveniently used as catalyst precursors for the present hydrosilylation. The reaction was carried out in a similar manner to that described in a previous paper [2].

Addition of trichlorosilane to styrene or cyclic conjugated dienes in the presence of a chiral palladium complex gave the respective addition product in an optically active form. The results are summarized in Table 1.

It is of interest that the addition of trichlorosilane to styrene catalyzed by the MDPP-palladium complex took place readily even at room temperature to give 1-phenylethyltrichlorosilane as the sole product (87% yield).



The adduct was converted into the trimethylsilyl derivative, $[\alpha]_{\text{D}}^{20} -5.30^\circ$ (neat); $[M]_{\text{D}}^{20} -9.44^\circ$. Previously [1], we have calculated the optical purity to be 5.1% of the *S* isomer on the basis of an empirical value, $[M]_{\text{D}}^{20} -184^\circ$, of molecular rotation in a series of (*S*)-1-phenylethyl derivatives [12]. Quite recently, however, we have shown that the maximum rotation of $\text{PhMe}\overset{*}{\text{C}}\text{HSiMe}_3$ is at the highest $[\alpha]_{\text{D}}^{20} 15.48^\circ$ (neat), $[M]_{\text{D}}^{20} 27.6^\circ$, based on a stereospecific transformation of 1-phenylethyltrichlorosilane to 1-phenylethyl alcohol via alkylpentafluorosilicate [13]. The optical yield of the present asymmetric hydrosilylation turned out to be at least 34%. When the NMDPP-palladium complex was used as catalyst, the enantiomeric *R* adduct was obtained, 22% enantiomeric excess (% e.e.), while $\text{PdCl}_2(\overset{*}{\text{P}}\text{R}_3)_2$ ($\overset{*}{\text{P}}\text{R}_3 = (R)\text{-(PhCH}_2\text{)MePhP}$) proved to be not very effective for inducing asymmetry in the adduct (1.6% e.e.). It is noteworthy that palladium-catalyzed hydrosilylation of styrene gives exclusively the 1-phenylethylsilane derivative regardless of the reaction conditions [14], whereas with nickel [15] or platinum [16] catalysts so far reported in the literature the addition always proceeds in two directions to form so-called α - and β -adducts. The ease with which reaction occurs and the ratios of α - to β -adducts depend on the conditions. These features also hold in the reac-

TABLE I
ASYMMETRIC HYDROSILYLATION OF OLEFINS WITH HSiCl_3 CATALYZED BY CHIRAL PHOSPHINE-PALLADIUM COMPLEXES

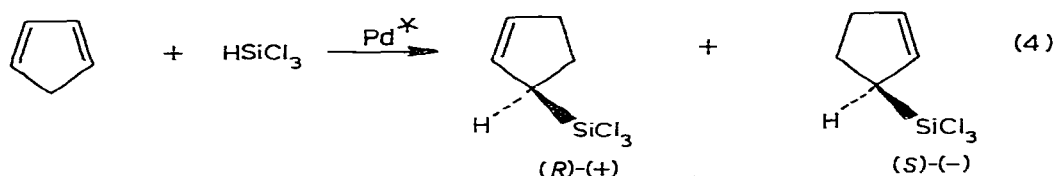
Olefin	Catalyst ^a PdII plus	Temp. (°C)	Time (h)	Product	Yield (%)	$[\alpha]_D^{20}$ (deg.) ^b of methylated	Configuration
Styrene	MDPP	r.t.	5	PhMeCHSiCl ₃	87	-5.30	S (34% e.e.) ^c
Styrene	NMDPP	r.t.	5	PhMeCHSiCl ₃	87	+3.38	R (22% e.e.) ^c
Styrene	PR ₃ ^d	120	12	PhMeCHSiCl ₃	70	+0.25	R (1.6% e.e.) ^c
Cyclopentadiene	MDPP	120	44	2-C ₅ H ₇ SiCl ₃ ^e	69	-11.84	S
Cyclopentadiene	NMDPP	120	58	2-C ₅ H ₇ SiCl ₃ ^e	81	-7.54	S
Cyclopentadiene	PR ₃ ^d	120	48	2-C ₅ H ₇ SiCl ₃ ^e	41	+8.71	R
1,3-Cyclohexadiene	MDPP	120	63	2-C ₆ H ₉ SiCl ₃ ^f	64	-11.08	S
1,3-Cyclohexadiene	NMDPP	120	63	2-C ₆ H ₉ SiCl ₃ ^f	56	-3.66	S
1,4-Cyclohexadiene	MDPP	135	58	2-C ₆ H ₉ SiCl ₃ ^f	58	-2.31	S
1,4-Cyclohexadiene	NMDPP	135	66	2-C ₆ H ₉ SiCl ₃ ^f	80	-0.29	S

^a PdCl₂(PhCN)₂ plus chiral phosphine (1:2); catalyst concentration was 2×10^{-3} mole per mole of olefin.

^b Measured neat. ^c Based on the maximum rotation of PhMeCHSiMe₃, $[\alpha]_D^{20}$ 15.48° (see text). ^d (R)-(+)-(PhCH₂)MePhP (67% optical purity). ^e 2-Cyclopentenyltrichlorosilane. ^f 2-Cyclohexenyltrichlorosilane.

tions catalyzed by chiral phosphine complexes of the nickel triad and this strongly suggested that a different mechanism is operative in the case of palladium-catalyzed addition to styrene from that with nickel or platinum.

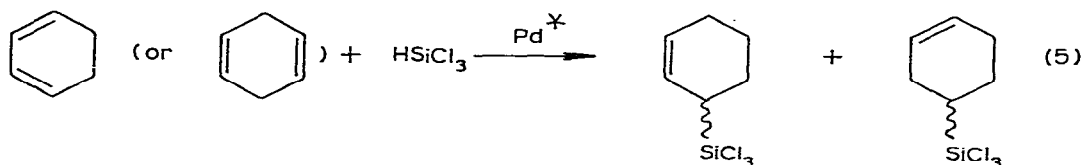
The palladium complex with either MDPP or NMDPP was also useful for asymmetric hydrosilylation of cyclic conjugated dienes with trichlorosilane, although a much higher reaction temperature was required. Of particular interest was that the reaction always gave 2-cycloalkenyltrichlorosilanes with an enantiomeric excess of the *S*-isomer regardless of the phosphine epimers (MDPP and NMDPP) used in the catalyst. This is not the case with styrene (see Table 1). Thus, addition of trichlorosilane to cyclopentadiene catalyzed by Pd-NMDPP at 120°C for 58 h yielded almost exclusively 2-cyclopentenyltrichlorosilane (81%), which was not contaminated with a possible 3-isomer but a trace of a cyclopentadiene dimer (eq. 4). When we accomplished this reaction none of the metal-catalyzed hydrosilylation of cyclopentadiene had been reported [17]; the same reaction but with a nickel catalyst was found to result in dimerization of cyclopentadiene prior to addition of a hydrosilane used.



The optical rotation of 2-cyclopentenyltrimethylsilane obtained upon methylation of the adduct was $[\alpha]_D^{20} -7.54^\circ$ (neat). The crucial structural proof for 2-cyclopentenyltrimethylsilane was given by treatment with trifluoroacetic acid which gave rise to facile cleavage of the trimethylsilyl group [18].

Interestingly, $\text{PdCl}_2(\bar{P}R_3)_2$ ($\bar{P}R_3 = (R)\text{-(PhCH}_2\text{)MePhP}$) was found to be exceptionally effective for asymmetric induction in the hydrosilylation of cyclopentadiene, the result being shown in Table 1.

Hydrosilylation of 1,3-cyclohexadiene with excess trichlorosilane catalyzed by Pd-MDPP gave two isomeric cyclohexenyltrichlorosilanes (2- and 3-isomers in a ratio of 9 : 1 by GLC analysis) in 71% combined yield (eq. 5). Methylation followed by preparative GLC gave pure 2-cyclohexenyltrimethylsilane, $[\alpha]_D^{20} -11.08^\circ$ (neat). Furthermore, hydrosilylation of 1,4-cyclohexadiene with tri-



chlorosilane also gave 2- and 3-cyclohexenyltrichlorosilane in a ratio of 9:1, which led, upon methylation, to 2-cyclohexenyltrimethylsilane, $[\alpha]_D^{20} -2.31^\circ$ (neat). These results concerning the product ratio are in marked contrast to those obtained with a nickel catalyst [3].

Brewster [19] already has reported conformational asymmetry of endocyclic olefinic compounds and predicted that the molecular rotation at 598 nm for

such a configuration of compounds as shown below will have a positive sign: Therefore, 2-cyclopentenyltrimethylsilane and 2-cyclohexenyltrimethylsilane obtained here would have the (*S*)-(-) configuration, the extent of asymmetric induction being unknown.

It seems likely that the intervention of π -allylic metal intermediates is crucial for the present palladium-catalyzed hydrosilylation, since the catalytic action of palladium complexes in hydrosilylation of butadiene and isoprene also differs distinctly from that of platinum for which π -allylic complexes are rather unusual [20]. Furthermore, it has been reported that even aromatic ring carbons can be involved in the formation of a π -benzyl complex with palladium [21] and nickel [22].

The formation of 1-phenylethyltrichlorosilane as sole product in the palladium complex-catalyzed hydrosilylation of styrene may thus be ascribed to the migration of a silyl group bound to the palladium into a benzylic position of a π - α -methylbenzyl-palladium complex. In the light of current views of the mechanisms of metal-catalyzed hydrosilylation [23], the diastereomeric intermediate which leads to partial asymmetric induction would be this π -benzylic palladium complex, which now contains chiral phosphine ligands [24].

Some significant features follow from the above argument. MDPP and NMDPP as ligands, which have configurations opposite to each other only at the chiral C(3) center adjacent to the diphenylphosphino group, gave enantiomeric products, (*S*)-(+)- (34% e.e.) and (*R*)-(-)-1-phenylethyltrichlorosilane (22% e.e.) respectively, in the hydrosilylation of styrene with trichlorosilane. However, this is not the case for 2-cycloalkenylsilane formation, the (*S*)-(-) enantiomer being preferred [25]. Possible π -enyl intermediates again play a key role in the asymmetric hydrosilylation of cyclopentadiene. It is difficult at present to ascertain the pattern of addition which determines the configuration of the product as a result of both olefins and phosphine ligands having multiple chiral centers. However, provided that the cyclic π -enyl system is conformationally fixed and the silyl group transfers necessarily to a π -enyl carbon atom in a *cis* coordination site with respect to the silicon, to give rise to the (*S*)-enantiomer in excess, asymmetric induction must arise from the selective coordination of a cyclic π -enyl group which is controlled by chiral ligand molecules as a whole, despite the meso configuration of 1,3-carbon atoms in the cyclic π -enyl moiety. There is an alternative where the cyclic π -enyl palladium moiety is in free rotation and can find a local plane of symmetry including a silyl-palladium bond. In this case the last silyl group transfer step from the metal center to the π -enyl carbon must involve diastereomeric transition states or intermediates, which control the stereochemical outcome of the present reaction.

Experimental

Preparation of chiral phosphines and palladium complexes

All manipulations for preparing phosphines and complexes were carried out in an atmosphere of dry nitrogen.

*Neomenthyl*diphenylphosphine (NMDPP). Morrison and Masler [9] have reported details of the preparation of this compound. To a tetrahydrofuran (THF) solution of lithium diphenylphosphide prepared from 24 g (0.11 mol) of

diphenylchlorophosphine and a large excess of lithium sand in 50 ml of THF was added 57 g (0.33 mol) of freshly distilled menthyl chloride, $[\alpha]_{\text{D}}^{20} -45.5^\circ$ (neat) (lit. [7] $[\alpha]_{\text{D}}^{20} -53.0^\circ$). The mixture was maintained with magnetic stirring at 40°C for 40 h, during which time the deep red color of the solution gradually disappeared. The reaction mixture was hydrolyzed, worked up in the usual manner, and distilled under reduced pressure to give 12.0 g (34%) of a crude product, b.p. $170-179^\circ\text{C}/0.3$ Torr. The product was purified by column chromatography (silica-gel) to give 8.5 g (24%) of pure neomenthyl-diphenylphosphine, m.p. $96-97^\circ\text{C}$ (in an evacuated tube), $[\alpha]_{\text{D}}^{20} +82.9^\circ$ (c 1.20, CH_2Cl_2) *. (Found: C, 81.14; H, 8.96; P, 9.26. $\text{C}_{22}\text{H}_{29}\text{P}$ calcd.: C, 81.44; H, 9.01; P, 9.55%.)

Menthyl-diphenylphosphine (MDPP). In a similar manner, a THF solution of lithium diphenylphosphide was prepared from 9.0 g (0.041 mol) of diphenylchlorophosphine and 1.0 g of lithium sand in 15 ml of THF. To this solution with stirring was added dropwise 15.5 g (0.089 mol) of neomenthyl chloride, $[\alpha]_{\text{D}}^{20} +48.5^\circ$ (neat), $[\alpha]_{\text{D}}^{20} +48.0^\circ$ (c 1.40, n-octane) (lit. [8] $[\alpha]_{\text{D}}^{25} +53.7^\circ$ (c 1.27, n-octane)) at such a rate as to maintain the reaction temperature below 30°C . The reaction mixture was then allowed to stand overnight and then hydrolyzed, worked up in the usual manner. Fractional distillation gave 3.3 g (25%) of a crude product, b.p. $130-136^\circ\text{C}/0.02$ Torr. After elution of the distillate with benzene through a silica-gel column, 2.0 g (15%) of pure menthyl-diphenylphosphine was obtained, m.p. $64-65^\circ\text{C}$, $[\alpha]_{\text{D}}^{20} -95.7^\circ$ (c 1.07, CH_2Cl_2) **. (Found: C, 80.85; H, 8.82; P, 9.38. $\text{C}_{22}\text{H}_{29}\text{P}$ calcd.: C, 81.44; H, 9.01; P, 9.55%.)

Dichlorobis(menthyl-diphenylphosphine)palladium(II). A mixture of MDPP (0.207 g, 0.64 mmol) and dichlorobis(benzonitrile)palladium(II) (0.122 g, 0.32 mmol) in 20 ml of benzene was heated at reflux for 0.5 h. The solvent was removed by evaporation and the residue was recrystallized from ethanol to give 25 mg (7.6%) of the product as yellow powder. (Found: C, 64.40; H, 7.23. $\text{C}_{44}\text{H}_{58}\text{Cl}_2\text{P}_2\text{Pd}$ calcd.: C, 63.96; H, 7.08%.)

Dichlorobis[(R)-benzylmethylphenylphosphine]palladium(II). To a solution of 0.50 g (1.7 mmol) of sodium tetrachloropalladate in 5 ml of water was added with stirring 0.75 g (3.5 mmol) of (R)-benzylmethylphenylphosphine [26] (67% optical purity) dissolved in 4 ml of ethanol, and the mixture was allowed to stand for 24 h. The precipitates formed were taken up with dichloromethane. After removal of the solvent, the residual mass was recrystallized from ethanol to give 0.22 g (22%) of pure complex as yellow needles, m.p. $165-166^\circ\text{C}$ (in a sealed tube), $[\alpha]_{\text{D}}^{20} -144.1^\circ$ (c 1.03, CH_2Cl_2). (Found: C, 55.28; H, 5.00; Cl, 11.50. $\text{C}_{28}\text{H}_{30}\text{Cl}_2\text{P}_2\text{Pd}$ calcd.: C, 55.51; H, 4.99; Cl, 11.70%.)

Asymmetric hydrosilylation of styrene and cyclic conjugated dienes

Hydrosilylation was carried out as described in the previous papers [2,3]. A mixture of dichlorobis(benzonitrile)palladium(II) with two equivalents of

* Morrison and Masler [9] obtained NMDPP (94–95% pure), $[\alpha]_{\text{D}}^{23} +94.4^\circ$ (c 1.26, CH_2Cl_2).

** Recent literature (ref. 9) gives $[\alpha]_{\text{D}}^{20} -93.5^\circ$ (c 1.56, CH_2Cl_2).

NMDPP or MDPP was used as catalyst precursor. The reaction conditions, yields and optical data of the methylated products are summarized in Table 1.

1. *Styrene*. The following is typical. Addition of trichlorosilane (8.0 g, 59 mmol) to styrene (3.0 g, 20 mmol) at room temperature in the presence of $\text{PdCl}_2(\text{PhCN})_2$ (22 mg, 0.057 mmol) and MDPP (37 mg, 0.114 mmol) gave 6.0 g (87%) of 1-phenylethyltrichlorosilane [27], b.p. $80^\circ\text{C}/7$ Torr, $[\alpha]_{\text{D}}^{20} +2.72^\circ$ (neat), which was converted into the trimethylsilyl derivative [2], b.p. $90^\circ\text{C}/17$ Torr, $[\alpha]_{\text{D}}^{20} -5.30$ (neat). Using methyldichlorosilane no appreciable reaction was observed under identical conditions.

2. *Cyclopentadiene*. A mixture of 12.0 g (89 mmol) of trichlorosilane, 3.0 g (46 mmol) of freshly distilled cyclopentadiene, and $\text{PdCl}_2(\text{PhCN})_2$ -NMDPP (0.091 mmol) was heated at 120°C for 58 h to give 7.4 g (81%) of 2-cyclopentenyltrichlorosilane, b.p. $60-70^\circ\text{C}/23$ Torr, which contained a small amount of dicyclopentadiene. The product was converted by methylation into 2-cyclopentenyltrimethylsilane, b.p. $137-139^\circ\text{C}$, $n_{\text{D}}^{20} 1.4485$, $d_4^{20} 0.8131$. (Found: C, 68.13; H, 11.30. $\text{C}_8\text{H}_{16}\text{Si}$ calcd.: C, 68.48; H, 11.49%.)

2-Cyclopentenyltrimethylsilane (0.438 g) was allowed to react with trifluoroacetic acid (0.60 g) in carbon tetrachloride (2.5 ml) [18] to give trimethylsilyl trifluoroacetate and cyclopentene, which were identical with the authentic samples.

3. *1,3-Cyclohexadiene*. Addition of 7.0 g (52 mmol) of trichlorosilane to 2.0 g (25 mmol) of 1,3-cyclohexadiene in the presence of $\text{PdCl}_2(\text{PhCN})_2$ -MDPP (0.05 mmol) at 120°C for 63 h gave 3.8 g (71%) of an isomeric mixture of cyclohexenyltrichlorosilane [28], b.p. $88-90^\circ\text{C}/23$ Torr. The mixture (area ratio of 9:1 by GLC) was methylated and isolated by preparative GLC to give pure 2-cyclohexenyltrimethylsilane [15b], $n_{\text{D}}^{20} 1.4629$, $d_4^{20} 0.8361$.

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