(bp 30–60°) to remove oil]. The mixture was heated at reflux for 3 hr after the initial exothermic reaction subsided, and then cooled. Butyl bromide (3.7 g, 0.027 mol) in toluene (10 ml) was added over 10 min and the resultant mixture was heated at reflux for 17 hr. The usual work-up gave a yellow oil [3.9 g crude, vpc (at 240° on 20% SE-30) 62% alkylated β-keto ester, 38% starting β-keto ester]. The crude product was hydrolyzed with NaOH (4.0 g, 0.1 mol) in $C_2H_5OH$–$H_2O$ (100 ml each), acidified with dilute HCl, and extracted with ether to give 2-methyl-6-butylcyclohexanone (*ca.* 2.3 g, 0.007 mol, 29%): bp 85° (2.5 mm); ir (film) 5.87 μ; nmr ($CCl_4$) τ 7.5–9.35 (m, 20) with apparent doublet at 9.06 ($J = 6$ Hz) which was shifted to 9.64 (d, 3, $CH_3CH$, $J = 6$ Hz) with 0.038 equiv of Pr(DPM)$_3$. In comparison the nmr ($CCl_4$) of 2-methylcyclohexanone has τ 9.06 (d, 3, $CH_3$, $J = 6$ Hz). No separation of **32** and **33** by vpc was noted on 20% SE-30 (175–217°) or 5% Carbowax (100–135°) columns under isothermal or temperature-programmed conditions. *Anal.* Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.40; H, 11.94. The 2,4-DNP of **33** formed with difficulty (in contrast to that of **32** which formed readily) and was an oil: uv max (95% $C_2H_5OH$) 363 and 228 nm; ir (film) 6.15 μ (C=N); tlc (silica gel $HF_{254}$) $R_f$ 0.3 (ether–hexane) while 2,4-DNPH had $R_f$ 0; uv max (95% $C_2H_5OH$) 350, 260 nm; nmr ($CDCl_3$) τ −1.2 (s, 1, NH), 0.8 (d, 1, aryl $H_c$), 1.6–2.1 (AB quartet, 2, aryl $H_{a,b}$), 6.8–9.3 (m, 20).

**2-Butylcycloheptanone (36)**[32] was collected by vpc (on 20% SE-30) from the cleavage–alkylation of **34**[4b] (Table VI): mass spectrum (20 eV) $m/e$ (rel intensity) 168 (M·$^+$, 37), 153 (M − $CH_3$, 3), 112 [$CH_2{}^+(CH_2)_2CH$·–$C_4H_9$, 56], 111 [$^+O≡CC(C_4H_9)=CH_2$, 33], 97 ($C_6H_9O$, 100), 55 ($^+O≡CC=CH_2$, 89); calcd M + 1 for $C_{11}H_{20}O$, 12.1; found, 12.2.

**2-Methylbutyraldehyde (40)** was separated from butyraldehyde [out of the mixture resulting from the cleavage (0°, 1 min), alkylation (25°, 1 min) of **39**] by its greater solubility in ether. It was identified by its vpc retention time (5.1 min at 85° on 20% SE-30) which was identical with that of a genuine sample and by conversion to its 2,4-DNP: mp 120–121°; mmp 121–122° with that of a genuine sample (lit.[33] mp 120°).

(32) W. von E. Doering and C. F. Hiskey, *J. Amer. Chem. Soc.*, **74**, 5688 (1952).

(33) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1967, p 320.

**2-Heptanone (38).**—The lithium enolate of acetone, generated from the butyl phenylphosphonate **37**, was alkylated with butyl iodide for 3 hr at 25° to give **38** (79% as determined by a vpc calibration curve using genuine samples). No polyalkylated material was detected. The vpc of **38** had a retention time of 5.8 min at 130° on 20% SE-30. The yield of recovered acetone could not be determined because of its nonseparation from other volatile components (vpc).

**2-Methyl-6-bromocyclohexanone (42).**—To pyrrolidino-6-methylcyclohexene (**43**, 25.0 g, 0.15 mol) in $CHCl_3$ (200 ml) and glacial acetic acid (90 ml), cooled to 0–5° in a salt–ice bath, bromine (28.0 g, 0.15 mol) in $CHCl_3$ (50 ml) was added dropwise with stirring under nitrogen. The reaction temperature was kept below 5° during the addition and for another 10 min, water (200 ml) was added and the reaction mixture was poured into saturated $NaHCO_3$ solution (400 ml). The organic layer was washed with water (3 × 200 ml), dried ($MgSO_4$), and usually directly converted to vinyl phosphate **24**. Removal of the solvent at 25° *in vacuo* gave a dark red oil: nmr ($CCl_4$) τ 8.91 (d, *ca.* 3, $CH_3$, $J = 6.5$ Hz), 7.0–8.4 (m, 7, $CH_2$), 5.22 (m, *ca.* 1, CHBr). Yields were *ca.* 80% of mixtures of 8–9 parts of **42** and 1–2 parts of 2-methyl-2-bromocyclohexanone (**46**). Rearrangement of **42** to **46** occurred in part upon attempted vpc and slowly at 25° (complete conversion in 24 hr). Reaction of **42** with lithium bromide, lithium carbonate, dimethylformamide, or collidine gave only 2-methylcyclohexenone, 2,4-DNP mp 208° (lit.[34] mp 207.5–208.5°).

**Registry No.**—**5**, 30758-39-5; **6**, 30758-40-8; **9**, 2042-85-5; **11**, 26709-97-7; **14**, 36504-01-5; **15**, 30758-45-3; **16**, 36504-02-6; **17**, 30842-23-0; **18**, 36504-03-7; **19**, 30758-41-9; **20**, 30758-44-2; **21**, 4452-32-8; **22**, 36504-04-8; **23**, 30908-58-8; **24**, 30908-59-9; **25**, 36504-06-0; **26**, 36547-04-3; **27**, 30758-42-0; **32**, 1197-78-0; **33**, 36504-08-2; **33** DNP, 36504-09-3; **34**, 31327-27-2; **36**, 36504-11-7; **42**, 36504-12-8; cyclohexanone lithium enolate, 21300-30-1; 2-methylcyclohexanone lithium enolate, 13670-83-2; cycloheptanone lithium enolate, 36504-15-1.

(34) E. W. Warnhoff and H. P. Landerl, *J. Amer. Chem. Soc.*, **75**, 494 (1953).

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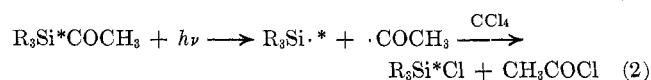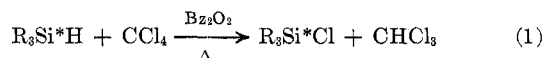# Chirality and Structure of Organosilicon Radicals

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Pyramidal structure for triorganosilyl radicals ($R_3Si$·) in general is indicated by chirality studies on five optically active organosilicon systems containing asymmetric silicon. Reactions of five different optically active silanes, $R_3Si$*H, with carbon tetrachloride, catalyzed by benzoyl peroxide, gave optically active $R_3Si$*Cl compounds. Progressively greater dilution of the carbon tetrachloride with benzene or cyclohexane demonstrated the capacity of the α-NpPhMeSi·* radical to invert. Also, for reasons presently unknown $Ph_3SiSi$*(Ph)(Me)H gave optically inactive $Ph_3SiSi$*(Ph)(Me)Cl.

Recent studies by Brook[1] and Kumada[2] have provided evidence that the α-naphthylphenylmethylsilyl radical as generated in reactions 1 and 2 below is chiral and nonplanar. In these studies $R_3Si$*Cl is optically active α-NpPhMeSi*Cl.

$$R_3Si\text{*}H + CCl_4 \xrightarrow[\Delta]{Bz_2O_2} R_3Si\text{*}Cl + CHCl_3 \qquad (1)$$

$$R_3Si\text{*}COCH_3 + h\nu \longrightarrow R_3Si\cdot\text{*} + \cdot COCH_3 \xrightarrow{CCl_4}$$
$$R_3Si\text{*}Cl + CH_3COCl \qquad (2)$$

In both reactions the optically active organosilicon reactants gave the product chlorosilane, $R_3Si$*Cl, with

(1) A. G. Brook and J. J. Duff, *J. Amer. Chem. Soc.*, **91**, 2118 (1969).

(2) H. Sakurai, M. Murakami, and M. Kumada, *ibid.*, **91**, 319 (1969).

*retention* of configuration. For reactions 1 and 2, respectively, optical purities of product $R_3Si$*Cl were 86 and 64%.

However, both of the above studies were limited to generation and reaction of the same radical, α-NpPhMeSi·, and we wish now to report results which demonstrate (a) chirality for a wide variety of monosilane radicals; (b) nonchirality or rapid inversion for a disilane radical; (c) capacity of the α-NpPhMeSi·* radical to invert under conditions of progressively greater dilution of the $CCl_4$ in reaction 1 by benzene and cyclohexane.

Results for reaction 1 using a wide variety of $R_3Si$*H compounds and pure $CCl_4$ as solvent-reactant are reported in Table I. References listed in Table I

### TABLE I
#### RADICAL REACTIONS OF $R_3Si^*H$ WITH $CCl_4$ TO GIVE $R_3Si^*Cl$

| No. | $R_3Si^*H$ reactant | $R_3Si^*H$,[a] [α]D, deg | $R_3Si^*Cl$,[a] [α]D, deg | $R_3Si^*Cl$,[b] optical purity, % | Ref |
|---|---|---|---|---|---|
| 1 | α-NpPhMeSi*H | +35.0 | -5.9 | 92 | 3 |
| 2 | neo-C5H11PhMeSi*H | +1.6 | +4.6[d] | 100 | 4 |
| 3 | PhFPhMeSi*H[c] | +3.5 | -16.0[d] | 84 | 5 |
| 4 | α-NpPhFMeSi*H[c] | +22.4 | +25.7[d] | 90 | 5 |
| 5 | Ph2CHPhMeSi*H | +3.1 | +13.6 | 100 | 4 |
| 6 | Ph3SiSi*(Ph)(Me)H | +7.3 | 0.0 | 0 | 6 |

[a] All rotations taken in pentane unless otherwise noted. [b] First five reactions proceed with predominant *retention* of configuration. [c] Ph$_F$ is perfluorophenyl, $C_6F_5$. [d] Rotation in $CCl_4$.

report the syntheses, optical rotations, and correlations of configuration for the $R_3Si^*H$ reactants and $R_3Si^*Cl$ products.[3-7]

All of the reactions in Table I were run in refluxing $CCl_4$ using benzoyl peroxide as the initiator. Reaction times required for complete reaction, as monitored by glpc, varied from 0.25 to 24 hr. This reaction was chosen for study because of the moderately long chain lengths (50-80) and lack of side reactions.[8]

For reactions 1-5 (Table I) the optical purities and signs of rotation show predominant *retention* of configuration and high stereospecificity. In these reactions, then, the organosilicon radicals maintain chirality. Thus, these radicals prefer a pyramidal geometry and their rate of reaction with $CCl_4$ in pure $CCl_4$ solvent–reactant is faster than their rate of inversion. Since the structural variation of the monosilyl radicals in reactions 1-5 (Table I) is fairly wide, it is reasonable to conclude that *a pyramidal geometry generally obtains for $R_3Si\cdot$* and that optically active $R_3Si\cdot^*$ can maintain chirality.

Previously, esr[9,10] and ir[11,12] data have been interpreted as indicating a pyramidal structure for monosilane radicals. Thus, the present data provide important confirmation of this interpretation and establish beyond any doubt the general pyramidal nature of such radicals.
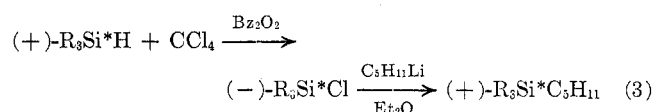
Since $Ph_3SiSi^*(Ph)(Me)H$ is a relatively reactive silane with $CCl_4$ and since the other silanes have configuration stability under the reaction conditions, it seems highly unlikely that $Ph_3SiSi^*(Ph)(Me)H$ can, itself, be racemized by the reagent prior to formation of the chlorosilane.

Concerning reaction 6 in Table I, formation of racemic $R_3Si^*Cl$ was shown not to be due to racemization of initially optically active chlorosilane. The latter was found to be optically stable under the reaction conditions. Thus, the lack of optical activity in the

product must be due either to a preferred planar geometry for the disilane radical or to rapid inversion of its pyramidal geometry. There is some esr evidence for preferred planar geometry for disilane radicals,[9] but more extensive study is certainly necessary. We consider that the result of reaction 6 suggests, but certainly does not prove, that the disilanyl radical is planar. If this radical were pyramidal, its rate of inversion might exceed its rate of reaction with $CCl_4$ and thus give the observed result. For example, see the studies discussed below.

In our next experiments we investigated the point just raised concerning possible competitive rates of inversion and reaction for chiral $R_3Si\cdot^*$. Reaction rates of the radicals were decreased by progressive dilution of the $CCl_4$ with benzene and the optical purity of the product $R_3Si^*Cl$ was determined by trapping the chloro silane by reaction with neopentyllithium. The coupling product was separated from the unreacted $R_3Si^*H$, and from the specific rotation of the $R_3Si^*C_5H_{11}$[4] the optical purity of the product was calculated.

The two-step stereoreaction sequence is given in eq 3 and the second step proceeds with excellent stereospecificity[4] and inversion of configuration.[4]
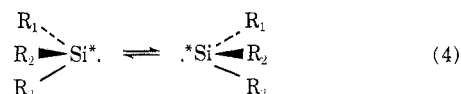
$$(+)\text{-}R_3Si^*H + CCl_4 \xrightarrow{Bz_2O_2}$$

$$(-)\text{-}R_3Si^*Cl \xrightarrow[Et_2O]{C_5H_{11}Li} (+)\text{-}R_3Si^*C_5H_{11} \quad (3)$$

Results of these studies are reported in Table II.

### TABLE II
#### EFFECTS OF BENZENE DILUTION ON THE STEREOSPECIFICITY OF REACTION OF $(+)\text{-}R_3Si^*H$ WITH $CCl_4$

| % CCl4 (v/v) | [α]D, $R_3Si^*C_5H_{11}$, deg | Optical purity, % |
|---|---|---|
| 100 | +21.4 | 92 |
| 75 | +20.1 | 87 |
| 50 | +18.4 | 79 |
| 25 | +15.3 | 66 |
| 10 | +10.4 | 45 |

From Table II it is clear that there is a dramatic decrease in product optical purity as the $CCl_4$ is diluted with benzene. Therefore, inversion of the chiral radical can compete with reaction. To eliminate the possibility of a specific solvent effect with benzene, such as radical complexation, which would lower the radical's reactivity and perhaps favor its racemization prior to reaction, a second series was performed with cyclohexane. The decrease in optical purity on dilution with cyclohexane paralleled the results given in Table II.

We conclude that the rates of eq 4 below can be competitive with reaction of the radical in certain cases.

$$\begin{array}{c} R_1 \\ R_2 \end{array}\!\!\!\!\!\!\!\!\text{—} Si^* \cdot \quad \rightleftarrows \quad \cdot^* Si \text{—}\!\!\!\!\!\!\!\!\begin{array}{c} R_1 \\ R_2 \\ R_3 \end{array} \qquad (4)$$

### Experimental Section

**A. Radical Reactions of Optically Active Organosilanes with CCl₄. Reaction of $(+)\text{-}α\text{-Naphthylphenylmethylsilane}$ with Carbon Tetrachloride.**—In a 100-ml one-necked round-bottom

(3) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, **86**, 3271 (1964).

(4) L. H. Sommer, K. W. Michael, and W. D. Korte, *ibid.*, **89**, 868 (1967).

(5) Unpublished work of L. H. Sommer and M. A. Silverman; see M. A. Silverman, Ph.D. Thesis, University of California at Davis, 1970.

(6) L. H. Sommer and K. T. Rosborough, *J. Amer. Chem. Soc.*, **91**, 7067 (1969).

(7) A. G. Brook and G. J. D. Peddle, *ibid.*, **85**, 2338 (1963).

(8) Y. Nagai, K. Yamazaki, I. Shiojima, N. Kobori, and M. Hayashi, *J. Organometal. Chem.*, **9**, 21 (1967).

(9) S. W. Bennett, C. Eaborn, A. Hussain, and R. A. Jackson, *ibid.*, **16**, 36 (1969).

(10) For recent esr work and pertinent recent references, see S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc. A*, 348 (1970).

(11) M. E. Jacox and D. E. Milligan, *J. Chem. Phys.*, **49**, 3130 (1968).

(12) D. E. Milligan and M. E. Jacox, *ibid.*, **49**, 5330 (1968).

flask equipped with a reflux condenser and a nitrogen inlet tube were placed 5.0 g (0.02 mol) of (+)-R₃Si*H, [α]D +35.0° (c 4.0, pentane), and 0.6 g (0.0025 mol) of benzoyl peroxide in 40 ml of carbon tetrachloride. The solution was refluxed for 10 hr and the solvent was removed under vacuum. The remaining oil, [α]D −6.3° (c 4.0, pentane), had ir and nmr spectra identical with those of authentic R₃SiCl. The optical purity is 97%.

**Reaction of (+)-Phenylneopentylmethylsilane with CCl₄.—**In a 25-ml round-bottom flask equipped with a reflux condenser and nitrogen inlet tube were placed 1.8460 g (9.61 mmol) of C₅H₁₁-PhMeSiH, [α]D +1.56° (c 9.6, pentane), and 0.2326 g (0.961 mmol) of benzoyl peroxide in 10 ml of carbon tetrachloride. The solution was refluxed under nitrogen for 9.5 hr and then transferred quantitatively to a polarimeter tube, and a rotation was taken. Calculation yielded [α]D +4.59° (c 7.75, CCl₄). Ir and nmr spectra were identical with those of authentic phenylneopentylmethylchlorosilane and thus no R₃SiH remained unreacted. The product was 100% optically pure from its specific rotation.

**Reaction of (+)-α-Naphthylpentafluorophenylmethylsilane with CCl₄.—**In a 25-ml round-bottom flask equipped with a reflux condenser and a nitrogen inlet tube were placed 0.598 g (1.77 mmol) of (+)-α-naphthylpentafluorophenylmethylsilane, [α]D +22.4° (c 1.75, CCl₄), and 0.05 g (0.21 mmol) of benzoyl peroxide in 3 ml of carbon tetrachloride and the solution was refluxed for 7 hr. Nmr indicated 34.1% conversion of the silane to the chlorosilane. A rotation of the mixture was taken, and calculation yielded φ = 82.8° (c 2.4, CCl₄). Calculations (see Treatment of Cyclohexane Dilution Experiments) showed that the specific rotation of the chlorosilane was [α]D +25.7°, which indicated an optical purity of 90%. The product was identified by nmr and glpc analyses.

**Reaction of (+)-1,2,2,2-Tetraphenyl-1-methyldisilane with CCl₄.—**In a 25-ml round-bottom flask equipped with a reflux condenser and a nitrogen inlet tube were placed 1.6744 g (4.40 mmol) of (+)-Ph₃SiPhMeSi*H, [α]D +7.27° (c 4.0, CCl₄), and 0.02662 g (0.11 mmol) of benzoyl peroxide in 5 ml of carbon tetrachloride and the solution was refluxed for 0.5 hr. The solution was transferred quantitatively to a polarimeter tube. The observed rotation was 0.0°. Nmr and ir spectra were identical with those of authentic Ph₃SiPhMeSiCl.

**Reaction of Racemic 1,2,2,2-Tetraphenyl-1-methyldisilane and (−)-1,2,2,2-Tetraphenyl-1-methyl-1-chlorodisilane with CCl₄.—**The specific rotation of a solution of 1.57 g (3.8 mmol) of (−)-Ph₃SiPhMeSi*Cl, 1.02 g (2.68 mmol) of (±)-Ph₃SiPhMeSiH, and 0.21 g (0.87 mmol) of benzoyl peroxide in 7 ml of carbon tetrachloride was [α]D −1.80° (c 12.0, CCl₄). The solution was refluxed under nitrogen in a 25-ml round-bottom flask for 2 hr and the contents were transferred quantitatively to a polarimeter tube for an observed rotation. Calculation yielded [α]D −1.74° (c 11, CCl₄). Therefore, the chlorodisilane wss optically stable under the conditions of the reaction.

**Reaction of (+)-Pentafluorophenylphenylmethylsilane with CCl₄.—**In a 25-ml round-bottom flask were placed 1.6 g (5.6 mmol) of C₆F₅PhMeSi*H, [α]D +3.53°, and 0.15 g (0.62 mmol) of benzoyl peroxide in 7 ml of carbon tetrachloride and the solution was refluxed under nitrogen for 3.5 hr. The contents were transferred quantitatively to a polarimeter tube and an observed rotation was taken; calculations yielded φ = −7.06°. Nmr indicated 27.8% conversion to the chlorosilane which, therefore, calculating from the molecular rotation (see Treatment of Cyclohexane Dilution Experiments), would have a specific rotation of [α]D −16.0° and an optical purity of 84%. Products were confirmed by nmr and ir analyses compared to those of authentic material.

**Reaction of (+)-Benzhydrylphenylmethylsilane with CCl₄.—**In a 25-ml round-bottom flask were placed 0.8996 g (3.1 mmol) of benzhydrylphenylmethylsilane, [α]D +3.09° (c 11.0, C₅H₁₂), and 0.0726 g (0.31 mmol) of benzoyl peroxide in 5 ml of CCl₄ and the solution was refluxed for 22 hr. After removal of CCl₄ under vacuum, the product was purified by recrystallization from pentane, which yielded 0.5818 g of white solid which was shown by nmr to consist of 27 wt % SiH and 73 wt % SiCl. Calculation gave [α]D SiCl + 13.6°, and this corresponded to 100% retention of configuration.

**B. Dilution Experiments. Preparation of Neopentyllithium.—**In a 500-ml three-necked flask equipped with reflux condenser, mechanical stirrer, dropping funnel, and nitrogen inlet tube were placed 17.35 g (2.5 g-atoms) of lithium wire (pounded flat under dry pentane and cut immediately prior to reaction into the flask under a stream of nitrogen) and 300 ml of anhydrous

ether (distilled from LiAlH₄). To this mixture was added slowly 49 g (0.46 mol) of neopentyl chloride over 2.5 hr with rapid stirring. The solution was stirred for an additional 2.5 hr and an aliquot was removed and poured into distilled water. This solution was titrated with standard acid and found to be 1.4 N in the organometallic.

**Reaction of (+)-α-Naphthylphenylmethylsilane and 100% CCl₄.—**In a 100-ml round-bottom flask equipped with a nitrogen inlet tube were placed 5.0 g (0.02 mol) of (+)-α-naphthylphenylmethylsilane, [α]D +35.0°, and 0.6 g (0.0025 mol) of benzoyl peroxide in 40 ml of carbon tetrachloride and the solution was refluxed under nitrogen for 10 hr. The solvent was stripped off under vacuum and the remaining viscous oil was taken up in 40 ml of anhydrous ether and cooled with an ice bath. To this solution was added rapidly 29 ml (0.04 mol) of the previously prepared neopentyllithium solution, which had been cooled by an ice bath, and the mixture was allowed to stand with occasional swirling for 20 min. The dark gray solution was then poured onto a slurry of ice, dilute HCl (5%), and pentane and the organic layer was washed three times with water. The organic layer was dried over sodium sulfate overnight and the solvent was then removed on the steam bath. The yellow oil remaining was taken up in 50 ml of pentane, adsorbed on a 19 × 50 cm silica gel column, and eluted with 300 ml of pentane followed by 500 ml of a pentane–benzene solution, 85:15 (v/v). The solvent was removed on the steam bath, leaving a clear, viscous oil, [α]D +21.4° (c 3, pentane), 5.7 g (90%). The ir spectrum was identical with that of authentic α-naphthylneopentylphenylmethylsilane.

**Reaction of (+)-α-Naphthylphenylmethylsilane, 75% Carbon Tetrachloride, and 25% Benzene.—**In a 100-ml round-bottom flask equipped with a nitrogen inlet tube and a reflux condenser were placed 5 g (0.02 mol) of (+)-R₃Si*H, [α]D +35.0°, and 0.6 g (0.0025 mol) of benzoyl peroxide in 30 ml of carbon tetrachloride and 10 ml of benzene, and the solution was refluxed under nitrogen for 10 hr. The procedure and work-up described above for formation and isolation of the (+)-α-naphthylneopentylphenylmethylsilane yielded 5.6 g (88%) of a viscous oil, [α]D +20.1° (c 4.5, pentane). The infrared spectrum was identical with that of an authentic sample.

**Reaction of (+)-α-Naphthylphenylmethylsilane, 50% Carbon Tetrachloride, and 50% Benzene.—**In a 100-ml round-bottom flask equipped with a nitrogen inlet tube and a reflux condenser were placed 5 g (0.02 mol) of (+)-R₃Si*H, [α]D +35.0°, and 0.6 g (0.0025 mol) of benzoyl peroxide in 20 ml of carbon tetrachloride and 20 ml of benzene and the solution was refluxed under nitrogen for 10 hr. The procedure and work-up described previously for the formation and isolation of (+)-α-naphthylneopentylphenylmethylsilane yielded 5.8 g (91%) of a clear, viscous oil, [α]D +18.4° (c 4.4, pentane). The infrared spectrum was identical with that of an authentic sample.

**Reaction of (+)-α-Naphthylphenylmethylsilane, 25% Carbon Tetrachloride, and 75% Benzene.—**In a 100-ml round-bottom flask equipped with a nitrogen inlet tube and a reflux condenser were placed 5.0 g (0.02 mol) of (+)-α-naphthylphenylmethylsilane, [α]D +35.0°, and 0.6 g (0.0025 mol) of benzoyl peroxide in 10 ml of carbon tetrachloride and 30 ml of benzene and the solution was refluxed under nitrogen for 10 hr. The procedure and work-up described previously for the formation and isolation of (+)-α-naphthylneopentylphenylmethylsilane yielded 5.6 g (88%) of a clear, viscous oil, [α]D +15.3° (c 4.2, pentane). The infrared spectrum was identical with that of an authentic sample.

**Reaction of (+)-α-Naphthylphenylmethylsilane, 10% Carbon Tetrachloride, and 90% Benzene.—**In a 100-ml round-bottom flask equipped with a nitrogen inlet tube and reflux condenser were placed 5.0 g (0.02 mol) of (+)-α-naphthylphenylmethylsilane, [α]D +35.0°, and 0.6 g (0.0025 mol) of benzoyl peroxide in 4 ml of carbon tetrachloride and 36 ml of benzene and the solution was refluxed under nitrogen for 10 hr. The procedure and work-up previously described for the formation and isolation of (+)-α-naphthylneopentylphenylmethylsilane yielded 5.4 g (85%) of a clear, viscous oil, [α]D +10.4° (c 3.2, pentane). The infrared spectrum was identical with that of an authentic sample.

**Treatment of Cyclohexane Dilution Experiments.—**In the reaction of (+)-R₃Si*H and carbon tetrachloride diluted with cyclohexane, the final solution contains both (+)-R₃Si*H and (−)-R₃Si*Cl. If it is assumed that the unreacted silane has retained its original rotation (this has been shown to be correct), the rota-

tion of the chlorosilane can be calculated from the following equation

$$\frac{[\alpha]_D \; MW \; moles}{100} + \frac{[\alpha]_D' \; MW' \; moles'}{100} = \phi \; moles''$$

where $[\alpha]_D$ = specific rotation of the remaining (+)-$R_3Si^*H$, MW = molecular weight of $R_3Si^*H$, moles = moles of $R_3Si^*H$ remaining after reaction, $[\alpha]_D'$ = specific rotation of (−)-$R_3Si^*Cl$, MW' = molecular weight of $R_3Si^*Cl$, moles' = moles of $R_3Si^*Cl$ formed in reaction, $\phi$ = molecular rotation of reaction mixture = (observed rotation) (ml)/(path length, dm) (moles'') (100), and moles'' = total moles of reactant.

Therefore, from the gross molecular rotation of the reaction mixture and an $[\alpha]_D$ of +35.0° for $R_3Si^*H$, the specific rotation of the formed (−)-$R_3Si^*Cl$ can be calculated. The amount of silane remaining (moles) and the amount of chlorosilane formed (moles') can be obtained from glpc or nmr analysis.

**Reaction of (+)-α-Naphthylphenylmethylsilane and CCl₄.—** In a 25-ml round-bottom flask equipped with a reflux condenser and a nitrogen inlet tube were placed 2.0 g (0.008 mol) of (+)-α-naphthylphenylmethylsilane, $[\alpha]_D$ +35.0°, and 0.19 g (0.0008 mol) of benzoyl peroxide in 8 ml of carbon tetrachloride. The resulting solution was refluxed for 14 hr under nitrogen. The reaction mixture was transferred quantitatively to a polarimeter tube and a rotation was taken. Calculations yielded $\phi$ = −6.60° (c 6.6, CCl₄). The solvent was removed, the remaining oil was taken up in cyclohexane, and a known quantity of phenanthrene was added [TCF = phenanthrene/$R_3SiH$ = 1.05 (weight basis), phenanthrene/$R_3SiCl$ = 1.42, $R_3SiH$/$R_3SiCl$ = 1.34]. The solution was analyzed by glpc and 0.18 g of $R_3Si^*H$ and 2.1 g of $R_3Si^*Cl$ were found to be present. Calculation using the equation previously described yielded $[\alpha]_D$ −5.5° for the chlorosilane produced. Nmr, ir, and glpc analyses were consistent with the assigned structures.

**Reaction of (+)-α-Naphthylphenylmethylsilane with 50% Carbon Tetrachloride and 50% Cyclohexane.—** In a 25-ml round-bottom flask equipped with a reflux condenser and a nitrogen inlet tube were placed 2.0 g (0.008 mol) of (+)-$R_3Si^*H$, $[\alpha]_D$ +35.0°, and 0.19 g (0.0008 mol) of benzoyl peroxide in 4 ml of carbon tetrachloride and 4 ml of cyclohexane. The solution was refluxed for 14 hr under nitrogen. Following the procedure described above yielded $\phi$ = −1.34° (c 6.6, CCl₄) for the molecular rotation of the reaction mixture and $[\alpha]_D$ −3.84 for the

$R_3Si^*Cl$ formed (0.21 g of $R_3Si^*H$ remaining and 2.0 g of $R_3Si^*Cl$ formed).

**Reaction of (+)-α-Naphthylphenylmethylsilane with 33% Carbon Tetrachloride and 67% Cyclohexane.—** In a 25-ml round-bottom flask equipped with a reflux condenser and a nitrogen inlet tube were placed 2.0 g (0.008 mol) of (+)-$R_3Si^*H$, $[\alpha]_D$ +35.0°, 0.19 g (0.0008 mol) of benzoyl peroxide in 2.6 ml of carbon tetrachloride, and 5.4 ml of cyclohexane, and the solution was refluxed for 14 hr under nitrogen. The procedure described previously yielded $\phi$ = +17.2° (c 6.6, CCl₄) for the molecular rotation of the reaction mixture and $[\alpha]_D$ −2.78° for the $R_3Si^*Cl$ formed (0.54 g of $R_3Si^*H$ remaining and 1.8 g of $R_3Si^*Cl$ formed).

**Reaction of α-Naphthylphenylmethyldeuteriosilane and Carbon Tetrachloride.—** In a 25-ml round-bottom flask were placed 1.1000 g (4.42 mmol) of $R_3SiD$ and 0.1000 g (0.414 mmol) of benzoyl peroxide in 5 ml of carbon tetrachloride. The solution was refluxed for 11 hr under nitrogen. The volatile material was removed under vacuum and trapped in a flask cooled by a Dry Ice–acetone bath. The chloroform formed was isolated by preparative glpc and a mass spectrum was taken. The results indicated that 98% of the hydrogen in the chloroform was deuterium.

**Reaction of α-Naphthylphenylmethyldeuteriosilane and Cyclohexane.—** In a 25-ml round-bottom flask were placed 0.3000 g (1.2 mmol) of α-naphthylphenylmethyldeuteriosilane and 0.0300 g (0.124 mmol) of benzoyl peroxide in 4 ml of cyclohexane and the solution was refluxed for 17 hr under nitrogen. Infrared examination of the reaction mixture indicated that no $R_3SiH$ formed.

**Reaction of α-Naphthylphenylmethyldeuteriosilane, Chloroform, Toluene, Benzene, and 1,3,5-Trimethylbenzene.—** In a manner analogous to that described above, $R_3SiD$ and benzoyl peroxide were treated with $CHCl_3$, PhMe, PhH, and PhMe₃. Infrared analysis indicated that no $R_3SiH$ formed in any of the reactions.

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# Stereochemistry of Addition Reactions of Allenes. VI.
# Orientation and Stereochemistry of Radical Addition

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Products of radical addition of *p*-toluenesulfonyl iodide, ArSO₂I, to various allenes (propadiene, 1,2-butadiene, 3-methyl-1,2-butadiene, 2,3-pentadiene, 2-methyl-2,3-pentadiene, and 1,2-cyclononadiene) have been identified. Each allene except propadiene gave an allylic iodide by way of central attack on the allenic system by arylsulfonyl radicals. Evidence supporting the intervention of symmetrical allylic radicals was obtained from a study of the addition of ArSO₂I to optically active 2,3-pentadiene and 1,2-cyclononadiene. Radical addition of halomethanes, CF₃I, CH₃I, and CCl₃Br, to 2,3-pentadiene gave products of terminal attack by CX₃ radicals (X = F, H, Cl) accompanied by 41-49% central attack in the case of CCl₃Br. The stereospecificity of addition of BrCCl₃ to (+)-2,3-pentadiene was found to be almost negligible, indicating that the products are formed from symmetrical allylic radicals and configurationally unstable vinylic radicals. The factors that influence the orientation of radical addition to allenes are discussed.

Radical-chain additions to allenes are presumed to involve radical intermediates of allylic structure by way of initial attack at the central allenic carbon, and of vinylic structure by attack at the terminal carbons. The degree to which radicals of either structure are involved depends on the structure of the starting allene,

the nature of the attacking radicals, and the reaction conditions.[3] Nevertheless, orientation data for the addition of various radical reagents to propadiene do not reveal any obvious correlation between the nature of the attacking radical and its regioselectivity. For example, under kinetic control, where reversibility

(3) (a) M. C. Caserio in "Selective Organic Transformations," Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1970, p 239. (b) For a thoughtful review on structure and reactivity in free-radical chemistry, see C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).