Basic Elimination of Hydrogen Chloride from 9-Halodecalins.—A 4.4-mg sample (0.0256 mmole) of *cis*- (or *trans*-) 9-chlorodecalin was weighed into a small tube fitted with a cold-finger condenser and 50 μl. of 5.1 *M* (0.255 mmole) potassium hydroxide in ethanol was added. The solution was heated at 55–60° for 24 hr. Water was added and the resulting, cloudy water layer was washed twice with pentane (or hexane or ethyl ether), the organic layer was dried ($MgSO_4$), and the bulk of the solvent was removed on a steam bath using a Vigreux column. The solution was further concentrated under a stream of nitrogen and the products were analyzed[36] by vapor phase chromatography without further work-up. In determination of yields a standard, *o*-dichlorobenzene, was added to the reaction before the addition of water. *cis*-9-Chlorodecalin gave a ratio of $\Delta^{9,10}$-octalin to $\Delta^{1,9}$-octalin of 1 to 9; *trans*-9-chlorodecalin gave the same octalins in the ratio 3.7 to 1; 9-bromodecalin (18 hr at 40° in 3.5 *M* ethanolic KOH) gave these octalins in the ratio 3 to 1.

Registry No.—*cis*-9-Decalylcarbinyl hypochlorite, 7731-61-5; *trans*-9-decalylcarbinyl hypochlorite, 7731-62-6; methyl *cis*-9-decalincarboxylate, 4630-78-8; methyl *cis*-9-decalyl ketone, 5682-42-8; 2-(*cis*-9-decalyl)propene, 7731-65-9; methyl(*cis*-9-decalyl)carbinol, 7775-55-5; *cis*-9-chlorodecalin, 5597-83-1; *trans*-9-chlorodecalin, 5597-82-0; 11-oxatricyclo[5.3.2.$0^{2,7}$]dodecane, 7771-18-8; 11-oxatricyclo[7.2.1.$0^{4,9}$]dodecane, 7731-68-2; 9-bromodecalin, 7731-69-3.

Stereoselectivity in Hydrogen Atom Transfer. Reduction of *cis*- and *trans*-9-Chlorodecalins with Organotin Hydrides[1a]

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The free-radical chain reaction of *trans*- and *cis*-9-chlorodecalin with tri-*n*-butyltin hydride affords in high yield the same mixture from each chloride of *trans*- and *cis*-decalin in which *trans* predominates (3.5/1 at 130°, 6/1 at 60°, 11/1 at 0°). The same product ratio is obtained by use of triphenyltin hydride or dibutyltin dihydride. The reductions may be effected at 0° with initiation by azobisisobutyronitrile and weak ultraviolet irradiation. Reaction of 9-chlorodecalin with tri-*n*-butyltin deuteride in toluene affords 9-deuteriodecalin; this process constitutes a specific method for the introduction of deuterium, and indicates a high hydrogen atom transfer activity for tri-*n*-butyltin hydride.

Organotin hydrides effect the reduction of a variety of organic functional groups,[2] probably by a range of mechanisms. For the reduction of alkyl halides to alkanes, the evidence points to a free-radical chain reaction, for which the chain-propagating steps of eq 1 and 2 have been suggested.[2] This reaction has been

$$RX + R'_3SnH \longrightarrow RH + R'_3SnX$$

$$R\cdot + HSnR'_3 \longrightarrow RH + \cdot SnR'_3 \quad (1)$$

$$RX + \cdot SnR'_3 \longrightarrow R\cdot + XSnR'_3 \quad (2)$$

of interest to us in that it provides an opportunity for studying the stereochemistry of hydrogen atom transfer to specific radicals (R·). The present study describes the application of this reaction to 9-decalyl radicals.

Results

trans- and *cis*-9-chlorodecalin[3] were prepared by the addition of anhydrous hydrogen chloride to $\Delta^{9,10}$-octalin or by the decomposition of *cis*-9-decalylcarbinyl hypochlorite and separated by preparative-scale glpc. Reaction of either of the 9-chlorodecalins with tri-*n*-butyltin hydride afforded in high yield a mixture of *trans*- and *cis*-decalin in which the former predominated. The same product ratio, *trans*-RH/*cis*-RH, was obtained from each chloride. As with previous cases, the reductions appear to proceed by free-radical chain reaction.[2,4] At 80° a source of radical initiators is needed. Azobisisobutyronitrile was employed at 0.5 to 1 mole % of the hydride. Reduction was complete in 0.5 hr at 80° under these conditions; thus the chain length is long. At 130°, the AIBN may be omitted; probably the reaction is self-initiated. Reduction may also be effected at 0° with chain initiation by means of photochemical decomposition of azo compound. Irradiation of 9-chlorodecalin and tri-*n*-butyltin hydride in the absence of added azo compound was not effective.

Reductions of *trans*- and *cis*-9-chlorodecalin with di-*n*-butyltin dihydride and triphenyltin hydride were examined to see if the use of these hydrides, more reactive[2,4a] than tri-*n*-butyltin hydride, would result in any dependence of the product ratio, *trans*-RH/*cis*-RH, on the stereochemistry of the initial chloride. *cis*- and *trans*-9-chlorodecalin still afforded a common product composition, and the ratio of *trans*-decalin to *cis*-decalin was essentially the same as that obtained from the tri-*n*-butyltin hydride in spite of the rather different steric situations in the three hydrides. The use of di-*n*-butyltin dihydride as solvent also did not alter the product ratio. The results are summarized in Table I.

Although one of the products of the reaction (R_3SnCl) is a weak Lewis acid, no isomerization of the tertiary chlorides occurs prior to their reduction. Both chlorides were shown to be stable to the reaction conditions by analysis for alkyl chloride after partial reaction. The products were also shown to be stable to the reaction conditions. (Free-radical isomerization of *cis*- to *trans*-decalin has been observed but requires more severe conditions than those employed here.)[5]

(1) (a) Supported in part by the Atomic Energy Commission under Contract No. AT(30-1)-905. Reproduction is permitted for any purpose of the U. S. Government; (b) National Institutes of Health Predoctoral Fellow, 1962–1965.

(2) H. G. Kuivila. "Advances in Organometallic Chemistry," Vol. 1, Academic Press Inc., New York, 1964, pp 47–87; see also C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966).

(3) F. D. Greene and N. N. Lowry, *ibid.*, **32**, 875 (1967).

(4) (a) H. G. Kuivila and L. W. Menapace, *ibid.*, **28**, 2165 (1963); (b) L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).

(5) R. M. Roberts and J. J. Madison, *ibid.*, **81**, 5839 (1959).

TABLE I

RATIOS OF PRODUCTS, *trans*-DECALIN/*cis*-DECALIN, FROM REDUCTION OF 9-CHLORODECALINS BY ORGANOTIN HYDRIDES IN TOLUENE

Reactants: Tin hydride	RCl[a]	Temp, °C	Initiator[b]	Product ratio, *trans*-RH/*cis*-RH	Yield of RH, %
$(n\text{-Bu})_3SnH$	*cis*	130	None	3.5[c]	
	trans	130	None	3.6[c]	
	trans	80	AIBN	5.3[d,e]	96
	trans	80	None	(No redn)[e]	
	cis	60	AIBN	6.2	
	trans	60	AIBN	5.8	97
	cis	0	AIBN, $h\nu$	10	
	trans	0	AIBN, $h\nu$	11	
$(n\text{-Bu})_3SnD$	*trans*	0	AIBN, $h\nu$	11	
$(n\text{-Bu})_2SnH_2$	*cis*	0	AIBN, $h\nu$	11	
	trans	0	AIBN, $h\nu$	11	
$(Ph)_3SnH$	*cis*	0	AIBN, $h\nu$	11	
	trans	0	AIBN, $h\nu$	12	
$(n\text{-Bu})_2SnH_2$	*cis*	10	AIBN, $h\nu$	11.5,[f] 12.3[g]	
	trans	10	AIBN, $h\nu$	12.0,[h] 12.0[i]	

[a] 0.1–0.2 *M*. [b] AIBN 0.5 to 1 mole % of the tin hydride. [c] Three hours. [d] Variation of RCl/R′$_3$SnH from 0.5 to 2 did not alter the product ratio. [e] Thirty minutes. [f] R_2SnH_2, 0.33 *M*. [g] R_2SnH_2, 4 *M*. [h] R_2SnH_2, 0.15 *M*. [i] R_2SnH_2, 3.7 *M*.

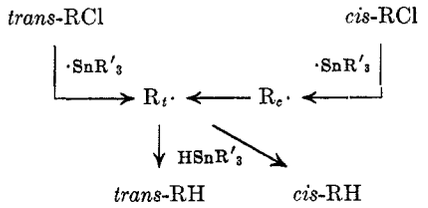
The rate of consumption of *trans*-chloride exceeds that of *cis*-chloride by *ca.* 1.5 to 1, based on an internal competition experiment employing *cis*- and *trans*-chloride and insufficient hydride. (The relative reactivity of *t*-butyl bromide *vs.* *n*-butyl bromide is 7 to 1.)[4]

Identification of Source of Hydrogen Involved in the Transfer Step.—Reaction of tri-*n*-butyltin deuteride with 9-chlorodecalin in toluene afforded the 9-deuteriodecalins (>95% monodeuterated) showing that tri-*n*-butyltin hydride is a better hydrogen donor than the solvent, toluene. The experiment also shows that the proteum abstracted from the organotin hydride is that attached to the tin rather than, for example, hydrogen on carbon α to the tin followed by rearrangement.

Discussion

These results provide further support for the free-radical chain route for the alkyl halide–organotin hydride reaction and for its formulation in terms of eq 1 and 2.[6] The reaction of tri-*n*-butyltin hydride with the 9-chlorodecalins at 0° results in a tenfold preference for formation of the *trans* product. Formation of the more stable of two stereochemically related products may not be general for this reaction, however, since the hydrogen-transfer step is expected to be exothermic. Although the desired bond-dissociation energies are not known for the organotin derivatives of interest here, estimates may be made:[7] for the average bond energy of the tin–hydrogen bond, 65 kcal/mole; for the tin–chlorine bond, 76[8] to 90[7] kcal/mole. A recent report[9] has indicated that actual bond energies exceed average bond energies in a series of organotin derivatives by *ca.* 20 kcal/mole. In spite of the uncertainties involved, it is highly probable that both reactions (eq 1 and 2) are exothermic. A minimum value for the exothermicity of the step of stereochemical interest (eq 1) is about 10 kcal/mole.

Studies of decomposition of *trans*- and *cis*-*t*-butyl 9-decalinpercarboxylate in the presence of oxygen[10] and of decomposition of *trans*- and *cis*-9-decalylcarbinyl hypochlorite[3] provided evidence for the formation from the *cis* precursors of a radical ($R_1\cdot$) that, at high oxygen and hypochlorite concentrations, respectively, reacted with these substrates to afford predominantly *cis* product. In the reduction of *trans* and *cis*-9-chlorodecalin by organotin hydrides, the observation of a common product composition under all conditions indicates that the activation energy for abstraction of hydrogen from organotin hydride exceeds the barrier for isomerization of the radical derived from the *cis* series ($R_c\cdot$) to that from the *trans* series. This situation also obtains with the other hydrogen atom transfer reactions to the 9-decalyl radical.[10] The following reaction sequence is applicable to the organotin hydride reductions. This pathway may be compared with that outlined for the reactions of hypochlorite and of peresters in the presence of oxygen.[3,10]



A summary of the stereoselectivity observed with 9-decalyl radicals under conditions of low concentration of atom transfer reagent[3] is given in Table II. The fact that the product ratio varies only slightly with changes in the nature of the scavenger should be noted. It is interesting that in this restricted series the reactions of lower activation energy (oxygen and hypochlorite reactions) show the greater selectivity, although the differences are small.

TABLE II

STEREOSELECTIVITY IN REACTIONS OF 9-DECALYL RADICAL WITH VARIOUS SUBSTRATES[a]

Substrate	Temp, °C	Product ratio[a] of *trans*/*cis*
O_2	50	7[b]
ClOR	50	11[c]
	0	15[c]
$HSn(n\text{-Bu})_3$	50	7[d]
	0	11[d]
$HSC_6H_5CH_3$	50	5.5[b]
$HC(CH_3)_2C_6H_5$	50	2[b]
$HCH_2C_6H_5$	50	5.5[b]
H-cyclohexyl	50	5[b]

[a] Product ratios for low initial concentration of substrate. [b] Reference 10. [c] Reference 3, estimated for 50° (actual value measured at 0 and 80°). [d] This work, estimated for 50° (actual value measured at 0 and 60°).

Synthetic Applications.—The general utility of the tin hydride reduction of organic halides has been well established.[2,4] It may be of value to emphasize here

(6) The possibility of R· + $HSnR'_3 \rightarrow [HSnR'_3R]\cdot \rightarrow RH + \cdot SnR'_3$ is rendered unlikely by the formation of *n*-octane in 80% yield from reaction of *n*-octyl bromide with tri-*n*-butyltin hydride,[4a] and by the insensitivity of the ratio of trans- to *cis*-decalin to variations in the structure of the organotin hydride in the reductions of Table I.

(7) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 91.

(8) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths and Co. (Publishers), Ltd., London, 1958, p 257.

(9) A. L. Yergey and F. W. Lampe, *J. Am. Chem. Soc.*, **87**, 4204 (1965).

(10) P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *ibid.*, **87**, 2590 (1965).

its use in the preparation of specifically deuterated (or tritiated) compounds, perhaps of special advantage in the preparation of compounds with deuterium at a tertiary position. Replacement of tertiary halide by hydrogen may also be effected in some cases by solvolysis in the presence of borohydride ion.[11] This latter sequence has the disadvantage of possible carbonium ion rearrangements prior to hydride transfer from borohydride to the cationic species. Furthermore, elimination may predominate over the hydride transfer. (Efforts to capture the 9-decalylcarbonium ion with borohydride ion resulted only in the formation of octalins.)

Secondly, in conjunction with the Hunsdiecker reaction[12] (or the Cristol–Firth or Kochi methods),[13] the sequence of eq 3 constitutes a convenient method for the replacement of carboxyl by hydrogen, a transformation that may also be effected by the sequence of eq 4.[14] For R = tertiary (other than bridgehead), yields in the Hunsdiecker reaction are usually poor,[12] and the sequence of eq 5 may be preferred (*e.g.*, a mixture of *cis*- and *trans*-9-chlorodecalin may be obtained in 85% yield from decomposition of *cis*-9-decalylcarbinyl hypochlorite at 0°;[3] efforts to convert *cis*-9-decalincarboxylic acid to 9-chloro or 9-bromodecalin by the Hunsdiecker or Cristol–Firth reactions were largely unsuccessful). For the conversion of RCOOH to RCl when R is primary or secondary, the hypochlorite decomposition of eq 5 leads to many side reactions; use of the sequence of eq 6 has been found satisfactory.[15]

$$\mathrm{RCOOH} \longrightarrow \mathrm{RCOOAg} \xrightarrow[X_2]{} \mathrm{RX} \xrightarrow{R'_3SnH} \mathrm{RH} \quad (3)$$

$$\mathrm{RCOOH} \longrightarrow \mathrm{RCOO\text{-}}t\text{-butyl} \xrightarrow[\Delta]{\text{cymene}} \mathrm{RH} \quad (4)$$

$$\mathrm{RCOOH} \longrightarrow \mathrm{RCH_2OH} \longrightarrow \mathrm{RCH_2OCl} \longrightarrow \mathrm{RCl} \xrightarrow{R'_3SnH} \mathrm{RH} \quad (5)$$

$$\mathrm{RCOOH} \longrightarrow \mathrm{RC(CH_3)_2OH} \longrightarrow \mathrm{RC(CH_3)_2OCl} \longrightarrow \mathrm{RCl} \quad (6)$$

Experimental Section

Organotin Hydrides.—From 17.8 g (0.055 mole) of tri-*n*-butyltin chloride and 2.4 g (0.06 mole) of lithium aluminum hydride a total of 11.54 g (0.0397 mole) of tri-*n*-butyltin hydride was obtained in a yield of 72%, bp 44–47° (0.05–0.075 mm) [lit.[16] bp 76° (0.7 mm)]. The dihydride was obtained from lithium aluminum hydride reduction of di-*n*-butyltin dichloride in 67% yield, bp 76–77° (13 mm) [lit.[16] bp 75–76° (12 mm)]. Alkyltin hydrides are sensitive to air, moisture, and silicone stopcock grease; they were stored under nitrogen in the refrigerator. Triphenyltin hydride was prepared by the reduction of triphenyltin chloride with lithium aluminum hydride as described[17] by Kuivila. Distillation was carried out by immersing the flask in an oil bath preheated to 150° and then raising the temperature. The distillate, obtained in 78% yield, boiled at 140–149° (0.03 mm) [lit.[17] bp 162–168° (0.5 mm)]. The hydride is a viscous liquid. Tri-*n*-butyltin deuteride was prepared by G. J. Nolfi by the reduction of tri-*n*-butyltin chloride with lithium aluminum deuteride, bp 70–74° (0.5 mm) 88%.

9-Chlorodecalins were prepared by the methods previously described.[3] The *cis* and *trans* isomers may be separated and analyzed without decomposition by use of vapor phase chromatography employing columns described in ref 3.

Reaction of 9-Chlorodecalins with Organotin Hydrides.—A 3.5-mg sample (0.0204 mmole) of *trans*-9-chlorodecalin was weighed into a dry, stoppered test tube flushed with nitrogen and 8.3 mg (0.0285 mmole) of tri-*n*-butyltin hydride was added. To this solution was added 0.23 ml of a 0.19 *M* solution of azobisisobutyronitrile (AIBN) in toluene. The test tube was stoppered with a ground-glass top, sealed with wax, placed in an ice bath, and irradiated with a weak ultraviolet source.[18] (For thermal reductions, sealed tubes were placed in an oil bath at the appropriate temperature.) The contents were analyzed by vpc, and the *cis*- and *trans*-decalins were confirmed by collection from the column and infrared comparison with authentic samples. Quantitative analysis was made by vpc employing *o*-dichlorobenzene as an internal standard (added at the end of the reduction reaction). The results are summarized in Table I.

It was found that if the reaction had not proceeded to completion prior to analysis by vapor phase chromatography, a slight reaction on the column preheater tended to make the ratio of *trans*-decalin to *cis*-decalin low and erratic. Adding carbon tetrachloride to the reaction mixture before analysis (approximately doubling the reaction volume) consumed all unreacted hydride, and consistent product ratios could be obtained. Addition of carbon tetrachloride to the dihydride must be done carefully and with cooling.

Control Experiments. A. Stability of the Chlorodecalins to the Reaction Conditions.—In the vapor phase chromatograms of reaction mixtures from partial reaction, the chloride observed is the starting chloride; hence, isomerization of the chlorides during the reaction does not occur. When the *trans*-chloride was heated at 130° with tri-*n*-butyltin chloride extensive dehydrohalogenation took place.

B. Stability of the Decalins to the Reaction Conditions.—To a reaction mixture containing *trans*-9-chlorodecalin, di-*n*-butyltin dihydride, and AIBN in toluene a weighed amount of *cis*-decalin was added and the solution was irradiated at 0°. After 2.5 hr carbon tetrachloride was added and the solution was analyzed by vapor phase chromatography. The amount of *cis*-decalin present was equal to the original amount plus that expected from reduction of the 9-chlorodecalin.

Competition between *cis*- and *trans*-9-Chlorodecalin for Tri-*n*-butyltin Hydride.—A solution of 9-chlorodecalins (24.7 mg, 0.14 mmole, 50% *trans*-9-chlorodecalin, 44% *cis*-9-chlorodecalin, 6% octalin) and tri-*n*-butyltin hydride (29.6 mg, 0.10 mole) in 0.1 ml of toluene containing AIBN (0.082 *M*) was irradiated with a weak ultraviolet lamp under nitrogen for 5 hr at room temperature. Vapor phase chromatographic analysis of the product indicated the presence of 26% *cis*-chloride, 23% *trans*-chloride, 4% olefin, and 47% decalin. Thus, during the reaction time, 54% of the *trans*-chloride reacted and 41% of the starting *cis*-chloride reacted. The ratio of *trans*- to *cis*-decalin was 10.6.

Solvolysis of *trans*-9-Chlorodecalin in the Presence of Sodium Borohydride.[11]—To a solution of 0.25 ml of water, 0.50 ml of ethanol, and 63.0 mg of sodium borohydride (1.6 mmoles) at 40° was added 17.4 mg (0.10 mmole) of *trans*-9-chlorodecalin. The solution was stirred for 2 hr and quenched with water, and then ether was added to obtain two layers, The ether layer, was extracted several times with oxalic acid solution and water, dried ($MgSO_4$), and filtered. The solution obtained was analyzed by vapor phase chromatography. Over 95% of the product was octalin, which was shown by infrared and vapor phase chromatography to be predominantly the $\Delta^{9,10}$ isomer. *trans*-9-Chlorodecalin was found to be stable to the acidic work-up conditions and to injection onto the vapor phase chromatography column with small amounts of oxalic acid.

The original procedure[11] employed diglyme–water as solvent

(11) H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962); H. M. Bell and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 1473 (1966).

(12) C. V. Wilson, *Org. Reactions*, **9**, 332 (1957); R. G. Johnson and R. K. Ingham, *Chem. Rev.*, **56**, 219 (1956).

(13) S. J. Cristol, J. R. Douglass, W. C. Firth, Jr., and R. E. Krall, *J. Org. Chem.*, **27**, 2711 (1962); S. J. Cristol and W. C. Firth, Jr., *ibid.*, **26**, 280 (1961); J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 2500 (1965).

(14) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *ibid.*, **83**, 3998 (1961). For recent applications, see J. C. Barborak, L. Watts, and R. Pettit, *ibid.*, **88**, 1328 (1966), and P. E. Eaton and T. W. Cole, Jr., *ibid.*, **86**, 3157 (1964).

(15) *E.g.*, see F. D. Greene, C-C. Chu, and J. Walia, *J. Org. Chem.*, **29**, 1285 (1964).

(16) G. J. M. van der Kerk, J. G. Noltes, and L. J. A. Luitjen, *J. Appl. Chem.* (London), **7**, 366 (1957).

(17) H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.*, **83**, 1246 (1961).

(18) Burton Manufacturing Co., Van Nuys, Calif., 2.2 w.

and potassium hydroxide to prevent hydrolysis of the borohydride. It was found that diglyme interfered with octalin on analysis by vapor phase chromatography, and the presence of the base was not needed. Under Brown's conditions, however, the same large yield of octalin was obtained.

Registry No.—*cis*-9-Chlorodecalin, 5597-83-1; *trans*-9-chlorodecalin, 5597-82-0; $(N\text{-}Bu)_3SnH$, 688-73-3; $(N\text{-}Bu)_3SnD$, 6180-99-0; $(N\text{-}Bu)_2SnH_2$, 1002-53-5; $(Ph)_3SnH$, 892-20-6.

Silacyclopentadiene Chemistry. I. 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene[1]

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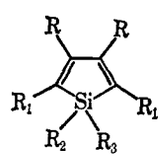
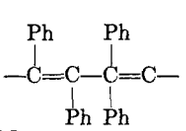
The preparation of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (VII) together with a brief investigation of the chemistry of this compound is described. In addition, a comparison of the ultraviolet properties of VII with those of other silacyclopentadienes is presented.

Unlike cyclopentadienes, the study of silacyclopentadienes has received little attention. The first silacyclopentadiene, 1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene (hexaphenylsilole I[2]), was prepared in 1959 by Braye and Hübel[2a] *via* reaction of a diphenylacetylene–iron–carbonyl complex $[Fe_2(CO)_6(PhC_2Ph)_2]$ with dichlorodiphenylsilane. Several years thereafter, these same workers[2b] synthesized I by treatment of 1,4-dilithiotetraphenylbutadiene with dichlorodiphenylsilane. The strong fluorescence and ultraviolet spectrum of I were reported at this time. A spirooctaphenyl-1-silacyclopentadiene derivative (II) was also prepared[2b,c] in low yield (*ca.* 1%).



I, R = R_1 = R_2 = R_3 = Ph

II, R = R_1 = Ph; R_2 = R_3 = 

III, R = R_1 = H; R_2 = R_3 = Me
IV, R = R_1 = Ph; R_2 = R_3 = Me
V, R = R_1 = Ph; R_2 = Me; R_3 = H
VI, R = R_1 = R_2 = Ph; R_3 = H
VII, R = H; R_1 = Ph; R_2 = R_3 = Me
VIII, R = R_1 = R_2 = Ph; R_3 = Me

1,1-Dimethyl-1-silacyclopentadiene (III) has been prepared by the catalytic dehydrogenation of 1,1-dimethyl-1-silacyclopentane[3] at high temperature. Compound III decolorized bromine solutions and reduced silver nitrate; however, the reaction products were not identified.[3a]

The reaction of 1,4-dilithiotetraphenylbutadiene with dichlorodimethylsilane was employed for the synthesis of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (IV).[4] This latter compound underwent Diels–Alder reactions with acetylenic dienophiles to give 7-silanorbornadienes.[4] A similar study has been carried out with 1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene (I).[5]

In a recent report,[6] 1,4-dilithiotetraphenylbutadiene was utilized in the synthesis of silacyclopentadienes functionality at the silicon, 1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (V) and 1,2,3,4,5-pentaphenyl-1-silacyclopentadiene (VI). In addition, numerous attempts[7] to prepare lesser substituted silacyclopentadienes by dehydrohalogenation of silacyclopentanes and silacyclopentenes have been reported by Benkeser, *et al.*

We now wish to report full details concerning the preparation and properties of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (VII), together with some reactions of the silacyclopentadiene ring system.[1,8]

Results and Discussion

1,1-Dimethyl-2,5-diphenyl-1-silacyclopentane (IX) was prepared from styrene, dichlorodimethylsilane, and lithium according to a published procedure.[9,10] Treatment of IX with N-bromosuccinimide (NBS) gave *trans*-2,5-dibromo-1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (X). Refluxing X in the presence of potassium acetate gave high yields of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (VII).

(1) Presented in part at the Division of Organic Chemistry, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstracts, p 100K.

(2) Since the silacyclopentadienes can be regarded as members of a general class of compounds designated as metaloles, the term "silole" has been used previously in naming these derivatives: (a) E. H. Braye and H. Hübel, *Chem. Ind. (London)*, 1250 (1959); (b) E. H. Braye, W. Hübel, and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961); (c) U. S. Patent 3,151,140 (1964); *Chem. Abstr.*, **61**, 16097 (1964).

(3) (a) J. Groubeau, T. Kolmar, and H. Hofman, *Ann.*, **659**, 39 (1962). (b) O. M. Nefedov and M. N. Manakov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 769 (1963); *Chem. Abstr.*, **59**, 8781 (1963).

(4) H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 1956 (1964).

(5) H. Gilman, S. G. Cottis, and W. H. Atwell, *ibid.*, **86**, 5584 (1964).

(6) K. Ruhlmann, *Z. Chem.*, **5**, 354 (1965).

(7) (a) R. A. Benkeser and G. M. Stanton, *J. Am. Chem. Soc.*, **85**, 834 (1963); (b) R. A. Benkeser, L. Noe, and Y. Nagai, *J. Org. Chem.*, **30**, 378 (1965); (c) R. A. Benkeser, Y. Nagai, J. L. Noe, R. F. Cunico, and Peter H. Gund, *J. Am. Chem. Soc.*, **86**, 2446 (1964).

(8) For a preliminary report of compound VII, see H. Gilman and W. H. Atwell, *J. Organometal. Chem.*, **2**, 291 (1964).

(9) D. R. Weyenberg, L. H. Toporcer, and A. E. Bey, *J. Org. Chem.*, **30**, 4096 (1965).

(10) O. M. Nefedov, M. N. Manakov, and A. D. Petrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1228 (1962). These workers did not determine the position of the phenyl substituents in IX. For a reported dehydrogenation of this 1,1-dimethyl-*x*,*x*′-diphenyl-1-silacyclopentane, see ref 3b.