room temperature, the opaque red suspension was titrated. There was 0.791 equivalent of acid and 0.239 equivalent of ester. The product was flashed under vacuum using a hot water bath. There was taken overhead 70 g. of distillate leaving 15 g. of somewhat viscous liquid residue. Titration of the distillate showed 0.701 equivalent of acid and 0.194 equivalent of ester and 2.1 g. of acrolein.

Oxidation of acrolein with selenium dioxide. To a suspension of 55.5 g. (0.5 mole) of selenium dioxide in 350 g. of *tert*-butyl alcohol was added 56 g. (1.0 mole) of acrolein all at once. The reaction was warmed and maintained at 40°. The color changed from white to red in about 0.5 hr. After standing overnight at room temperature, filtration of the mixture gave 40.7 g. of selenium. The filtrate was distilled at 50° (25 mm.). The colorless distillate contained no acid as shown by titration.

Formic acid catalyzed oxidation of acrolein. A slow consumption of peroxide took place when 1.15 moles of acrolein, 1.15 moles of hydrogen peroxide, and 1.0 mole of formic acid in 500 cc. of water was left at room temperature. After 8 days 77.5% of the H_2O_2 was gone and 0.84 mole of acid had been generated. Evaporation of the solvents at less than 50° left 84 g. of a very viscous water-soluble polymer with analysis indicative of a crude poly(acrylic acid).

Anal. Calcd. for $C_3H_4O_2$: C, 50.00; H, 5.59; Neut. equiv. 72. Found: C, 49.25; H, 6.31; Neut. equiv. 109.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

Studies in Organosilicon Chemistry. XXXIV. The Reaction of Trimethylsilylmethyl Metallic Compounds with Trichlorosilane

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Trichlorosilane and trimethylsilylmethylmagnesium bromide react in 2.5:1 molar ratio to form trimethylsilylmethyldichlorosilane, in 0.33:1 ratio to give bis(trimethylsilylmethyl)chlorosilane and in 0.30:1 ratio giving an 18.6% yield of tris(trimethylsilylmethyl)silane. Trichlorosilane and trimethylsilylmethyllithium react in 0.22:1 molar ratio forming tris(trimethylsilylmethyl)silane in 71% yield. The product undergoes bromination giving tris(trimethylsilylmethyl)bromosilane which can be hydrolyzed by aqueous ammonium hydroxide in acetone to form tris(trimethylsilylmethyl)silanol. Trimethylsilylmethyldichlorosilane undergoes hydrolysis to poly(trimethylsilylmethyl)siloxanes. Infrared absorption curves are presented for tris(trimethylsilylmethyl)silane, tris(trimethylsilylmethyl)silanol and poly(trimethylsilylmethyl)siloxanes, I(fraction 1), II(fraction 2), and III(fraction 3).

The steric effect of highly-branched groups in aliphatic organosilicon compounds is manifested in the reactivity or non-reactivity of certain functional groups attached to the silicon.[1,2,3,4,5] In line with some of this previously reported work, a series of compounds has been prepared and studied in which the trimethylsilylmethyl group has been substituted for one or more chlorines in trichlorosilane. Silanols containing large groups attached to silicon are quite stable toward condensation, in contrast with those with smaller groups.[6,7]

Trimethylsilylmethylmagnesium bromide reacts with trichlorosilane in various proportions, to form the mono-, the di-, and the trisubstitution products. Tris(trimethylsilylmethyl)silane reacts with bromine to form tris(trimethylsilylmethyl)bromosilane and this compound undergoes hydrolysis to form the corresponding silanol, isolable as such. (Trimethylsilylmethyl)dichlorosilane undergoes hydrolysis to give the trimeric and tetrameric forms of (trimethylsilylmethyl)siloxane. Trimethylsilylmethyllithium reacts with trichlorosilane to form tris(trimethylsilylmethyl)silane.

TABLE I

TRIMETHYLSILYLMETHYLSILANES

	B.P. °C	Mm.	n_D^{25}	d_4^{25}
$(CH_3)_3SiCH_2SiHCl_2$	52.0-53.5	24		
	146–148			
$[(CH_3)_3SiCH_2]_2SiHCl$	79–80	5		
$[(CH_3)_3SiCH_2]_3SiH$	108[a]	9[a]	1.4495[a]	0.8221[a]
	103–107[b]	8[b]	1.4498[b]	
$[(CH_3)_3SiCH_2]_3SiBr$	110	1.8	1.4725	
$[(CH_3)_3SiCH_2]_3SiOH$	112–113	5.0	1.4540	0.8594

[a] Through the Grignard reagent. [b] Through the organolithium compound.

Infrared absorption curves (Fig. 1) are presented for the first of the polymeric materials listed in Table II, as well as for tris(trimethylsilylmethyl)silane, and for tris(trimethylsilylmethyl)silanol. The scanning speed was one micron per minute, with a normal slit, and a sample cell of 0.025 mm. The reference was air at 24° with no solvent.

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TABLE II

POLYMERIC HYDROLYSIS PRODUCTS

	B.P., °C	Mm.	n_D^{25}	d_4^{25}	Mol. Wt.	MR
$[(CH_3)_3SiCH_2SiHO]_x$	105–108	1	1.4383	0.9027	368	115.2
$[(CH_3)_3SiCH_2SiHO]_y$	143	1	1.4433	0.9283	490 516	150.9
$[(CH_3)_3SiCH_2SiHO]_z$	166–168	1	1.4458	0.9355	517	150.4
Calculated for trimer					396	113.5
Calculated for tetramer					528	151.3

EXPERIMENTAL

Trimethylbromomethylsilane. This compound was prepared by the method of Speier,[8] and of Noller and Post.[9]

Trimethylsilylmethylmagnesium bromide was prepared in accordance with a procedure outlined by Willard Keeber[10] of the University of Buffalo, by the action of magnesium on trimethylbromomethylsilane, in absolute ether, under an atmosphere of dry nitrogen.

Lithium (6.9 g., 1.0 mole) and 250 cc. of mineral oil were placed in a dry 500 cc. three-necked flask and blanketed with dry oxygen-free, nitrogen. The flask was heated until the lithium had melted, then closed and shaken until the lithium had solidified in the form of a dry sand. After cooling, the mineral oil was decanted and the lithium was washed by repeated addition and decantation of 50 cc. portions of anhydrous ether, under a stream of nitrogen. Trimethylbromomethylsilane (73.5 g., 0.44 mole) dissolved in 200 cc. anhydrous ether was then added dropwise over a period of 3 hr. Cooling was provided to maintain the reaction temperature at −15° to −5°. After the addition had been completed, the reaction mixture was allowed to warm up to room temperature and stand overnight, forming trimethylsilylmethyllithium.

Trimethylsilylmethyldichlorosilane. Trimethylsilylmethylmagnesium bromide (0.2 mole) was prepared as described above and added to 50 cc. (0.5 mole) of trichlorosilane in 200 cc. of anhydrous ether, dropwise, over a 3-hr. period. The temperature was maintained below 10° by means of an ice bath but after addition had been completed, the mixture was allowed to warm to room temperature and stand overnight. The liquid was then decanted under an atmosphere of nitrogen and distilled yielding trimethylsilylmethyldichlorosilane, 24 g., 64% yield, b.p. 52.0–53.5° (24 mm.), 146–148° (760 mm.).

Anal. Calcd. for $C_4H_{12}Cl_2Si_2$: Cl, 37.94. Found: Cl, 34.50.

Bis(trimethylsilymethyl)chlorosilane. In a manner similar to that described above, 10 cc. (0.1 mole) of trichlorosilane was allowed to react with 0.3 mole of trimethylsilylmethylmagnesium bromide. Fractionation yielded only 0.8 g. (13.3% yield) of contaminated bis(trimethylsilymethyl)-chlorosilane, b.p. 79–80° (5 mm.).

Anal. Calcd. for $C_8H_{23}Si_3Cl$: Cl, 14.9. Found: Cl, 13.9. A higher fraction, 9.5 g., 32.7% yield, b.p. 100–106° (6 mm.), n_D^{25} 1.4501, was probably tris(trimethylsilylmethyl)-silane. It contained no chlorine.

Tris(trimethylsilylmethyl)silane. Trimethylsilylmethylmagnesium bromide (0.5 mole) in 300 cc. of absolute ether was prepared as before. Trichlorosilane (15 cc., 0.15 mole) dissolved in 100 cc. of absolute ether was then added dropwise over a period of 2 hr. A slightly positive nitrogen pressure was maintained throughout, and the reaction temperature was kept at between 0° and 5° by means of an ice bath. After addition had been completed the reaction mixture was allowed to warm to room temperature and stand overnight. After pouring into 100 cc. of cold water with 5 cc. of concentrated sulfuric acid the organic layer was separated. Fractionation yielded 27.3 g. of tris(trimethylsilylmethyl)silane, 18.6%, b.p. 100° (6 mm), 110–112° (10 mm), n_D^{25} 1.4489–1.4495, d_4^{25} 0.8221.

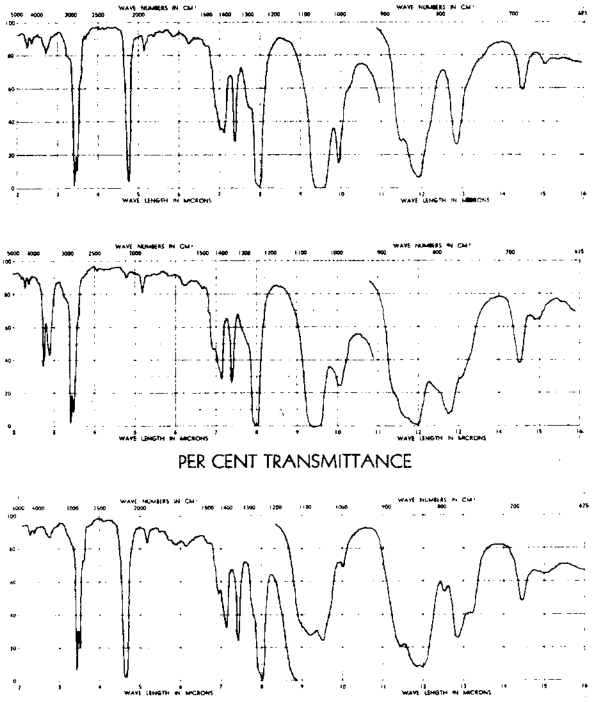

FIG. 1. INFRARED SPECTRA OF: $[(CH_3)_3SiCH_2]_3SiH$ (TOP), $[(CH_3)_3SiCH_2]_3SiOH$ (CENTER), AND $[(CH_3)_3SiCH_2SiHO]_4$ (BOTTOM)

Anal. Calcd. for $C_{12}H_{34}Si_4$: C, 49.66; H, 11.7; Si, 38.68; Mol. wt., 290; M.R., 97. Found: C, 50.08; H, 11.62; Si, 37.8, 38.2; Mol. wt., 286, 283, 272; M.R. 96.

Trimethylsilylmethyllithium (0.44 mole) was prepared as described above and treated with 10 cc. (0.1 mole) of trichlorosilane in 10 cc. of absolute ether, added dropwise over a 2-hr. period. Cooling was required to maintain the temperature between −15° and −10°. A slight positive pressure of dry oxygen-free nitrogen was also maintained. After addition had been completed, the system was allowed to warm to room temperature and was stirred for 2 hr. After distillation of the ether, the temperature was kept at 70° for an additional hour, then poured into acidified water. The solids were washed with three 100 cc. portions of ether and the washings added to the decanted organic layer. Alcohol was added to the solids remaining in the reactor and the mixture slowly poured into water. There is danger of fire at this point. Organic layer and ether were stirred with water for 15 min., then separated and the organic layer dried over sodium sulfate. Fractionation gave 20.7 g. 71% yield, of tris-(trimethylsilylmethyl)silane, b.p. 103–107° (8 mm), n_D^{25} 1.4498.

Poly(trimethylsilylmethyl)siloxane. Trimethylsilylmethyldichlorosilane (24.0 g., 0.13 mole) was added dropwise, with stirring, to 200 cc. of ether containing 20 cc. of water. The *p*H of the resulting system was adjusted to approximately

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(9) D. C. Noller and H. W. Post, *J. Org. Chem.*, **17**, 1393 (1952).

(10) W. H. Keeber, Private Communication.

seven by the addition of 32.0 g. of two percent aqueous ammonium hydroxide. The ether layer was separated and dried over sodium sulfate. After removal of the ether by distillation, 18.2 g. of liquid remained. Fractionation produced 1.1 g. of product, b.p. 105–108° (1 mm) n_D^{25} 1.4383, d_4^{25} 0.9027, 3.0 g. of material, b.p. 143° (1 mm), n_D^{25} 1.4433, d_4^{25} 0.9283 and 1.8 g., b.p. 166–168° (1 mm), n_D^{25} 1.4458, d_4^{25} 0.9355.

Anal. Calcd. for trimer, Mol. wt., 396; M.R. 113; for tetramer, Mol. wt., 538; M.R., 151. Found: *first fraction,* Mol. wt., 368; M.R., 115.2. Second fraction, mol. wt., 503 (average); M.R., 150.9. Third fraction, Mol. wt., 517; M.R., 150.4.

The second fraction is probably a mixture of the first and third.

Tris(trimethylsilylmethyl)bromosilane. Tris(trimethylsilylmethylsilane (18 g., 0.06 mole), in 300 cc. of carbon tetrachloride was placed in a 500 cc. three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. Bromine (13 g., 0.08 mole) in 100 cc. of carbon tetrachloride was added dropwise over a 2-hr. period. After approximately one half of the bromine had been added the reaction slowed up markedly. The flask was then illuminated with a 200 watt bulb, then allowed to stand for 50 hr. at room temperature with continued illumination. It was then heated to reflux and a stream of nitrogen passed through it for 1 hr. After cooling, a 5% aqueous solution of ammonium hydroxide (60 cc.) was then added and this mixture stirred for 30 min. The aqueous layer was then removed (*p*H approximately 10 by Alkacid test paper). Fractionation produced tris(trimethylsilylmethyl)bromosilane, 4.3 g., b.p. 110° (1.8 mm), n_D^{25} 1.4725, 20% yield.

Anal. Calcd. for $C_{12}H_{33}BrSi_4$: Br, 21.7. Found: Br, 22.1.

Tris(trimethylsilylmethyl)silanol. Tris(trimethylsilylmethyl)bromosilane (10 g., 0.03 mole) in 30 cc. of acetone was treated with 6.6 g. of 10% aqueous ammonium hydroxide (0.046 mole). The mixture was stirred for 2 hr. at room temperature, and the layers separated. The aqueous layer was slightly basic. The organic layer was dried over sodium sulfate and the acetone evaporated. There remained 9 g. of liquid which was fractionated yielding 3.7 g. of tris(trimethylsilylmethylsilyl)silanol, b.p. 112–113° (5.0 mm.), n_D^{25} 1.4540, d_4^{25} 0.8594, yield 40%.

Anal. Calcd. for $C_{12}H_{34}OSi_4$: C, 47.06, H, 11.11; Si, 36.68; Mol. wt., 306; M.R. 97. Found: C, 47.87; H, 10.93; Si, 35.8, 36.6, 36.5; mol. wt., 295; M.R., 96.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Stable Organic Biradicals

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The preparations of seventeen glycols, two of the corresponding glycol ethers and eleven of the corresponding chlorides are described. While only somewhat more than half of these substances constitute new compounds, the present procedures are superior to previously reported methods of synthesis and are of general applicability to all compounds of this type, bis-triarylmethanol where the alcohol centers are separated by at least one aromatic ring. Ten of the chlorides were converted by treatment with "molecular" silver to potential biradicals of the bis-triarylmethyl type. Of these, seven had been previously prepared and declared to be non-radical in character. One of them, the Tschitschibabin hydrocarbon (XXIX A), however, has more recently been shown to possess radical character by its paramagnetic resonance (ESR) spectrum. All ten potential radicals were examined by the ESR technique, and all but one, the Thiele hydrocarbon (XVII), were shown to absorb micro waves of the resonant frequency. The results make it clear that if no interaction between the two "odd" electrons of a biradical (*e.g.*, quinoidation) can be envisioned in terms of Kekule structures, the substance will be a biradical. If interaction is possible, the detectability of radical character will depend upon the energy difference between the state involving interaction and the state in which the electrons are unpaired.

The problem posed by the possible interconversion of singlet (quinoid) and triplet (biradical) states in certain types of organic molecules is an intriguing one, and the type of compound potentially capable of such interconversion is very nearly as old as the stable free radical itself.[2] However, from the period 1904–1907 when the first attempts to prepare the quinoid forms (see below) were published until the late 1920's, no interest seems to have attached to the problem. As will become apparent in the sequel (see Discussion) early attempts to provide criteria for judging the radical character of biradicals were not altogether satisfactory. Of the ten potential biradicals selected for the present study seven had been examined before and considerable confusion is apparent in the literature as to the problem of quinoid-biradical interconvertibility and the nature of biradicals with "insulated" radical centers. It is the purpose of this paper and the previously published theoretical treatment of the paramagnetic resonance study[3] to provide an answer to the question posed by earlier work: When can one expect interaction between the "odd" electrons of a biradical? The present paper does not treat the theoretical findings in detail but is chiefly concerned with improved methods for the preparations of certain organic biradicals and the intermediates necessary for their syntheses, and with the general conclusions based upon the ESR data.

The species of biradical selected for study are of the bis-triarylmethyl type where the radical centers are separated by various groups which serve

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