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NEW COMPOUNDS

Tetraalkylsilanes via Hydrosilylation of 1-Alkenes

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Tetraalkylsilanes carrying one short and three long alkyl groups were synthesized via a two-step hydrosilylation procedure, which appears more suited for commercial production than previously employed Grignard or alkyllithium routes. The viscosities of two component blends were adequately treated by the ASTM D-341 procedure. The thermal stabilities of some silahydrocarbons and model paraffins, as measured by the loss of their 40 °C viscosity, were determined at 371 °C.

Synthesis of Tetraalkylsilanes

We have prepared a series of tetraalkylsilanes, referred to as silahydrocarbons to stress their hydrocarbon-like properties, via a two-step hydrosilylation procedure, and found their viscosities comparable to similar compounds prepared via the Grignard or alkyllithium routes (*1*, *2*). For example, reaction of methyldichlorosilane with 1-octene or 1-decene gave the corresponding dialkyldichlorosilanes (eq 1), which were then reduced to dialkylsilanes (eq 2), and the latter were subjected to a second hydrosilylation with 1-octene or 1-decene to give the desired silahydrocarbon (eq 3). The advantage of using a two-step hydrosilylation lies in the commercial availability of methyldichlorosilane and because the higher molecular weight dialkylsilane intermediates are not pyrophoric and are easy to handle on a large scale. Reduction of chlorosilanes was conveniently carried out with lithium aluminum hydride (LAH, 100% excess) (*3*), but less costly procedures based on sodium hydride could be developed (*4*-*9*). The catalyst used in the first reaction (eq 1) was platinum, and in the second reaction (eq 3) it was platinum or rhodium. The products were isolated by distillation in yields of ~75-86; our primary concern was to obtain purities of at least 98%.

$$CH_3SiCl_2H + H_2C{=}CHR \rightarrow CH_3SiCl_2CH_2CH_2R \qquad (1)$$

$$2CH_3SiCl_2CH_2CH_2R + LiAlH_4 \rightarrow 2CH_3SiH_2CH_2CH_2R + AlCl_3 + LiCl \qquad (2)$$

$$CH_3SiH_2CH_2CH_2R + 2H_2C{=}CHR \rightarrow CH_3Si(CH_2CH_2R)_3 \qquad (3)$$

Viscosity Correlations

A plot of viscosities against the carbon number of tetraalkylsilanes (Figure 1) for compounds listed in Table I, and some viscosities taken from the literature, gave a series of fan-shaped curves. Many of the tetraalkylsilanes had high melting points, which precluded measurement of their viscosities at temperatures below −20 °C. By synthesizing methyltrialkylsilanes, where R is a mixture of octyl and decyl groups, we found that the products were fluid even below −54 °C, the anticipated storage temperature in the Arctic region. A comparison of silahydrocarbon viscosities with a typical commercial fluid (4 mm^2/s Synfluid) is shown in Figure 2. The data show that, at temperatures above 38 °C, the viscosities for the two classes of fluids are about equivalent; at lower temperatures, however, the viscosities of silahydrocarbons were lower than those of the Synfluid.

The viscosity data for two component blends, either all silahydrocarbon (Table I) or silahydrocarbon/Synfluid mixtures (Table II), are adequately treated by the ASTM D-341 procedure, which is based on Walther's classical equations. This behavior may not be too surprising as both classes of fluids are considered to have geometries consisting of dense centers.

In our experience, D-341 procedure gave calculated viscosities that were close to the measured viscosities but the method was tedious to use without a computer. Calculations using Roegier's equation were just as effective and much simpler to carry out with a calculator. While the applicability of the Roegier's equation to untested fluids may be questionable, in our work with silahydrocarbons and Synfluids, a good correlation between the calculated and experimental viscosities was obtained at all temperatures (±2%). Calculations based on D-341 procedure showed deviations of up to ±5% at low temperature (-54 °C) (Table II), particularly when the viscosity difference between the fluids was large.

Thermal Stability

Along with viscosity, an important property of hydraulic fluids for use at elevated temperatures is the thermal stability, which is determined by exposing the fluid under nitrogen to 371 °C for 6 h and measuring the loss of its 40 °C viscosity (Penn State method) (*1*). The effect of structure of the fluid on thermal

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Table I. Viscosities of Some Silahydrocarbons

silahydrocarbon	bp, °C (mmHg)	viscosity, mm^2/s -54 °C	-40 °C	-18 °C	38 °C	99 °C
$CH_3Si(C_8H_{17})_3$	188–189 (0.9)	1417	388	80.11	7.98	2.35
$CH_3Si(C_8H_{17})_2(C_{10}H_{21})$	200 (0.55)	1944	529	102.6	9.50	2.70
$CH_3Si(C_8H_{17})(C_{10}H_{21})_2$	200–206 (0.3)	2954	733	134.0	11.45	3.09
$CH_3Si(C_{10}H_{21})_3$	230–233 (0.95)	(4060)[a]	969	169.5	13.39	3.47
$CH_3Si(C_8H_{17})_3/CH_3Si(C_{10}H_{21})_3$ (2:1 M)		2067	537	105.1	9.66	2.72
		2095[b]	546[b]	106[b]	9.69[b]	2.72[b]
		2027[c]	530[c]	103[c]	9.51[c]	2.68[c]
(1:2 M)		2937	731	134.6	11.50	3.11
		2960[b]	740[b]	136[b]	11.51[b]	3.08[b]
		2875[c]	719[c]	133[c]	11.30[c]	3.06[c]
$CH_3Si(C_8H_{17})_2(CH_2)_3CH(CH_3)_2$	170 (0.9)	1810	421	76.8	6.88	2.04
$C_2H_5Si(C_8H_{17})_3$	201–205 (1.2)	1474	412	87.1	8.71	2.43
$C_2H_5Si(C_{10}H_{21})_3$	228–230 (0.9)	(4400)[a]	978	180.4	14.33	3.63
$C_2H_5Si(C_8H_{17})_3/C_2H_5Si(C_{10}H_{21})_3$ (2:1 M)		2127	570	112.9	10.44	2.88
		2170[b]	569[b]	114[b]	10.52[b]	2.82[b]
		2100[c]	552[c]	112[c]	10.31[c]	2.78[c]
(1:2 M)		3031	756	144.5	12.29	3.27
		3123[b]	758[b]	145[b]	12.41[b]	3.23[b]
		2979[c]	737[c]	142[c]	12.17[c]	3.18[c]

[a] Extrapolated values. [b] Calculated viscosities according to ASTM D-341 blending equations. [c] Calculated viscosities according to Roegier's equation.

Table II. Viscosities of Silahydrocarbon/Synfluid Mixtures

fluid composition	viscosity, mm^2/s -54 °C	-40 °C	-18 °C	38 °C	99 °C
4 mm^2/s Synfluid	10974	2042	284	16.43	3.65
silahydrocarbon fluid	1788	469	93.6	8.89	2.54
75% Synfluid, 25% silahydrocarbon	6482	1349	210	13.91	3.31
	6684[a]	1376[a]	211[a]	13.92[a]	3.31[a]
	6565[b]	1346[b]	207[b]	13.81[b]	3.29[b]
50% Synfluid, 50% silahydrocarbon	3993	922	155.6	11.87	3.02
	4191[a]	942[a]	159[a]	11.89[a]	3.02[a]
	4102[b]	920[b]	156[b]	11.77[b]	3.00[b]
25% Synfluid, 75% silahydrocarbon	2599	650	120.8	10.25	2.77
	2696[a]	660[a]	121[a]	10.39[a]	2.77[a]
	2663[b]	648[b]	119[b]	10.17[b]	2.75[b]

[a] Calculated viscosities according to ASTM D-341 blending equations. [b] Calculated viscosities according to Roegier's equation.

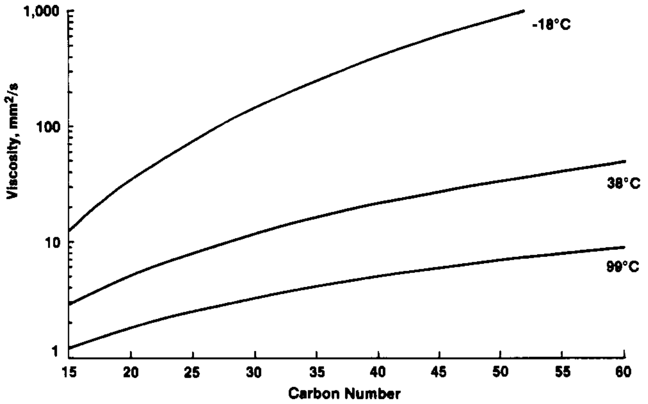

Figure 1. Silahydrocarbon viscosity vs carbon number.

stability is shown for several model hydrocarbons in Table III. It appears that as the number of tertiary hydrogens increases, the thermal stability decreases. This result is consistent with the fact that tertiary C–H bonds have the lowest bond dissociation energy (91 kcal/mol) (*11*) and therefore could be the weak links in the fluid. In the area of silahydrocarbons (Table IV), a similar behavior was observed as with the paraffins. Tetraalkylsilanes carrying no tertiary hydrogens were the most stable, while introduction of tertiary hydrogen into the structure of silahydrocarbon, depending on position, caused the stability

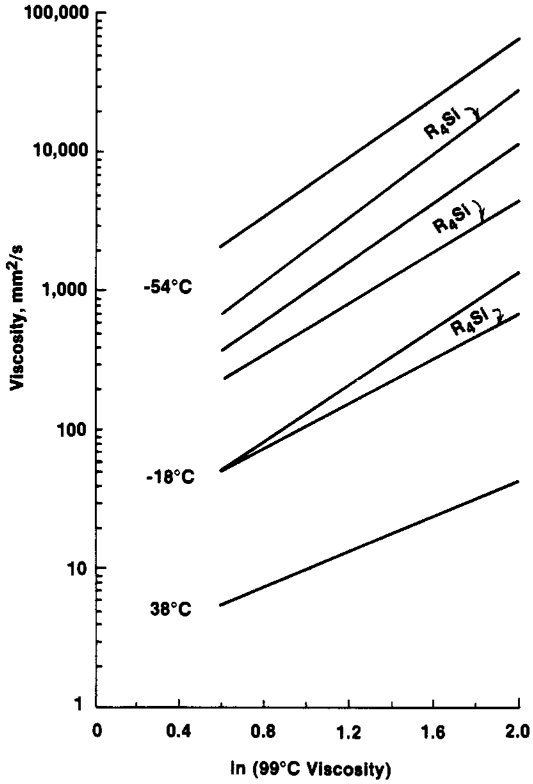

Figure 2. Comparison of silahydrocarbon and Synfluid viscosities.

Table III. Thermal Stability of Some Hydrocarbons[a]

fluid	carbon no.	40 °C viscosity loss, %
eicosane	20	3.6
9-methylnonadecane	20	11.1
2,4-dimethyloctadecane	20	15.1
2,6,10,14-tetramethylpentadecane	19	22.3
13-methylheptacosane	28	11.5
2,6,10,15,19,23-hexamethyltetracosane	30	41.8
hydrogenated 1-decene dimer[b]	20	29.0
hydrogenated 1-decene trimer[b]	30	58.6

[a] 371 °C, 6 h, N_2, sealed stainless steel tube. [b] Fraction isolated from commercial 4 mm^2/s Synfluid by distillation.

Table IV. Thermal Stability of Some Silahydrocarbons[a]

fluid	carbon no.	40 °C viscosity loss, %
$CH_3Si(C_8H_{17})_3$	25	10.8
$CH_3Si(C_{10}H_{21})_2(C_8H_{17})$	29	10.6
$(CH_3)_2CHSi(CH_3)_2C_{14}H_{29}$	19	10.6
$CH_3Si(C_8H_{17})_2(CH_2)_3CH(CH_3)_2$	23	14.1
$CH_3Si[CH_2CH(C_2H_5)(C_4H_9)]_3$	25	40.0 (ref *1*)

[a] 371 °C, 6 h, N_2, sealed stainless steel tube.

of the fluid to vary. For example, the presence of a tertiary hydrogen near the end of the alkyl chain (exposed) such as in $MeSi(C_8H_{17})_2(CH_2)_3CHMe_2$, or in the β-position relative to silicon as in $MeSi[CH_2CH(Et)Bu]_3$, made the molecule less stable. On the other hand, the presence of tertiary hydrogen in the α-position relative to silicon as in $Me_2CHSi(Me)_2C_{14}H_{29}$ made the molecule more stable. This appears to be due to the shielding effect of silicon with stabilizes radicals in the α-position (*12*). The products of thermal degradation of silahydrocarbons and the mechanisms by which they occur need to be determined before meaningful structure property relationships are developed.

Toxicology Study

Toxicology studies on tetraalkylsilanes were carried out to determine eye irritation and the dermal LD50 test on rabbits. In the eye test, a rating of 1 was observed on a scale of 0 to 5 (0 = nonirritating, 1 = mildly irritating, and 5 = extremely irritating), indicating the product to be only mildly irritating to washed and unwashed eyes. On a skin test after 24-h dermal exposure (2 g of R_4Si/kg), no adverse effects were noted, and no deaths of animals occurred, indicating tetraalkylsilanes to be essentially nontoxic.

Experimental Section

All reactions were carried out at atmospheric pressure in standard laboratory glassware under nitrogen. Chromatographic analyses were performed on a Hewlett-Packard 5880A (FID) chromatograph, using a 25-m, 2% OV-101, fused silica capillary column, programmed from 50 to 300 °C at 8 deg/min. The ^1H NMR spectra were recorded on a Varian T-60 spectrometer, usually in carbon tetrachloride or acetone-d_6. The chemical shifts are in δ units (ppm) relative to Me_4Si (s = singlet, d = doublet, t = triplet, m = multiplet). The IR spectra were recorded on a Perkin-Elmer Model 597 spectrometer. The platinum catalysts were purchased from various commerical sources.

***Preparation of Methyloctylsilane*.** To a stirred slurry of LAH (48 g) in ether (600 mL) was added methyloctyldichlorosilane (244 g) in ether (150 mL) over 3 h (*3*). The mixture was then heated at reflux (16 h) and cooled. The reaction product was treated cautiously with cold water (~200 mL) over 1 h. The ether layer was washed with water, dried (anhydrous $MgSO_4$), and stripped of solvent to give water white methyloctylsilane (166 g, 97%). GLC, 99.4%, retention time about half of the starting silane; IR, 2063 cm^{-1} (s) (R_2SiH_2); NMR, δ 3.62 (m, 2 H, SiH_2).

***A Typical Hydrosilylation Procedure*.** A mixture of methyloctylsilane (130 g), methyldecylsilane (60 g), 1-octene (510 g), and 1-decene (210 g) was stirred at 130 °C in the presence of 5% Pt/C (1.0 g, saturated with air for ~10 min prior to use in 10 mL of *n*-octane). After 2 h, the reaction stopped due to catalyst deactivation. The reaction mixture was cooled to room temperature, saturated with air for ~2 min, and then reheated to 130 °C. After 2 h, the reaction was complete. The product after filtering was distilled, bp 170–196 °C (~0.2 mmHg), to give an 85% yield of tetraalkylsilanes: methyltrioctylsilane, 48%; methyldioctyldecylsilane, 34%;, methyldidecyloctylsilane, 15%; and methyltridecylsilane, 3% (*13*).

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Appendix

Roegier's equation, ref *10*, is as follows

$$\eta_m = (\eta_L)(\eta_H/\eta_L)^{(KX_H/KX_H+1-X_H)}$$

where η_m is the viscosity of the mixture, mm^2/s, η_L is the viscosity of the lighter component, η_H is the viscosity of the heavier component, X_H is the weight fraction of the heavier component, and K is 0.845, the experimentally determined blending factor.

Registry No. $CH_3Si(C_8H_{17})_3$, 3510-72-3; $CH_3Si(C_8H_{17})_2(C_{10}H_{21})$, 83094-48-8; $CH_3Si(C_8H_{17})(C_{10}H_{21})_2$, 83584-71-8; $CH_3Si(C_{10}H_{21})_3$, 18769-78-3; Pt, 7440-06-4; $CH_3Si(C_8H_{17})_2(CH_2)_3CH(CH_3)_2$, 111324-79-9; $C_2H_5Si(C_8H_{17})_3$, 83094-46-6; $C_2H_5Si(C_{10}H_{21})_3$, 83094-47-7; $(CH_3)_2CHSi(CH_3)_2C_{14}H_{29}$, 111324-80-2; $CH_3Si[CH_2CH(C_2H_5)(C_4H_9)]_3$, 83094-43-3; methyloctyldichlorosilane, 14799-93-0; methyloctylsilane, 80204-10-0; methyldecylsilane, 109528-85-0; 1-octene, 111-66-0; 1-decene, 872-05-9; eicosane, 112-95-8; 9-methylnonadecane, 13287-24-6; 2,4-dimethyloctadecane, 61866-10-8; 2,6,10,14-tetramethylpentadecane, 1921-70-6; 13-methylheptacosane, 15689-72-2; 2,6,10,15,19,23-hexamethyltetracosane, 111-01-3.

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