maintained at 5°. An additional 29 g. of *p*-toluene sulfonyl chloride and 50 ml. of 25% sodium hydroxide were added during 1.5 hr. After additional stirring for 3 hr. at 5°, the mixture was poured into water and filtered. The solid product was dissolved in ether, dried with potassium carbonate, reprecipitated by cooling with Dry Ice, and centrifuged. Residual solvent was evaporated and the product was crystallized from benzene–hexane at low temperature. Yields by this procedure were about 70%. (Note: During one such run, the product polymerized spontaneously while being stored overnight in the refrigerator during recrystallization.)

The resulting benzyl-*α*-*d* tosylate was added to a solution of 20 g. of sodium azide in 58 ml. of water and 260 ml. of methanol and maintained at 60° for 1 day. The mixture was diluted with water and extracted with ether. The washed and dried ether solution was treated with 10 g. of lithium aluminum hydride in the usual manner. The reaction mixture was decomposed with water and the washed and dried ether solution was distilled giving 11.7 g. (54%) of amine, b.p. 72–95° (10–11 mm.), contaminated by some benzyl alcohol (infrared).

The combined product from two such runs was dissolved in dilute hydrochloric acid and washed with ether. The aqueous solution was made basic with sodium hydroxide and extracted with ether. The dried extract was distilled and the residue was fractionated giving two fractions: fraction 1, b.p. 79.5–81° (17 mm.), 9.6 g., $\alpha^{25}\mathrm{D}$ 0.940 ± 0.006°, $\alpha^{25}{}_{5463}$ 1.087 ± 0.003° (*l* 4); fraction 2, b.p. 81–83° (18–19 mm.), 9.5 g., $\alpha^{25}\mathrm{D}$ 0.941 ± 0.005° $\alpha^{25}{}_{5463}$ 1.105 ± 0.011° (*l* 4). The combined product had $n^{25}\mathrm{D}$ 1.5404; freshly fractionated benzylamine had $n^{25}\mathrm{D}$ 1.5410.

(−)-**Benzyl-*α*-*d* Alcohol from** (+)-**Benzylamine**-*α*-*d*.—A mixture of 9.8 g. of the benzylamine-*α*-*d*, 26.2 g. of 88% formic acid and 25.7 g. of 37% formalin was heated at 95–100° until a vigorous evolution of gas commenced. The flask was removed from the oil bath and when the reaction subsided, 25.7 g. of the formalin and 26.2 g. of 88% formic acid were added and the mixture was refluxed for 8 hr. After cooling, 75 ml. of 4 *N* hydrochloric acid was added and the mixture was evaporated *in vacuo* to a thick sirup. The mixture was diluted with water, made basic with sodium hydroxide, and extracted with ether. Evaporation of the solvent left a pale yellow liquid which was difficult to distil because of excessive foaming; hence, the crude product was stirred with 30 g. of methyl iodide and 90 ml. of ether for 2 hr. in an ice bath and 14 hr. at room temperature. The trimethylbenzyl-*α*-*d*-ammonium iodide was filtered, washed with ether, and dried *in vacuo;* yield, 22.7 g. (90% from amine).

A solution of this product in 250 ml. of water was treated with a suspension of silver oxide in 125 ml. of water prepared from 68 g. of silver nitrate.[8] After stirring for 8 hr., the mixture was filtered with Filter-aid and the solid was washed with water. To the combined aqueous solutions was added 69 g. of glacial acetic acid. The mixture was evaporated to a thick sirup which was distilled *in vacuo*. The distillate was dissolved in ether, washed, dried and distilled, yielding 7.5 g. (55% from amine) of benzyl-*α*-*d* acetate, b.p. 98–99° (10–11 mm.), identified by the infrared spectrum. Reduction in the usual way with lithium aluminum hydride gave benzyl-*α*-*d* alcohol, $\alpha^{27}\mathrm{D}$ −0.355 ± 0.004°, $\alpha^{25}{}_{5463}$ −0.431 ± 0.004° (*l* 2). The alcohol was converted to the hydrogen phthalate, recrystallized from benzene–cyclohexane and again reduced to alcohol with lithium aluminum hydride giving benzyl-*α*-*d* alcohol, b.p. 92–94° (7–8 mm.), $\alpha^{25}\mathrm{D}$ −0.352 ± 0.005°, $\alpha^{25}{}_{5463}$ −0.418 ± 0.012° (*l* 2).

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Organosilicon and Tin Alkylthiols

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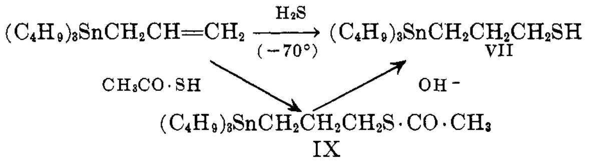
Only a few organometallic alkylthiols have been described previously. Marvel and Cripps[1] prepared bismethylbis(propyl-3-thiol)silane by saponification of the respective thiolacetate. Later[2] several additional silicon-containing thiols were synthesized by this method. Noller and Post[3] prepared methylthioltrimethylsilane by alkaline hydrolysis of its isothiouronium bromide; Cooper[4] and Schmidt and Wieber[5] described the synthesis of methylthiolsiloxanes from chloromethylsiloxanes and potassium hydrosulfide. Only one publication[6] has become known describing the direct addition of hydrogen sulfide to unsaturated organosilanes at high temperatures and under pressure. However, the principal reaction products were organosilicon sulfides. Organosilicon alkylthiols were only identified as by-products in yields below 10%.

No organotin alkylthiols are reported in the literature. Noltes and van der Kerk[7] attempted the synthesis of propyl-3-thioltriphenyltin by the addition of triphenyltin hydride to allyl mercaptan, but obtained propene, H_2S, and bis(triphenyltin)sulfide instead. And Seyferth[8] observed only cleavage of vinyltin compounds by mercaptans as well as other electrophilic reagents.

This note describes the synthesis of the first reported organotin alkylthiols by two different routes and a new method for the preparation of organosilicon alkylthiols. These methods consist of either radiation-induced free-radical ("anti-Markovnikov") addition of hydrogen sulfide to olefinic unsaturated organometallic compounds at Dry Ice bath temperatures, or free-radical addition of thiolacetic acid at or below room temperature, followed by alkaline hydrolysis. The alkylthiols obtained by both methods were identical as demonstrated with tributylallyltin in the following example.



$$\begin{tikzcd}
(C_4H_9)_3SnCH_2CH{=}CH_2 \arrow[rr, "H_2S", "(-70°)"'] \arrow[dr, "CH_3CO\cdot SH"'] & & \underset{\text{VII}}{(C_4H_9)_3SnCH_2CH_2CH_2SH} \\
& \underset{\text{IX}}{(C_4H_9)_3SnCH_2CH_2CH_2S\cdot CO\cdot CH_3} \arrow[ur, "OH^-"'] &
\end{tikzcd}$$

A quartz mercury vapor lamp was the most effective source of radiation, especially if used in connection with the quartz reactor described in the Experimental reaction. Considerably lower yields were obtained in Vycor flasks and also with long wave ultraviolet light.

The primary mercaptan structure was unequivocally confirmed by 60-Mc. n.m.r. spectra.[9]

Main by-product of the hydrogen sulfide addition was sulfide, which—as shown by independent experiments—was formed by the following reaction.

$$(C_4H_9)_3Sn(CH_2)_3SH + CH_2{=}CH{\cdot}CH_2Sn(C_4H_9)_3 \xrightarrow{h\nu} [(C_4H_9)_3Sn(CH_2)_3]_2S$$

In order to suppress this side reaction a larger excess of hydrogen sulfide was employed. The use of low-boiling aliphatic hydrocarbon diluents influenced favor-

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[1] C. S. Marvel and H. N. Cripps, *J. Polymer Sci.*, **9**, 53 (1952).

[2] V. F. Mironov and N. A. Pogonkina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.* 85 (1959).

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TABLE I

COMPOUNDS PREPARED

	Compound	B.p., °C. (mm.)	n^{25}D	Sulfur, %		Metal, %		Infrared SH frequency
				Calcd.	Found	Calcd.	Found	
I	$Me_3Si(CH_2)_2SH$[2]	40 (18) 143 (760)	1.4515	23.9	23.75	20.8	19.9	3.94
II	$(Me_3SiCH_2CH_2)_2S$	39 (0.05) 268 (760)	1.4620	13.75	13.70	24.05	23.85	
III	$Me_3Si(CH_2)_3SH$[2]	53 (16) 164 (760)	1.4538	21.65	21.60	18.95	18.64	3.94
IV	$(Me_3SiCH_2CH_2CH_2)_2S$	46 (0.05) 66 (0.5)	1.4621	12.24	12.25	21.41	21.19	
V	$(Me_3SiCH_2CH_2)_2SO_2$	123 (m.p.)		12.02	11.96	21.08	20.95	
VI	$Bu_3Sn(CH_2)_2SH$	70–80 dec. (0.2)	1.5068	9.10	8.73	33.76	33.9	(3.75) 3.80 (3.89)
VII	$Bu_3Sn(CH_2)_3SH$	91 (0.1)	1.5025	8.78	8.72	32.62	33.40	(3.76) 3.80 (3.90)
VIII	$Bu_3Sn(CH_2)_2S{\cdot}CO{\cdot}CH_3$	115 (0.2)	1.5006	8.18	8.14	30.20	30.20	
IX	$Bu_3Sn(CH_2)_3SCO{\cdot}CH_3$	120 (0.3)	1.4982	7.89	7.76	29.12	28.95	

ably the yield of mercaptan. The yields of ethyl-2-thiolsilicon and -tin compounds by hydrogen sulfide addition to the corresponding trialkylvinyl compounds were lower than those of propyl-3-thiol derivatives, although no cleavage of vinyl groups was observed. All compounds described were sufficiently stable to be distilled with the exception of ethyl-2-thioltributyltin, which decomposed at 70° (0.2 mm.).

The addition of thiolacetic acid to allyl- and vinyltributyltin proceeded with remarkable ease. Mixing at 0° in the presence of long wave ultraviolet light resulted in excellent yields of 3-(tributyltin)propyl thiolacetate and 2-(tributyltin)ethyl thiolacetate, respectively, which were both distillable. No cleavage of vinyl groups was observed. Since also the saponification of these thiol esters to the corresponding thiols proceeded easily and in good yields this latter procedure is the method of choice for organotin alkylthiols.

Experimental

General Procedure. Hydrogen Sulfide Addition.—The addition of hydrogen sulfide was studied in two different reactors. Low yields were obtained if a Vycor flask was used rotating in a Dry Ice bath and if the mixture of liquid hydrogen sulfide and vinyl- or allyltrialkylmetal was irradiated by a ultraviolet lamp. Better yields were obtained in a reactor constructed as follows. A double-wall quartz well, open at the top, was inserted into the center-neck of a graduated reaction flask. The reaction flask was equipped with a gas inlet tube leading to the bottom and an outlet at the top leading to a hydrogen sulfide scrubber. This flask—with the inserted quartz well and charged with the olefinic unsaturated compound, catalyst and solvent—was immersed in a Dry Ice bath. Hydrogen sulfide was then distilled into the flask through the gas inlet tube to the desired level. A 100-w. Hanovia (8A-1) quartz mercury vapor lamp was switched on and introduced into the quartz well. Heat transfer was minimized by a high vacuum between the walls of the double-wall quartz well.

Addition of Thiolacetic Acid.—In all cases this reaction was achieved in good yields between 0-25° by using a simple Vycor flask. As radiation source a long wave ultraviolet lamp or even an ordinary 100-w. bulb was sufficient, which was used during the controlled addition of thiolacetic acid to the vinyl- or allyltin or silicon compounds.

Propyl-3-thioltrimethylsilane (III).—The graduated reactor was charged with a mixture of 57 g. (0.5 mole) of allyltrimethylsilane, 1.5 g. of ethyl acetate (catalyst), and 60 ml. of pentane. It was cooled to −70° in a Dry Ice bath and hydrogen sulfide was distilled into this mixture until its volume had increased by approximately 40 ml. The ignited Hanovia quartz light was then inserted into the open center well, and the reaction mixture was irradiated for 2 hr. By removing the Dry Ice bath the excess of hydrogen sulfide was slowly evaporated into a sodium hydroxide scrubber. Pentane was removed by distillation at atmospheric pressure. Seventy-three grams of a colorless liquid remained which contained about 19% sulfur. The pure reaction product (55 g., 74.4%) was isolated by two fractionations through a 20-in. Vigreux column; b.p. 52–53° (16 mm.).

Anal. Calcd. for $C_6H_{16}SSi$: C, 48.62; H, 10.76; S, 21.65; 18.95. Found: C, 49.01; H, 10.23; S, Si, 21.60; Si, 18.64.

Bis(3-trimethylsilylpropyl) Sulfide (IV).—The combined pot residues of the two distillations were distilled at 0.05 mm. Pure colorless sulfide (14.5 g., 19.2%) boiled at 46–47°.

Anal. See Table I.

Ethyl-2-thioltrimethylsilane (I).—In the graduated quartz reactor, immersed in a Dry Ice bath, 50 g. (0.5 mole) of vinyltrimethylsilane, 40 ml. of liquid hydrogen sulfide, and 1 g. of ethyl acetate were irradiated with the Hanovia quartz lamp for a period of 2.5 hr. The excess hydrogen sulfide was then distilled into a scrubber by slowly raising the temperature in the reactor to 20°. In the reactor remained 65 g. of a clear, colorless oil, which was purified by two fractional distillations through a 20-in. Vigreux column; b.p. 40–41° (18 mm.); yield, 14 g. (21%).

Bis(3-trimethylsilylethyl) Sulfide (II).—The combined pot residues of the preceding distillations were distilled at 0.05 mm. Pure, colorless sulfide (23.5 g.) distilled at 39–40°.

Bis(2-trimethylsilylethyl) Sulfone (V).—This compound was prepared by oxidizing 23.3 g. (0.1 mole) of II, dissolved in 180 ml. of anhydrous acetic acid, with a 50% excess (38 g.) of 30% hydrogen peroxide in 2 hr. at 50–60°. Upon storage in the refrigerator 18.5 g. (71%) of pure sulfone crystallized (m.p. 122–123°). An additional 4 g. was obtained by concentrating the mother liquor *in vacuo*.

Propyl-3-thioltri-*n*-butyltin (VII). By Direct Addition of Hydrogen Sulfide.—About 20 ml. of liquid hydrogen sulfide was distilled into the mixture of 30 g. of allyltri-*n*-butyltin, 50 ml. of pentane, and 1 ml. of acetone. The mixture in the quartz reactor was irradiated for 2 hr. with a Hanovia mercury lamp at −70°. Then the excess of hydrogen sulfide and pentane was removed, and the reaction product was purified by high vacuum distillation through a 5-in. Vigreux column (see Table I).

3-(Tri-*n*-butyltin)propyl Thiolacetate (IX). By Addition of Thiolacetic Acid.—To 160 g. (0.5 mole) of allyltri-*n*-butyltin was added with stirring and outside ice-cooling 46 g. (0.59 mole) of distilled thiolacetic acid.[10] At 0–10° the agitated mixture was irradiated with ultraviolet light for 2 hr. Then the small excess of thiolacetic acid was removed by distillation. The remaining clear, colorless oil was distilled at reduced pressure, the main fraction (87%) boiling at 120° (0.2 mm.). The infrared spectrum of this compound has a strong carbonyl band at 1675 cm.$^{-1}$.

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(10) Stauffer Chemical Co.

Saponification.—In 25 ml. of ethanol was dissolved 20 g. (0.05 mole) of IX. The solution of 2.5 g. of potassium hydroxide in 5 ml. of water and 25 ml. of ethanol was added with agitation at room temperature. The clear solution was heated for 3 hr. at 50°. During this time two phases formed. The lower, oily phase was separated at room temperature, taken up in ether, washed with water, and dried over sodium sulfate. Ether was evaporated, and the remaining colorless oil was purified by high vacuum distillation. VII was obtained in 78% yield (14.2 g.).

A Hammett Study of Hydrogen Abstraction from Substituted Allylbenzenes

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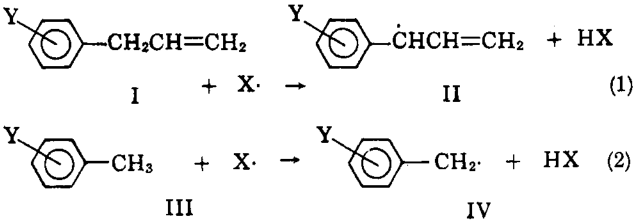
This study is a comparison of the polar effects operating in the abstraction of a hydrogen atom from a series of substituted allylbenzenes (reaction 1) and the more extensively investigated abstraction of a hydrogen atom from substituted toluenes (reaction 2).[2-7] The greater stability of the α-vinylbenzyl radical (II) compared to the benzyl radical (IV) would be expected to compress the activation energy scale for reaction 1 compared to reaction 2, and thereby decrease the effect of a polar substituent on reaction rate in the case of the allylbenzenes. In order to determine the extent to which this effect is reflected in the magnitude of the Hammett ρ-value for reaction 1 as compared to reaction 2, reaction constants have been determined for abstraction of a hydrogen atom from allylbenzenes by the trichloromethyl radical, generated from bromotrichloromethane, and by the bromine atom, generated from N-bromosuccinimide.[8]



Experimental

Materials.—The **substituted allylbenzenes** were all prepared by the coupling reaction of allyl bromide with an aryl Grignard reagent. The procedural details and properties of these compounds are reported elsewhere.[10] The **N-bromosuccinimide** was purified by recrystallization from petroleum ether (80°–100°), m.p. 179°. **Chlorobenzene** was purified by shaking with three portions of sulfuric acid, once with water, three times with 5% sodium bicarbonate, again with water, drying successively over calcium chloride, calcium sulfate, and phosphorus pentoxide, and distilling, b.p. 130–130.5°. Merck, Reagent **carbon tetrachloride** was used without further purification.

Products.—A mixture of 17.3 g. (0.147 mole) of allylbenzene, 26.1 g. (0.146 mole) of N-bromosuccinimide, and 100 ml. of carbon tetrachloride under nitrogen was refluxed for 24 hr. while being irradiated by a 275-w. General Electric sun lamp directed through the side of the reaction flask. At the end of this time the solution was cooled, whereupon 13.65 g. (94%) of succinimide, m.p. 124.5–126.5° (lit.[11a] 125–126°), separated. Solvent was removed from the liquid filtrate by distillation at reduced pressure, and the residue distilled through a Vigreux column, giving 25.8 g. (89%) of a liquid identified as cinnamyl bromide, b.p. 120–124° (30 mm.), m.p. 29° (lit.[11b] 31°). Vapor phase chromatography on a diethylene glycol succinate column indicated only one component, and the infrared spectrum was devoid of any absorption bands which would be characteristic of the possible isomeric product, phenylvinylcarbinyl bromide.

These results confirm the contention that the dominant reaction of an olefin with N-bromosuccinimide is allylic hydrogen abstraction and not addition to the double bond, and justifies the assumption in the kinetic studies that olefin disappears only by hydrogen abstraction without significant competition by addition.

Procedure for Kinetic Runs Using N-Bromosuccinimide.—Equimolar quantities of two allylbenzenes, N-bromosuccinimide and chlorobenzene (present as an inert internal standard for v.p.c. analysis) were sealed under a nitrogen in small Pyrex ampoules and placed in a horizontal position just beneath the surface of an oil bath maintained at 69.5 ± 0.2° and irradiated by a General Electric 275-w. sun lamp placed 19 cm. from the surfaces until anywhere from 45 to 70% of the total number of moles of allylbenzenes present had been consumed. An irradiation time of about 5 to 5.5 hr. was employed. After the ampoules had cooled, they were opened, the liquid portion decanted from undissolved solids, and analyses conducted by v.p.c. on a 6-ft. 10% diethylene glycol succinate column. *p*-Dimethylamino-, *p*-methoxy-, *p*-phenyl-, *m*-methoxy-, *p*-chloro-, and *m*-chloroallylbenzene were run in competition with the unsubstituted allylbenzene, whereas *p*-methyl-, *m*-methyl-, *p*-fluoro-, *p*-trifluoromethyl- and *m*-trifluoromethylallylbenzene were run against *m*-chloroallylbenzene to give better separation on v.p.c., and therefore better analytical results. The ratio of rate constants relative to the unsubstituted compound was then calculated from the expression

$$\frac{k_X}{k_0} = \frac{k_X}{k_{m\text{-Cl}}} \times \frac{k_{m\text{-Cl}}}{k_0}$$

where k_X is the rate constant for the substituted allylbenzene in question, k_0 the rate constant for the unsubstituted allylbenzene and $k_{m\text{-Cl}}$ the rate constant for *m*-chloroallylbenzene.

Determination of k_x/k_0.—The rate of hydrogen abstraction from the substituted compound relative to the unsubstituted compound was calculated from the expression

$$\frac{k_X}{k_0} = \frac{\log X_0/X_f}{\log U_0/U_f}$$

where X_0 and U_0 are the number of moles initially present of substituted and unsubstituted allylbenzene, respectively, and X_f and U_f are the number of moles present at the end of the irradiation period. The ratios X_0/X_f and U_0/U_f were determined by v.p.c. analysis from the expression

$$\frac{X_0}{X_f} = \frac{(\text{area under X peak/area under } C_6H_5Cl \text{ peak})_{\text{initially}}}{(\text{area under X peak/area under } C_6H_5Cl \text{ peak})_{\text{finally}}}$$

and the analogous one for the unsubstituted olefin. Areas were determined with the aid of a disk integrator.

Procedure for Kinetic Runs Using Bromotrichloromethane.—The experiments from which reactivity ratios for hydrogen abstraction by the trichloromethyl radical were determined are described elsewhere.[10] The results are included in this note for

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[8] Recent studies[4,9] have demonstrated that the bromine atom is the hydrogen abstracting species in benzylic brominations involving N-bromosuccinimide, and not the N-succinimidyl radical as had been originally believed.[2]

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