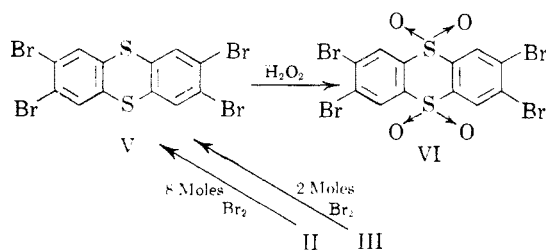
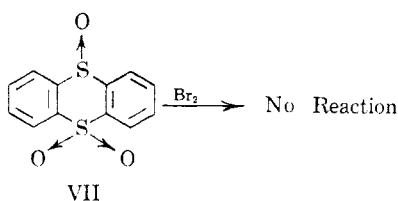


tions *para* to one or the other of the two sulfur atoms. Considering that the bromination should occur at one or more of the *para* positions,^{1,3,4} it is seen that the treatment of II with bromine should give one monobromo-, two dibromo-, one tribromo- and one tetrabromothianthrene. Hence, in the formation of a tri- or tetrabromothianthrene the difficulty of obtaining a sharp-melting product would not be encountered. We found that II and an excess of bromine gave a 41% yield of 2,3,7,8-tetrabromothianthrene (V), melting at 291–292°. The same product was also obtained in 28% yield by the action of two molar equivalents of bromine on III. Oxidation of V with hydrogen peroxide gave an excellent yield of 2,3,7,8-tetrabromothianthrene-5,5,10,10-tetroxide (VI), melting at 357–358° with decomposition.



Thianthrene-5-oxide,³ like other sulfoxides such as dibenzothiophene-5-oxide² and 10-ethylphenothiazine-5-oxide,⁴ is reduced during the process of bromination. Thianthrene-5,5-dioxide, a sulfone, does not react with bromine.³ It was considered interesting to study the action of bromine on thianthrene-5,5,10-trioxide (VII), which has both the sulfoxide and the sulfone groups. Bromine was found to have no action on VII when a mixture of the two was refluxed for a period of 16 hours.



EXPERIMENTAL⁵

Thianthrene (II) and bromine. To 6.48 g. (0.03 mole) of II⁶ was added 38.4 g. (0.24 mole) of bromine. The reaction commenced immediately with the evolution of hydrogen bromide. To the dark solid was added 20 ml. of glacial acetic acid and the resulting red suspension was refluxed for 16 hr. The mixture was treated with a dilute solution of sodium thiosulfate to remove the excess bromine. The white product was filtered, washed with water, and dried to give 15.32 g. of crude 2,3,7,8-tetrabromothianthrene (V) melting over the range 247–264°. Two recrystallizations from xylene (Norit-A) yielded 6.56 g. (41%) of nearly pure V melting

(4) H. Gilman and J. Eisch, *J. Am. Chem. Soc.*, **77**, 3862 (1955).

(5) All melting points reported herein are uncorrected.

(6) K. Fleischer and J. Stemmer, *Ann.*, **422**, 265 (1921).

at 288–290°. The analytical sample, obtained by an additional recrystallization from xylene, melted at 291–292°.

Anal. Calcd. for C₁₂H₄Br₄S₂: Br, 60.08; S, 12.03. Found: Br, 59.72, 59.53; S, 12.02.

Thianthrene-5,10-dioxide (III) and bromine. To 1.5 g. (0.006 mole) of the α -form⁷ of III⁸ was added 2 ml. of bromine. To the resulting dark solid was added 5 ml. of glacial acetic acid and the solution was refluxed for 5 hr. A crystalline product began to crystallize out soon after the solvent began to reflux. At the end of the reaction period the mixture was cooled and treated with a dilute solution of sodium thiosulfate to remove the unused bromine. The white product was filtered, washed with water, and dried to give 3.35 g. of the crude V. Successive recrystallizations from chloroform and xylene yielded 0.9 g. (28%) of pure V melting at 291–292°. A mixture of this product with that obtained from II and bromine melted undepressed.

2,3,7,8-Tetrabromothianthrene-5,5,10,10-tetroxide (VI). To a hot suspension of 2.13 g. (0.004 mole) of V in 50 ml. of glacial acetic acid was added a solution of 5 ml. of 30% hydrogen peroxide in 20 ml. of glacial acetic acid and the suspension was refluxed for 4 hr. The mixture was cooled and the white product was filtered and dried to give 2.25 g. (95%) of VI melting at 357–358° with decomposition.

Anal. Calcd. for C₁₂H₄Br₄O₄S₂: Br, 53.63; S, 10.73. Found: Br, 52.99, 52.91; S, 10.63, 10.61.

Thianthrene-5,5,10-trioxide (VII) and bromine. A mixture of 2.64 g. (0.01 mole) of VII,³ 2 ml. of bromine, and 2 ml. of glacial acetic acid was refluxed for 16 hr. The excess bromine was destroyed with a dilute solution of sodium thiosulfate. The white product was filtered, washed with water, and dried to yield 2.52 g. (95%) of crude VII melting over the range 210–221°. Recrystallization from glacial acetic acid yielded 2.14 g. (81%) of pure VII melting at 221.5–222.5°. A mixture of the product with authentic VII³ melted undepressed.

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(7) E. Bergmann and M. Tschudnowsky, *Ber.*, **65**, 457 (1932).

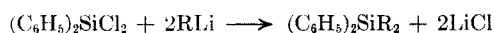
(8) K. Fries and W. Vogt, *Ber.*, **44**, 756 (1911).

Tetrasubstituted Higher Aliphatic and Phenyl Silanes

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We wish to report the synthesis and physical properties of a number of new tetra-substituted silanes prepared in connection with a study in this laboratory of the higher aliphatic silanes. These compounds, Table I, were prepared by treatment of a slight excess of a chlorosilane with an organolithium compound according to the usual procedure.



The intermediate organolithium compounds were obtained directly by the action of lithium on *n*-octyl-, 2-octyl-, 2-ethylhexyl- and 2-cyclohexylethylbromides in yields of 87, 76, 64 and 88%, respectively.

TABLE I
 TETRA-SUBSTITUTED SILANES

Reagent	Reaction Time (hr.) with RLi	Product	Yield, %	M.P., °C.	B.P.		n_D^{20}	d_4^{20}	MR _D		Silicon, %		
					°C.	Mm.			Calcd. ^a	Found	Calcd.	Found	
Triphenylchlorosilane	10	Triphenyl- <i>n</i> -octylsilane	76	73-75 ^a	182	0.02						7.54	7.51, 7.46
Triphenylchlorosilane	2	Triphenyl-2-octylsilane	44	153-155		.04	1.5748	1.009	122.2	122.0		7.54	7.57, 7.65
Triphenylchlorosilane	18	Triphenyl-2-ethylhexylsilane	50	163-166		.03	1.5734	1.005	122.2	122.3		7.54	7.67, 7.50
Triphenylchlorosilane	12	Triphenyl-2-cyclohexylethylsilane	63	58-59 ^a	168	.03						7.58	7.57, 7.64
Diphenyldichlorosilane	12	Diphenyldi- <i>n</i> -octylsilane	59	198		.12	1.5191	0.919	134.7	135.0		6.87	6.87, 6.85
Diphenyldichlorosilane	2	Diphenylbis(2-octyl)silane	86	141-156 ^c		.02	1.5305						
Diphenyldichlorosilane	6	Diphenylbis(2-ethylhexyl)silane	31	153-159 ^c		.06	1.5220	.931	134.7	134.5		6.87	6.88, 6.76
Diphenyldichlorosilane	12	Diphenylbis(2-cyclohexylethyl)silane	79	187		.03	1.5527	.925	134.7	134.9		6.87	6.95, 6.90
Phenyltrichlorosilane	12	Phenyltri- <i>n</i> -octylsilane	80	181		.02	1.4841	.993	130.5	130.3		6.94	7.04, 7.03
Phenyltrichlorosilane	18	Phenyltris(2-ethylhexyl)silane	70	150-157 ^c		.01	1.4887	.862	147.3	147.7		6.31	6.45, 6.31
Phenyltrichlorosilane	12	Phenyltris(2-cyclohexylethyl)silane	76	188		.02	1.5235	.875	147.3	146.8		6.31	6.38, 6.40
Silicon tetrachloride	18	Tetra- <i>n</i> -octylsilane	63	192		.15	1.4589	.954	140.9	140.7		6.40	6.45, 6.62
Silicon tetrachloride	24	Tetrakis(2-ethylhexyl)silane	50	135-155 ^c		.05	1.4612	.822	159.9	160.0		5.84	5.86, 5.85
Silicon tetrachloride	18	Tetrakis(2-cyclohexylethyl)silane	68	146-147 ^b	206	.02	1.4619	.842	159.9	157.0		5.84	5.94, 5.92
<i>n</i> -Dodecyltrichlorosilane	24	<i>n</i> -Dodecyltris(2-cyclohexylethyl)silane	57	211		.02	1.4885	.894	172.1	171.2		5.29	5.17, 5.22

^a Recrystallized from absolute ethanol. ^b Recrystallized from 1:1 benzene-absolute ethanol. ^c The crude product is possibly a mixture of stereoisomers. The purified sample was an arbitrarily selected distillation fraction. ^d Molar refractions were calculated from the values of E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

EXPERIMENTAL¹

n-Octyllithium.² A suspension of 13.7 g. (1.97 g.-atoms) of lithium wire, cut into 2–3 mm. lengths, in 320 ml. of ethyl ether was stirred at -15 to -30° while a solution of 155 g. (0.8 mole) of *n*-octyl bromide in 100 ml. of ethyl ether was added during 45 min. The temperature was maintained at -15 to -30° for 2 hr. and then at -5 to 0° for 1 hr. After filtration the yield was 87%, as determined by the double titration procedure.³

This method was also used for the preparation of 2-ethylhexyllithium and 2-cyclohexylethyllithium from 2-ethylhexylbromide and 2-cyclohexylethyl bromide, respectively.

2-Octyllithium.⁴ A solution of 74.3 g. (0.5 mole) of 2-octyl chloride in 200 ml. of pure pentane was added during 3 hr. to a stirred refluxing suspension of 13.9 g. (2.0 g.-atoms) of lithium foil in 200 ml. of pentane. The refluxing was continued for a further 2 hr. After filtration the yield was 76% according to the double titration procedure.

General synthetic method. A. Preparation of triphenyl-n-octylsilane. A suspension of 56 g. (0.19 mole) of triphenylchlorosilane in 235 ml. of ethyl ether was maintained at -20 to -10° while an ether solution of 0.21 mole of *n*-octyllithium was added during 15 min. The mixture was allowed to come to room temperature and stirred for 10 hr., by which time Color Test I⁵ was negative. After hydrolyzing the reaction mixture with cold dilute sulfuric acid, the ether layer was separated, dried over sodium sulfate, and distilled, giving a main fraction distilling at 182° (0.02 mm.) and melting at 72 – 74° . One recrystallization from absolute ethanol gave 54 g. (76%) melting at 73 – 75° .

Anal. Calcd. for $C_{26}H_{32}Si$: Si, 7.54. Found: Si, 7.51, 7.46.

This same procedure was used with all of the compounds, Table I, with the exception of those prepared from silicon tetrachloride.

B. Preparation of tetra-n-octylsilane. A solution of 14.1 g. (0.083 mole) of silicon tetrachloride in 170 ml. of ethyl ether was maintained at -20° while an ether solution of 0.39 mole of *n*-octyllithium was added rapidly. The mixture was kept at room temperature for 10 hr. and then was refluxed for 8 hr., by which time Color Test I was negative. Working up as in procedure A gave a main fraction of 25.3 g. (63%) distilling at 191 – 192° at 0.15 mm., n_D^{20} 1.4589, d_4^{20} 0.822.

Anal. Calcd. for $C_{32}H_{68}Si$: Si, 5.84. Found: Si, 5.86, 5.85.

Silicon analyses. The procedure usually used in this laboratory,⁶ in which about a 0.2-g. sample is wetted with a few drops of nitric acid, digested with 1 ml. of concentrated sulfuric acid, and finally ignited gave erratically low results with some of these compounds. Successful analyses were obtained by digestion of the samples in covered Vycor crucibles with 3 ml. of a 2:1 mixture of sulfuric and nitric acids. Additional nitric acid was added as necessary to complete the oxidation.

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(1) All melting and boiling points are uncorrected. All operations involving organolithium compounds were carried out under an atmosphere of dry oxygen-free nitrogen in sodium-dried solvents.

(2) For a general reference to the preparation of aliphatic lithium compounds see, H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

(3) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

(4) D. S. Tarbell and M. Weiss, *J. Am. Chem. Soc.*, **61**, 1203 (1939), obtained a 56% yield from the chloride by a similar procedure in ethyl ether solution.

(5) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

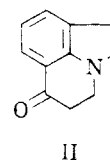
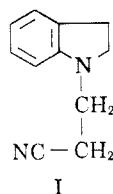
(6) H. Gilman, B. Hofferth, H. W. Melvin, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

A Synthesis of 5-Ketolilolidine¹

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Our interest in the synthesis of 5-ketolilolidine (II) arose from the consideration that this compound would be a useful intermediate in syntheses directed toward apo- β -erythroidine and related compounds.² Brauholtz and Mann have reported the cyclization of aromatic cyanoethyl amines to give ketojulolidine derivatives,^{3a,b} and it seemed likely that *N*-(β -cyanoethyl)indoline (I) would undergo cyclization in a similar manner to give 5-ketolilolidine (II).



Preparation of the starting material, *N*-(β -cyanoethyl)indoline, was readily accomplished by the addition of acrylonitrile to indoline. However, when *N*-(β -cyanoethyl)indoline was treated with aluminum chloride and hydrochloric acid in chlorobenzene, as described for the preparation of 1,6-diketojulolidine,³ the only apparent reaction was one of dissociation to indoline and acrylonitrile. The conditions for effecting cyclizations of this type seem to be quite critical and eventually it was found that, by the use of anhydrous aluminum chloride in *o*-dichlorobenzene, 5-ketolilolidine could be obtained consistently in yields varying from 8 to 13%. In the isolation procedure developed, 5-ketolilolidine was separated from the other reaction products by use of Girard's reagent and a product of high purity resulted. For purposes of characterization, the oxime and 2,4-dinitrophenylhydrazone derivatives were prepared. Also, to establish its identity, 5-ketolilolidine was reduced by the Wolff-Kishner procedure and the properties of the product were shown to be in agreement with those reported for lilolidine.⁴

Because of the low yields encountered in the cyclization step, alternate methods were investigated but without success. Hydrolysis of *N*-(β -cyanoethyl)indoline occurred smoothly to give the corresponding acid, *N*-(β -carboxyethyl)indoline. But,

(1) Aided by a grant from the United Cerebral Palsy Association, Inc.

(2) M. F. Grundon, G. L. Sauvage, and V. Boekelheide, *J. Am. Chem. Soc.*, **75**, 2550 (1953).

(3) (a) J. T. Brauholtz and F. G. Mann, *J. Chem. Soc.*, 1817 (1953); (b) J. A. C. Allison, J. T. Brauholtz, and F. G. Mann, *J. Chem. Soc.*, 403 (1954).

(4) G. Barger and E. Dyer, *J. Am. Chem. Soc.*, **60**, 2414 (1938).