TABLE I

2,3-Dihydroxypropyl Alkyl Sulfide and Sulfone Diesters

Compound	Yield, %	M.P.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
(2,3-Distearoylpropyl octadecane sulfide)	82	62–63	$C_{57}H_{112}SO_4$	76.61	76.59	12.63	12.67	3.59	3.61
(2,3-Distearoylpropyl octadecane sulfone)	85	82–83	$C_{57}H_{112}SO_6$	73.96	73.81	12.20	12.24	3.46	3.55
(2,3-Dipalmitoylpropyl hexadecane sulfide)	72	53–54	$C_{51}H_{100}SO_4$	75.68	75.60	12.45	12.63	3.96	4.04
(2,3-Dipalmitoylpropyl hexadecane sulfone)	75	75–76	$C_{51}H_{100}SO_6$	72.79	73.00	11.98	11.84	3.81	3.90

the fatty acid chlorides and the calculated quantity of the corresponding alcohol.[5]

EXPERIMENTAL

Starting materials. The palmitoyl and stearoyl chlorides were obtained from Matheson, Coleman and Bell, East Rutherford, N. J., and were used without any further purification. The thiochimyl alcohol (2,3-dihydroxypropylhexadecane sulfide) and thiobatyl alcohol (2,3-dihydroxypropyloctadecane sulfide) were prepared from alkyl halide and 3-mercapto-1,2-propanediol under basic conditions. The sulfones were obtained by oxidation of the sulfides with 30% hydrogen peroxide, using acetic acid as a solvent.[6] All melting points were obtained on a Fisher-Johns melting point apparatus and all compounds reported are racemic.

General procedures for preparation of 2,3-dihydroxypropyl alkyl sulfide and sulfone diesters. A mixture of 0.05 mole of appropriate alcohol and 0.11 mole of the fatty acid chloride was heated to 100° (hydrogen chloride being evolved) for 15 min. The hot oily reaction mixture was then flushed with dry nitrogen to remove the dissolved hydrogen chloride and 200 ml. of acetone was carefully added to the hot reaction mixture. The reaction mixture was immediately filtered and allowed to crystallize. The diester was then recrystallized two more times from acetone to yield material which was homogeneous when examined by the silicic acid thin layer chromatoplates method of Stahl.[7] The solvent system employed consisted of 90 parts by volume of petroleum ether (b.p. 30–60°), 10 parts anhydrous diethyl ether, and 1 part acetic acid. The plates were developed by spraying with 25% sulfuric acid and heating at 105° for 10 min. The infrared spectra of these sulfones showed a characteristic absorption band at 1300–1350 cm.$^{-1}$.

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Reaction of Triphenylsilyllithium with Anthracene

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The selective nucleophilicity of triphenylsilyllithium has been demonstrated by 1,4-addition of the silylmetallic compound to pyridine[1] and quinoline,[2] whereas alkyl- and aryllithium derivatives undergo predominantly 1,2-addition with these compounds.[3] However, triphenylsilyllithium underwent 9,10-addition to acridine,[4] as in the case of alkyl- and aryllithium reagents.[5] The silyllithium reagent has also been found to add to the olefinic linkage of 1,1-diphenylethylene and of triphenylethylene, but not to tetraphenylethylene and some other aliphatic and alicyclic olefins.[6] Since dimethylphenylmethylpotassium was found to add to anthracene and triphenylmethylpotassium showed little tendency to add,[7] it was of interest to extend our studies of the reaction of triphenylsilyllithium with polynuclear compounds[8] to anthracene.

Subsequently, it was found that triphenylsilyllithium added smoothly to anthracene to give 9,10 - dihydro - 10 - lithio - 9 - (triphenylsilyl)-anthracene (I), which upon hydrolysis gave 9,10-dihydro - 9 - (triphenylsilyl)anthracene (II).

The structure of II was confirmed by an independent synthesis involving monometalation of 9,10-dihydroanthracene and treatment of the organolithium compound with chlorotriphenylsilane. This reaction also gave a small amount of hexaphenyldisilane resulting from a halogen-metal interconversion reaction. The NMR spectrum of II showed a one proton peak at 5.56 τ, representing the proton at position 9 (benzhydryltriphenylsilane showed a single proton peak at 5.6 τ), and a quartet centered at 6.92 τ, typical of an AB system, for the two protons at position 10. The coupling constant for these two protons was 17 c.p.s. The non-equivalence of the two protons at the

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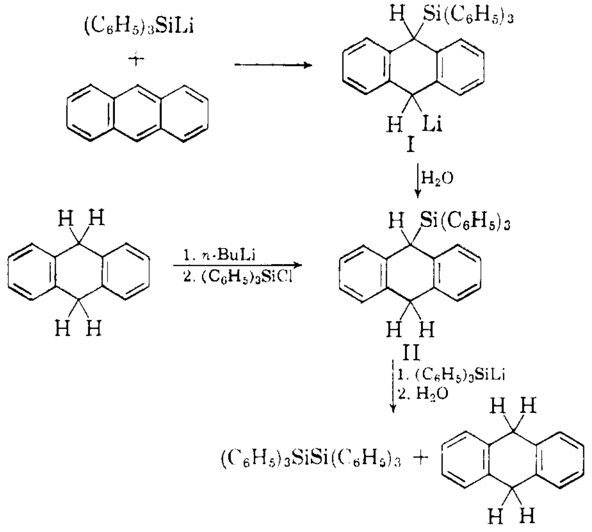

10-position is in accord with the proposed[9] folded structure of 9,10-dihydroanthracene compounds.

The reaction of triphenylsilyllithium with anthracene was complicated by the formation of some unidentifiable by-products. Furthermore, when the reaction mixture was allowed to stir for an extended length of time (nineteen hours at room temperature), the yield of II was lower and was more difficult to purify. Concurrently the yield of hexaphenyldisilane increased from 2.3%, when a reaction time of fifteen minutes was employed, to 10.6% for the longer reaction time. In the latter case, 9,10-dihydroanthracene, anthracene, anthraquinone, 4-hydroxybutyltriphenylsilane, and high-melting solids were isolated. These products, the increased yield of hexaphenyldisilane, and the decreased yield of II suggests that I probably undergoes disproportionation and polymerization, as well as oxidation. Mikhailov and Blokhina[10] have stated that polymerization and disproportionation reactions interfere in the reaction of alkyl halides with 9,10-dihydro-9,10-disodioanthracene, and Hock and Ernst[11] have recently observed the ready autoxidation of the dilithium adduct of anthracene, and, under more rigorous conditions, that of 9,10-dihydroanthracene. We also observed that II and the various high-melting by-products slowly turned yellow if exposed to air.

Since it has been observed that triphenylsilyllithium readily metalates 9,10-dihydroanthracene,[8] the silyllithium reagent was allowed to react with II for the purpose of producing the anion I, which would then be allowed to stir at room temperature in order to observe the disproportionation and/or oxidation of I. However, the preferred reaction was displacement of the dihydroanthracene grouping with the formation of hexaphenyldisilane.

Similar displacement of groups from silicon has been observed in the reaction of n-butyllithium with triphenyl(phenylethynyl)silane,[12] phenyllithium with triphenyl-β-styrylsilane,[6] and triphenylsilyllithium with phenylethynylsilanes[13,14] and benzhydrylsilanes.[15]

EXPERIMENTAL[16]

Reaction of triphenylsilyllithium with anthracene. Run 1. A solution of triphenylsilyllithium[17] (0.05 mole) in 100 ml. of tetrahydrofuran (THF) was added to 8.92 g. (0.05 mole) of anthracene suspended in 100 ml. of THF. A deep red solution was formed and Color Test I[18] was positive. The mixture was stirred 15 min. at room temperature and then poured into cold dilute sulfuric acid. Ether was added and the layers separated. Filtration of each layer gave 1.2 g. of a solid which turned black at 200°, but did not completely melt below 370°. Recrystallization of the solid from benzene gave 0.3 g. (2.3%) of hexaphenyldisilane, m.p. and mixed m.p. 362–364°.

The organic layer was allowed to stand and then filtered to give 0.65 g. of a flocculent solid melting over the range 236–240° (dec.). Attempts to purify this material failed. The infrared spectrum of the compound indicated the presence of a triphenylsilyl group. The material was not investigated further. The filtrate was dried over magnesium sulfate and concentrated. The residual solid was suspended in petroleum ether (b.p. 60–70°) and poured onto a column of alumina. Elution with 200 ml. of petroleum ether gave 12.17 g. of a solid, melting over the range 130–145°. Recrystallization from ethanol afforded 6.52 g. (29.7%) of a crystalline solid, m.p. 153–155°. The infrared spectrum of the compound as a carbon disulfide solution showed prominent absorption bands at 3.3, 3.5, and 9.06 μ, characteristic of aromatic and aliphatic C—H and the silicon-phenyl linkage, respectively. The melting point was not depressed when admixed with a sample of 9,10-dihydro-9-(triphenylsilyl)anthracene prepared by a different method (see below). The analytical sample melted at 153–154°.

Anal. Calcd. $C_{32}H_{26}Si$: Si, 6.40. Found: Si, 6.35, 6.36.

Concentration of the ethanolic filtrate gave 1.4 g. of a solid melting over the range 140–190°. Continued elution of the column with petroleum ether gave 3.45 g. of material with a similar wide melting point range. Attempted purification was unsuccessful. Using cyclohexane as the eluent, traces of a viscous oil were eluted. Benzene elution gave 0.4 g. of solid melting over the range 225–235° dec. Recrystallization from a n-propyl alcohol–benzene mixture yielded 0.2 g. of amorphous solid, m.p. 228–250°. The infrared spectrum of the solid showed aromatic C—H, weak aliphatic C—H, the silicon-phenyl linkage, and *ortho*-disubstitution bands.

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[12] H. Gilman and H. Hartzfeld, *J. Am. Chem. Soc.*, **73**, 5878 (1951).

[13] Dan Aoki, unpublished studies.

[14] Donald J. Peterson, unpublished studies.

[15] Frank K. Cartledge, unpublished studies.

[16] All melting points are uncorrected. The tetrahydrofuran was dried and purified by successively refluxing over sodium wire and lithium aluminum hydride. Anthracene was recrystallized from benzene before use. The recrystallized material melted at 217–218°. The NMR spectra were determined at 60 Mc. in carbon tetrachloride or deuterated chloroform using tetramethylsilane as the internal standard.

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

Final elution of the column with ethyl acetate afforded 0.55 g. (3.8%) of triphenylsilanol, m.p. and mixed m.p. 153–155°.

Run 2. Triphenylsillithium (0.05 mole) in 100 ml. of tetrahydrofuran was added to 8.92 g. (0.05 mole) of anthracene suspended in 100 ml. of the same solvent. Color Test I was positive. The mixture was stirred 7 hr. at room temperature during which time the color of the solution changed from deep red to yellow-brown and a solid was formed. After stirring an additional 12 hr., Color Test I was weakly positive. The mixture was hydrolyzed, ether was added, and the layers filtered to remove 6.0 g. of a solid. Treatment of the solid with hot benzene gave 2.8 g. of insoluble material-melting over the range 238–260°. Cooling and concentration of the benzene filtrate afforded 1.42 g. (10.6%) of hexaphenyldisilane, m.p. and mixed m.p. 356–359°, and 0.75 g. of residue. The organic layer was dried, concentrated, and chromatographed as above. However, 0.75 g. (8.3%) of 9,10-dihydroanthracene, m.p. and mixed m.p. 108–111°, and 1.51 g. (16.9%) of anthracene, m.p. and mixed m.p. 214–217°, were eluted first with petroleum ether, followed by 1.45 g. (6.6%) of impure 9,10-dihydro-9-(triphenylsilyl)-anthracene, melting over the range 130–150° (cloudy), and 1.5 g. (6.84%) of pure 9,10-dihydro-9-(triphenylsilyl)anthracene, m.p. 151–153°. Elution with cyclohexane afforded 1.1 g. of a solid, melting at 149–156° (cloudy). The first eluates of the benzene elution gave 3.59 g. of material, m.p. 211–220°, which was fractionally crystallized from a *n*-propyl alcohol–benzene mixture to give only solids melting over a similar wide ranges (225–275°). The infrared spectrum of the solid was similar to that of 9,10-dihydro-9-(triphenylsilyl)-anthracene. Continued elution with benzene yielded 0.05 g. of anthraquinone, identified by comparison of the infrared spectra, and a yellow solid (0.18 g.) which did not contain silicon and melted over the range 208–240° (dec.). Final elution with ethyl acetate gave 0.1 g. (0.6%) of 4-hydroxybutyltriphenylsilane, m.p. and mixed m.p. 109–111°.

9,10-Dihydro-9-(triphenylsilyl)anthracene. 9,10-Dihydroanthracene (10.8 g., 0.06 mole), prepared by the method of Wieland,[19] in 100 ml. of ether was metalated with 0.06 mole of *n*-butyllithium in a manner similar to that previously reported.[20] Color Test I was positive and Color Test II[21] was negative after refluxing the mixture for 12 hr.

The deep red solution was added to an excess (0.77 mole) of chlorotriphenylsilane suspended in ether. The color test was negative after stirring 1 hr. Hydrolysis was effected with water and the layers separated. The combined organic layer was filtered to remove 1.06 g. (2.7%) of hexaphenyldisilane, m.p. and mixed m.p. 355–358°. The filtrate was dried over anhydrous sodium sulfate and concentrated. The residual solid was taken up in petroleum ether (b.p. 60–70°) and chromatographed on alumina. Elution with the same solvent gave 8.5 g. of solid melting over a wide range, followed by 6.8 g. of material, m.p. 149–153°. Recrystallization from ethanol raised the melting point to 153–154°. A mixed melting point with the 9,10-dihydro-9-(triphenylsilyl)anthracene isolated in the previous experiment was not depressed. Further elution with petroleum ether gave 4.85 g. of impure product, m.p. 130–145°.

The first eluate was rechromatographed, but only 0.92 g. of pure product could be isolated.

The yield of crude product was 11.65 g. (44.2%) and that of the pure product was 7.72 g. (29.3%).

Benzene and methanol elution gave nonidentifiable solids melting over wide ranges.

Reaction of triphenylsilyllithium with 9,10-dihydro-9-(triphenylsilyl)anthracene. A tetrahydrofuran (THF) solution of triphenylsilyllithium (0.0046 mole) was added to 2.0 g. (0.0046 mole) of 9,10-dihydro-9-(triphenylsilyl)anthracene dissolved in 5 ml. of THF. The color of the solution became red and a solid formed during the addition. Color Test I was positive. The mixture was stirred 10 min. subsequent to complete addition and then was poured into dilute sulfuric acid. Ether was added and the layers were separated and filtered to afford 1.5 g. (63.3%) of hexaphenyldisilane, m.p. and mixed m.p. 362–364°. The organic layer was dried over magnesium sulfate and concentrated. The oily residue was treated with petroleum ether and chromatographed on alumina. Elution with 200 ml. of the same solvent gave 0.2 g. of slightly impure 9,10-dihydroanthracene, m.p. 106–108°, identified by mixed melting point and by comparison of the infrared spectra. Further concentration of the eluate and treatment with ethanol afforded 0.34 g. (total crude, 65.9%) of impure 9,10-dihydroanthracene, m.p. 85–105°. This material was contaminated with unchanged 9,10-dihydro-9-(triphenylsilyl)anthracene (infrared spectrum), which was eluted with the next 200-ml. portion of petroleum ether: 0.42 g. (21%), m.p. and mixed m.p. 151–153°. Benzene elution gave a trace of solid material.

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The Sulfomethylation of Indole

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The readiness with which indole forms gramine (ref. 1) suggests that it should also undergo sulfomethylation (ref. 2). This has been found to be the case. Treatment of indole with formaldehyde and sodium sulfite produced sodium 3-indolemethanesulfonate in 88% yield at a conversion of 59%. The compound could not be obtained in any appreciable yield with sodium bisulfite, although this situation was altered readily by the addition of alkali to convert the bisulfite to sulfite. The sodium 3-indolemethanesulfonate obtained was identified by comparison with a sample of the material prepared by a reported procedure (ref. 3) and by elemental and infrared analysis.

3-Indolemethanesulfonic acid, a relatively unstable compound, was obtained by passing the sodium salt over Amberlite IR-120 (acid form). Ammonium 3-indolemethanesulfonate, formed by

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