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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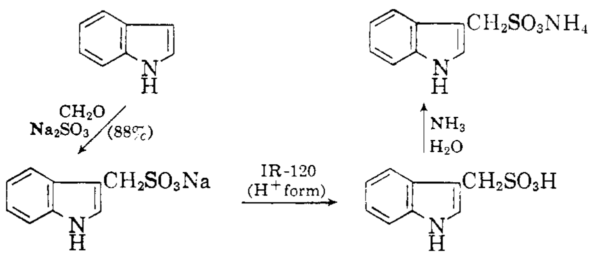
the addition of aqueous ammonia to a solution of the free acid, was found to be comparable in stability to the sodium salt. All efforts to react free 3-indolemethanesulfonic acid or either its sodium or ammonium salt with an alkali cyanide to produce 3-indoleacetonitrile were unsuccessful.



EXPERIMENTAL

Indole (30 g., 0.26 mole) and sodium sulfite (126 g., 1.00 mole) were placed in water (250 ml.) and heated to gentle reflux with stirring. Aqueous formaldehyde (50 ml. 36.2% solution equivalent to 18.1 g. or 0.60 mole) was added and the mixture refluxed gently for 18 hr. The reaction mixture was then cooled and the crystalline precipitate collected by filtration. Several extractions of the product first with ether, then methanol removed the unchanged indole (10 g.). The crystalline residue was dissolved in a minimum amount (800 ml.) of boiling water and saturated sodium bromide solution (200 ml.) added. The resulting solution was cooled to 0–5° and the precipitate of sodium 3-indolemethanesulfonate which formed collected by filtration. After air drying the white crystalline product amounted to 35 g. (0.16 mole, 88% yield at 59% conversion). A second recrystallization from water (300 ml.) and saturated sodium bromide solution (90 ml.) reduced the yield to 29.5 g. (0.13 mole).

Anal. Calcd. for $C_9H_8O_3NSNa$: C, 46.38; H, 3.43; N, 6.01; S, 14.35. Found: C, 46.16; H, 3.86; N, 6.10; S, 14.35.

The Preparation of Diethyl Peroxide. The Use of Dispersing Agents to Increase Yields in Heterogeneous Systems[1]

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The difficulties with regard to the preparation of diethyl peroxide have been described by Leadbeater.[2] According to this investigator, the usual yield of "pure" compound obtained after a number of fractionations was about 2–3%. The methods of preparations reported in the literature as also used by Minkoff[3] were employed to prepare this compound needed for kinetic studies. Unfortunately, all attempts using both methods were met with utter failure. With somewhat modified procedural details, we have been able to prepare the pure product in about 28–30% yields. The significant high yield resulted from the use of sodium stearate as a dispersing agent.

Experimental

To a three-neck Pyrex flask (500 ml.), containing 120 ml. of 30% hydrogen peroxide, was added about 50 mg. of sodium stearate dissolved in a few milliliters of distilled water. The flask was kept cool at or below −35° by using a bromobenzene–Dry Ice slush bath (usually, a simple Dry Ice bath proved equally good and handy, and was mostly used in later preparations). A solution of 56 g. of potassium hydroxide dissolved in 60 ml. of distilled water was added dropwise to the flask whose contents were kept stirred during this process. The result was an almost semifluid mass. The flask was transferred to a common salt-ice bath. Ethyl sulfate, 154 g., was added slowly (a few drops at a time, over a period of about 1 hr.), through another inlet tube. The contents became entirely liquid in the course of the addition of the ethyl sulfate. The temperature of the mixture was kept below −10° during the addition. After the addition, the contents were kept stirred overnight (for about 16 hr.) in the ice bath. No attempt was made to study the effect of period of stirring on the yield. The oily layer was extracted with anisole the next day and washed two to three times with distilled water to remove as much alkali as possible. The extract was transferred to a glass-stoppered flask, 1–2 drops of phenolphthalein were added and sulfuric acid (4 *N*) was added dropwise just to the disappearance of pink color. Anhydrous sodium sulfate (Analar grade), 10 g., was added to the extract. After 1 hr. of drying, the contents were vacuum-distilled (pressure = 20 mm.), raising the temperature of the distillation flask slowly to about 60° toward the end of the operation. The receiving set consisted of a series of traps; the first trap cooled in an ice bath could entrap any anisole that distilled, while the peroxide was found in the two successive traps at liquid nitrogen temperature. The peroxide from both the traps was transferred to a 100 ml. round-bottomed flask fitted with a Vigreux column which had a side-water-condenser and a fraction-cutter of four receivers. The product was fractionated using a water bath; the fraction distilling between 62–63° was collected for subsequent analysis. The infrared spectrum of the product was taken on an Infracord (Perkin-Elmer) and it matched with the one reported by Minkoff.[2] The refractive index also agreed with the value reported in the literature, $n^{20}\mathrm{D}$ 1.3698. A yield of 25.6 g. was obtained in one particular trial, and it ranged from 25 to 28 g.

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[1] This work has been supported by a Grant from the Atomic Energy Commission.

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A Stereospecific Photochemical Addition of Acetone to Norbornylene

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Photochemical addition reactions of olefins with carbonyl compounds were reported early in this century,[1] but only in recent years has the scope and variety of these transformations become

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