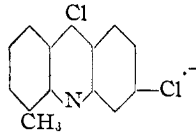

3,9-Dichloro-5-methylacridine, .—A mixture of 71 g. of 2-*o*-toluidino-4-chlorobenzoic acid and 350 g. of phosphorus oxychloride was refluxed for two hours at 120°. The excess of phosphorus oxychloride was distilled off *in vacuo*, and the residue was poured into ice and water kept basic with ammonia. After thirty minutes the acridine was collected on a filter, washed with dilute ammonia, ice water, and desiccated. Crystallization from benzene produced 58 g. (81%) of light yellow needle-shaped crystals of 3,9-dichloro-5-methylacridine, m. p. 146–147°, cor.

Anal. (Parr bomb) Calcd. for $C_{14}H_9Cl_2N$: Cl, 27.04. Found: Cl, 26.78, 26.61.

3,9-Dichloroacridine.—Similar directions were followed, starting with 80 g. of 2-anilino-4-chlorobenzoic acid and 400 g. of phosphorus oxychloride. Light yellow needles, m. p. 168–170°, cor., were obtained after crystallization of the product from benzene. The yield was 55 g. or 69%. Albert and Linnell[2] prepared this compound in another way.

Yields of 65–76% were also obtained in similar syntheses of 9-chloroacridine[3] and 9-chloro-4-methoxyacridine.[4]

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[2] Albert and Linnell, *J. Chem. Soc.*, 1614 (1936).

[3] Magidson and Grigorowsky, *Ber.*, **66**, 869 (1933). We found that the method of Graebe and Lagodzinski, *Ann.*, **276**, 35 (1893), gave much poorer yields.

[4] Gleu and Nitsche, *J. prakt. Chem.*, **153**, 200 (1939), who prepared this substance, listed no yield.

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RECEIVED OCTOBER 9, 1946

Some New Organosilicon Compounds

Dimethylethylcholorosilane and Dimethylethylbromosilane.—A Grignard reagent prepared from 2 kg. (18.35 moles) of ethyl bromide in ether was added to 2900 g. (24.0 moles) of dimethyldichlorosilane. The mixture was filtered and distilled and from the distillation analysis the following yields were calculated: 8.33 moles of dimethylethylchlorosilane, 0.723 mole of dimethyldiethylsilane, and 1.506 moles of dimethylethylbromosilane. The formation of a bromosilane by halogen interchange between silicon and magnesium has not been previously reported. The recovery of ethyl groups (61%) was low because of an accidental loss during the reaction. Redistillation of the product gave a fraction boiling at 89.2° (cor.).

Anal. Calcd. for $C_4H_{11}SiCl$: Cl, 28.90. Found: Cl, 28.90.

Another fraction was obtained at 110.0–110.4° (cor.).

Anal. Calcd. for $C_4H_{11}SiBr$: Br, 21.21. Found: Br, 21.04, 21.03.

Phenyldichlorosilane. (A) Chlorobenzene–Silicon Reaction.—In the reaction between 100 kg. of chlorobenzene with silver and silicon,[1] 100 g. of material boiling between 136° and 190° was obtained. Redistillation gave a small amount boiling about 173° having an odor of *p*-dichlorobenzene but containing 27% hydrolyzable chlorine. The presence of phenyldichlorosilane was qualitatively established by the evolution of hydrogen when a sample was hydrolyzed with water and treated with alkali.

(B) Grignard Reaction.—A Grignard reagent made from 58 g. (0.37 mole) of bromobenzene was added slowly to 107 g. (0.80 mole) of trichlorosilane. The reaction mixture was distilled at reduced pressure giving 17.2 g. (26%) of a product boiling at 104–125° (100 mm.). On redistillation it boiled at 184° (cor.) at 760 mm.

Anal. Calcd. for $C_6H_6SiCl_2$: Cl, 40.04. Found: Cl, 39.2.

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[1] E. G. Rochow and W. F. Gilliam, THIS JOURNAL, **67**, 1772 (1945).

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2,3-Dimethoxy-6-chloro-9-phenanthrenecarboxylic Acid

A mixture of 11 g. of potassium *p*-chlorophenylacetate 11 g. of 6-nitroveratraldehyde[1] and 50 cc. of acetic anhydride was heated on the steam-bath for fifteen hours (stirring was essential at first) and poured into about 100 cc. of ice-cold, dilute hydrochloric acid. After thorough cooling the semi-solid was recrystallized from acetic acid to give 12.8 g. of α-(*p*-chlorophenyl)-2-nitro-4,5-dimethoxycinnamic acid of m. p. 200–202.5°; yellow prisms from ethanol, m. p. 202–203.5°.

Anal. Calcd. for $C_{17}H_{14}ClNO_6$: C, 56.12; H, 3.88. Found: C, 56.13; H, 4.04.

The foregoing nitro acid (13 g.) was reduced[2] with 90 g. of ferrous sulfate to yield, from ethanol, 11.8 g. of α-(*p*-chlorophenyl)-2-amino-4,5-dimethoxycinnamic acid of m. p. 207–210°; pale, greenish-yellow leaflets from ethanol, m. p. 208–211° with gas evolution to a solid which remelted at *ca.* 280°.

Anal. Calcd. for $C_{17}H_{16}ClNO_4$: C, 61.18; H, 4.83. Found: C, 61.22; H, 5.04.

A mixture of 5.5 g. of the above amino acid and 80 cc. of 5 *N* sulfuric acid was stirred at 0° while adding a solution of 2 g. of sodium nitrite in 25 cc. of water (fifteen minutes). After stirring for two hours the yellow solid was collected and stirred for one-half with 50 cc. of ethanol and 2 g. of copper-bronze. The temperature rose to 37°. The mixture was cooled, filtered and the precipitate digested with about 50 cc. of boiling dioxane. From the dioxane filtrate, 1.8 g. of 6-chloro-2,3-dimethoxy-9-phenanthrenecarboxylic acid of m. p. 264–267° separated. After sublimation in a high vacuum followed by recrystallization from dioxane, the acid appeared in short, prismatic rods of m. p. 268–269°

Anal. Calcd. for $C_{17}H_{13}ClO_4$: C, 64.48; H, 4.14. Found: C, 64.67; H, 4.13.

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[1] Cassaday and Bogert, THIS JOURNAL, **61**, 2461 (1939).

[2] For a detailed procedure of this type of reduction see May and Mosettig, *J. Org. Chem.*, **11**, 441 (1946).

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Esters of Long-chain, Hydroxy Aliphatic Acids

The esters listed in Table I were prepared by the azeotropic method previously reported.[1] 9,10-Dihydroxyoctadecyl 12-hydroxystearate was prepared from 9,10-dihydroxyoctadecanol,[2] m. p. 84.5–86°, and 12-hydroxystearic acid, m. p. 80–81°, prepared from hydrogenated castor oil. 9,10-Dihydroxyoctadecyl 9,10,12-trihydroxystearate was prepared from 9,10-dihydroxyoctadecanol and 9,10,12-trihydroxystearic acid,[3] m. p. 110°. Tetrahydrofurfuryl 9,10-dihydroxystearate was prepared from tetrahydrofurfuryl alcohol, b. p. 115.7° (100 mm.), and 9,10-dihydroxystearic acid,[4] m. p. 95°. The crude esters were obtained in quantitative yields and were hard,

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[1] Swern and Jordan, THIS JOURNAL, **67**, 902 (1945).

[2] Swern, Findley and Scanlan, *ibid.*, **66**, 1925 (1944).

[3] Scanlan and Swern, *ibid.*, **62**, 2309 (1940).

[4] Swern, Billen, Findley and Scanlan, *ibid.*, **67**, 1786 (1945).