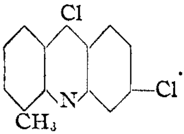
3,9-Dichloro-5-methylacridine, 

.—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]

---

[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.

CHEMICAL LABORATORY — CHARLES D. HURD
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS — OTIS E. FANCHER

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.

---

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

RESEARCH LABORATORY
GENERAL ELECTRIC COMPANY
SCHENECTADY, NEW YORK — RICHARD N. LEWIS

RECEIVED NOVEMBER 20, 1946

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.

---

[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).

DIVISION OF PHYSIOLOGY
NATIONAL INSTITUTE OF HEALTH
BETHESDA 14, MARYLAND — EVERETTE L. MAY

RECEIVED NOVEMBER 6, 1946

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,

---

[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).

TABLE I

ESTERS OF LONG-CHAIN, HYDROXY ALIPHATIC ACIDS

Ester	Formula,	Yield,[a] %	M. p., °C.	Saponification no. Calcd.	Saponification no. Found	Carbon[b] Calcd.	Carbon[b] Found	Hydrogen[b] Calcd.	Hydrogen[b] Found
9,10-Dihydroxyoctadecyl 12-hydroxystearate	$C_{36}H_{72}O_5$	60	86–87	95.9	95.0	73.9	73.6	12.4	11.7
9,10-Dihydroxyoctadecyl 9,10,12-trihydroxystearate	$C_{36}H_{72}O_7$	40	103.5–104.2	90.9	90.2	70.1	70.5	11.8	11.7
Tetrahydrofurfuryl 9,10-dihydroxystearate	$C_{23}H_{44}O_5$	30	59.8–60.6	140.1	142.7	69.0	68.8	11.1	11.3

[a] Purified products after at least three crystallizations from 95% ethanol. [b] Analyses were made by Mary Jane Welsh of this Laboratory.

waxy solids. The purified products were white, odorless solids with the same solubility characteristics as the esters previously reported.[1,5]

---

(5) Swern, Jordan and Knight, THIS JOURNAL, **68**, 1673 (1946).

EASTERN REGIONAL RESEARCH LABORATORY, PHILADELPHIA 18, PA., ONE OF THE LABORATORIES OF THE BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE

H. B. KNIGHT
E. F. JORDAN, JR.
DANIEL SWERN

RECEIVED JANUARY 2, 1947

New Compounds as Plant Growth Regulators

The compounds listed below were prepared for testing for plant growth regulating activity under a contract between the Chemical Warfare Service and the Ohio State University Research Foundation. The activity of some of these compound has been reported in the *Botanical Gazette*, **107**, June (1946).

Methods

A. The phenol was condensed with ethyl bromoacetate in ethanol in presence of an excess of concentrated aqueous potassium carbonate solution at room temperature. The ester formed was isolated and saponified in the usual way. The yield of acid reported is based on the original phenol used. In some cases the reaction mixture was saponified without any attempt at isolation of the ester.

B. *p*-Chlorophenol containing a catalytic amount of sodium *p*-chlorophenolate was treated at 130° with acrylonitrile.[1]

C. The halophenyl γ-bromopropyl ether was prepared from the sodium halophenolate in ethanol and 1,3-dibromopropane. An ethanol solution of the ether was converted to the nitrile[2] by sodium cyanide in the usual manner. The yield of nitrile reported is based on the original phenol used.

D. A solution of the nitrile in glacial acetic acid was hydrolyzed by boiling with aqueous sulfuric acid during six to eighteen hours.

E. A solution of the phenol in pyridine was treated with an equimolecular quantity of ethyl chlorocarbonate at 0°; followed by stirring while allowing to warm to room temperature during one to three hours.

F. (a) Esterification was carried out by refluxing the acid in benzene solution with an excess of the alcohol in presence of a little *p*-toluenesulfonic acid, while removing the water produced in the reaction as fast as formed. (b) Concentrated sulfuric acid was used as catalyst. (c) In the preparation of a methyl ester F(a) was followed, with omission of benzene.

G. A crude sample of 2,4-diiodophenol[3] was converted to the phenoxyacetic acid by Method S. The product was esterified by Method F(a) saponified and the resulting mixture of mono- and diiodophenoxyacetic acids separated by partial precipitation as the potassium salts. Pure 2,4-diiodophenoxyacetic acid was obtained by recrystallization of the free acid from benzene–Skellysolve-B. The yield of acid reported is based on the phenol used for iodination.

H. The corresponding allyl ester was chlorinated in carbon tetrachloride solution at 0°.

I. Reaction of alkali halophenolates with halogenated esters or alcohols. (a) The sodium halophenolate was refluxed with diethyl chlorofumarate in xylene and the resulting ester saponified.[4] (b) Dry potassium 2,4-dichlorophenolate was heated with an equimolecular quantity of ethylene bromohydrin in xylene at 150° for five hours. (c) The sodium halophenolate in ethanol was treated at 75° with ethyl α-bromoheptoate and heated at 75–100° for two hours. The resulting ester was then saponified.

J. A solution of the ketoxime in dioxane and a suspension of the calculated quantity of sodamide in dioxane

---

(1) I. G. Farbenindustrie, French Patent 833,734; *Chem. Zentr.*, **110**, I, 1451 (1939).

(2) Lohmann, *Ber.*, **24**, 2631 (1891).

(3) Brenans, *Bull. soc. chim.*, [3] **25**, 629 (1901).

(4) Ruhemann, *Ber.*, **54**, 912 (1921).

TABLE I

FSA no.	Compound	Method	Yield, %	B. p., °C.	B. p., Mm.	M. p., cor., °C.	t°	n^t_D	Mol. formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, halogen or neutral equivalent Calcd.	Nitrogen, halogen or neutral equivalent Found
80	3,5-Dichlorophenoxyacetic acid	A	50.7			117.5–118			$C_8H_6Cl_2O_3$	43.5	43.6	2.7	3.3	221	227
430	2,4-Dichloromandelic acid	O	15			119.5–120.5			$C_8H_6Cl_2O_3$					221	222
93	2-Bromo-4-chlorophenoxyacetic acid	T	27.9			139–140.5			$C_8H_6ClBrO_3$	36.2	36.5	2.3	2.5	266	267
94	2-Chloro-4-bromophenoxyacetic acid	T	60			144.5–146.5			$C_8H_6ClBrO_3$	36.2	36.4	2.3	2.4	266	270
142	2-Iodo-4-chlorophenoxyacetic acid	A	40.3[c]			136–140			$C_8H_6IClO_3$	30.7	30.7	1.9	2.2	313	314
150	2-Chloro-4-iodophenoxyacetic acid	A	[d]			138–141			$C_8H_6IClO_3$	30.7	30.8	1.9	2.2	313	310
71	2,4-Dibromophenoxyacetic acid	A	65[b]			151.8–153.5			$C_8H_6Br_2O_3$	31.0	30.8	1.9	2.0	310	309
145	2,4-Diiodophenoxyacetic acid	G	2			165–167			$C_8H_6I_2O_3$					404	402