TABLE I

Substituted 2-pyrrolidone R	R^1	R^2	Yield, %	B. p., °C.	Mm.	Formula	Nitrogen, %[a] Calcd.	Found
Dodecyl[b]	H	H	83	202–205	11	$C_{16}H_{31}NO$	5.5	5.8
Tridecyl[c]	H	H	61	210–213	9.5	$C_{17}H_{33}NO$	5.2	5.3
Tetradecyl[d]	H	H	72	201–201.5	2.5	$C_{18}H_{35}NO$	5.0	5.0
Hexadecyl[d]	H	H	72	213–215	2.5	$C_{20}H_{39}NO$	4.5	4.5
Octadecyl[b,d]	H	H	78	219–221	1.5	$C_{22}H_{43}NO$	4.2	4.0
Benzyl[b]	H	H	33	168–170	14	$C_{11}H_{13}NO$	8.0	7.9
4-Diethylamino-1-methylbutyl	H	H	77	162–166	11	$C_{13}H_{26}N_2O$	12.4	12.4
Dodecyl	H	CH_3	56	185–187	3.5	$C_{17}H_{33}NO$	5.2	5.1
Tetradecyl	H	CH_3	45	189–190	1.5	$C_{19}H_{37}NO$	4.7	4.8
Hexadecyl[d]	H	CH_3	31	200–201	1	$C_{21}H_{41}NO$	4.3	4.2
Octadecyl[d]	H	CH_3	33	219–222	1.2	$C_{23}H_{45}NO$	4.0	3.8
Dodecyl	CH_3	C_2H_5	48	162–172	4	$C_{19}H_{37}NO$	4.7	4.9

[a] The analyses were performed by Mrs. J. D. Nevins and Mrs. R. C. Schropp of the Monsanto Analytical Laboratory. [b] Preparation mentioned, but compound not described, in ref. (1b). [c] Prepared by Mr. H. L. Morrill. [d] Waxy solid.

tested *in vitro*, were found to have no bacteriostatic activity. The 2-pyrrolidones with the dodecyl, tetradecyl, octadecyl and 4′-diethylamino-1′-methylbutyl groups in the 1-position were inactive against experimental tuberculosis in guinea pigs. These products were evaluated for chemotherapeutic and pharmacologic action in The Lilly Research Laboratories.

Experimental

Preparation of 2-Pyrrolidones.—Equimolar quantities of the amine and the lactone were heated with agitation at 110–130° for about three hours and then at 250–270° for three to six hours while distilling off water. The excess reactants were distilled off under reduced pressure and the N-substituted pyrrolidone was distilled.

Long chain amines,[2] benzylamine and 1-diethylamino-4-aminopentane reacted satisfactorily, giving 35–85% yields of the corresponding pyrrolidones.

γ-Butyrolactone, γ-valerolactone and γ-ethyl-γ-valerolactone[3] reacted without difficulty with the amines used, although it is clearly seen that under the same conditions γ-valerolactone gives lower yields than does γ-butyrolactone.

The several pyrrolidones prepared were high-boiling liquids or waxy solids.

(2) Gift from Armour and Company. Tridecylamine was prepared in 55% yield by Dr. E. L. Hatlelid using the procedure of Ralston, Selby, Pool and Potts, *Ind. Eng. Chem.*, **32**, 1093 (1940); the ditridecylamine (35%) obtained as a by-product boiled at 240–242° (8 mm.), while Hoerr, Harwood and Ralston, *J. Org. Chem.*, **9**, 201 (1944), reported m. p. 56.5°. Didodecylamine, b. p. 263–265° (27 mm.), was obtained in a preparation of dodecylamine; Wibaut, Heierman and Wagtendonk, *Rec. trav. chim.*, **57**, 456 (1938), reported 195° (0.7 mm.).

(3) Grignard, *Compt. rend.*, **135**, 629 (1902). See Cason, Adams, Bennett and Register, THIS JOURNAL, **66**, 1764 (1944), for an improved method of making γ,γ-dialkyl-butyrolactones.

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NEW COMPOUNDS

Cadalene and Eudalene Trinitrotoluates

Cadalene (50 mg.) and trinitrotoluene (58 mg.) were heated in methanol solution on the water-bath for a few minutes. On cooling, long yellow glistening needles of cadalene trinitrotoluate crystallized out, m. p. 83°, not raised by further crystallization from methanol.

Anal. Calcd. for $C_{15}H_{18}\cdot C_7H_5N_3O_6$: C, 62.12; H, 5.45. Found: C, 62.04; H, 5.56.

Eudalene trinitrotoluate, similarly prepared from eudalene (87 mg.) and trinitrotoluene (103 mg.), formed short, dull yellow needles, m. p. 62–63°, not raised by further crystallization.

Anal. Calcd. for $C_{14}H_{16}\cdot C_7H_5N_3O_6$: C, 61.31; H, 5.15; N, 10.21. Found: C, 61.02; H, 5.15; N, 10.4.

We are indebted to Mr. A. R. Penfold for a specimen of eudesmol from which the eudalene was prepared by dehydrogenation, to the Chemical Society and the Australian and New Zealand Association for the Advancement of Science for grants and one of us (W. I. T.) for a Duffus Lubecki Scholarship.

The analyses are by Drs. Weiler and Strauss.

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RECEIVED NOVEMBER 5, 1946

2-Arylamino-4-chlorobenzoic Acids and 9-Chloroacridines[1]

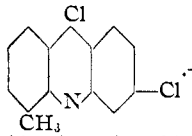
2-Anilino-4-chlorobenzoic Acid, $C_6H_5NHC_6H_3ClCOOH$.—A mixture of 153 g. (0.8 mole) of 2,4-dichlorobenzoic acid, 93 g. (1 mole) of freshly distilled aniline, 111 g. (0.8 mole) of anhydrous potassium carbonate, 4 g. of copper bronze and 600 ml. of *n*-pentyl alcohol was heated under reflux with stirring for five hours. One hundred ml. of 35% potassium hydroxide solution was added, and the excess aniline and pentyl alcohol was removed by steam distillation. The residue was filtered and acidified (concentrated hydrochloric acid). The purple solid which separated was removed by filtration and washed with water. Crystallization of the moist product from alcohol gave purple needles, and a second recrystallization from benzene gave 105 g. (53% yield) of slightly grey needles melting at 201°, cor.

Anal. Calcd. for $C_{13}H_{10}ClNO_2$: Cl, 14.31; neut. equiv., 247.7. Found: Cl, 14.08; neut. equiv., 247.6, 248.5.

2-*o*-Toluidino-4-chlorobenzoic Acid.—Similar directions were followed. From 0.8 mole of 2,4-dichlorobenzoic acid and *o*-toluidine was obtained 75 g. (36%) of the desired acid, m. p. 208°, cor. after crystallization from alcohol.

Anal. Calcd. for $C_{14}H_{12}ClNO_2$: Cl, 13.54; neut. equiv., 261.7. Found: Cl, 13.40; neut. equiv., 262.1, 260.3.

(1) This report is based on work done under contracts, recommended by the National Defense Research Committee and the Committee on Medical Research, between the Office of Scientific Research and Development and Northwestern University.

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.

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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.

(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.

(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,

(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).