Anal. Calcd. for $C_6H_{15}SiBr$: Br, 40.95; neut. equiv., 195. Found: Br, 40.93; neut. equiv., 196.

An ether solution of α-chloroethyldiethylaminosilane, 24 g. (0.145 mole) was treated with dry hydrogen bromide to give 12 g. (0.052 mole) of α-chloroethyldiethylbromosilane, b. p. 194–196°, n^{20}_D 1.4762, a yield of 26%. A product of higher purity was obtained in the reaction with hydrobromic–sulfuric acid mixture.

Anal. Calcd. for $C_6H_{14}SiClBr$: Br, 34.81; neut. equiv., 230. Found: Br, 33.99; neut. equiv., 234.

E. With Hydrobromic-Sulfuric Acid Mixture.—In a one-liter three-necked flask equipped with reflux condenser, mercury-sealed stirrer, and dropping funnel, there was placed 300 cc. of 48% hydrobromic acid. This was cooled in an ice-bath and 200 cc. of concentrated sulfuric acid was added. To the mixture there was then added through the dropping funnel 41 g. (0.31 mole) of triethylaminosilane. After stirring the reaction mixture for twenty minutes, the resulting two layers were separated and the organic layer dried over sodium sulfate. Fractionation gave 33.5 g. (0.17 mole) of triethylbromosilane, b. p. 78–79° (45 mm.), n^{20}_D 1.4561, Br, 40.8% (calcd. 40.95%), a yield of 55%.

α-Chloroethyldiethylaminosilane, 52 g. (0.31 mole), was treated with hydrobromic–sulfuric acid by a procedure similar to that used for triethylaminosilane. Distillation of the product gave 58.5 g. (0.255 mole) of α-chloroethyldiethylbromosilane, b. p. 105–106° (46 mm.), n^{20}_D 1.4784, d^{20} 1.2661, Br, 34.8% (calcd. 34.81%), a yield of 81%.

DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA RECEIVED MAY 17, 1947

Conductivities of Aqueous Solutions of Dodecylammonium Chloride

BY A. W. RALSTON AND D. N. EGGENBERGER

We are currently engaged in a study of the effects of inorganic electrolytes and of various organic compounds upon the electrical behavior of solutions of cationic colloidal electrolytes. During the course of this investigation we have redetermined the equivalent conductivities of aqueous solutions of dodecylammonium chloride at various temperatures and have found that the values are somewhat lower than those which we have previously reported.[1,2] We are of the opinion that the dodecylammonium chloride which was used in our earlier work contained traces of impurities, since our present values have been reproduced with several quite pure samples of this amine salt prepared by different investigators. The values herein reported, when plotted against the square root of the volume normality, $\sqrt{N_v}$, show a decidedly less steep slope within the first range, although the concentrations of amine salt at the critical points for micelle formation are in agreement with those reported previously.

The values of the equivalent conductivities of aqueous solutions of dodecylammonium chloride at various temperatures are shown in Table I.

TABLE I

EQUIVALENT CONDUCTIVITIES OF AQUEOUS SOLUTIONS OF DODECYLAMMONIUM CHLORIDE

N_v 20°	Λ	N_v 25°	Λ	N_v 30°	Λ	N_v 40°	Λ	N_v 50°	Λ	N_v 60°	Λ
0.000507	87.6	0.000777	96.0	0.000985	106.4	0.000801	127.7	0.000968	148.6	0.000905	172.1
.00127	86.5	.00177	95.2	.00179	105.7	.00186	126.0	.00212	147.4	.00194	169.5
.00284	85.0	.00398	93.1	.00335	104.8	.00405	124.0	.00445	145.5	.00466	166.7
.00402	84.4	.01003	91.3	.00384	104.4	.00728	123.0	.00820	142.4	.01433	160.6
.00635	83.0	.01025	90.9	.00608	103.5	.00806	121.5	.00933	141.8	.0180	155.0
.00934	81.7	.0156	86.6	.00842	102.4	.01455	119.7	.01417	140.7	.0248	130.0
.01025	81.4	.0168	83.1	.01137	101.5	.0177	107.2	.0181	128.6	.0439	96.0
.0170	74.1	.0172	80.7	.01354	100.7	.0207	96.5	.0223	112.5	.0729	79.7
.0181	70.3	.0196	73.5	.0150	98.9	.0480	61.8	.0240	109.0	.1345	70.8
.0208	64.1	.0223	68.4	.0173	90.5	.0796	52.1	.0423	80.5		
.0265	54.3	.0437	45.7	.0226	75.4	.1353	47.2	.0682	67.0		
.0484	38.1	.0769	36.3	.0235	72.9			.1383	58.4		
.0782	31.1	.1371	31.7	.0384	54.9						
.1397	26.8			.0622	43.7						
				.1008	38.7						
				.1493	36.4						

Experimental

Preparation of Dodecylammonium Chloride.—Commercially distilled dodecylamine was fractionated through a Stedman packed column and the fraction boiling at 111.5° at 4 mm. retained. This fraction melted at 28.30°. The amine (200 g.) was dissolved in benzene (2 liters) and treated with dry hydrogen chloride. Upon cooling, crystals of dodecylammonium chloride precipitated. The crystals were removed by filtration and crystallized three times from benzene. The sample was analyzed by a previously described procedure.[3] (*Anal.* Calcd. for $C_{12}H_{25}NH_2$, 83.54; Cl, 16.00. Found: . $C_{12}H_{25}NH_3$, 83.84; Cl, 16.06).

Conductivity Determinations.—Conductivities were determined in the manner and with the equipment previously described.[1]

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(1) Ralston, Hoerr and Hoffman, THIS JOURNAL, **64**, 97 (1942).

(2) Ralston and Hoerr, *ibid.*, **64**, 772 (1942).

(3) Ralston and Hoerr, *Ind. Eng. Chem., Anal. Ed.*, **16**, 459 (1944).

RESEARCH LABORATORY OF ARMOUR AND COMPANY
CHICAGO, ILLINOIS RECEIVED JULY 14, 1947

Trimethylgermanium Chloride

BY EUGENE G. ROCHOW[1]

The preparation of methylgermanium trichloride and dimethylgermanium dichloride by the

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(1) Research Laboratory, General Electric Company.

action of methyl chloride upon elementary germanium in the presence of a copper catalyst has been described in a previous paper.[2] In that investigation, no trimethylgermanium chloride was found in the product of the direct reaction, although the compound may have been present in an amount too small to be recovered in the distillation.

In order to round out the series of methylgermanium chlorides, some of the pure dimethylgermanium dichloride obtained in the direct reaction has been methylated with Grignard reagent.

Experimental

One-half mole of methylmagnesium chloride was allowed to drip slowly into a solution of 0.5 mole of dimethylgermanium dichloride in 300 cc. of dry ether. The mixture stood overnight and the magnesium chloride was filtered off. Ether was distilled from the liquid product, and the residue was fractionated. Nineteen grams of trimethylgermanium chloride was isolated. *Anal.* Calcd.: Cl, 23.15. Found: Cl, 23.3, 23.5. Because of the complete analysis of its progenitor[2] and the impossibility of halogen exchange in the system used, no further analyses were considered necessary.

Trimethylgermanium chloride is a colorless liquid which boils at 115°, melts at −13°, and has a refractive index of 1.4314 at 29° for sodium light. It hydrolyses rather slowly in water to form volatile products.

This compound completes the series

$GeCl_4$	b. p.	83.1°
CH_3GeCl_3	b. p.	111°
$(CH_3)_2GeCl_2$	b. p.	124°
$(CH_3)_3GeCl$	b. p.	115°
$(CH_3)_4Ge$	b. p.	43.4°

It is seen that the substitution of methyl groups for chlorine in $GeCl_4$ does not bring about a gradual lowering of the boiling point to that of $(CH_3)_4Ge$, but causes a rise and then a decline, with a maximum at $(CH_3)_2GeCl_2$. The "abnormally" high maximum boiling points for the disubstituted compounds $(CH_3)_2SiCl_2$ and $(CH_3)_2GeCl_2$ correspond to a lower reactivity in some reactions,[3] and the association therefore may be considered as a form of self-stabilization.

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[2] Rochow, This Journal, **69**, 1729 (1947).

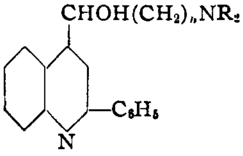
[3] Fuoss, *ibid.*, **65**, 2406 (1943).

SCHENECTADY, NEW YORK RECEIVED JUNE 27, 1947

Synthesis of Antimalarials. VIII.[1] 1-(7-Chloro-2-phenylquinolyl-4)-6-diethylaminohexanedione-1,3 and Certain Other Compounds

BY JOSEPH C. SHIVERS[2] AND CHARLES R. HAUSER

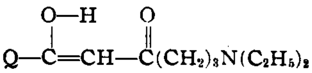
Various workers[3] have synthesized 4-quinolinemethanols (I) certain of which possess considerable antimalarial activity. The present note describes the synthesis of the β-diketone (II),[4] which, in its enol form (III),[4] resembles 4-quinolinemethanols. An attempt was made to prepare the 1,3-diol (IV)[4] from the β-diketone but a pure product was not isolated.



(I)

$Q{-}COCH_2CO(CH_2)_3N(C_2H_5)_2$

(II)



$$Q{-}\overset{\overset{\displaystyle O{-}H}{|}}{C}{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_3N(C_2H_5)_2$$

(III)

$Q{-}CHOHCH_2CHOH(CH_2)_3N(C_2H_5)_2$

(IV)

$CH_3CO(CH_2)_3N(C_2H_5)_2$

(V)

$Q{-}CO_2C_2H_5$

(VI)

The crude β-diketone (II–III)[4] was obtained in good yield by acylating ketone (V) with ester (VI)[4] by means of sodium amide; however, the pure product was isolated in only 15% yield. The acylation practically failed in the presence of sodium ethoxide. An attempt to acylate ketone (V) with ethyl 2-(3′-nitrophenyl)-cinchoninate by means of sodium amide produced tars.

Experimental[5]

2-Phenyl-7-chlorocinchoninic acid was prepared from benzaldehyde, *m*-chloroaniline and pyruvic acid by the Doebner reaction using a modification of the procedure kindly furnished by Elderfield, Gensler and Brody of Columbia University who based their procedure on that of earlier workers.[6] Our modification[7] consisted in first isolating N-benzal-3-chloroaniline and in treating it in refluxing commercial absolute ethanol with the pyruvic acid; the yield of 2-phenyl-7-chlorocinchoninic acid was 30%. The intermediate anil, b. p. 155° at 2 mm. (reported b. p. 338° at atm. press.)[8] was obtained in 90% yield by allowing a mixture of benzaldehyde and *m*-chloroaniline to stand overnight, extracting with ether and distilling the dried ether solution.

Ethyl 2-phenyl-7-chlorocinchoninate (VI), m. p. 88° (reported m. p. 89–89.5°)[9] was obtained in 75% yield by esterification of the crude acid using the common sulfuric acid method.

2-(3′-Nitrophenyl)-cinchoninic acid was obtained in 47% yield from pyruvic acid and 3-nitrobenzalaniline (m. p. 68°, reported m. p. 66°)[10] which was prepared in 86% yield from 3-nitrobenzaldehyde and aniline. After recrystallization from glacial acetic acid, a sample of the acid melted at 257°, darkening at 245°.

Anal. Calcd. for $C_{16}H_{10}O_4N_2$: C, 65.30; H, 3.43; N, 9.52. Found: C, 65.12; H, 3.72; N, 9.70.

Ethyl 2-(3′-nitrophenyl)-cinchoninate, m. p. 110–112°, was obtained in 70% yield by the esterification of the crude acid by the sulfuric acid method, and recrystallization from ethanol–water using charcoal. A second recrystallization gave light tan crystals, m. p. 112–113°.

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[1] Part of this work was done under an O. S. R. D. contract. For paper VII of this series see This Journal, **68**, 1544 (1946).

[2] Present address: E. I. du Pont de Nemours and Company, Inc., Pioneering Research Section, Buffalo, New York.

[3] See especially King and Work, *J. Chem. Soc.*, 1307 (1940); 401 (1942); Lutz, *et al.*, This Journal, **68**, 1813 (1946); Winstein, Jacobs, *et al.*, *ibid.*, **68**, 1831 (1946); Campbell and Kerwin, *ibid.*, **68**, 1837 (1946); Campbell, Helbing and Kerwin, *ibid.*, **68**, 1840 (1946); Buchman, Sargent, Meyers and Seneker, *ibid.*, **68**, 2692 (1946).

[4] Q = 7-chloro-2-phenyl-4-quinolyl.

[5] Analyses by Oakwold Laboratories, Alexandria, Va.

[6] Borsche, *Ber.*, **41**, 3884 (1908); John, *J. prakt. Chem.*, [2] **130**, 314 (1931).

[7] This was devised by M. J. Weiss and G. A. Reynolds of this Laboratory.

[8] Lachowicz, *Monatsh.*, **9**, 697 (1889).

[9] Tarbell and co-workers, This Journal, **67**, 1583 (1945).

[10] Schwalbe, *Chem. Zentr.*, **74**, I, 231 (1903).