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[3] 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.

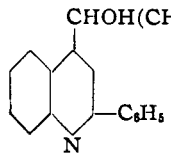
(2) Rochow, THIS JOURNAL, **69**, 1729 (1947).
(3) Fuoss, *ibid.*, **65**, 2406 (1943).

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—C(OH)=CH—$C(CH_2)_3N(C_2H_5)_2$
(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°.

(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).

Anal. Calcd. for $C_{18}H_{14}O_4N_2$: C, 67.07; H, 4.38; N, 8.70. Found: C, 67.39; H, 4.50; N, 8.86.

1-(7'-Chloro-2'-phenylquinoline-4')-5-diethylaminohexanedione-1,3 (II) was prepared by acylating 1-diethylaminopentanone-4 (V) with ethyl 2-phenyl-7-chlorocinchoninate (VI) by means of sodium amide according to an adaptation of the method developed in this Laboratory.[11] To a stirred suspension of 0.4 mole of sodium amide[11] in 500 ml. of liquid ammonia was added rapidly 0.4 mole of the ketone in 75 ml. of dry ether. After replacing the ammonia by ether,[11] 0.2 mole of the ester in one liter of dry ether was added and the mixture refluxed five hours and then allowed to stand overnight. The mixture was poured onto 750 ml. of 10% acetic acid and crushed ice; after shaking thoroughly, the ether phase was extracted with 500 ml. of 10% acetic acid and combined with the aqueous phase. To the combined acetic acid solution was added cold 20% sodium hydroxide solution to a *p*H of 11 (oil separating). Carbon dioxide was passed into the mixture to a *p*H of 9, and the oil extracted with ether. The solvent was distilled from the dried ether solution leaving the crude oily β-diketone (79%) which, after drying over phosphorus pentoxide in a vacuum desiccator, was recrystallized from a mixture of benzene and 30–60° petroleum ether, freezing out with dry ice. There was obtained a 15% yield of pure β-diketone, melting at 88°; this melting point was not raised by further recrystallization but was depressed by admixture with the cinchoninic ester (VI).

Anal. Calcd for $C_{31}H_{27}O_2Cl$: C, 70.98; H, 6.44; N, 6.62. Found: C, 70.96, 70.61; H, 6.34, 6.17; N, 6.63, 6.40.

The β-diketone gave a deep red enol test with alcoholic ferric chloride, and formed a 2,4-dinitrophenylhydrazone which soon became oily. Attempts to convert the crude β-diketone to a picrate, pyrazole, hydrochloride or a copper salt failed. The crude β-diketone, which was entirely soluble in dilute hydrochloric acid, appeared to decompose on distillation at 0.1 mm., since the distillate, b. p. 175–190°, was not entirely soluble in the acid.

Hydrogenation of the crude β-diketone in glacial acetic acid at room temperature and low pressure in the presence of Adams catalyst[12] absorbed the calculated amount of hydrogen within two hours and produced an oil, b. p. 240–250° at 0.1 mm., which, as should be expected, failed to give the enol test with alcoholic ferric chloride; however, the pure 1,3-diol or a solid derivative of it has not been isolated.

(11) Adams and Hauser, THIS JOURNAL, **66**, 1220 (1944); Levine, Adams, Conroy and Hauser, *ibid.*, **67**, 1510 (1945).

(12) Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. I, 463 (1946).

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY
DURHAM, NORTH CAROLINA RECEIVED JUNE 5, 1947

Identification of Esters of Dibasic Acids by the Use of Ethanolamine

BY WILLIAM H. RAUSCHER AND WILLIAM H. CLARK

In an attempt to find a rapid and satisfactory method for the identification of esters, their ammonolysis by ethanolamine in the absence of water has been investigated. It was hoped that on refluxing esters with ethanolamine that solid amides which would suitably characterize the acid would be formed, and that the alcohol simultaneously formed could be distilled out of the reaction mixture in such a state of purity that it could be easily identified in the usual manner.

On refluxing a number of esters with ethanolamine it was found that they were rapidly ammonolyzed, and that the alcohol could be distilled from the reaction mixture at a temperature very close to its boiling point. A redistillation of the alcohol from a simple distilling flask gave a product of correct boiling point from which a standard solid derivative of correct melting point was made. The reaction mixture from which the alcohol had been distilled did not yield solid amides on cooling in the case of most esters of monobasic acids which were investigated. However, the series of esters of dibasic acids shown in the table did give solid amides on cooling the reaction mixture after distilling off the alcohol. After a recrystallization the amides proved to have melting points suitable for purposes of identification.

Experimental

The reflux apparatus consisted of a 50-cc. flask and water cooled reflux condenser, both with ground joints. A mixture of 5 g. of the ester and 15 g. of ethanolamine was refluxed for fifteen minutes. After cooling below the boiling point of the alcohol, the condenser was replaced by a short Vigreux column and the alcohol distilled off. The residue was cooled to room temperature to obtain a solid product in the case of the esters of dibasic acids listed in the table. The amides were recrystallized from a 1:1 solution of alcohol and benzene. The alcohol which had been distilled from the reaction mixture was redistilled from a simple distilling flask, its boiling point checked and at least one solid derivative prepared from the distillate by standard procedures.

TABLE I

N,N'-DI-β-HYDROXYAMIDES OF DIBASIC ACIDS

Ester	M. p. (cor.), °C.	Nitrogen, % Calcd.	Found
Methyl oxalate[a]	169–169.2	15.95	15.90–16.03
Ethyl oxalate[a]	169–169.2	15.95	
n-Butyl oxalate[a]	169–169.2	15.95	
Ethyl malonate	127.0–127.5	14.71	14.73–14.81
Ethyl succinate	156.2–156.7	13.69	13.55–13.61
Ethyl glutarate[b]	119.6–120.0	12.85	12.86–12.99
Ethyl adipate	130.2–130.7	12.08	12.02–12.05
Ethyl suberate	138.5–138.9	10.77	10.88–10.79
Ethyl azelate	125.5–125.9	10.22	10.33–10.81
Methyl sebacate	144.5–145.0	9.72	9.77– 9.89

[a] Required no refluxing. [b] Dioxane used for recrystallization of amide.

DEPARTMENT OF CHEMISTRY
RENSSELAER POLYTECHNIC INSTITUTE
TROY, N. Y. RECEIVED AUGUST 12, 1947

NEW COMPOUNDS

α-Amino-β-mercapto-*n*-valeric Acid Hydrochloride

α-Amino-β-mercapto-*n*-valeric acid hydrochloride was prepared by following the procedure of Carter, Stevens and Ney[1] for the corresponding butyric acid.

2-Phenyl-4-*n*-propylidene-5-oxazolone was synthesized by the method of Carter, Handler and Melville[2] using

(1) Carter, Stevens and Ney, *J. Biol. Chem.*, **139**, 247 (1941).

(2) Carter, Handler and Melville, *ibid.*, **129**, 359 (1939).