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 $C_{25}H_{27}O_2Cl$: 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.

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[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
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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.	Nitrogen, % 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
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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

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

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

slight modifications. The mixture of 72 g. of hippuric acid, 33 g. of anhydrous sodium acetate and 200 ml. of acetic anhydride was maintained at 30° under a reflux condenser while 250 ml. of propionaldehyde was added over a period of one hour. The mixture was then heated about forty-five minutes at 50–60° until an almost clear orange solution resulted. Decomposition with ice yielded a semi-crystalline mass which was washed several times with ice water. The small amount of oil present was dissolved by adding 300 ml. of 70% ethanol and the resulting mixture was filtered by suction to give light yellow crystals. These crystals were sucked as dry as possible, washed several times with water and air dried. The yield of crude azlactone was 30–33 g., m. p.[3] 79–81°. Recrystallization from 50% ethanol gave white needles, m. p. 81–83°.

Anal. Calcd. for $C_{12}H_{11}NO_2$: N, 6.96. Found: N, 6.94.

If the temperature of the reaction were allowed to rise above 60° or the time of heating were prolonged, the yield suffered markedly and the majority of the resultant product was the dark red oil. The crude material was entirely satisfactory for the next step.

α-Benzoylamino-β-benzylmercapto-*n*-valeric Acid.—To a solution of 0.67 g. of sodium in 140 ml. of dry methanol was added 17.2 g. of benzyl mercaptan. Then a solution of 27 g. of 2-phenyl-4-*n*-propylidene-5-oxazolone in 140 ml. of dry benzene was added, with stirring, over a period of one hour. The mixture was allowed to stand at room temperature for fourteen hours. The product was isolated as described for the butyric acid derivative[1] except that the mixture was stirred and heated on the steam-bath for five hours. It was chilled and diluted with 250 ml. of water. A dark brown, gummy mass precipitated and tended to solidify after standing for several hours. It was washed with water and dissolved in 150 ml. of benzene. The water which had been entrapped was removed and the benzene solution was filtered. The solution was diluted with 500 ml. of gasoline causing the separation of an oil that soon solidified into light gray crystals. The yield of crude α-benzoylamino-β-benzylmercapto-*n*-valeric acid was 15 g., m. p. 102–104°. A small sample was recrystallized from the benzene–gasoline mixture, m. p. 103–105°.

Anal. Calcd. for $C_{19}H_{21}NO_3S$: N, 4.08. Found: N, 3.84.

The crude material was sufficiently pure for use in the following step.

A larger run from 60 g. of the oxazolone yielded 60 g. of the acid melting at 102–104°.

α-Amino-β-benzylmercapto-*n*-valeric Acid.—A mixture of 30 g. of α-benzoylamino-β-benzylmercapto-*n*-valeric acid, 230 ml. of commercial formic acid (87%), 230 ml. of concentrated hydrochloric acid and 230 ml. of water was heated under reflux for twelve hours. After the mixture had been cooled in an ice-bath, starting material (15 g.) was removed by filtration. The clear filtrate was evaporated to dryness *in vacuo* and the residue was taken up in 500 ml. of water. A small amount of a brown insoluble substance was removed by filtration. The filtrate was made slightly alkaline with ammonium hydroxide and then was evaporated to remove excess ammonia. α-Amino-β-benzylmercapto-*n*-valeric acid crystallized in white plates, yield 7.5 g., m. p. 172–174°. A small sample was recrystallized from water, m. p. 177–179°.

Anal. Calcd. for $C_{12}H_{17}NO_2S$: N, 5.87. Found: N, 5.98.

α-Amino-β-mercapto-*n*-valeric Acid Hydrochloride.—Sodium (about 2.5 g.) in small pieces was added with vigorous stirring to a solution of 7 g. of the above acid in 100 ml. of liquid ammonia. The metal was added until a deep blue color persisted. This color was discharged by the addition of sufficient solid ammonium chloride. The ammonia was then allowed to evaporate, eventually at reduced pressure to remove final traces. The residue was washed with ether and again evaporated *in vacuo*. The white product was dissolved in 50 ml. of dilute hydrochloric acid and the solution was extracted twice with 50-ml. portions of ether. Again the solution was evaporated to dryness *in vacuo*.

This residue was extracted with 150 ml. of absolute ethanol and the ammonium and sodium chlorides were removed by filtration. The alcohol solution was evaporated to dryness at reduced pressure. The light yellow solid was redissolved in 100 ml. of absolute ethanol and this solution was treated with decolorizing charcoal, filtered and evaporated *in vacuo*.

The white crystalline solid was dissolved in 75 ml. of absolute ethanol. Anhydrous ether was added until a slightly cloudy solution resulted. After the mixture had stood for fiteen minutes, the amino acid hydrochloride began to crystallize in small, white platelets. The mixture was then chilled for several hours and filtered. The yield of white, crystalline α-amino-β-mercapto-*n*-valeric acid hydrochloride was 3 g., m. p. 154–156°. More acid was obtained by working up the ether–ethanol mother liquor. The product gave a strong nitroprusside test to indicate the presence of the sulfhydryl rather than sulfide group.

After two further recrystallizations, the melting point was 163–165°. The nitroprusside test was still strongly positive.

Anal. Calcd. for $C_5H_{11}NO_2S{\cdot}HCl$: N, 7.54. Found: N, 7.32.

Throughout this synthesis no attempt was made to separate the two theoretically possible racemic modifications in pure form or to determine if more than one form were present.

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(3) Melting points were determined by means of a Fisher–Johns melting-point block.

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4-Fluoroanthranilic Acid

4-Fluoro-2-nitrotoluene.—3-Nitro-4-toluidine (228 g., 1.5 moles)[1] was suspended in a mixture of 313.5 cc. of concd. hydrochloric acid and 450 cc. of water, chilled to 0° and diazotized using 130 g. of sodium nitrite (as a 35% solution). The filtered diazonium solution was stirred at 0° while 451 g. of 40% fluoboric acid solution was added (*ca.* ten minutes), and stirred for half an hour. After washing (ice-water, methanol, and ether), the cream-colored crystalline diazonium borofluoride was dried, first in air, then *in vacuo* (over paraffin and phosphoric anhydride); yield, 202 g. (54%).

The diazonium borofluoride was decomposed by heating it alone or mixed with an equal weight of acid-washed sand in an apparatus with wide-bore tubing (25 mm.) connected to several traps (*cf.* ref. 2). All products of the reaction, including the residual ashes in the decomposition flask, were combined and distilled with steam. The distillate was extracted with ether, and the extracts freed of phenolic matter by washing with 5% sodium hydroxide and saturated salt solution. After drying (Na_2SO_4), the extract was fractionated[3]; 125–134 g. (67–71%) of yellow liquid was collected at 75–76° (5 mm.) or 108–109° (23 mm.), n^{25}_D 1.5212. 4-Fluoro-2-nitrotoluene was previously obtained by the nitration of 4-fluorotoluene[4]; b. p. 102.4° (20 mm.), n^{25}_D 1.51997.

5-Fluoro-2-acetotoluidide.—Reduction of 4-fluoro-2-nitrotoluene by the method of West,[5] using aqueous

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(1) Noelting and Collin, *Ber.*, **17**, 263 (1884).

(2) Flood, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 295.

(3) A 25 cm. vacuum-jacketed Vigreux column was used in the distillation.

(4) Desirant, *Bull. sci. acad. roy. Belg.*, **19**, 325 (1933); *C. A.*, **27**, 4781^8 (1933).

(5) West, *J. Chem. Soc.*, 494 (1925).