heated at 250–260° in a distilling flask having a wide side-arm sealed to a receiver. After half an hour, when evolution of hydrogen sulfide had ceased, the product was distilled at 0.5 mm. pressure. Recrystallization of the distillate from benzene yielded 5 g. of 1-acetylaminophenanthrene in the form of colorless needles; m. p. 219–220°. From the benzene filtrate there was obtained 1.5 g. of unchanged tetrahydro derivative which can be used in another dehydrogenation reaction. The 1-acetylaminophenanthrene was identical with the product obtained by acetylation of 1-aminophenanthrene prepared through the Beckmann rearrangement.[1] On hydrolysis by twenty-four hour boiling with an alcoholic solution of hydrochloric acid the acetyl derivative was converted completely to 1-aminophenanthrene; m. p. 146–147°.

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The Action of Benzylamine on Aliphatic Esters

BY C. A. BUEHLER AND CHARLES A. MACKENZIE

In an attempt to develop an improved method for the identification of aliphatic esters, they were treated with benzylamine in aqueous solution. This scheme is similar to that already in use for certain halogenated aliphatic esters which, with ammonium hydroxide in the cold, form the corresponding amides. Both these reagents possess approximately the same dissociation constants, but it appeared that benzylamine, in contrast to ammonia, might be employed successfully at boiling temperatures with the esters of weaker acids because of its higher boiling point.

From Tables I and II it can be seen that benzylamine reacts with the esters studied either to form the N-benzylamide or the benzylamine hydrohalide. With the polyhalogenated esters investigated, the corresponding N-benzylamides form readily even in the cold. Of the monohalogenated esters studied, only one, ethyl chloroacetate, could be induced to undergo a similar reaction. This type, by the more vigorous treatment used for non-halogenated esters or, preferably, by heating with the amine in the absence of water, yields the benzylamine hydrohalide, a reaction[1] which has been represented as

$$XCH_2COOR + 2C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH_2NHCH_2COOR + C_6H_5CH_2NH_2{\cdot}HX$$

By refluxing from one to five hours, depending upon the strength of the acid present in the ester, the non-halogenated esters produced N-benzylamides. All the esters, save those of the higher fatty acids, gave satisfactory yields.

TABLE I

N-BENZYLAMIDES FROM ESTERS OF NON-HALOGENATED ACIDS

Ester	Formula	M. p., °C. Obsd.	M. p., °C. Corr.	Lit.	Nitrogen, % Calcd.	Nitrogen, % Found
Ethyl formate	$HCONHCH_2C_6H_5$	59.6–60.2	59.8–60.4	49[a]	10.37	10.46
Methyl acetate[b]	$CH_3CONHCH_2C_6H_5$	60.4–61.0	60.7–61.3	60–61[c]		
Ethyl propionate	$C_2H_5CONHCH_2C_6H_5$	42.6–43.7	42.6–43.7		8.58	8.46
Ethyl *n*-butyrate	$C_3H_7CONHCH_2C_6H_5$	36.9–38.0	36.9–38.0		7.91	7.89
Ethyl *i*-butyrate	$C_3H_7CONHCH_2C_6H_5$	86.3–87.3	87.0–88.0		7.91	8.07
Ethyl *n*-valerate	$C_4H_9CONHCH_2C_6H_5$	41.1–41.8	41.1–41.8		7.33	7.38
Ethyl *n*-caproate	$C_5H_{11}CONHCH_2C_6H_5$	50.1–51.2	50.3–51.4		6.83	6.88
Ethyl crotonate	$C_3H_5CONHCH_2C_6H_5$	111.1–112.2	112.5–113.6		8.00	7.96

[a] Holleman, *Rec. trav. chim.*, **13**, 415 (1894). [b] Identical results were obtained with ethyl, propyl, butyl, isobutyl, *s*-butyl, amyl and isoamyl acetates. [c] Amsel and Hofmann, *Ber.*, **19**, 1286 (1886).

TABLE II

COMPOUNDS FROM ESTERS OF HALOGENATED ACIDS

Ester	Formula	M. p., °C. Obsd.	M. p., °C. Corr.	Lit.	Nitrogen, % Calcd.	Nitrogen, % Found
Ethyl chloroacetate	$ClCH_2CONHCH_2C_6H_5$[a]	92.2– 92.8	93.0– 93.6	93.5– 94.5 (corr.)[b]		
Ethyl chloroacetate	$C_6H_5CH_2NH_2{\cdot}HCl$[c]	257.0–259.0	263.6–265.7	255.5–258.0[d]	9.75	9.79
Ethyl bromoacetate	$C_6H_5CH_2NH_2{\cdot}HBr$[e]	218.0–219.0	223.0–224.1	215–216[f]	7.45	7.52
Ethyl dichloroacetate	$Cl_2CHCONHCH_2C_6H_5$	94.2– 95.0	94.8– 95.6	95–96[g]		
Ethyl trichloroacetate	$Cl_3CCONHCH_2C_6H_5$	92.8– 93.6	93.6– 94.4	90–91[h]	5.55	5.59

[a] Prepared by method described for polyhalogenated esters. [b] Jacobs and Heidelberger, *J. Biol. Chem.*, **20**, 686 (1915). [c] Ethyl α-chloropropionate gave the same product. [d] Hoogewerff and van Dorp, *Rec. trav. chim.*, **5**, 253 (1886). [e] Ethyl β-bromopropionate and ethyl α-bromo-*n*-butyrate gave the same product. [f] Wallach, *Ann.*, **259**, 308 (1890). [g] Mannich and Kuphal, *Arch. Pharm.*, **250**, 544 (1912). [h] Braun, *Ann.*, **453**, 143 (1927).

Experimental

Preparation of Ester Derivatives

(a) Polyhalogenated Esters.—A mixture of 0.5 cc. of ester, 2 cc. of benzylamine and 0.5 cc. of water was im-

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(1) Mason and Winder, *J. Chem. Soc.*, **65**, 187 (1894).

mersed in an ice-bath and shaken vigorously at intervals of a few minutes until a solid formed. Purification of the solid was effected by recrystallization from ligroin.

(b) **Monohalogenated Esters.**—Although the derivatives of monohalogenated esters may be prepared as in (c), a better procedure is to heat 2 mols of the amine with 1 mol of the ester for a few minutes when the hydrohalide forms. To obtain the salt in pure form, it was dissolved in hot ethyl acetate containing sufficient ethyl alcohol to effect solution, after which the solid crystallized from the cooled solution upon the addition of a few cc. of ether.

(c) **Non-halogenated Esters.**—The ester, 2 cc., mixed with 4 cc. each of benzylamine and water and, when necessary, sufficient ethyl alcohol or dioxane to effect solution, was refluxed one hour (for formates), two hours (for acetates) or from four to five hours (for higher esters like caproates). The excess of reagents was removed by distilling up to 200°, after which the derivative[2] in the distillation flask was crystallized from hot ligroin by cooling to room temperature or lower.

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[2] Before final crystallization, derivatives melting below 50° were distilled off over a range beginning at 290° and continuing until decomposition occurred in the distillation flask.

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The Thermal Decomposition of Gaseous Hydrogen Peroxide

BY G. B. KISTIAKOWSKY AND S. L. ROSENBERG[1]

The thermal decomposition of gaseous hydrogen peroxide was investigated semi-quantitatively by a static method at 85 and 98°. A very pure, 70% peroxide was used. The reaction in a quartz flask is heterogeneous, with an almost negligible temperature coefficient. Times for 50% reaction varying from one to thirty minutes were obtained, the reaction rate increasing with time due to changes in the reaction vessel surface. No stopping of the reaction at about 15% completion as described by Elder and Rideal[2] could be detected. Furthermore, the pressure increase accompanying the reaction proved to be the theoretical value of 50% (based on hydrogen peroxide present), rather than the somewhat astonishing value of about 1000% found by these authors.

Some experiments were tried, where the reaction vessel was flushed with oxygen prior to the reaction. This had no effect, so that neither oxygen from the reaction nor other oxygen leads to a stoppage of the reaction before completion. In another experiment a thin coating of paraffin wax was applied to the interior of the quartz reaction bulb. This slowed down the reaction somewhat, demonstrating its heterogeneity.

We take this opportunity of thanking Mr. P. Giguere of McGill University for the gift of some very pure 70% hydrogen peroxide.

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[1] McGill University Moyse traveling fellow.

[2] Elder and Rideal, *Trans. Faraday Soc.*, **23**, 545 (1927).

Syntheses from Ethanolamine. IV. A Synthesis of β-Chloroethyl Phthalimide

BY HENRY WENKER

This paper presents a convenient method of preparing β-chloroethyl phthalimide, an intermediate which can be used for most purposes in place of the less readily accessible β-bromo analog.[1] The reactions involved are: phthalic anhydride and ethanolamine react in molar proportions to form β-hydroxyethylphthalimide; this compound reacts with one mole of phosphorus pentachloride to yield β-chloroethyl phthalimide.

Experimental

Garelli and Racciu[2] obtained β-hydroxyethyl phthalimide from phthalic anhydride and ethanolamine, using absolute ethanol as a solvent. It has been found that by omitting the solvent and heating both components[3] for about thirty minutes to 210°, a quantitative yield is obtained. On cooling, the product solidifies in crystalline form, melting at 127–128° (lit. 127–128°). Through the action of phosphorus pentachloride, β-chloroethyl phthalimide was obtained from this product in the usual way. The yield was 94%, the melting point 81° (lit. 79–81°).

ELIZABETH, N. J.
RECEIVED DECEMBER 4, 1936

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[1] "Organic Syntheses," John Wiley and Sons, Inc., 1932, Coll. Vol. I, p. 114.

[2] Garelli and Racciu, *Atti acad. sci. Torino, Classe sci. fis, mat. nat.*, **69**, I, 358–63 (1934).

[3] Technical monoethanolamine, boiling at 169–171°, from Carbide and Carbon Chemicals Corporation, was used.