to express his gratitude to McGill University, Montreal, for its award of the Moyse Travelling Scholarship, which enabled him to do this work. We are particularly indebted to Professor F. H. MacDougall for his aid in the derivation of the equations presented in the first part of this paper.

Summary

An expression has been derived for the e. m. f. E of cells involving silver halide membranes, of the type

$$Ag/AgX(s),\ X^-(a_1)/\overset{\text{membrane/}}{AgX/X^-(a_2)}/KNO_3(sat.)//KCl(sat.),\ Hg_2Cl_2/Hg$$

It was found that

$$E = E^0 + RT/F \ln (a_2)$$

The experimental results obtained with fused silver halide membranes over a wide range of values of a_2 showed that $E = E^0 + A \ln(a_2)$ in which A was found to be slightly less than the theoretical value.

MINNEAPOLIS, MINN. RECEIVED DECEMBER 3, 1936

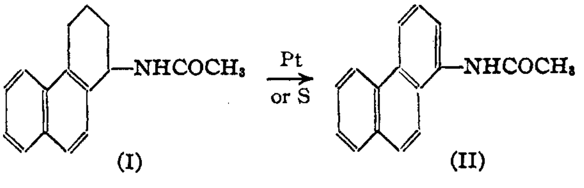
NOTES

A New Synthesis of 1-Aminophenanthrene

BY W. E. BACHMANN

Recently[1] we described the preparation of 1-aminophenanthrene, starting from phenanthrene. This new phenanthrylamine can also be obtained from naphthalene through the intermediate compound, 1-keto-1,2,3,4-tetrahydrophenanthrene. The oxime of this cyclic ketone is reduced by sodium amalgam and alcohol to 1-amino-1,2,3,4-tetrahydrophenanthrene[2] and the acetyl derivative (I) of the amine is dehydrogenated to 1-acetylaminophenanthrene (II). The free base, 1-aminophenanthrene, can be obtained by hydrolysis of the acetyl derivative.

Complete dehydrogenation of 1-acetylamino-1,2,3,4-tetrahydrophenanthrene takes place rapidly when the compound is heated with half its weight of platinum black at 320°; the 1-acetylaminophenanthrene is obtained pure by a single recrystallization from benzene. We have also employed sulfur for the dehydrogenation; with this reagent some oily by-products are formed in the reaction, but the 1-acetylaminophenanthrene can be isolated in pure form in yields of 50–60%.



(I) (II)

Experimental

1 - Acetylamino - 1,2,3,4 - tetrahydrophenanthrene.—A mixture of 13 g. of 1-keto-1,2,3,4-tetrahydrophenanthrene,[3] 6 g. of hydroxylamine hydrochloride and 8 cc. of pyridine in 80 cc. of absolute alcohol was heated on a steam-bath for three hours. The solution was evaporated to dryness and the residue was digested with water. The oxime, which was formed in quantitative yield, was filtered off and when dried was sufficiently pure for the next step.

A mixture of 13 g. of the oxime and 180 cc. of alcohol was warmed to 50–60° and treated with 150 g. of 2% sodium amalgam in portions in the course of half an hour. Throughout the reaction the temperature was kept below 60° by external cooling and the solution was kept acidic by addition of acetic acid. Any sodium acetate that precipitated was brought back into solution by addition of small amounts of water. When the reaction was complete, the solution was separated from the mercury and the alcohol was evaporated. The residue was taken up in water and a small amount of oily impurities was removed by extraction with carbon tetrachloride. The aqueous solution was made alkaline and the 1-amino-1,2,3,4-tetrahydrophenanthrene was extracted by benzene. Evaporation of the benzene left the amine as an oil which quickly solidified. A mixture of the crude amine and 15 cc. of acetic anhydride was refluxed for five minutes. The acetic acid and the excess of acetic anhydride were removed by directing a jet of air onto the warm solution. The crystalline residue of the acetyl derivative was digested with cold acetone and the colorless crystals were filtered off; yield, 10 g. 1-Acetylamino-1,2,3,4-tetrahydrophenanthrene crystallizes from acetone in colorless needles; m. p. 176°. The compound is not very soluble in cold acetone but dissolves in benzene and in acetic acid.

Anal. Calcd. for $C_{16}H_{17}ON$: N, 5.9. Found: N, 6.0.

Dehydrogenation of 1-Acetylamino-1,2,3,4-tetrahydrophenanthrene.—A mixture of 10 g. of 1-acetylamino-1,2,3,4-tetrahydrophenanthrene and 2.5 g. of sulfur was

---

[1] Bachmann and Boatner, THIS JOURNAL, 58, 2097 (1936).

[2] Our experiments on the preparation of this compound were already completed at the time Burger and Mosettig [*ibid.*, 58, 1570 (1936)] reported its preparation by the same method.

[3] Haworth, *J. Chem. Soc.*, 1128 (1932).

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°.

CHEMISTRY LABORATORY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN
RECEIVED DECEMBER 14, 1936

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.	Corr.	Lit.	Nitrogen, % Calcd.	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.	Corr.	Lit.	Nitrogen, % Calcd.	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-

---

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