2. α-Naphthylethylaminoacetonitrile reacts with potassium cyanate in glacial acetic acid to form the nitrile of α-naphthylethylhydantoic acid. When this compound is heated with 1:1 hydrochloric acid it is converted into 5,5-α-naphthylethylhydantoin.

3. 5,5-α-Naphthylethylhydantoin does not possess the properties of an hypnotic.

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Studies in the Phenanthrene Series. III. Hydroxy Aldehydes and Hydroxy Ketones[1]

BY ERICH MOSETTIG AND ALFRED BURGER

The preparation of the series of hydroxyphenanthrene ketones and aldehydes described in this communication was undertaken in order to obtain the starting materials for the synthesis of phenolic β-ethylamines, amino ketones and amino alcohols of the phenanthrene series. These amino derivatives will be the subject of pharmacological investigation, as part of the program of study of the physiological action of phenanthrene derivatives which is being carried on at the University of Michigan[2] in collaboration with this Laboratory.

3-Hydroxyphenanthrene-4-aldehyde has been previously prepared by Smith[3] by the Gattermann aldehyde synthesis.

Smith used aluminum chloride as catalyst, and stated that the yield drops to 10% when zinc chloride is used. In agreement with this, our attempts to apply Adams'[4] modified Gattermann synthesis with zinc chloride to the hydroxyphenanthrenes gave very unsatisfactory results.

We made use of the Smith procedure for the preparation of the aldehydes of 2- and 9-hydroxyphenanthrenes, in the expectation that the aldehyde group would enter the 1- and 10-positions, respectively. That this actually took place was proved by converting the 2-hydroxyaldehyde to 1,2-dihydroxyphenanthrene, and the 9-hydroxyaldehyde to 9,10-phenanthrenequinone.

It was possible in most cases to carry out the preparation of the hydroxyphenanthrene ketones in two ways, by Fries rearrangement and by Friedel–Crafts reaction.

3-Acetoxyphenanthrene, treated with aluminum chloride or bromide

(1) This investigation was supported by a grant from the Committee on Drug Addiction of the National Research Council from funds provided by the Bureau of Social Hygiene, Inc.

(2) N. B. Eddy, *J. Pharmacol.*, **45**, 3 (July, 1932); and others in press.

(3) Smith, *J. Chem. Soc.*, **109**, 568 (1916).

(4) Adams and co-workers, THIS JOURNAL, **45**, 2373 (1923); **46**, 1518 (1924).

under widely varying conditions of time, temperature, and solvent, does not undergo the Fries rearrangement to any extent. The starting material is undoubtedly attacked, but under the most favorable conditions only about 20% yield of alkali-soluble products could be separated, from which no crystalline material was obtained. Applying the Friedel–Crafts reaction, acetyl chloride and 3-hydroxyphenanthrene, we observed that the first mole of acetyl chloride is used entirely in acetylating the phenolic hydroxyl group. When 3-hydroxyphenanthrene was treated with 2 moles, or 3-acetoxyphenanthrene with one mole of acetyl chloride, a 3-acetoxy-X-acetylphenanthrene was obtained in 30% yield. Contrary to expectation, the acetyl group did not enter the 4-position, as was shown by converting the compound to the corresponding 3-methoxyphenanthrene-X-carboxylic acid, of m. p. 238.5–239°. The 3-methoxyphenanthrene-4-carboxylic acid which is obtained by oxidation of 3-methoxyphenanthrene-4-aldehyde melts at 153–154°. Since the constitution of 3-hydroxyphenanthrene-4-aldehyde was proved[5] by its conversion to 3,4-dihydroxyphenanthrene, the 4-position for the ketone group in 3-acetoxy-X-acetylphenanthrene does not come into question. The 9- and 10-positions are impossible, for chromic acid oxidation leads to a 3-acetoxy-X-acetyl-9,10-phenanthrene quinone. The 2-position is likewise excluded, because 3-methoxyphenanthrene-X-carboxylic acid methyl ester (colorless, m. p. 125–126°) is different from 3-methoxyphenanthrene-2-carboxylic acid methyl ester (yellow, m. p. 133–135°).

By treating sodium-3-phenanthrolate with carbon dioxide under pressure, Werner and Kunz[6] obtained a hydroxyphenanthrene carboxylic acid, to which, on speculative considerations, the structure of a 3-hydroxy-2-carboxylic acid was assigned. We were able to prove that Werner's assumption of a position other than 4- for the carboxyl group is correct, for 3-hydroxyphenanthrene-4-carboxylic acid prepared from the 3-acetoxy-4-aldehyde is white and decomposes at 125°, while Werner's acid is yellow and decomposes at 312°. The blue-green color test observed with ferric chloride, and the reluctance of the hydroxyl to form a methyl ether support an ortho position to the carboxyl group in Werner's acid. The O-methyl ether could be obtained only with silver oxide and methyl iodide.[7] We are therefore justified in saying that Werner's acid is actually the 3,2-derivative, although no strict proof has been offered. Coupling reactions with the 3-hydroxy-2-carboxylic acid and the 3-hydroxy-4-carboxylic acid, which might be of interest in view of Fieser's[8] arguments concerning the fixation of the double bonds in the phenanthrene nucleus, have not been carried out.

For the location of the acetyl group in 3-hydroxy-X-acetylphenanthrene there remain the positions 1, 5, 6, 7 and 8. As meta-position, 1- seems to us quite unlikely; on the basis of other phenanthrene studies we consider the 6- or 7-position as most probable.

(5) Smith, *J. Chem. Soc.*, **109**, 568 (1916); *cf.* Barger, *ibid.*, **113**, 218 (1918).

(6) Werner and Kunz, *Ber.*, **35**, 4419 (1902).

(7) 3-Hydroxyphenanthrene-4-carboxylic acid could be converted to the methyl ether methyl ester by the action of diazomethane.

(8) Fieser and Young, THIS JOURNAL, **53**, 4120 (1931).

From the Friedel–Crafts reaction with 3-methoxyphenanthrene, a new methoxy ketone is obtained in good yield. It is different from the 3-methoxy-X-acetylphenanthrene described above, and will be designated as 3-methoxy-Y-acetylphenanthrene. A comparison of the methoxy-Y-carboxylic acid derived from it with the above-mentioned 3-methoxy-2- and 4-carboxylic acids showed its acetyl group not to be at 2-, or 4-. We were not able to isolate a 9,10-quinone by oxidation of the methoxy ketone.

In the studies of Werner,[9] difficulties met in the preparation of 3-alkoxyphenanthrene quinones were mentioned. While we could not oxidize 3-methoxy-X-acetylphenanthrene to a quinone, the corresponding acetoxy-X-acetyl compound was converted almost quantitatively to 3-acetoxy-X-acetylphenanthrene quinone by chromic acid oxidation. We therefore attempted to demethylate 3-methoxy-Y-acetylphenanthrene and the corresponding carboxylic acid, but without success.

Since the known 3-methoxyphenanthrene-10-carboxylic acid of Pschorr[10] (m. p. 235°) is different from 3-methoxyphenanthrene-Y-carboxylic acid (m. p. 200°), the 10-position for the acetyl group is also excluded. There remain as possibilities the bridge-position 9, four positions in ring III, and the improbable meta-position 1. Because of the relative inaccessibility of these hydroxy ketones, we have not yet been able to demonstrate the location of the X- and Y-substituents through the corresponding dihydroxyphenanthrenes.

The failure to obtain a 3-hydroxy-4-ketone may be explained by the assumption that the acetyl group in a primarily-formed 4-acetyl derivative migrates under the influence of aluminum halide. Werner accounted for the fact that he could not obtain 3-hydroxyphenanthrene-4-carboxylic acid as due to the ease of removal of substituents in the 4-position, and we have found that this acid does indeed lose carbon dioxide with relative ease.

The Fries rearrangement of 2-acetoxyphenanthrene leads to a crystalline but inseparable mixture of phenolic ketones. From this mixture, after methylation, only one individual, m. p. 175°, could be separated, in 10% yield. It proved to be 2-methoxy-1-acetylphenanthrene, giving on oxidation a methoxycarboxylic acid identical with 2-methoxyphenanthrene-1-carboxylic acid (m. p. 244–246°). The constitution of the latter is certain through its preparation from the 2-methoxy-1-aldehyde. The Friedel–Crafts reaction on 2-hydroxyphenanthrene gives similar results.

When 2-acetoxyphenanthrene is subjected to the Friedel–Crafts reaction, a 2-acetoxy-X-acetylphenanthrene can be isolated. The corresponding 2-methoxy derivative (m. p. 117°) is different from 2-methoxy-1-acetylphenanthrene. In order to determine whether the X-substituent occupied the other ortho-position (3), the ketone was oxidized to 2-methoxy-X-carboxylic acid. This proved to be different from the methyl ether of

(9) Werner, *Ann.*, **322**, 145, 147 (1902).

(10) Pschorr, Wolfes and Buckow, *Ber.*, **33**, 174 (1900).

TABLE I

PHENANTHRENE DERIVATIVES

No.	Substituent	Solvent of recrystn.	Yield, %	M. p., °C.	Crystal form	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1	3-Methoxy-4-aldehyde[a]	CH_3OH	75	80	Long needles	$C_{16}H_{12}O_2$	81.32	81.29	5.13	5.32		
2	Semicarbazone[b]	B. dioxane		237–239 dec.		$C_{17}H_{15}O_2N_3$	69.60	69.50	5.16	5.61	14.34	14.62
3	3-Acetoxy-4-aldehyde[c]	Dil. CH_3OH	Quant.	98–99	Almost colorless	$C_{17}H_{12}O_3$	77.24	77.15	4.58	4.61		
4	2-Hydroxy-1-aldehyde[d]	Toluene or $CHCl_3$-CH_3OH	63–70	172–173	Needles	$C_{15}H_{10}O_2$	81.05	81.14	4.54	4.67		
5	Schiff base[e]	C_2H_5OH		160–161	Orange needles	$C_{21}H_{15}ON$					4.72	4.88
6	2-Methoxy-1-aldehyde	C_2H_5OH		160	Light brown cryst.	$C_{16}H_{12}O_2$	81.32	81.55	5.13	5.49		
7	Semicarbazone	C_2H_5OH		300–315[f]	Faintly pink needles	$C_{17}H_{15}O_2N_3$					14.34	14.54
8	9-Hydroxy-10-aldehyde[g]	C_2H_5OH	50	133–134	Yellow	$C_{15}H_{10}O_2$	81.05	81.22	4.54	4.73		
9	Schiff base	C_2H_5OH		160–161	Long yellow needles	$C_{21}H_{15}ON$	84.81	84.77	5.09	5.58	4.72	4.99
10	9-Methoxy-10-aldehyde	Dil. C_2H_5OH		79–81	Yellow needles	$C_{16}H_{12}O_2$	81.32	81.65	5.13	5.19		
11	Semicarbazone	Dil. C_2H_5OH		211	Yellow needles	$C_{17}H_{15}O_2N_3$	69.59	69.53	5.16	5.53	14.34	14.70

[a] Prepared by methylation of the hydroxyaldehyde [J. W. Smith, *J. Chem. Soc.*, **109**, 568 (1916)] with methyl sulfate and potassium hydroxide. Crude product distilled at 1 mm. pressure. Remainder of the hydroxyaldehyde recovered unchanged. [b] Sparingly soluble in boiling alcohol. [c] From the hydroxyaldehyde with acetic anhydride in pyridine. [d] Prepared in the way described by Smith except that double the amount of benzene was necessary. Alkali salts sparingly soluble in water. [e] From the aldehyde with aniline in boiling alcohol. [f] Depending upon the mode of heating. [g] Prepared like the isomers, but reaction was allowed to proceed at room temperature. Purification by extraction with boiling 0.3% potassium hydroxide solution.

TABLE II

PHENANTHRENE DERIVATIVES

No.	Substituent	Solvent of recrystn.	Yield, %	M. p., °C.	Crystal form	Formula	Methoxyl, % Calcd.	Methoxyl, % Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
12	1,2-Diacetoxy[a]	CH_3OH		147		$C_{18}H_{14}O_4$			73.44	72.96	4.80	4.68
13	1,2-Dimethoxy			100–102	Colorless	$C_{16}H_{14}O_2$			80.64	81.07	5.93	5.88
14	9,10-Quinone[i]			204–206		$C_{14}H_8O_2$			80.75	81.25	3.88	4.03
15	3-Methoxy-4-carboxylic acid[b]	B. toluene	94	153–154 dec.	Almost colorless needles	$C_{16}H_{12}O_3$			76.16	76.26	4.80	4.95
16	Methyl ester[c]	Dil. CH_3OH		122	Almost colorless needles	$C_{17}H_{14}O_3$			76.66	76.48	5.30	5.30
17	3-Acetoxy-4-carboxylic acid[d]	Dil. CH_3OH		162–163 dec.		$C_{17}H_{12}O_4$			72.83	72.81	4.32	4.35
18	3-Hydroxy-4-carboxylic acid[e]	Dil. alc.		125 dec.	White leaflets	$C_{15}H_{10}O_3$			75.61	75.80	4.23	4.55
19	3-Methoxy-2-carboxylic acid methyl ester[f]	CH_3OH		133–133.5	Yellow leaflets	$C_{15}H_8O(OCH_3)_2$	23.31	22.67				
20	2-Methoxy-1-carboxylic acid	C_2H_5OH	60	244–246 dec.	Colorless needles	$C_{16}H_{12}O_3$			76.16	76.63	4.80	5.08
21	Methyl ester	C_2H_5OH		145–146	Colorless needles	$C_{15}H_8O(OCH_3)_2$	23.31	22.90				
22	2-Methoxy-1-carboxylic acid methyl ester[g]	Dil. CH_3OH (ligroin)		143	Colorless needles	$C_{15}H_8O(OCH_3)_2$	23.31	23.15				
23	9-Methoxy-10-carboxylic acid[h]	Bz-pet. ether		113	Colorless	$C_{16}H_{12}O_3$			76.16	75.89	4.80	4.84

[a] Prepared by refluxing the dihydroxyphenanthrene with acetic anhydride and sodium acetate for two hours; purified by distillation at 1 mm.

[b] All oxidations of aldehydes to the corresponding acids were carried out according to the directions of Heads and Robertson, *J. Chem. Soc.*, 2432 (1931).

[c] From the acid with diazomethane.

[d] Crystallizes with 1 molecule of water, m. p. 105–115°. The water is lost by drying at 95° in a vacuum. Calcd. for $C_{17}H_{12}O_4 \cdot H_2O$: H_2O, 6.04. Found: H_2O, 6.19.

[e] Obtained by saponification of the acetyl derivative with 10% sodium hydroxide in the cold. When saponification is carried out hot, partial decarboxylation with formation of 3-hydroxyphenanthrene takes place. Heating to 130° for five minutes results in quantitative decarboxylation. Treatment with a large excess of diazomethane in ether–methanol solution yields ester No. 16.

[f] Prepared by boiling 3-hydroxyphenanthrene-2-carboxylic acid with a large excess of silver oxide and methyl iodide in dry benzene solution for six hours. Lacking an autoclave of the type described by Werner we prepared the hydroxycarboxylic acid by the Kolbe method, heating sodium phenanthrolate in a retort under carbon dioxide to 260° for four hours and separating the acid by its solubility in sodium bicarbonate solution. The hydroxycarboxylic acid methyl ester described by Werner is conveniently prepared by the action of diazomethane in ether–methanol solution.

[g] Prepared by the action of silver oxide and methyl iodide on 2-hydroxy-1-carboxylic acid which was obtained by Kolbe synthesis. Werner assigned to this acid the structure of 2-hydroxyphenanthrene-3-carboxylic acid. The m. p. of the acid and its methyl ester (with diazomethane) checked with Werner's data. The methoxy carboxylic acid and its methyl ester (No. 22) derived from this so-called 2-hydroxy-3-carboxylic acid were identical (m. p. and mixed m. p.) with acid No. 20 and methyl ester No. 21, respectively.

[h] Very soluble in ether, alcohol or benzene.

[i] Substances Nos. 12, 13, 14 obtained from the corresponding aldehydes.

TABLE III

FRIEDEL–CRAFTS REACTION AND FRIES REARRANGEMENT WITH 2-, 3- AND 9-HYDROXYPHENANTHRENES AND THEIR ACETYL DERIVATIVES AND METHYL ETHERS

No.	Substituents	Solvent of recrystn.	Yield, %	M. p., °C.	Crystal form	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Methoxyl, % Calcd.	Methoxyl, % Found
24	2-Methoxy-1-acetyl[a]	CH_3OH		175–176	Shining leaflets	$C_{17}H_{14}O_2$	81.57	81.65	5.64	5.84				
25	2-Acetoxy-X-acetyl[b]	Dil. alc.	29	120–122.5	White	$C_{18}H_{14}O_3$	77.67	77.49	5.07	5.13				
26	2-Acetoxy-X-acetyl-9, 10-quinone	CH_3COOH	70	238–240 dec.	Red needles	$C_{18}H_{12}O_5$	70.11	69.93	3.93	3.91				
27	2-Hydroxy-X-acetyl[c]	Dil. alc.		186	White needles	$C_{16}H_{12}O_2$	81.32	81.37	5.13	5.32				
28	2-Methoxy-X-acetyl[d,g]	Dil. CH_3OH		117	Colorless needles	$C_{17}H_{14}O_2$	81.57	81.71	5.64	5.87				
29	Semicarbazone	Alc.		241–242		$C_{18}H_{17}O_2N_3$					13.68	14.00		
30	2-Methoxy-X-carboxylic acid[e]	Alc.		251–252	Colorless	$C_{16}H_{12}O_3$	76.16	76.01	4.80	4.96				
31	Methyl ester	Dil. CH_3OH		79–80	Needles	$C_{15}H_8O(OCH_3)_2$							23.31	22.66
32	2-Methoxy-Y-acetyl[g]	Alc.		132–133	Long needles	$C_{17}H_{14}O_2$	81.57	80.81	5.64	5.71				
33	Semicarbazone[f]	Alc.		223		$C_{18}H_{17}O_2N_3$					13.68	13.93		
34	3-Acetoxy-X-acetyl[h]	Alc.	41	155	White	$C_{18}H_{14}O_3$	77.67	77.69	5.07	5.09				
35	Semicarbazone	Alc.		218	White needles	$C_{19}H_{17}O_3N_3$					12.54	12.41		
36	3-Acetoxy-X-acetyl-9, 10-quinone	CH_3COOH		206–208[i]	Yellow glittering leaflets	$C_{18}H_{12}O_5$	70.11	69.66	3.93	3.98				
37	3-Hydroxy-X-acetyl[c]	Dil. alc.		180–181	Light yellow leaflets	$C_{16}H_{12}O_2$	81.32	81.25	5.13	5.20				
38	3-Methoxy-X-acetyl[d,g]	Dil. CH_3OH		106–107	Yellowish leaflets	$C_{17}H_{14}O_2$	81.56	81.37	5.64	5.67				
39	Semicarbazone	Dil. alc.		203–205	Almost colorless	$C_{18}H_{17}O_2N_3$	70.32	70.24	5.58	5.83	13.68	13.72		
40	3-Methoxy-X-carboxylic acid[e]	B. toluene		238.5–239[j]	Needles	$C_{16}H_{12}O_3$	76.16	76.31	4.80	5.11				
41	Methyl ester	CH_3OH		125–126	Long needles	$C_{15}H_8O(OCH_3)_2$							23.31	23.47
42	3-Methoxy-Y-acetyl[g,k]	CH_3OH	74	98–99	Slightly yellow prisms	$C_{17}H_{14}O_2$	81.56	81.26	5.64	5.45				
43	Semicarbazone[f]	Alc.		217–219		$C_{18}H_{17}O_2N_3$					13.68	13.77		
44	3-Methoxy-Y-carboxylic acid[e,l]	Alc.		200	Colorless needles	$C_{16}H_{12}O_3$	76.16	75.86	4.80	4.75				
45	Methyl ester	Dil. CH_3OH		81.5–82.5		$C_{15}H_8O(OCH_3)_2$							23.31	23.43
46	9-Hydroxy-10-acetyl	CH_3OH	72	96	Yellow needles	$C_{16}H_{12}O_2$	81.32	81.11	5.12	5.19				
47	The same[m]	CH_3OH		101.5–102	Yellow blades	$C_{16}H_{12}O_2$	81.32	81.34	5.12	5.24				
48	9-Methoxy-10-acetyl[d,n]				Oily	$C_{17}H_{14}O_2$	81.57	81.82	5.64	5.77				
49	Picrate	CH_3OH			Brick-red	$C_{23}H_{17}O_9N_3$					8.77	8.31		
50	9-Hydroxy-10,3(6)-diacetyl[o,p]	C_2H_5OH	40	175.5–176.5	Yellow needles	$C_{18}H_{14}O_3$	77.67	77.65	5.07	5.21				
51	9-Methoxy-10,3(6)-diacetyl[d,p]	CH_3OH		111.5–112.5	Long white needles	$C_{19}H_{16}O_3$	78.05	77.83	5.52	5.66				

[a] (a) Obtained from Fries rearrangement of 2-acetoxyphenanthrene with aluminum bromide in nitrobenzene and subsequent methylation of the inseparable mixture of hydroxy ketones with diazomethane in 10% yield. (b) From Friedel–Crafts reaction on 2-hydroxyphenanthrene with aluminum chloride and acetyl chloride in nitrobenzene and subsequent methylation. The yield was poor. (c) Obtained as main reaction product from Friedel–Crafts reaction on 2-methoxyphenanthrene with acetyl chloride (in nitrobenzene, sixteen hours at 0°, five hours at 25°). Separation by crystallization from alcohol, yield 36%. Oxidation with sodium hypochlorite yields acid No. 20. Comparison of acids and methyl esters by mixed m. p.

[b] Prepared by Friedel–Crafts reaction on 2-acetoxyphenanthrene (in nitrobenzene, twenty hours at room temp.). Purification by distillation in a high vacuum. Soluble in alcohol, benzene, sparingly soluble in ether.

[c] Formed by saponification of the O-acetyl derivative with hot dilute alkali.

[d] From the hydroxy ketone with diazomethane.

[e] From the corresponding methoxy ketone with sodium hypochlorite.

[f] Prepared by boiling the components for three hours.

[g] Oxidation of this methoxy ketone with chromic acid to a quinone was unsuccessful.

[h] Formed in Friedel–Crafts reaction with an excess over 2 moles of acetyl chloride on 3-hydroxyphenanthrene (in nitrobenzene, at 0° for six days). Purification of the black reaction product by recrystallization from alcohol with boneblack.

[i] Mixed m. p. with 3-acetoxy-9,10-phenanthrene quinone (m. p. 200–201°) showed 20–30° depression.

[j] Mixed m. p. with 3-methoxyphenanthrene-10-carboxylic acid of m. p. 235° (prepared by the direction of Pschorr, Wolfes and Buckow, *Ber.*, **33**, 174 (1900)) was between 200 and 210°.

[k] From Friedel–Crafts reaction with acetyl chloride on 3-methoxyphenanthrene in nitrobenzene solution (sixteen hours at 0°, four hours at 20°).

[l] Demethylation with boiling hydrobromic acid yields 3-hydroxyphenanthrene by simultaneous decarboxylation.

[m] Prepared by Fries rearrangement of 9-acetoxyphenanthrene (5 g.) in 100 cc. of nitrobenzene with aluminum bromide (14 g.), two and one-half hours at room temp. or by Friedel–Crafts reaction on 9-hydroxyphenanthrene (m. p. 155° after high-vacuum sublimation) with exactly one mole of acetyl chloride. Yields 9,10-phenanthrene quinone by oxidation with chromic acid. Exists in two modifications (Nos. 46 and 47). The lower melting form can be converted to the stable higher melting one by fusion.

[n] n_D^{22} 1.6584. Forms no semicarbazone.

[o] Formed by Friedel–Crafts reaction with 9-hydroxyphenanthrene and an excess over two moles of acetyl chloride in nitrobenzene, or with one mole of acetyl chloride and 9-acetoxyphenanthrene, or 9-hydroxy-10-acetylphenanthrene. Slightly soluble in ether, more soluble in benzene.

[p] Chromic acid oxidation yields 3-acetyl-9,10-phenanthrene quinone of m. p. 221–222° (evac. tube), identical with the quinone obtained by Mosettig and van de Kamp (THIS JOURNAL, **52**, 3704 (1930)).

[q] See footnote a, part (c). From the mother liquors of 2-methoxy-1-acetylphenanthrene. Isolated and purified by repeated fractionation in high vacuum and crystallization.

Werner's[11] so-called 2-hydroxyphenanthrene-3-carboxylic acid, but the point in question was nevertheless still unsettled, for Werner's acid was found to be actually 2-hydroxyphenanthrene-1-carboxylic acid. Chromic acid oxidation, leading to a 2-acetoxy-X-acetyl-9,10-quinone, eliminates

(11) Werner, *Ber.*, **35**, 4419 (1902).

the 9- and 10-positions from consideration. The meta-position, 4-, seems improbable, and we believe 6- or 7- to be the most likely positions for the entrance of the acetyl group.

2-Methoxyphenanthrene, on the other hand, yields 2-methoxy-1-acetylphenanthrene as the main product from the Friedel–Crafts reaction. By an elaborate process of separation, another methoxyacetylphenanthrene (m. p. 132–133°) could be separated, but in such small amount that its structural proof was not attempted.

By the Fries rearrangement of 9-acetoxyphenanthrene, or Friedel–Crafts reaction on 9-hydroxyphenanthrene, a hydroxy ketone is obtained in good yield. Its constitution as 9-hydroxy-10-acetylphenanthrene was proved by chromic acid oxidation, which led to phenanthrene-9,10-quinone.

The reaction of 9-acetoxy- or 9-hydroxyphenanthrene with one and two moles, respectively, of acetyl chloride yields a 9-hydroxydiacetylphenanthrene. Since the latter can be oxidized to 3-acetyl-9,10-phenanthrene quinone, it must be 9-hydroxy-10,3-(or 6)-diacetylphenanthrene.

Structural Proofs

(a) 2-Hydroxyphenanthrene-1-aldehyde was converted to the dihydroxyphenanthrene by the reaction of Dakin, modified by Barger[12] using twice as much pyridine as called for in the case of 3-hydroxyphenanthrene-4-aldehyde. The dihydroxyphenanthrene was purified by high vacuum sublimation; m. p. 178–179° (evac. tube). The mixed m. p. of the dihydroxy compound, the diacetyl and dimethyl derivatives showed no depression with Fieser's[13] 1,2-dihydroxy, 1,2-diacetoxy and 1,2-dimethoxy phenanthrenes, respectively.

(b) A sample of 9-hydroxyphenanthrene-10-aldehyde was converted to the hydroquinone with hydrogen peroxide in pyridine. Without purification this was converted to the quinone by bubbling oxygen through its alkaline solution. Chromic acid oxidation of the aldehyde in acetic acid solution yielded also 9,10-phenanthrene quinone.

Summary

1. The preparation of 2,1- and 9,10-hydroxyphenanthrene aldehydes is described and proof of their constitution given.

2. The Friedel–Crafts reaction on 2-, 3-, and 9-hydroxyphenanthrenes, and the Fries rearrangement of the corresponding acetoxyphenanthrenes have been investigated.

3-Hydroxyphenanthrene yields two ketones, in one of which the acetyl group is probably in position 6- or 7-, in the second of which it may be at 6-, 7- or 9-.

From 2-hydroxyphenanthrene the products are 2-hydroxy-1-acetyl-

(12) Barger, *J. Chem. Soc.*, **113**, 218 (1918).

(13) Fieser, THIS JOURNAL, **51**, 1896 (1929).

phenanthrene, and a second ketone which is probably 2-hydroxy-6- or 7-acetylphenanthrene.

9-Hydroxyphenanthrene gives a mono- and a diacetyl derivative. The former is 9-hydroxy-10-acetylphenanthrene, the latter 9-hydroxy-10,3-(or 6-)diacetylphenanthrene.

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Some Factors that Influence the Conversion of Cellulosic Materials to Sugar[2]

BY GEO. J. RITTER, R. L. MITCHELL AND R. M. SEBORG

When cellulosic materials are treated with strong sulfuric acid at room temperature and then with boiling dilute sulfuric acid, the sugar yields that are obtained vary considerably among different investigators.[3,4,5,6]

Results described in this paper indicate that with a given concentration of acid such variations in sugar yields may be due to differences in (a) the temperature of the strong acid during its contact with the cellulose, (b) the time during which the cellulose remains in the strong acid, and (c) the cellulosic materials.

Materials Used.—Spruce cellulose, isolated from sawdust by means of the modified chlorination method,[7] was used for the study.

Experimental Procedure

Spruce cellulose was treated with 72% sulfuric acid (20 cc. of acid to 1 g. of cellulose) for periods of both two and six hours at temperatures ranging from 8 to 45°. The solution was then diluted with water to 4% acid concentration and hydrolyzed for four hours at boiling temperature. The reducing number of the sugar solution was determined according to the standard method[8] using the electrolytic procedure for the deposition of the reduced copper from a nitric acid solution. The glucose equivalent of the reducing number found was divided by the theoretical glucose yield (hexosan × 1.1) to obtain the efficiency of the conversion. In reporting the sugar yields in terms of glucose equivalent no correction has been applied for a small percentage of xylan and mannan that was present in the cellu-

(1) Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

(2) Presented before the joint meeting of the Divisions of Organic Chemistry and Cellulose Chemistry at the 84th meeting of the American Chemical Society, Denver, Colo., August 22–26, 1932.

(3) Braconnot, *Ann. chim. phys.*, **25**, 81 (1827).

(4) Flechsig, *Z. physiol. Chem.*, **7**, 528 (1883).

(5) Monier-Williams, *J. Chem. Soc.*, **119**, 803 (1921).

(6) Ost and Wilkening, *Chem.-Ztg.*, **34**, 461 (1910).

(7) Ritter and Fleck, *Ind. Eng. Chem.*, **16**, 147 (1924).

(8) U. S. Dept. Agr., Bur. Chem., Bull. 107 (revised), p. 49 (1912).