for this was suggested on the basis of an assumed shift of the partition equilibrium of the dissolved substance between the bacteria and the aqueous-alcoholic phase. The effect of diluted alkali in the preparation of the solutions upon their germicidal action was also studied.

BLOOMFIELD, NEW JERSEY

[CONTRIBUTION NO. 93 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

STUDIES IN THE PHENANTHRENE SERIES. II. PHENANTHRENE CARBOXYLIC ACIDS AND 9-BROMOPHENANTHRENE DERIVATIVES[1]

BY ERICH MOSETTIG AND JACOB VAN DE KAMP

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These investigations have been carried out in order to find a practicable way of preparing the phenanthrene carboxylic acids, whereby an adequate supply of starting material for further syntheses in this series would be assured.

Of the hitherto known preparative methods, that of Pschorr[2] is the best for the phenanthrene-9-carboxylic acid, while the -2- and -3-carboxylic acids were best prepared through the corresponding phenanthrene-2- and 3-sulfonic acids.[3,4] Neither of these methods is suitable however for large scale preparation of the carboxylic acids.

Recently, Mosettig and van de Kamp[5] found a way of preparing phenanthrene-2- and -3-carboxylic acids by oxidizing 2- and 3-acetylphenanthrenes, respectively, with sodium hypochlorite, a method which seemed much simpler than those hitherto employed because of the relatively easy separation of the acetylphenanthrenes on a large scale and the good yields obtained in their oxidation.

Liebermann and Zsuffa[6] described the preparation of a phenanthrene carboxylic acid from phenanthrene with oxalyl chloride and aluminum chloride. These authors claimed for their acid the constitution of phenanthrene-9-carboxylic acid and mentioned that besides this acid another one, containing the carboxyl group "in the nucleus," was found in smaller quantities.

In consideration of the results which we obtained from the acetylation of phenanthrene,[5] where it was shown that the acetyl group enters the

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[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] Pschorr, *Ber.*, **29**, 496 (1896).

[3] Werner and co-workers, *Ann.*, **321**, 248 (1902).

[4] Fieser, THIS JOURNAL, **51**, 2460 (1929).

[5] Mosettig and van de Kamp, *ibid.*, **52**, 3704 (1930).

[6] Liebermann and Zsuffa, *Ber.*, **44**, 207 (1911).

phenanthrene nucleus in the 2- and 3-positions, but not in any detectable degree in the 9-position, it seemed desirable to test Liebermann's results.

When phenanthrene was treated with oxalyl chloride in the presence of aluminum chloride in carbon disulfide solution, under certain conditions a mixture of phenanthrene-3-, -2- and -9-carboxylic acids was formed in an approximate ratio of 75:18:4. Besides these acids, an acid which might be a phenanthrene monocarboxylic acid was formed, whose structure has not as yet been determined because of the small amount obtained (yield about 2%). This acid was compared with a sample of the phenanthrene-1-carboxylic acid[7] which Dr. L. F. Fieser kindly sent us for comparison. No agreement in properties was found, so the formula of the 1-carboxylic acid for our acid is excluded.

These facts are to some extent in accord with the results of the action of acetyl chloride on phenanthrene, where the 3-position is favored, and the 2-position is the next in order of preference. We may remark that nitrobenzene, which gave such good results in the acetylation of phenanthrene, did not prove to be so useful in the case of oxalyl chloride, apparently because of the fact that in this medium we could not run the reaction at the desired low temperature (−15°). Unfortunately it appeared that this interesting formation of the acids was not a practicable method of preparation, first because of the high cost of oxalyl chloride, and second because of the extremely complicated procedure necessary in separating the reaction mixture.

As was shown by Staudinger,[8] oxalyl chloride decomposes in the presence of aluminum chloride into phosgene and carbon monoxide, so that the action of oxalyl chloride on hydrocarbons under these conditions may be considered essentially as the action of phosgene under the catalytic influence of aluminum chloride, whereby the acid chlorides are formed, which in turn are converted into the acids when the reaction mixture is decomposed. Therefore the direct action of phosgene and aluminum chloride on phenanthrene was investigated. The conditions of the experiment were exactly the same as those in the experiment involving oxalyl chloride and phenanthrene, but we did not succeed in isolating any of the expected phenanthrene carboxylic acids.

Phenanthrene, phosgene and aluminum chloride were allowed to react at −15° for twenty-four hours. Not a trace of acid could be isolated from this reaction. The phenanthrene had changed completely. The brown amorphous mass obtained from the reaction mixture could not be crystallized in any way, nor did a high vacuum distillation give a product which could be crystallized.

[7] Prepared from phenanthrene-1-sulfonic acid (private communication from Dr. L. F. Fieser).

[8] Staudinger, *Ber.*, **41**, 3558 (1908).

The action of cyanogen bromide and aluminum chloride, which gave good results with anthracene,[9] gave practically no product in the case of phenanthrene. Under the most varied experimental conditions it was not possible to obtain the expected nitriles. At low temperature and short duration, no reaction took place, whereas with higher temperatures and longer time the phenanthrene was changed completely and only traces of nitrile could be detected (hydrolysis to the carboxylic acids).

It was found, however, that the reaction of Rosenmund,[10] the replacement of nuclear halogen by the cyano group with potassium cyanide in the presence of a cuprous salt as catalyst, could be applied in the phenanthrene series with satisfactory results. We were greatly assisted here by E. I. du Pont de Nemours and Company, Wilmington, Del., who were so kind as to carry out this reaction on a large scale in a high pressure autoclave, and to whom we wish to express our sincere thanks. An even better method, and one requiring no autoclave, was found in the modification of the Rosenmund procedure, recently published by von Braun and Manz.[11] By heating 9-bromophenanthrene with the calculated amount of cuprous cyanide at 260° for six hours, phenanthryl-9-cyanide was obtained in a yield of 90–95% of the theoretical. Because of its simplicity, this method is especially adapted for the production of phenanthrene-9-carboxylic acid in large quantities.

This substitution of nuclear bromine by the cyano group probably can be accomplished also on other bromophenanthrenes, but is of particular advantage for the preparation of phenanthrene-9-carboxylic acid (from the easily accessible 9-bromophenanthrene), which until now has been prepared either by Pschorr's method[12] or through the difficultly obtainable phenanthrene-9-sulfonic acid.[13]

The 9,10-double bond in phenanthrene has a well-marked olefinic character, as is shown in the formation of a 9,10-dibromo addition product[14] and an ether of 10-nitro-9,10-dihydrophenanthrol (-9).[15,16] The polymerization of olefinic compounds which is caused by aluminum halides under certain conditions might account for the unsatisfactory yields of acids or acid chlorides, respectively, in the action of oxalyl chloride on phenanthrene with aluminum chloride. Therefore one might expect that the formation of polymerization products, which appear in the form of unpleasant non-crystallizable and tarry products, would be minimized when the ac-

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[9] Karrer and Zeller, *Helv. Chim. Acta*, **2**, 482 (1919).

[10] Rosenmund and Struck, *Ber.*, **52**, 1749 (1919).

[11] Von Braun and Manz, *Ann.*, **488**, 111 (1931).

[12] Pschorr, *Ber.*, **29**, 496 (1896).

[13] Werner, *Ann.*, **321**, 327 (1902); Fieser, Ref. 4; and others.

[14] Hayduck, *Ann.*, **167**, 180 (1873); and others.

[15] Schmidt, *Ber.*, **33**, 3251 (1900).

[16] Wieland and Rahn, *ibid.*, **54**, 1770 (1921).

tivity of the 9,10-double bond is decreased by the introduction of an appropriate substituent, like bromine,[17] in the 9-position. We find, in fact, that when the Friedel–Crafts reaction is carried out on 9-bromophenanthrene with oxalyl chloride or with acetyl chloride[18] in carbon disulfide solution with aluminum chloride, it gives exclusively crystalline compounds.

When oxalyl chloride reacts with 9-bromophenanthrene in carbon disulfide solution under the catalytic influence of aluminum chloride at −15°, the main product formed is a monobromo-monocarboxylic acid of m. p. 283–284°, which appears to be 9-bromophenanthrene-3(or 6)-carboxylic acid. Besides this acid at least two other acids which have not been identified are formed in small quantities. The yield of crystalline material in this reaction is from 90 to 95%. The structure of this monocarboxylic acid was proved by oxidizing its methyl ester with chromic acid in glacial acetic acid solution, whereby a substituted phenanthrene-9,10-quinone was formed, which proved to be identical with the known[19] phenanthrene-9,10-quinone-3-carboxylic acid methyl ester. Furthermore, the bromine atom in the methyl ester of this acid could be replaced by hydrogen, catalyzed with palladium. The reduction resulted in phenanthrene-3-carboxylic acid methyl ester which, as well as the oxidation with chromic acid, shows that the carboxyl group has entered the molecule in the 3- or 6-position.

The reaction between 9-bromophenanthrene and acetyl chloride in carbon disulfide solution in the presence of aluminum chloride at −15° yielded a solid reaction mixture, free from tars and resins, which consisted mainly of 9-bromo-3(or 6)-acetylphenanthrene of melting point 150–151°. The position of the acetyl group was proved by the oxidation of this compound with chromic acid in glacial acetic acid solution, which yielded 3-acetylphenanthrene-9,10-quinone of melting point 217–218.5°, identical with the quinone obtained on oxidation of 3-acetylphenanthrene.[5] The structure could also be demonstrated by oxidation with a 2% sodium hypochlorite solution, which gave an acid which was identical with the 9-bromophenanthrene 3(or 6)-carboxylic acid obtained from 9-bromophenanthrene and oxalyl chloride. Here likewise, besides this main product, at least one other ketone was formed.

The separation and purification of these by-products, as well as of the by-products from the reaction of 9-bromophenanthrene and oxalyl chloride, involved extreme difficulties, however, and were not pursued, and the

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[17] *Cf.* Ingold and Ingold, *J. Chem. Soc.*, 2354 (1931).

[18] Although this reaction carried out in nitrobenzene solution on phenanthrene itself gives excellent yields of crystalline products, the same reaction, when run in carbon disulfide solution, leads chiefly to light yellow, heavy oils which could not be crystallized by any means. We hope to collect more experimental material to provide a satisfactory explanation for this remarkable difference in the influence of the solvents.

[19] Fieser, THIS JOURNAL, 51, 3101 (1929).

question of the position taken by the new substituent (3 or 6) in the main reaction product was likewise left unsettled, since we were mainly interested in showing the quantitative effect of the 9-bromine atom on these two Friedel–Crafts reactions.

Experimental

Phenanthrene with Oxalyl Chloride

Phenanthrene-2-, -3- and -9-Carboxylic Acids.—Twenty-five grams of phenanthrene dissolved in 150 cc. of carbon disulfide in a 500-cc. flask fitted with a mercury-sealed stirrer and a calcium chloride tube was placed in a freezing mixture of ice and salt. Sixty grams of oxalyl chloride was slowly added and to the mixture which was vigorously stirred at $-15°$ was added 12 g. of aluminum chloride in small portions in the course of one-half hour. Immediately after the addition of the aluminum chloride the reaction mixture turned dark green and a rapid stream of hydrogen chloride was liberated. After one-half hour 100 cc. of carbon disulfide and 25 g. of aluminum chloride were added in small portions over a period of forty-five minutes. The evolution of hydrogen chloride which was quite violent in the beginning of the reaction slowed down toward the end, and when the hydrogen chloride had practically ceased to escape (after fourteen hours' stirring at $-15°$), the dark green viscous reaction mixture was decomposed very cautiously and slowly on cracked ice (under the hood). Violent streams of hydrogen chloride and possibly of phosgene were liberated in the decomposition. The mixture was then treated with 25 cc. of concentrated hydrochloric acid.

In all, 100 g. of phenanthrene was so treated and the decomposed reaction mixtures combined afterward. The carbon disulfide solution of the decomposed reaction mixture had a dark red color. After separating the two layers and removing the carbon disulfide *in vacuo*, a dark brown, sticky, partly solidified residue was obtained. This residue was extracted with 10% sodium carbonate solution until practically no precipitate was obtained on acidifying the filtered alkaline extracts with hydrochloric acid. The precipitate of acids obtained from these extractions will be designated A.

As it appeared that the residue still contained a small amount of an acid in the form of an almost insoluble sodium salt, it was extracted several times by boiling with water. These aqueous extracts were also filtered and acidified and yielded a precipitate of acid, designated B.

The final residue was dissolved in ether and the ethereal solution dried over sodium sulfate. On evaporation of the ether, crystals separated which were filtered and washed with cold ether. After one crystallization from benzene a homogeneous product was obtained, yellow needles melting at 233–234° (uncorr.), yield, 2.0 g. This product, which showed no acid properties, might have been a mono or diketone. The properties and analyses of this compound, however, do not confirm this.

Anal. Subs., 0.0822, 0.0760: CO_2, 0.2618, 0.2421; H_2O, 0.0349, 0.0321. Calcd. for monoketone $C_{14}H_9COC_{14}H_9$: C, 91.06; H, 4.75; for diketone $C_{14}H_9COCOC_{14}H_9$: C, 87.77; H, 4.42. Found: C, 86.86, 86.88; H, 4.75, 4.73.[20]

After this substance had been isolated from the ethereal solution, the latter was evaporated to dryness. Upon standing, the residue crystallized partly to a red cake. From it, by extraction with methyl alcohol, 27 g. of phenanthrene could be recovered, while the remainder consisted of a dark red viscous oil, weighing 16 g., sparingly soluble in most of the common organic solvents, with the exception of pyridine, from which, however, it could not be recrystallized. The investigation of this oil offered little pros-

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[20] We did not succeed in the preparation of a quinoxaline derivative which would indicate the presence of an α-diketone.

pect of success and has not been carried further. (If the temperature in this reaction is not kept as low as −15°, the product consists almost entirely of this red oil, and hardly any acid is formed.)

The mixture of acids A consisted of a yellowish-brown flocculent precipitate. In order to purify this precipitate, it was treated with dilute sodium carbonate solution, and the small insoluble residue taken up in ether. The carbonate solution was extracted with ether until the ether came off colorless. The ether extracts contained more of the red oil mentioned above. On acidification of the sodium carbonate solution, a slightly yellow precipitate was obtained which after being filtered, washed with water and dried in air weighed 52 g.

Space does not permit a description of the exact method of working up the mixture of acids, since for the complete separation of the mixture a division into at least sixty fractions was necessary. Neither the solubilities of the acids nor those of their potassium or sodium salts were so different that one component could be easily removed completely. Nevertheless, advantage could be taken of the fact that phenanthrene-3-carboxylic acid is less soluble in xylene, glacial acetic acid or ethyl alcohol than the 2- and 9-isomers. Furthermore, the formation of characteristic micro-crystalline salts enabled us to follow the separation more or less and to identify under the microscope each fraction obtained. Besides these properties, the fact that phenanthrene-9-carboxylic acid methyl ester is much less soluble (and crystallizes much better) than the 2- and 3-isomers, proved to be of great advantage in this separation.

The 52 g. of A was extracted eight times by boiling with 250 cc. of xylene each time. From the last four fractions nearly colorless crystals of phenanthrene-3-carboxylic acid separated, which was purified through its potassium salt. Also the mother liquors of these fractions consisted almost entirely of the 3-acid (melting point 267–269°, melting point of the methyl ester, after one recrystallization, 95–95.5°; mixed melting point with the 3-acid or its methyl ester, obtained on oxidation of 3-acetylphenanthrene[5] 267–269° and 95–95.5°, respectively). The fourth fraction, which had a slight yellow color, also yielded some phenanthrene-3-carboxylic acid. Fractions I, II and III (dark brown) gave only a very small crystalline precipitate of this acid.

The xylene mother liquor of fraction IV was combined with the mother liquors of fractions I, II and III, evaporated to dryness in a vacuum and the remaining residue brought into solution with a little dilute sodium hydroxide solution. With an excess of concentrated sodium hydroxide solution (50%), a very sparingly soluble sodium salt was precipitated which was not homogeneous. Enough water was added therefore to dissolve it again and the mixture of acids was precipitated with hydrochloric acid. After drying, this mixture was esterified with methyl alcohol and concentrated sulfuric acid. In this esterification a resinous product separated out which caused a loss of 5 to 10% of the material. (As yet the cause of this resin formation is unknown. As the original product was entirely alkali-soluble, one may assume that only products of an acid character are present, which, however, can in no way be separated from the phenanthrene-carboxylic acids.)

The brown oily mixture of esters was saponified with a concentrated aqueous sodium hydroxide solution, whereupon the sparingly soluble sodium salt of phenanthrene-2-carboxylic acid separated in shining white leaflets. This salt was uniform and gave, after digesting with hydrochloric acid, pure phenanthrene-2-carboxylic acid, melting point 256–258° (melting point of its methyl ester after one recrystallization from methyl alcohol 95.5–96°; mixed melting points with the 2-acid, or its methyl ester, obtained on oxidation of 2-acetylphenanthrene[5] 257–259° and 95.5–96°, respectively).

From the mother liquors of the sparingly soluble sodium phenanthrene-2-carboxylate the free acids were regenerated; these free acids were put into solution with the calculated amount of dilute potassium hydroxide and by gradual addition of 50% potassium hydroxide solution, several fractions of potassium salts were precipitated. The first salt fractions consisted of practically pure potassium-3-carboxylate. The last fractions contained a small amount of the 3-acid and a mixture of some other acids, and were dissolved in water again and precipitated with hydrochloric acid. This precipitate was a yellowish-brown crystalline mass and weighed after drying 24 g. It was extracted with hot ethyl alcohol and yielded thus 4 g. of almost white, insoluble crystals. This appeared to be practically pure phenanthrene-3-carboxylic acid, which was further purified through the potassium salt in the usual way. The alcoholic mother liquor was evaporated to dryness and treated with alkali, giving a trace of phenanthrene-3-carboxylic acid in the form of the potassium salt. The remaining mixture was acidified, and the mixture of acids which separated esterified with methyl alcohol and sulfuric acid. A further purification by fractional crystallization of the ester mixture could not be effected. Therefore the mixture of esters was distilled in oil pump vacuum. The slightly yellow distillate was taken up in methyl alcohol, from which a small amount of white needles was deposited. These were collected and after one more distillation in oil pump vacuum melted at 114–115°; a mixed melting point with the methyl ester[5] of phenanthrene-9-carboxylic acid (synthesized according to Pschorr[21]) showed no depression (yield, 1.5 g.).

From the mother liquors of this ester a homogeneous product could not be obtained by fractional crystallization. On saponification of these fractions with sodium hydroxide, a small amount of sodium phenanthrene-2-carboxylate could be collected, whereupon the residual alkaline mother liquors were acidified separately, and from each a yellow mixture of acids was obtained.

Some of these fractions of acid gave a potassium salt crystallizing in shining leaflets, which was purified by two recrystallizations from water. On acidification of its colorless aqueous solution a yellow oil precipitated which upon cooling solidified to yellow needles. After drying in a desiccator, the melting point of the acid was found to be between 70 and 75°. Apparently it contained water of crystallization; after drying at 100° in a vacuum and recrystallizing from benzene, the acid melted at 123–125°.[22] It was analyzed in the form of its potassium salt, which was dried at 100° in a vacuum.

Anal. Subs., 0.0586: K_2SO_4, 0.0193. Calcd. for phenanthrene monocarboxylic acid potassium salt $C_{15}H_9O_2K$: K, 15.03. Found: K, 14.78.

The precipitate B consisted of practically pure phenanthrene-2-carboxylic acid, which was purified through its sodium salt; melting point of the acid 258–260°, of the methyl ester 95.5–96°.

Whether acids were formed in the oxalyl chloride reaction which could not be esterified or were unstable under the conditions of separation could not be determined. From the original mixture of 52 g. of acids, 22.5 g. of pure acids was obtained: 17 g. of phenanthrene-3-carboxylic acid, 4 g. of phenanthrene-2-carboxylic acid, 1 g. of phenanthrene-9-carboxylic acid and 0.5 g. of the yellow acid of m. p. 123–125°.

Preparation of Phenanthrene-9-carboxylic Acid from 9-Bromophenanthrene.—A mixture of 50 g. of 9-bromophenanthrene (m. p. 63°), 30 g. of cuprous cyanide, 75 g. of potassium cyanide, 100 cc. of methyl alcohol and 40 cc. of water was heated at 210° for eight hours in an autoclave of 500 cc. capacity. The autoclave was heated in a bath of refluxing nitrobenzene (205–210°). After the autoclave had cooled down to room temperature the excess pressure was released (strong odor of ammonia). The reaction mixture was removed from the autoclave by pouring the liquid part into water

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[21] Pschorr, *Ber.*, **29**, 496 (1896).

[22] The phenanthrene-1-carboxylic acid prepared by Dr. L. F. Fieser melts at 232° (private communication).

and washing out the solid crystalline cake with water. After evaporation of the alcohol the mixture was filtered. From the filtrate a small amount (10–15%) of phenanthrene-9-carboxylic acid could be thrown out and purified through its potassium salt. The precipitate on the filter was extracted with ether. After drying and evaporating the ether, the residue was hydrolyzed by boiling with a 25% methyl alcoholic potassium hydroxide solution, which yielded the 9-acid. The acid thus collected combined with the small amount already obtained weighed 36 g. (yield, 83% of the theoretical). Recrystallized from glacial acetic acid, the acid melted at 251–252°.

The following procedure, which does not necessitate the use of an autoclave, was found to be most convenient. Thirty grams of 9-bromophenanthrene was mixed with 12 g. (1 mole + 10%) of finely powdered cuprous cyanide and heated at 260° for six hours. The reaction mixture, which solidified entirely upon cooling to room temperature, was finely powdered and extracted with ethyl alcohol or with chloroform. On evaporation of the solvent and removal of the last traces in a vacuum, 22.1 g. of phenanthryl-9-cyanide was obtained, which after one recrystallization from alcohol melted at 103–104°; yield, 93% of the theoretical. This nitrile was hydrolyzed to phenanthrene-9-carboxylic acid by boiling with 25% methyl alcoholic potassium hydroxide; yield, 90% of the theoretical.

9-Bromophenanthrene with Oxalyl Chloride.—Fifteen grams of 9-bromophenanthrene in 125 cc. of carbon disulfide, 25 cc. of oxalyl chloride, and 25 g. of aluminum chloride were allowed to react in the way described above. After decomposition of the reaction mixture a slightly yellow crystalline mixture of acids resulted which was filtered and brought into solution with dilute alkali. The alkaline solution was extracted with ether to remove unchanged 9-bromophenanthrene, and the acids were precipitated with hydrochloric acid. After drying, 15.5 g. of a mixture of acids was obtained; yield, 85% of the theoretical. (Ten to twelve per cent. of bromophenanthrene was recovered.) In all, 85 g. of 9-bromophenanthrene was so treated. The separation of the mixture of acids was carried out through their methyl esters.

9-Bromophenanthrene-3(or 6)-carboxylic Acid Methyl Ester, $C_{14}H_8BrCOOCH_3$.—Thirty grams of the mixture of acids described above, 600 cc. of methyl alcohol and 45 g. of concentrated sulfuric acid were boiled for four hours. During this esterification, part of the esters crystallized out. The esterification mixture was worked up in the usual way. Because of its slight solubility in methyl alcohol the methyl ester of 9-bromophenanthrene-3(or 6)-carboxylic acid was easily isolated and purified as white needles of m. p. 155–155.5°, sparingly soluble in methyl alcohol and ether, more soluble in glacial acetic acid, dioxane and chloroform.

Anal. Subs., 0.0904, 0.0798: AgI, 0.0657, 0.0577. Calcd. for $C_{16}H_{11}O_2Br$: one methoxyl, 9.83. Found: 9.60, 9.55.

9-Bromophenanthrene-3(or 6)-carboxylic Acid, $C_{14}H_8BrCOOH$.—The ester was saponified to the acid with 25% methyl alcoholic potassium hydroxide; yield, quantitative. The acid is recrystallized from glacial acetic acid, in which it is sparingly soluble, as white needles of m. p. 283–284° (uncorr.).

Anal. Subs., 0.1492: AgBr, 0.0942. Calcd. for $C_{15}H_9BrO_2$: Br, 26.55. Found: Br, 26.87.

This acid forms well-crystallized potassium and sodium salts, which are only sparingly soluble in water.

By treating the 9-bromophenanthrene-3(or 6)-carboxylic acid methyl ester with chromic acid in the usual way, a quinone was obtained which after recrystallization from glacial acetic acid melted at 210–212°. The mixed melting point with phenanthrene-9,10-quinone-3-carboxylic acid methyl ester, obtained from phenanthrene-3-carboxylic acid methyl ester, gave no depression.

Debromination of 9-Bromophenanthrene-3(or 6)-carboxylic Acid Methyl Ester with Hydrogen.—To a suspension of 0.1 g. of palladous hydroxide–calcium carbonate catalyst (Pd content 1%) in a mixture of 3 cc. of ethyl alcohol and 1 cc. of water, 0.1 g. of 9-bromophenanthrene-3(or 6)-carboxylic acid methyl ester dissolved in a mixture of 10 cc. of ethyl alcohol and 5 cc. of pyridine was added under a stream of hydrogen. On shaking the mixture with hydrogen, the calculated absorption was reached in about twenty minutes. Upon filtering the reaction mixture from the palladium–calcium carbonate and pouring the filtrate into 250 cc. of 10% hydrochloric acid, phenanthrene-3-carboxylic acid methyl ester separated practically pure. After one recrystallization from methyl alcohol the melting point is 95–95.5°. A mixed melting point with a sample of ester prepared from 3-acetylphenanthrene showed no depression.

The separation of the mixture of methyl esters contained in the mother liquors of 9-bromophenanthrene-3(or 6)-carboxylic acid methyl ester was attempted by laborious fractional crystallization from several solvents. A uniform product could not be obtained.

9-Bromophenanthrene with Acetyl Chloride

9-Bromo-3(or 6)-acetylphenanthrene, $C_{14}H_8BrCOCH_3$.—Twenty-five grams of 9-bromophenanthrene in 200 cc. of carbon disulfide, 10 g. of acetyl chloride and 40 g. of aluminum chloride were allowed to react in the way described above. After decomposition of the reaction mixture a light yellow oil was obtained, which soon solidified to an almost white crystalline cake. Fractional crystallization of this cake from methyl alcohol yielded mainly 9-bromo-3(or 6)-acetylphenanthrene (±70% yield), besides a small amount of unchanged bromophenanthrene and a mixture of other ketones. The 9-bromo-3(or 6)-acetylphenanthrene was purified by two more recrystallizations from methyl or ethyl alcohol (with animal charcoal), from which solvents it crystallizes in long white needles of m. p. 150–151°. It is easily soluble in dioxane or glacial acetic acid, sparingly soluble in ether, methyl or ethyl alcohol and chloroform.

Anal. Subs., 0.1610: AgBr, 0.1023. Calcd. for $C_{16}H_{11}OBr$: Br, 26.73. Found: Br, 27.04.

9-Bromo-3(or 6)-acetylphenanthrene Semicarbazone.—The semicarbazone which was prepared in the usual way was recrystallized from methyl alcohol in which it is very sparingly soluble; white needles of m. p. 265–265.5° (uncorr.).

Anal. Subs., 0.1351: 14.65 cc. of N (29°, 746 mm.). Calcd. for $C_{17}H_{14}ON_3Br$: N, 11.80. Found: N, 12.03.

9-Bromo-3(or 6)-acetylphenanthrene Oxime.—Recrystallized from methyl alcohol it forms white needles of m. p. 142.5–143° (uncorr.).

Anal. Subs., 0.1541: 6.5 cc. of N (28°, 746 mm.). Calcd. for $C_{16}H_{12}ONBr$: N, 4.46. Found: N, 4.70.

Oxidation with Sodium Hypochlorite.—One gram of 9-bromo-3(or 6)-acetylphenanthrene was oxidized with a 2% sodium hypochlorite solution.[5,23] The acid obtained melted after one recrystallization from glacial acetic acid at 283–284°. A mixed melting point with the 9-bromophenanthrene-3(or 6)-carboxylic acid described above showed no depression; yield, almost quantitative. One-half gram of this acid esterified with methyl alcohol and sulfuric acid yielded a methyl ester of m. p. 155–155.5°. This methyl ester gave no depression in melting point with the methyl ester of 9-bromophenanthrene-3(or 6)-carboxylic acid described above.

Oxidation with Chromic Acid.—The oxidation with chromic acid of 9-bromo-3-(or 6)-acetylphenanthrene was carried out in the usual way. The quinone obtained

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[23] Graebe, *Ber.*, **35**, 2753 (1902).

melted after two recrystallizations from glacial acetic acid at 217–218.5°. A mixed melting point with the quinone obtained by oxidation of 3-acetylphenanthrene showed no depression.

Summary

1. The action of oxalyl chloride on phenanthrene described by Liebermann and Zsuffa has been shown to yield not phenanthrene-9-carboxylic acid as the main product, but phenanthrene-3-carboxylic acid, accompanied by smaller quantities of the 2- and 9-isomers and an acid of melting point 123–125° whose structure has not yet been determined.

2. A good preparative method for phenanthrene-9-carboxylic acid is described.

3. The influence of bromine substitution in the 9-position on Friedel–Crafts reactions in this series has been investigated.

4. 9-Bromophenanthrene-3(or 6)-carboxylic acid and 9-bromo-3(or 6)-acetylphenanthrene are described.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF PURDUE UNIVERSITY AND THE PURDUE RESEARCH FOUNDATION]

PRODUCTION OF BUTENES BY PYROLYSIS OF THE NORMAL MONOCHLOROBUTANES

BY PAUL E. WESTON[1] AND H. B. HASS

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Introduction

In recent years normal butane has become available in large quantities at a low price. It is conceivable that this butane can be converted into more valuable substances through the butenes as intermediates, for example into *sec.*-butyl alcohol, by chlorination of the *n*-butane, splitting off hydrogen chloride from the monochlorobutanes, and hydration of the resulting butenes. In addition to the direct economic importance, this method of producing the butenes is of fundamental importance to the general chemistry of the olefins, for the butenes are the simplest substances in which it is possible to have the shifting of a hydrogen atom from one carbon atom to another (shifting of a double bond), stereomutation between *cis* and *trans* forms and shifting of a methyl group. A survey of the literature has shown that almost no information at all is available concerning the conditions governing these changes.[2] Lucas and his associates[3] have been at-

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[1] Research Chemist with the Purdue Research Foundation, J. K. Lilly Research Fellowship.

[2] Egloff, Schaad and Lowry, *J. Phys. Chem.*, **35**, 1825, 1860, 1866 (1931).

[3] Young and Lucas, THIS JOURNAL, **52**, 1964 (1930); Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930); Lucas, Dillon and Young, *ibid.*, **52**, 1949 (1930).