thiouronium chloride in methanol precipitated the salt. Recrystallization gave 0.75 g. (68%) of the product as white needles, m.p. 150°.

Anal. Calcd. for $C_{17}H_{24}O_2N_2S$: N, 8.74. Found: N, 8.98.

6-Butyl-4-methyl-5,6-dihydro-2-pyrone.—5-Carboxy-6-butyl-4-methyl-5,6-dihydro-2-pyrone was decarboxylated in 2,4-lutidine with cupric acetate by the procedure given above for the 6-propyl analog given above. The mixture of lactone and acid, b.p. 115–117° (4 mm.), obtained from 20 g. of starting material was dissolved in alkali and extracted with ether to obtain 6.7 g. (42.5%) of the product, b.p. 124° (4 mm.), $n^{11}D$ 1.4935. The pure acid could not be obtained from the alkaline solution.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.88; H, 9.73.

6-Butyl-4-methyltetrahydro-2-pyrone.—A solution of 4.5 g. of the crude dihydro-2-pyrone obtained as described in the preceding paragraph in 50 ml. of ether was hydrogenated over palladium-on-charcoal catalyst. The crude product was neutralized and extracted with ether. The ether extracted oil was fractionated to give 1.6 g. (35%) of the product, b.p. 114° (4 mm.), $n^{10}D$ 1.4517. This compound shows infrared absorption bands in carbon tetrachloride at 2959 (C–H stretching), 1712 (carbonyl stretching), 1381 (unassigned) and 1238 cm.$^{-1}$ (C–O stretching) as does also 4,6-dimethyltetrahydro-2-pyrone.[10]

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66; sapn. equiv., 170.2. Found: C, 70.37; H, 10.64; sapn. equiv., 169.

6-(1′-Ethylamyl)-4-methyl-5,6-dihydro-2-pyrone.—Four grams of 4-carboxy-6-ethyl-3-methyl-2,4-dodecanoic acid was decarboxylated in 10 ml. of 2,4-lutidine with 0.01 g. of cupric acetate at 100°. The lutidine was removed by distillation. The residue was acidified and extracted with ether. The ether-extracted oil on fractionation gave 2.6 g. of a mixture of the lactone and acid. The acid was extracted from an ether solution of the mixture with dilute alkali. The ether extracts were evaporated and the residue fractionated to give 1.7 g. (51%) of the product, b.p. 141–143° (5 mm.), $n^{25}D$ 1.4641.

Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54; sapn. equiv., 210.3. Found: C, 74.38; H, 10.48; sapn. equiv., 205.

The infrared absorption spectra were determined using potassium bromide pellets, except as otherwise noted, and a Baird double beam recording infrared spectrometer with sodium chloride optics.

LOUISVILLE 8, KENTUCKY

[CONTRIBUTION FROM THE CHARLOTTE DRAKE CARDEZA FOUNDATION, JEFFERSON MEDICAL COLLEGE]

Synthesis of Acids Containing Hydrophenanthrene and Hydroacephenanthrylene Rings

BY D. L. TURNER

RECEIVED OCTOBER 25, 1956

The Reformatsky reaction with methyl 3-carbomethoxy-2-keto-3-methyl-6-phenylcyclohexane-1-acetate yields an unsaturated acid which can be cyclized either to a keto-anhydride (IV) or to an acephenanthrylene phenol (VI). The structure of the latter was shown by an independent synthesis from the α-form of 2-methyl-2-carbomethoxy-9-methoxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid. The β-stereoisomer of the acephenanthrylene also was prepared.

The cyclic keto-ester I described previously[1] was allowed to react with ethyl bromoacetate in the Reformatsky reaction. The principal crystalline material obtained from this reaction was the lactone ester II. The presence of the lactone ring was indicated by the infrared spectrum $\lambda_{\max}^{CS_2}$ 5.56, 5.75 μ. This is similar to the result obtained by Johnson and Christiansen[2] in a similar reaction.

Hydrolysis of the lactone II with alcoholic potassium bicarbonate gave the unsaturated acid III. The ultraviolet absorption spectrum of this acid showed a band at 209 mμ (ϵ 16520), supporting the structure indicated[3] containing a conjugated double bond. The infrared spectrum of the methyl ester of the acid showed a band at 5.75 μ but no absorption at 5.56 μ and a new weak band, not present in the lactone, at 6.12 μ and probably caused by the double bond. The double bond was resistant to oxidation by permanganate under the conditions described by Johnson and Hunt,[4] a method which proved successful with unhindered double bonds.[1] When III was hydrogenated in acetic acid in the presence of Adams catalyst and hydrochloric acid, a product was obtained in which the aromatic ring was reduced but not the hindered double bond.

The acid III was cyclized with polyphosphoric acid, and the product was not an ester, but instead the keto-anhydride IV. Since the product is not phenolic, the double bond must be exocyclic as indicated in the structural formula. This is confirmed by the ultraviolet absorption spectrum, which shows the characteristics of the phenyl and carbonyl chromophores in conjugation,[5,6] and deviates from the spectrum of 9-keto-1,2,3,4,4a,-9,10,10a-octahydrophenanthrene[7] only at the lower minimum where the molecular extinction is greater, reaching 21000 at 212 mμ, the limit of measurement.

The anhydride IV was recovered unchanged after boiling with alcoholic alkali and acidifying. If the double bond were in the nucleus, the substance might be expected to isomerize to a phenol under these conditions. Another substance that exists only in anhydride form and not as the free acid has been obtained in the α-amyrin series by Ruzicka's group.[8,9] It seems probable that the anhydride IV belongs to the same stereochemical series as the major products described by Johnson and Christiansen[2] and it is of interest that it would then conform to the stereochemical arrangement in the Ruzicka anhydride.

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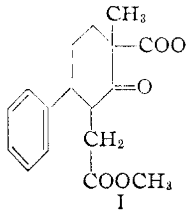
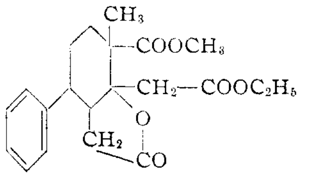


I



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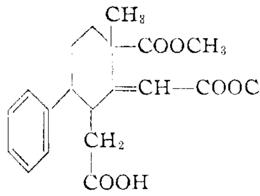

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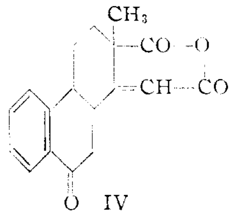
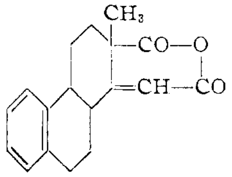
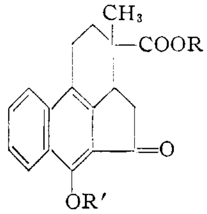


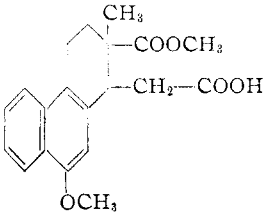
IV



V



VIa, R = R' = H
VIb, R = CH3; R' = H
VIc, R = R' = CH3



VII

The carbonyl group in the anhydride IV was hydrogenated in the presence of perchloric acid[10] to form the anhydride V. This anhydride was dehydrogenated with palladium to 1,2-dimethylphenanthrene. The anhydride V shows the same resistance to reduction of the double bond exhibited by the acid III. Reduction with dissolving alkali metals[11] might be expected to succeed; perhaps it failed because of the extreme insolubility of the alkali metal salts formed from the anhydride.

When the acid III was cyclized by the Friedel–Crafts reaction, the resulting neutral product was a mixture, which was not easily separated. This mixture was hydrolyzed with alkali, producing isomers of the anhydride IV with phenolic properties. The two pure substances resulting from this reaction are assigned the structures VIa and VIb. The substance VIa could be converted to the second product VIb by esterification. These substances were soluble in alkali to give green fluorescent solutions. It was difficult to methylate the phenolic hydroxyl in VIa or VIb, and this could not be done with methyl sulfate or methyl *p*-toluenesulfonate in alkaline solution, but succeeded when diazomethane was employed in an ether–methanol solution. The methyl ether VIc was prepared by an independent method and this constitutes the proof of structure for these substances as acephenanthrylenes.

The monomethyl ester VII of Bachmann and Holmes[12] exists in two stereochemical forms α and β. Both of these were cyclized by the thionyl chloride–stannic chloride method. Since the acid chlorides were prepared at low temperature, it seems improbable that any rearrangement took place[13] and the cyclization products should be the acephenanthrylenes of structure VIc. The identity of the acephenanthrylene derived from the α-acid of Bachmann and Holmes and the product VIc from the Reformatsky acid was established by comparison of melting points and infrared spectra. Hirschmann and Johnson[14] have suggested that the α-series of Bachmann and Holmes has rings C and D fused in the *trans* configuration as in natural estrone.

The ultraviolet absorption spectrum of the methyl ether VIc shows a pronounced hypsochromic shift, when compared with that of the phenolic materials VIa and VIb, which have identical spectra. The hypsochromic shift produced by methylating the phenolic hydroxyl probably indicates chelation in the phenolic substances.[15] This effect is shown in a pronounced form by purpurogallin and its methyl ether,[16] which also has a carbonyl group adjacent to a phenolic hydroxyl. Many substances with this type of structure also show similar chemical properties, particularly characterized by difficulty in methylating the phenolic hydroxyl (quercetin[17]) and easy removal of the methyl group (purpurogallin).[18,19] It should be noted, however, that Haworth[19] ascribes the difficulty in methylating the third phenolic hydroxyl of purpurogallin to steric hindrance, rather than to the chelation effect. The easy removal of the methyl group in VIc was shown by the formation of greenish fluorescent solutions on saponification.

The infrared spectrum of VIa showed bands at 3.0 μ (hydroxyl), 5.93 μ (carboxyl carbonyl) and 6.09 μ (chelate). The band attributed to chelation agrees with the assignment of Bellamy and Beecher[20] for 1-tetralone-2-carboxylate esters. This band disappears in the methyl ether, which has a new band at about 6.2 μ possibly caused by the aromatic system.[21]

Experimental

Ultraviolet absorption spectra were determined in 95% ethanol and infrared spectra in carbon disulfide.

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[11] G. E. Arth, G. I. Poos, R. M. Lukes, F. M. Robinson, W. F. Johns, M. Feurer and L. H. Sarett, THIS JOURNAL, **76**, 1715 (1954).

[12] W. E. Bachmann and D. W. Holmes, *ibid.*, **62**, 2750 (1940).

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[14] R. Hirschmann and W. S. Johnson, *ibid.*, **73**, 327 (1951).

[15] R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1940).

[16] G. D. Thorne and L. R. C. Barclay, *Can. J. Chem.*, **30**, 251 (1952).

[17] J. H. Locker, A. L. Krieger and K. C. Kennard, *J. Org. Chem.*, **19**, 1741 (1954).

[18] J. A. Barltrop and J. S. Nicholson, *J. Chem. Soc.*, 116 (1948).

[19] R. D. Haworth, B. P. Moore and P. L. Pauson, *ibid.*, 1045 (1948).

[20] L. J. Bellamy and L. Beecher, *ibid.*, 4487 (1954).

[21] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1954, p. 55.

Lactone of Ethyl 2-Carbomethoxy-6-carboxymethyl-1-hydroxy-2-methyl-5-phenylcyclohexane-1-acetate.—A solution of 55 g. of the ester I in 500 ml. of dry ether and 450 ml. of dry benzene was treated with 70 g. of activated zinc[22] and 3 g. of iodine, while stirring and refluxing under nitrogen. Two additional portions of 50 g. of zinc and a crystal of iodine were added at two-hour periods, and the mixture was stirred for a total of six hours. The mixture was treated by the method of Bachmann, Cole and Wilds.[23] After the evaporation of the solvent from the neutral fraction, the product was crystallized from isopropyl alcohol, m.p. 125–127.5°.

Anal. Calcd. for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 67.76; H, 6.98.

Ethyl 2-Carbomethoxy-6-carboxymethyl-2-methyl-5-phenyl-cyclohexylidene-acetate (III) (a).—A solution of the preceding ester (3 g.) in 100 ml. of methanol was refluxed with a solution of 5 g. of potassium bicarbonate in 15 ml. of water. After one hour, the mixture was evaporated *in vacuo,* treated with water, and acidified with 10% hydrochloric acid. The acid fraction was isolated with ether, the ethereal solution was dried and the ether was removed. The residue was crystallized from benzene, giving 1.28 g., m.p. 154–155°, λ_{max} 209 mμ (log ϵ 4.22).

Anal. Calcd. for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00; neut. equiv., 374. Found: C, 67.49, 67.41; H, 6.88, 6.83; neut. equiv., 375, 375.

An attempt to oxidize the material by the method of Johnson and Hunt[4] using potassium permanganate in acetone, gave a 63% recovery of the starting material.

(b).—The mother liquors from the preceding Reformatsky reaction were dissolved in 100 ml. of pyridine and refluxed for 45 minutes with 28 ml. of phosphorus oxychloride. After treating with ice and extracting with ether, the ethereal extract was washed with 10% hydrochloric acid, saturated bicarbonate and dried. The residue from the distillation of the ether was hydrolyzed with potassium bicarbonate (30 g.) in 90 ml. of water and 600 ml. of methanol. This gave 6 g. of material, m.p., alone and mixed with (a), 152–154°.

The methyl ester of the acid was made with ethereal diazomethane and crystallized from ethanol; m.p. 70–72°.

Anal. Calcd. for $C_{22}H_{28}O_6$: C, 68.02; H, 7.26. Found: C, 67.93, 68.00; H, 7.16, 7.12.

2-Carboxy-6-carboxymethyl-2-methyl-5-phenylcyclohexylideneacetic Acid.—The complete hydrolysis of the preceding acid was effected by refluxing in 5% aqueous sodium hydroxide for four hours. After cooling, it was acidified and isolated with ether in the normal manner. Crystallized from ethyl acetate it melted at 181–183°.

Anal. Calcd. for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07. Found: C, 64.78; H, 6.27.

The trimethyl ester of this acid, prepared with ethereal diazomethane, was crystallized from ether–pentane; m.p. 65–66°.

Anal. Calcd. for $C_{21}H_{26}O_3$: C, 67.36; H, 7.00. Found: C, 67.29; H, 7.12.

Hydrogenation of the Reformatsky Lactone Ester. (II).—The material was recovered unchanged after attempts to hydrogenate using Adams catalyst or palladium catalysts in ethanol or acetic acid.

3-Carbomethoxy-2-keto-3-methyl-6-phenylcyclohexane-1-acetic Acid.—This was prepared for comparison with products of Reformatsky reactions by hydrolysis of the starting ester I using potassium bicarbonate in aqueous methanol as described above. It was crystallized from benzene; m.p. 147–148°.

Anal. Calcd. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.63; neut. equiv., 304. Found: C, 67.15; H, 6.57; neut. equiv., 304.

Ethyl 2-Carbomethoxy-5-cyclohexyl-2-methyl-6-carboxymethylcyclohexylidene-1-acetate.—The acid from the bicarbonate hydrolysis of the Reformatsky ester (4.7 g.) was hydrogenated for 2 hours in 100 ml. of acetic acid in the presence of 1 ml. of concentrated hydrochloric acid and 0.5 g. of Adams catalyst. The acetic acid was distilled *in vacuo,* and the residue was purified by a partition chromatograph using nitroethane–heptane on silicic acid–Celite (1:3 by weight)[24] with the nitroethane as the stationary phase.[25] Early eluates gave crystals, m.p. 132–134° after recrystallization from acetone–pentane (1.4 g.).

Anal. Calcd. for $C_{21}H_{34}O_6$ (completely reduced): C, 65.94; H, 8.96; neut. equiv., 382. Calcd. for $C_{21}H_{32}O_6$ (one double bond): C, 66.29; H, 8.48; neut. equiv., 380.5. Found: C, 65.96; H, 8.33; neut. equiv., 374.

Another fraction obtained from later eluates was crystallized from acetone–pentane; m.p. 163–165°.

Anal. Calcd. for $C_{20}H_{32}O_6$ (completely reduced): C, 65.18; H, 8.73; neut. equiv. (dibasic), 246. Calcd. for $C_{20}H_{30}O_6$ (one double bond): C, 65.55; H, 8.25; neut. equiv. (dibasic), 227. Found: C, 65.60; 65.65; H, 8.31, 8.26; neut. equiv., 278.

This substance is considered to be a monoethyl ester because of the analysis and neutralization equivalent. Both of the substances from the chromatograph gave the same acid on hydrolysis.

2-Carboxy-5-cyclohexyl-2-methyl-6-carboxymethylcyclohexylidene-1-acetic Acid.—The preceding dibasic acid was refluxed in 10% aqueous sodium hydroxide solution for 4 hours. The solution was cooled, acidified, and the product filtered. After several recrystallizations from acetone–carbon tetrachloride it had m.p. 184–185.5°. A similar hydrolysis of the preceding monobasic acid gave a substance which was crystallized from acetone–carbon tetrachloride; m.p. 182–184°. The m.p. of a mixture was 182–184°. For analysis, it was crystallized from ether–pentane; m.p. 185–186°.

Anal. Calcd. for $C_{18}H_{28}O_6$: C, 63.89; H, 7.75; neut. equiv. (tribasic), 113. Found: C, 63.99; H, 7.90; neut. equiv., 114.

Anhydride of 2-Carboxy-9-keto-2-methyl-1,2,3,4,4a,9,10,-10a-octahydrophenanthrylideneacetic Acid.—To 310 g. of phosphorus pentoxide was added 20 ml. of 85% phosphoric acid with cooling. After the reaction had subsided, the mixture was heated on the steam-bath for 2 hours and poured over 26 g. of the Reformatsky unsaturated acid III. The mixture was heated on the steam-bath with frequent swirling for 2 hours and then poured into ice-water. The precipitated solid was filtered, dried and crystallized from ethyl acetate, giving 9.5 g., m.p., 258–260° dec.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44; sapon. equiv., 148.1. Found: C, 73.07; H, 5.54; sapon. equiv., 148.

The substance did not react with diazomethane. The ultraviolet absorption spectrum showed λ_{max} 293, 247 mμ (log ϵ 3.31, 4.10); λ_{min} 275 and 226 mμ (log ϵ 3.12, 3.90). The spectrum resembled that of α-tetralone.

The semicarbazone, m.p. 300° dec., was extremely insoluble in the usual solvents. The **2,4-dinitrophenylhydrazone** was made by the method of Reich, Crane and Sanfilippo[26] and recrystallized from dimethylformamide–ethanol; m.p. 282°. It was extremely insoluble in most solvents.

Anhydride of 2-Carboxy-2-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrylideneacetic Acid.—The unsaturated anhydride (9 g.) was hydrogenated in the presence of 3 g. of 5% palladium chloride on carbon (Wilkens–Anderson Co.) in 250 ml. of acetic acid and 10 ml. of 60% perchloric acid. The calculated amount of hydrogen was absorbed in three hours. The solution was filtered from the catalyst and poured into 100 ml. of 5% sodium carbonate solution and the product was filtered giving 4.4 g., m.p. 195–210°. This could not be purified by recrystallization. It was treated with ethereal diazomethane and the part which did not react was removed by filtration and crystallized from acetone; m.p. 208–210°, yield 3.4 g.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43; sapon. equiv., 141.2. Found: C, 76.52; H, 6.10; sapon. equiv., 149.

This anhydride could not be esterified by the method of Clinton and Laskowski[27] or by the sodium methylate method

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[22] L. F. Fieser and W. S. Johnson, THIS JOURNAL, **62**, 575 (1940).

[23] W. E. Bachmann, W. Cole and A. L. Wilds, *ibid.*, **62**, 824 (1940).

[24] Celite no. 545, a product of Johns Manville, Inc.

[25] *Cf.* J. K. N. Jones and S. R. Stitch, *Biochem. J.*, **53**, 679 (1953).

[26] H. Reich, K. F. Crane and S. J. Sanfilippo, *J. Org. Chem.*, **18**, 822 (1953).

[27] R. O. Clinton and S. C. Laskowski, THIS JOURNAL, **70**, 3135 (1948).

of Herr and Miescher.[28] Attempts to reduce the double bond catalytically failed as with the unsaturated acid III. Sodium and *n*-butyl alcohol was not effective possibly because the anhydride gave a very insoluble sodium salt.

1,2-Dimethylphenanthrene.—The preceding anhydride of carboxy-2-methyloctahydrophenanthrylideneacetic acid (600 mg.) was heated with 1 g. of palladium chloride on Darco, a catalyst containing 5% palladium,[29] to 350° for 20 minutes. The product was dissolved in acetone and filtered from the catalyst. The acetone was evaporated and the residue was crystallized from methanol; m.p. 145°,[30] yield 300 mg.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.18; H, 6.84. Found: C, 92.99; H, 6.93.

The **picrate** of this hydrocarbon was crystallized from ethanol; m.p. 153–154°.[31]

Anal. Calcd. for $C_{22}H_{17}O_7N_3$: C, 60.69; H, 3.94. Found: C, 60.82; H, 4.08.

Cyclization of Ethyl 2-Carbomethoxy-6-carboxymethyl-2-methyl-5-phenylcyclohexylideneacetate by the Friedel-Crafts Method.—Using the method of Johnson and Glenn,[32] 23 g. of phosphorus pentachloride was added to a solution of 36.8 g. of the acid in 100 ml. of dry benzene. The acid chloride, after the removal of the solvents, was dissolved in 100 ml. of fresh benzene and the solution was added dropwise to a stirred solution of 18.5 g. of aluminum chloride in 50 ml. of benzene at a temperature below 10°. After 2 hours at this temperature and 3 hours at room temperature, the mixture was hydrolyzed with ice and hydrochloric acid, and extracted with ether. The ethereal solution was washed with hydrochloric acid, water, saturated sodium bicarbonate and dried. Partial removal of the ether gave crystals, m.p. 126–135°, yield 27 g. Because this was difficult to purify, it was hydrolyzed by refluxing in 200 ml. of methanol with 30 ml. of 15% sodium hydroxide solution. After 30 minutes, water was added, and the insoluble salt, which separated on cooling, was filtered and treated with 10% hydrochloric acid. The oily yellow crystals produced were filtered and crystallized from benzene; m.p. 159–170° dec., yield 9 g. Repeated recrystallization of this material gave VIa, better prepared by retreatment with alkali as described later.[33] The mother liquor from the benzene solution gave a second crop of 5 g., m.p. 241–248°, which was recrystallized from acetone; m.p. 252–253°. This is **3-carboxy-6-hydroxy - 5 - keto - 3 - methyl - 1,2,3,3a,4,5 - hexahydroacephenanthrylene (VIa).**

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44; neut. equiv. (dibasic), 148. Found: C, 72.87; H, 5.49; neut. equiv., 149.

Alternative Preparation of 3-Carboxy-6-hydroxy-5-keto-3-methyl-1,2,3,3a,4,5-hexanydroacephenanthrylene (VIa).—The intermediate above, m.p. 159–170°, was converted to the phenol by standing in solution, or by the following treatment with alkali. The crystals (600 mg.) were heated on the steam-bath for 1 hour with 10 ml. of 10% sodium hydroxide solution. The solution was acidified with 2 *N* hydrochloric acid, and filtered, giving 0.5 g., m.p. 248–252°. This was recrystallized from acetone–pentane, m.p. alone, and mixed with the phenol from the mother liquor of the starting material, 252–253.5°. The absorption spectrum showed λ_{max} 381, 300, 290, 265 mμ (log ε 3.74, 2.76, 3.64, 4.67).

3-Carbomethoxy-6-hydroxy-5-keto-3-methyl-1,2,3,3a,4,5-hexahydroacephenanthrylene (VIb) (a).—The benzene mother liquor from the hydrolysis of the Friedel–Crafts reaction products was evaporated, and the residue was crystallized from nitromethane, rejecting material insoluble in hot nitromethane. This gave 2.7 g., m.p. 104–109.5°; recrystallized from methanol, m.p. 111–114°.

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.64; H, 5.69.

The ultraviolet absorption spectrum was the same as that of the preceding phenol.

(b).—To 2.1 g. of the free acid VIa, was added 50 ml. of ethylene chloride, 20 ml. of methanol and 2 ml. of concentrated sulfuric acid. This was refluxed for 5 hours, diluted with water and extracted with ethylene chloride.

The ethylene chloride solution was washed with saturated sodium bicarbonate, and dried over sodium sulfate. The solvent was evaporated and the residue was crystallized from ethyl acetate–pentane, m.p., alone and mixed with (a) above 111–114°. The ultraviolet absorption spectrum was identical with that of (a). The yield was 1.1 g. This esterification could also be performed using methanol and boron trifluoride etherate.

This substance, like the free acid, dissolved in alkali to give a greenish-yellow fluorescent solution.

3-Carbomethoxy-5-keto-6-methoxy-3-methyl-1,2,3,3a,4,-5-hexahydroacephenanthrylene (VIc).—The phenolic ester VIb was esterified with diazomethane in ether-methanol to give a dark red oil. This was crystallized from isopropyl alcohol and then from methanol; m.p. 106–107°. The very faintly yellow crystals formed a solution in alcohol with violet fluorescence; λ_{max} 372, 311, 299, 257, 221 mμ (log ε 3.62, 3.76, 3.84, 3.67, 4.38).

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22; mol. wt., 324. Found: C, 74.26; H, 6.61; mol. wt. (Rast), 317.

The **2,4-dinitrophenylhydrazone** of this keto-ester was prepared by heating in acidified ethanol with Brady's reagent. It had m.p. 273° dec. It was too insoluble to recrystallize and was extracted with hot ethyl acetate and ethanol to purify it.

Anal. Calcd. for $C_{26}H_{24}N_4O_7$: C, 61.90; H, 4.80. Found: C, 61.86; H, 5.02.

Synthesis of the Preceding Acephenanthrylene (VIc) from the α-Form of 2-Methyl-2-carbomethoxy-9-methoxy-1,2,3,4-tetrahydrophenanthrene-1-acetic Acid.—To 4 g. of the half ester of Bachmann and Holmes[12] was added 125 ml. of anhydrous ether, 10 drops of pyridine and 7 ml. of purified[34] thionyl chloride. After 30 minutes at room temperature, the solvents were distilled *in vacuo* below 35°, 35 ml. of dry benzene was added and the solvents were distilled again. The residual acid chloride was dissolved in 55 ml. of benzene, the solution was cooled until the benzene began to crystallize, and 13 ml. of stannic chloride was added. After swirling for 3 minutes, the mixture was hydrolyzed with ice and hydrochloric acid. The product was taken up in ether and benzene, washed with 10% hydrochloric acid, 4% sodium carbonate solution, water, saturated sodium chloride and then dried. The solvents were removed and the residue was crystallized from methanol, yield 2.9 g. (76%), m.p. 106–107° undepressed when mixed with the preceding acephenanthrylene (VIc). The ultraviolet and infrared absorption spectra of the two substances were identical.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 74.09; H, 6.19.

β-Form of 3-Carbomethoxy-5-keto-6-methoxy-3-methyl-1,2,3,3a,4,5-hexahydroacephenanthrylene.—Using a pro-

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[28] J. Heer and K. Miescher, *Helv. Chim. Acta*, **31**, 234 (1948).

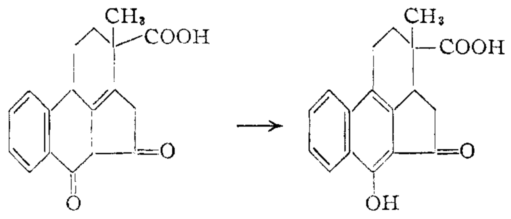
[29] Catalyst C of R. Mozingo, *Org. Syntheses*, **26**, 77 (1946).

[30] Reported 142–143°, A. Butenandt, H. A. Weidlich and H. Thompson, *Ber.*, **66**, 601 (1933); R. D. Haworth, C. R. Marvin and G. Sheldrick, *J. Chem. Soc.*, 457 (1934).

[31] Reported m.p. 153–154° (Haworth, Marvin and Sheldrick).

[32] W. S. Johnson and H. J. Glenn, THIS JOURNAL, **71**, 1094 (1949).

[33] This impure material may contain VIa mixed with an isomer of VIa with the structure of 3-carboxy-5,6-diketo-3-methyl-1,2,3,4,5,-5a-hexahydroacephenanthrylene, easily converted to the phenolic substance VIa by migration of the double bond



The ultraviolet absorption spectrum showed λ_{max} 341 mμ (log ε 3.93), 239 mμ (log ε 4.09) λ_{min} 281 mμ (log ε 3.33), 224 mμ (log ε 3.95). This supports the hypothetical compositon of the material as does the analysis. *Anal.* Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.88; H, 5.49.

[34] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1955, p. 345. This purification is important: *cf.* B. H. Chase and D. H. Hey, *J. Chem. Soc.*, 553 (1952).

cedure similar to that employed for the α-form, the β-form of 2-methyl-2-carbomethoxy-9-methoxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid[12] was converted to the acephenanthrylene in 50% yield. It was crystallized from ethyl acetate; m.p. 173–174°. The ultraviolet absorption spectrum and that of the α-form were identical.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 74.18; H, 6.21.

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PHILADELPHIA, PA.

[CONTRIBUTION FROM LINWOOD LABORATORY, REMINGTON RAND DIVISION, SPERRY RAND CORPORATION]

Cyanine Dyes. I. Absorption of Cyanines Derived from Pyranothiazole and Thiopyranothiazoles[1]

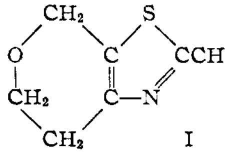
BY ROBERT H. SPRAGUE

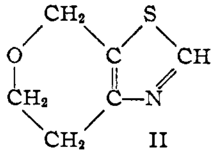
RECEIVED JULY 27, 1956

Three new thiazole bases have been prepared by condensing thioacetamide with 3-bromotetrahydro-4-pyrone, 3-bromotetrahydro-1-thio-4-pyrone and 2-bromotetrahydro-1-thio-3-pyrone. Quaternary salts of the products have given rise to new cyanine dyes, some of which are powerful photographic sensitizers. The absorptions of the new dyes are compared with those of similar dyes from benzothiazole and tetrahydrobenzothiazole.

The well known synthesis of 2-methylthiazoles by condensation of thioacetamide with α-haloketones[2] has been employed to prepare thiazole bases from 3-bromotetrahydro-4-pyrone, 3-bromotetrahydro-1-thio-4-pyrone and 2-bromotetrahydro-1-thio-3-pyrone.

Thus 3-bromotetrahydro-4-pyrone was treated with thioacetamide giving 2-methyl-6,7-dihydro-4-H-pyrano[4,3d]thiazole (I). Although (I) has not been reported in the literature, the corresponding unsubstituted thiazole II has been prepared by Sorkin and Erlenmeyer[3] by condensing thioformamide with 3,5-dibromotetrahydro-4-pyrone. The enol forms of the reactants condense with elimination of water and hydrobromic acid.


I


II

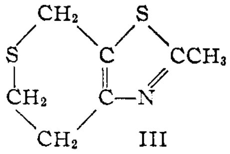
Since the product contained no bromine, Erlenmeyer postulated that the extra bromine atom in the five position of the pyrone ring was eliminated by "reductive splitting" and replaced by hydrogen.

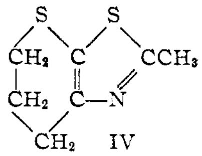
Erlenmeyer isolated only the 3,5-dibromo ketone on treatment of tetrahydro-4-pyrone with N-bromosuccinimide (36% yield, m.p. 156–157°); however, attempts to repeat his work in this Laboratory led to a mixture of the dibromo derivative with a monobromo compound, in which the latter predominated. The mixture was purified by vacuum distillation giving a 24% yield of 3-bromotetrahydro-4-pyrone in the form of a colorless liquid (b.p. 76–80° at 2 mm.) which darkened rapidly and solidified on standing.

In a second experiment the crude product was recrystallized from ethanol without previous distillation resulting in a small yield of the dibromo compound melting at 159–161°.

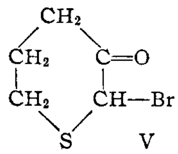
Both products condensed readily with thioacetamide in ethanol solution. Contrary to Erlenmeyer's findings in the analogous thioformamide reaction, a bromine-substituted thiazole was obtained from the dibromopyrone. The bases gave crystalline quaternary salts with ethyl iodide and were analyzed in this form.

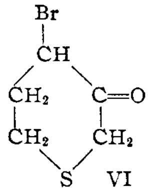
Bromination of tetrahydro-1-thio-4-pyrone[4] with N-bromosuccinimide gave a very unstable bromoketone, which nevertheless could be condensed with thioacetamide at low temperature. The product, 2-methyl-6,7-dihydro-4-H-thiopyrano[4,3d]thiazole (III), formed quaternary salts with alkyl halides which were very reluctant to crystallize. However, a crystalline hydrochloride was obtained on saturating a solution of the base in ether with hydrogen chloride and this derivative was used for analysis.


III


IV

A base IV, isomeric with III, was similarly prepared by condensing thioacetamide with the bromoketone derived from tetrahydro-1-thio-3-pyrone.[5] Of the two possible monobromo derivatives of the latter the product isolated is believed to be the 2-bromo compound V, rather than the 4-bromo isomer VI, for the following reasons:


V


VI

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[1] Presented in part before the Organic Division, American Chemical Society, at Minneapolis, Minn., Sept. 12, 1955.

[2] A. Hantzsch, *Ann.*, **250**, 265 (1889).

[3] E. Sorkin and H. Erlenmeyer, *Helv. Chim. Acta*, **31**, 96 (1948).

[4] G. M. Bennett and I. V. D. Scorah, *J. Chem. Soc.*, 196 (1927).

[5] E. H. Fehnel, THIS JOURNAL, **74**, 1569 (1952).