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Reduction Product and Leuco-form of Flavanthrone[*1]

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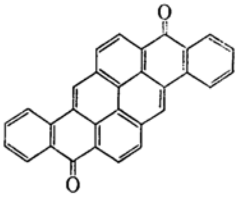
By reducing flavanthrone (II), 8,16-diazapyranthrene (V) (denoted as flavanthrene) was obtained. On the other hand, leucoflavanthrone dibenzoate was also prepared. Since these two substanses give nearly identical absorption spectra, the leucobenzoate is considered to have the VI formula (5,13-dibenzoyloxy-8,16-diazapyranthrene) and to belong to the same conjugated system as flavanthrene. Consequently, it may be considered that the leuco-form of flavanthrone corresponds to the IV formula (5,13-dihydroxy-8,16-diazapyranthrene) in which two carbonyl groups are reduced, but not the III formula (8-hydro-13-hydroxy-5-oxo-8,16-diazapyranthrene) previously presented. In addition, the leucobenzoate can also be synthesized by boiling the quinone with zinc dust and benzoyl chloride in *o*-dichlorobenzene containing pyridine. This method, devised by the author, is easy to perform and gives a good yield.

Flavanthrone (II) is a yellow vat color and is also the diaza compound equivalent to pyranthrone (I) in the field of the polycyclic system. Studies of this substance and of related compounds have already been carried out by Scholl *et al.*1) There are, however, some doubtful points in their results. For example, the leuco-form was assigned the III formula, in spite of the fact that the IV formula is more reasonable. Furthermore, diazapyranthrene (V) which corresponds to the skeleton of flavanthrone, has not yet been synthesized.

The present investigation was undertaken in order to prepare this reduction product and the related compounds; it has been found during this work that the leuco-form of flavanthrone corresponds to the IV formula.

As is well known, the leuco compound is very unstable in air. It is, therefore, very difficult to isolate it, but it is possible to prepare a kind of ester, "leuco-ester," by adding acid chloride to the vat. The leuco-ester (VIII) may be considered to be a derivative of the corresponding hydrocarbon, since it is not a compound of a quinonoid form (VII) but belongs to a conjugated system of the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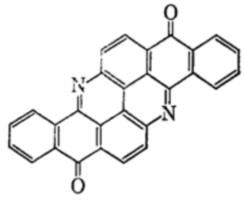
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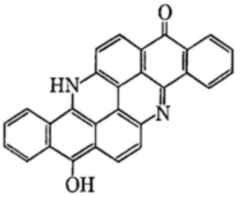
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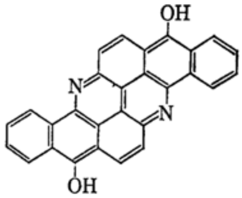
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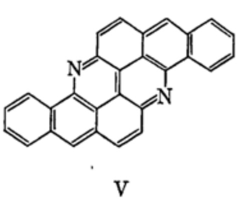
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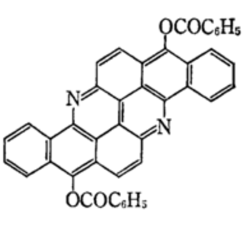

VI

[*1] Presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, Aprill, 1964.

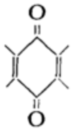
1) R. Scholl *et al.*, *Ber.*, **40**, 933 (1907); **41**, 2304, 2534 (1908); **44**, 1727 (1911).

Table 1. The wavelength (mμ) of the peaks in the absorption spectra of the hydrocarbons and their related leucobenzoates

Solvent: anthracene and its related benzoate, benzene; the others, 1, 2, 4-trichlorobenzene

Anthracene	311	325	341	359	378		
Leucoanthraquinone dibenzoate	324	339.5	356.5	375.5	396.5		
Pyranthrene	340	358	415	438	468		
Leucopyranthrone dibenzoate	342	360	423	448	480		
Violanthrene	347	365	385	409	434	462	496
Leucoviolanthrone dibenzoate	351	368	391.5	417	442	471	506
Leuco-16,17-dihydroxy-violanthrone tetrabenzoate	360	381	402	428	459	489	526
Flavanthrene	347	365	391	412	437	469	500
Leucoflavanthrone dibenzoate	348	367	395	416	442	475	508

hydrocarbon type (IX). In addition, it may be supposed that the ionization energy of the substituent (–$OCOC_6H_5$) is not small. It may, therefore, be considered that the absorption spectrum of the leuco-ester is about the same in appearance as that of the hydrocarbon and that the former appears in the region of somewhat longer wavelengths than the latter.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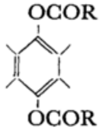
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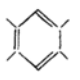
IX


X

The present author synthesized the lecuobenzoates of anthraquinone, pyranthrone, violanthrone, *etc.*,[2]) examined their absorption spectra, and confirmed the suggestion mentioned above: these leucobenzoates gave absorption spectra nearly identical with those of the corresponding hydrocarbon, although they were somewhat red-shifted, as is shown in Table 1. These facts are not only useful for examining the structure of the leuco compound, but also give proof that the hydrocarbon[*2] belongs to the aromatic hydrocarbon type (IX), but not its dihydro form (X).

Concerning flavanthrone (II), when the leucobenzoate was sysnthesized by the author's method, brown needles were obtained. On the other hand, when the zinc-dust fusion was applied to flavanthrone, a reduction product of the hydrocarbon type, a product which might be called "flavanthrene," was obtained as reddish brown needles which melted at 386—388°C. These two substances gave the absorption spectra shown in Fig. 1 and Table 1. By comparing these spectra, it may be found that the absorption spectrum of leucobenzoate is nearly identical with that of flavanthrene, although somewhat red-shifted.

As has been described above, this fact means that these two substanses belong to the same polycyclic conjugated system. The absorption band of flavanthrene is situated in a region of longer wavelengths than that of pyranthrene; the results of

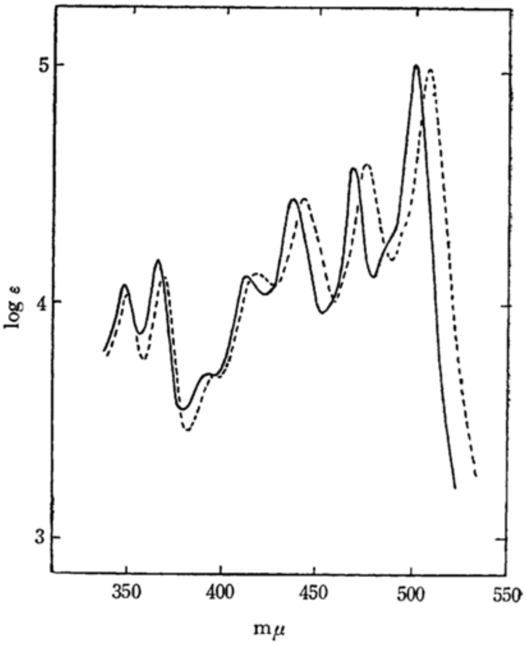

Fig. 1. Absorption spectra of flavanthrene and leucoflavanthrone dibenzoate (broken line) in 1, 2, 4-trichlorobenzene.

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2) The synthesis of "leuco-ester" is generally carried out by adding acid chloride or acid anhydride to the vat, but a large excess of the reagent is necessary and still the yield is low. The following method, devised by the author, is easy to perform and gives a good yield.

A mixture of quinone (1 part), pyridine (1 part), and *o*-dichlorobenzene (30—50 parts) is refluxed, and then zinc dust (1 part) is added little by little. After several minutes, benzoyl chloride (1 part) is added, and the mixture is refluxed for 10—30 min; after cooling, the same volume of ethanol is added. After the mixture has stood overnight, the precipitate is collected and boiled with ethanol to remove the soluble impurities. Finally, it is recrystallized from a suitable solvent.

In addition, pyridine is indispensable for this reaction; indeed, more of it is necessary than the mole ratio of benzoyl chloride.

[*2] Many kinds of condensed polycyclic hydrocarbons are prepared by the zinc-dust fusion of quinones. In this case, it is possible also to produce the dihydro compound.

the elementary analysis indicate that flavanthrene does not contain oxygen. From these facts, flavanthrene may be considered to be a compound with the V formula, 8,16-diazapyranthrene. Since the leucobenzoate corresponds to the derivative of flavanthrene and since the analysis indicates that it is dibenzoate, this ester may be considered to have the VI formula.

In addition, the author synthesized leucobenzoate by adding benzoyl chloride to the vat.[*3] Since flavanthrone is readily vatted, the synthesis was carried out under six sets of conditions, from 20°C to 75°C; all the products gave absorption spectra identical with that of the ester described above.

These results mean that the author's method was useful in this case also and, further, confirm that the leuco-form of flavanthrone has the IV formula in which two carbonyl groups are reduced, not the III formula hitherto proposed.

Experimental

The melting points were measured in a liquid bath or in an air bath and are uncorrected.

Anthracene. The synthesis was carried out by the method described in Ref. 3. Colorless fine plates with a violet fluorescence were obtained by recrystallization from xylene. Mp 212.5°C (Ref. 3, 213°C).

Leucoanthraquinone Dibenzoate. A mixture of 5.0 g of anthraquinone, 5.0 g of zinc dust, 5.0 g of pyridine, and 200 m*l* of *o*-dichlorobenzene was refluxed for about 10 min. Then 5 g of benzoyl chloride was added, and boiling was continued for 30 min. After hot filtration, 200 m*l* of ethanol was added to the filtrate and the mixture was allowed to stand overnight. The crude product (5.2 g) was recrystallized from *o*-dichlorobenzene, giving pale yellow needles which melted at 292—293°C (Ref. 4, 293°C). This product is soluble in concentrated sulfuric acid with a yellow color.

Found: C, 80.62; H, 4.51%. Calcd for $C_{28}H_{18}O_4$: C, 80.37; H, 4.34%.

Pyranthrene. The synthesis was carried out by the method described in Ref. 5.

Leucopyranthrone Dibenzoate. Synthesis was carried out by the method described in Ref. 2 (pyranthrone: 2.0 g; *o*-dichlorobenzene: 80 m*l*). The crude product was recrystallized from trichlorobenzene, giving 1.4 g of fine, yellow-brown needles which colored at about 400°C but which did not melt below 450°C. This product is soluble in an organic solvent, giving a yellow color and a green fluorescence, while in a concentrated sulfuric acid solution it is blue.

Found: C, 85.86; H, 4.03%. Calcd for $C_{44}H_{24}O_4$: C, 85.70; H, 3.92%.

Violanthrene. The synthesis of the authentic sample has already been reported.[6]

Leucoviolanthrone Dibenzoate. The synthesis was carried out by a method similar to that used for pyranthrone. The crude product was recrystallized from *o*-dichlorobenzene, giving fine, red-brown needles which did not melt below 450°C, although they sintered at 358—364°C.[*4] Although this product is hardly soluble in an organic solvent, its solution gives a yellow-green fluorescence, while a concentrated sulfuric acid solution shows a blue color.

Found: C, 86.71; H, 4.10%. Calcd for $C_{48}H_{26}O_4$: C, 86.47; H, 3.93%.

Leuco - 16, 17 - dihydroxyviolanthrone Tetrabenzoate. A mixture of 1.0 g of 16,17-dihydroxyviolanthrone dibenzoate,[6] 2 g of pyridine, 1.5 g of benzoyl chloride, and 200 g of *o*-dichlorobenzene was boiled, and then 1.0 g of zinc dust was added little by little. After the mixture had been refluxed for 10 min, the zinc dust was removed by hot filtration. The filtrate was concentrated and ethanol was added, whereupon 1.2 g of red crystals were obtained. They were recrystallized from chlorobenzene, giving fine, red leaflets which melted at 333°C (decomp.). This product is soluble in an organic solvent, giving a strong yellow fluorescence, while in a concentrated sulfuric acid solution it shows a violet-blue color.

Found: C, 82.02; H, 3.91%. Calcd for $C_{62}H_{34}O_8$: C, 82.11; H, 3.78%.

Flavanthrene (V). The synthesis was performed by the zinc-dust fusion of flavanthrone (II). A mixture of 1.0 g of flavanthrone, 1.0 g of zinc dust, 5 g of zinc chloride, and 1 g of sodium chloride was fused at 280—290°C for 10 min. After cooling, the reaction mixture was dissolved in water and the insoluble part was filtered off. Then, it was treated with an alkaline hydrosulfite solution and the unchanged material was removed as the soluble part. The excess of zinc dust was dissolved by treatment with a diluted hydrochloric acid solution. Yield, 0.90 g of a grey black powder. It was recrystallized from trichlorobenzene, giving 0.35 g of reddish-brown needles which melted at 386—388°C. This product is soluble in an organic solvent, giving a yellow color and a stronger and more yellowish-green fluorescence than pyranthrene, while in a concentrated sulfuric acid solution it is blue-green.

Found: C, 88.72; H, 3.82; N, 7.34%. Calcd for $C_{28}H_{14}N_2$ (V): C, 88.87; H, 3.73; N, 7.40%.

Leucoflavanthrone Dibenzoate (VI). *Method Performed in a Solvent.* A mixture of 0.5 g of flavanthrone, 0.6 g of zinc dust, 1 g of pyridine, and 50 m*l* of *o*-dichlorobenzene was refluxed for 10 min. Then, 0.6 g of benzoyl chloride was added, after which the reaction mixture was further refluxed for 30 min. After the mixture had then cooled, 50 m*l* of ethanol was added and the mixture was allowed to stand overnight. The precipitate was collected, and this crude product (1.05 g, containing zinc dust) was recrystallized from trichlorobenzene, giving 0.26 g of fine, brown needles which did not melt below 450°C, although they sintered at 358—362°C.[*4] This product is soluble in an organic solvent with a strong yellowish-green fluorescence,

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[*3] The leucobenzoate prepared from a vat is an authentic sample equivalent to the actual leuco compound.

3) E. L. Martin, *J. Am. Chem. Soc.*, **58**, 1438 (1936).

4) Y. Nagai, Report of the Institute of Industrial Science, The University of Tokyo, **16** (Serial No. 104), 30 (1966).

5) E. Clar, *Ber.*, **72**, 1648 (1936).

6) J. Aoki, This Bulletin, **37**, 1356 (1961).

[*4] It is considered that, during sintering, the original quinone with a high melting point is reproduced. Hence, the sintering may be regarded as a kind of decomposition.

while a concentrated sulfuric acid solution shows a green color.

Found: C, 80.93; H, 3.92; N, 4.41%. Calcd for $C_{42}H_{22}O_4N_2$ (VI): C, 81.54; H, 3.58; N, 4.53%. (Calcd for monobenzoate of III, $C_{35}H_{18}O_3N_2$: C, 81.70; H, 3.53; N, 5.44%)

Method Performed in a Vat. Flavanthrone (0.1 g) was vatted in 20 m*l* of an alkaline hydrosulfite solution (NaOH, 4%; $Na_2S_2O_4$, 2%). After the substance had then been kept at the reaction temperature (Table 2) for 20 min, 0.7 g of benzoyl chloride was added and the reaction mixture was further kept at the same temperature for 2 hr. Then, after cooling, the precipitate was filtered off and washed, successively, with an alkaline hydrosulfite solution and with water. Since it was inevitable that the crude product obtained by this method would contain considerable amounts of the unchanged material, further purification was carefully carried out by recrystallization from trichlorobenzene; the results shown in Table 2 were obtained.

TABLE 2. THE RESULTS OF VATTING METHOD

Reaction temp., °C	20	30	40	50	60	75
Yield, g	0.05	0.01	0.05	0.04	0.03	0.01

However, all of products gave absorption spectra identical with that of the sample prepared in a solvent.

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