[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE ORIENTATION OF CHRYSENE[1]

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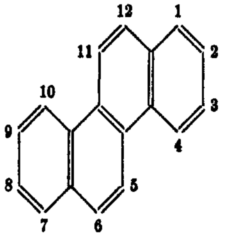
Almost all of the monosubstitution products of chrysene (I) have been made by direct introduction of the substituent into the chrysene nucleus or by simple transformation of a substituent thus introduced. In most of these cases it has been assumed that the entering group occupied the 6 position.[3] However, proof of the positions which these groups occupy has not been furnished to date. It was therefore deemed important to establish conclusively the structure of certain monosubstitution products of chrysene.



I. Chrysene numbering system

The assumption that chrysene is attacked at the 6 position was originally made by Weitzenbock and Lieb (1). These authors had synthesized 5-chrysenecarboxylic acid by the reliable Pschorr method and found it to melt at 222–223°, uncorr., whereas the chrysenecarboxylic acid of Liebermann and Zsuffa (2), prepared by the condensation of oxalyl chloride with chrysene, melted at 303°. Influenced by the knowledge that chrysene on oxidation formed a quinone having carbonyl groups at the 5 and 6 positions, they made the assumption that the higher-melting acid was 6-chrysenecarboxylic acid. Since that time, most workers in the chrysene field have assumed that other substituents directly introduced likewise occupied the 6 position.

Quite a few chrysene derivatives have been correlated by interconver-

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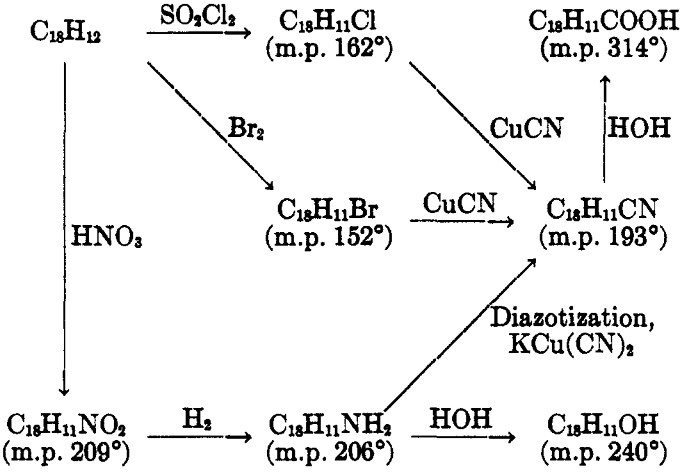
[1] Part of the subject matter herein described was presented to the Organic Division of the American Chemical Society at the meeting in Cincinnati, April, 1940.

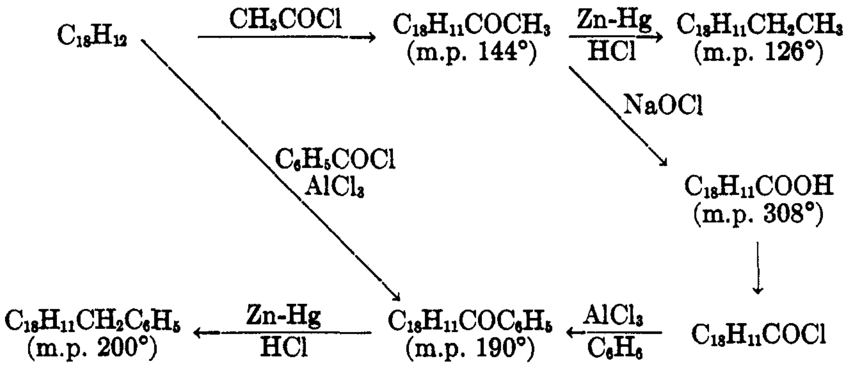
[2] The Elizabeth Clay Howald Scholar at The Ohio State University, 1939–1940.

[3] Chemical Abstracts numbering system.

sions, and it is of some interest to summarize this work, for if the structure of any one of this series is established, then the structures of all are known. In recent patents (3, 4) the following transformations have been demonstrated:



Funke and Müller (5) carried out the reactions indicated below.



In the present work we have shown that only one nitrochrysene (6) is formed on direct nitration. Since reduction to aminochrysene and hydrolysis yielded a chrysenol identical with authentic 6-chrysenol (7), the structure of the above nitration-product is established as 6-nitrochrysene. This finding also provides firm basis for assigning the 6 position to all of the above mentioned substituents. Further evidence is provided by the observation that synthetic 6-ethylchrysene (7) has the same melting point as that recorded for the ethylchrysene of Funke and Müller (5). It is of interest to note that the ethylchrysene, m.p. 236°, of these authors is not the 5 derivative as tentatively suggested, for 5-ethylchrysene has been synthesized and shown to melt at 92° (8).

In addition, we have sulfonated chrysene (9), isolated pure chrysene-6-sulfonic acid, and characterized it as a *p*-toluidine salt. The position of the entering sulfonic acid group was established by an alkaline fusion which resulted in the formation of 6-chrysenol, identified as its acetate.

EXPERIMENTAL[4]

6-Nitrochrysene. The chrysene used was a commercial product[5], m.p. 253.2–254.2°. It was converted into a finely divided form suitable for reactions by pouring a pyridine solution (10%) into water. The chrysene thus precipitated was thoroughly dried in an oven. Of the many conditions examined the following proved the most satisfactory for nitration. To a mechanically stirred suspension at 40° of 25 g. of chrysene in 700 cc. of glacial acetic acid, was added, all at once, a solution of 20 cc. of nitric acid (sp. gr. 1.42) and 25 cc. of concentrated sulfuric acid in 200 cc. of acetic acid. Within five minutes there was a small rise in temperature, the color became yellow, and flocculation of the suspended solid occurred. After a total of twenty minutes, the solid was collected by filtration, washed with acetic acid and water, and dried in an oven. This product melted at 210.8–212.8°. On one crystallization from 300 cc. of pyridine 21.8 g. (73%) of orange-yellow needles of 6-nitrochrysene, m.p. 213.7–214.2° was obtained. A portion dissolved in pyridine-xylene and purified by means of chromatographic adsorption on activated alumina, formed bright yellow needles, m.p. 214.0–214.6°.

Anal. Calc'd for $C_{18}H_{11}NO_2$: C, 79.10; H, 4.06; N, 5.13.
Found: C, 79.07; H, 4.06; N, 5.10.

Although an extended series of fractional recrystallizations was carried out, no evidence for the presence of a second nitrochrysene was found.

5-Nitrochrysophenazine[3]. The oxidation of 6-nitrochrysene with chromic acid or sodium dichromate in acetic acid resulted in the formation of deep red solids. Although 6-nitrochrysenequinone was undoubtedly present, we were unable to isolate an analytically pure sample. However, treatment with *o*-phenylenediamine yielded the phenazine derivative, which crystallized from pyridine-alcohol as fine yellow needles, m.p. 277.6–279.6°.

Anal. Calc'd for $C_{24}H_{13}N_3O_2$: C, 76.80; H, 3.49.
Found: C, 76.69; H, 3.71.

6,12-Dinitrochrysene. To a stirred suspension at 45–50° of 1 g. of chrysene in 35 cc. of acetic acid containing 1 cc. of concentrated sulfuric acid was added 10.5 cc. of fuming nitric acid over a period of six hours. After standing overnight, the mixture was heated for four hours on the steam-bath and then cooled and poured into water. The solid was crystallized from pyridine to yield 0.90 g. of fine bright yellow needles, m.p. 380.5–382.5° (10).

Anal. Calc'd for $C_{18}H_{10}N_2O_4$: C, 67.92; H, 3.17; N, 8.80.
Found: C, 68.10; H, 3.15; N, 8.79.

6-Aminochrysene. A mixture of 20 g. of 6-nitrochrysene, 5 g. of red phosphorus, 50 cc. of hydriodic acid (sp. g. 1.5), and 250 cc. of acetic acid was refluxed in an all-

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[4] All melting points corrected. The analyses were performed by Mr. J. H. Walker whose assistance was made possible by the Ohio State W.P.A. project 65–1–42–89.

[5] Frankel and Landau, Berlin.

glass apparatus until the color was gray (two to three hours). The solid was collected, washed well with acetic acid and water, dried, and extracted with 350 cc. of hot alcohol. This filtered extract was made slightly alkaline with alcoholic potassium hydroxide (color change to orange-red with a blue fluorescence) and cooled quickly. The pale tan leaflets of 6-aminochrysene weighed 15.3 g. (86%) and melted at 210.0–211.0° (11). A product having a lighter color was obtained by shaking a benzene solution of the crude product with sodium bisulfite solution.

Anal. Calc'd for $C_{18}H_{13}N$: C, 88.86; H, 5.38; N, 5.76.
Found: C, 89.08; H, 5.66; N, 5.83.

6-Acetylaminochrysene. A solution of 0.28 g. of 6-aminochrysene in 20 cc. of ethyl acetate was concentrated until solid began to appear, whereupon 15 cc. of hot acetic acid was added to bring the amine into solution. Then 0.1 g. of fused sodium acetate and 2 cc. of acetic anhydride were added. After heating for a few minutes, crystals appeared; cooling to room temperature and filtering gave 0.27 g. (82%) of pale tan needles, m.p. 296.5–299.0°. A sample recrystallized from acetic acid for analysis melted at 299.5–301.0° (12).

Anal. Calc'd for $C_{20}H_{15}NO$: C, 84.18; H, 5.30; N, 4.91.
Found: C, 83.88; H, 5.20; N, 4.86.

6-Diacetylaminochrysene. A solution of 0.14 g. of 6-aminochrysene in 20 cc. of acetic anhydride was refluxed for two hours, cooled somewhat, and diluted to cloudiness with water. There separated 0.15 g. (80%) of glistening tan needles, m.p. 215.8–217.8°. A sample for analysis, recrystallized twice from benzene-petroleum ether, using decolorizing carbon, formed large colorless prisms, m.p. 221.8–223.0° after sintering at 218° (12).

Anal. Calc'd for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.24; N, 4.28.
Found: C, 80.95; H, 4.95; N, 4.24.

6-Chrysenol. In a typical experiment, 2.44 g. of 6-aminochrysene and 15 cc. of 10% sulfuric acid were heated at 220–225° in a sealed tube for six hours. After cooling, the solid was collected and extracted with methyl alcoholic potassium hydroxide. On acidification of this filtered extract, 1.86 g. (76%) of tan solid was obtained. This was recrystallized from acetone-benzene to yield pale tan needles of 6-chrysenol, m.p. and mixed m.p. 248–250° (7). Portions of this product were converted into the acetate, m.p. 158.6–159.2° (7) and the methoxy derivative, m.p. 127.2–127.8° (7). Neither of these derivatives showed a depression of melting point when mixed with authentic specimens (7).

6-Chrysenesulfonic acid. To a well-stirred suspension at 0–5° of 11.4 g. of finely divided chrysene in 100 cc. of *s*-tetrachloroethane was added dropwise over a period of one hour 3.5 cc. of chlorosulfonic acid (9). As the drops came in contact with the suspension a local purple color was produced. The color of the reaction-mixture became gray and darkened as the reaction proceeded. An additional 50 cc. of solvent was used during this time to wash down the sides of the flask. The stirring was continued for five hours at 0–5° and for fifteen hours at room temperature. Ice was then added and the solvent was removed by steaming. To the hot solution (about 1 l.) was added about 30 g. of sodium bicarbonate and then about 400 g. of salt. The precipitate which formed was collected after cooling, and was crystallized from a minimal amount of water, filtering from substances insoluble in water. On cooling, 13.8 g. (83%) of pale tan sodium 6-chrysenesulfonate was obtained. A sample for analysis was further recrystallized from water.

Anal. (13). Calc'd for $C_{18}H_{11}NaO_3S$: Na, 6.96; Found: Na, 6.55.

6-Chrysenesulfonic acid was obtained in 65% yield by strongly acidifying a solution of the sodium salt with hydrochloric acid. The acid was thoroughly dried *in* *vacuo* over solid sodium hydroxide and then recrystallized from ethyl acetate-ligroin, separating as stout transparent pale yellow hydrated prisms. Some decomposition took place on recrystallization. On drying *in vacuo* at 110° the solvent was removed and the crystals, now almost colorless, opaque and powdery, melted at 193–194° when heated at the rate of 4° per minute.

Anal. Calc'd for $C_{18}H_{12}O_3S$: C, 70.11; H, 3.92.
Found: C, 69.62; H, 4.19.

This acid was further characterized by the formation of its *p*-toluidine salt (14), m.p. 273–274.5° with decomposition, when heated at the rate of 5° per minute.

Anal. Calc'd for $C_{25}H_{21}NO_3S$: C, 72.27; H, 5.10; N, 3.37.
Found: C, 72.40; H, 5.19; N, 3.27.

6-Chrysenyl acetate from 6-chrysenesulfonic acid. Into a melt of 7 g. of potassium hydroxide at 220° was stirred 0.5 g. of sodium 6-chrysenesulfonate. The temperature was raised slowly to 250° with constant stirring by which time the salt had changed to a viscous dark oil. After the temperature was raised to 270° during three minutes, the melt was cooled somewhat and poured into water. The alkaline solution was acidified, and the precipitate when dry amounted to 0.24 g. This crude product was acetylated to yield 0.22 g. of a crude acetate which upon sublimation and recrystallization from dioxane-water melted at 158.0–158.6°. The melting point was not depressed when the substance was mixed with an authentic sample of 6-chrysenyl acetate (7).

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