[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ALBERTA]

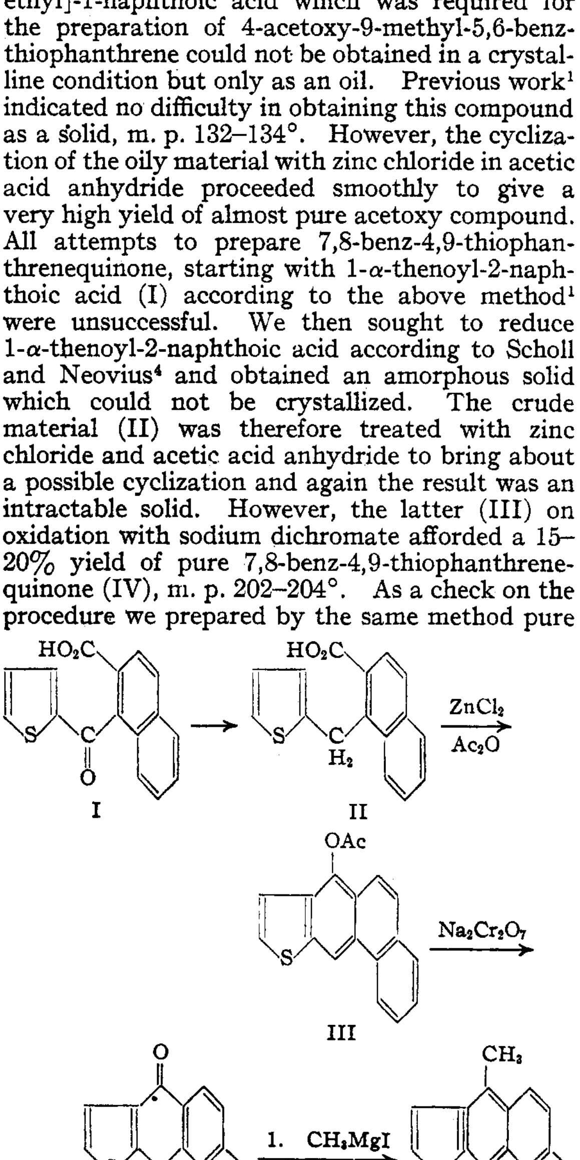
The Synthesis of Some 9,10-Dialkylanthracenes and 4,9-Dialkylbenzthiophanthrenes

BY REUBEN B. SANDIN AND ROSS KITCHEN

The method which Sandin and Fieser developed for the synthesis of 9,10-dimethyl-1,2-benzanthracene and 4,9-dimethyl-5,6-benzthiophanthrene[1] appears to be a fairly general one for the preparation of *meso*-methylanthracene derivatives. Hershberg and Fieser[2] have used it in the preparation of isologs of 9,10-dimethyl-1,2-benzanthracene in which the 1,2-benz ring is replaced by a thiophene and by a selenophene ring. Recently, Sandin, Kitchen and Fieser[3] used this procedure for the preparation of 1,2,9,10-tetramethylanthracene. In order to get more information regarding the adaptability of the method, we have now employed it to prepare 9,10-dimethylanthracene, 1,9,10-trimethylanthracene, 2,-9,10-trimethylanthracene, 2,3,9,10-tetramethylanthracene, 2,3-dimethyl-9,10-diethylanthracene, and 4,9-di- methyl-7,8-benzthiophanthrene (V). Isomeric with the latter compound we have also prepared 4,9-dimethyl-5,6-benzthiophanthrene, an active carcinogen,[1,2] from pure 5,6-benz-4,9-thiophanthrenequinone, in much higher yields than previously recorded.

The procedure involves, in each case, the interaction of the 9,10-anthraquinone or the 4,9-thiophanthrenequinone with excess alkyl Grignard reagent and treatment of the resulting magnesio halide derivative of the diol with methanol, hydriodic and acetic acids to give the solid alkyl-iodoalkyl compound. The latter on reduction with stannous chloride in dioxane affords the desired end-product. The yields of the *meso*-alkyl compounds calculated on the quinones were found to vary from 20% in the case of the 4,9-dimethyl-7,8-benzthiophanthrene to almost theoretical for 2,3,9,10-tetramethylanthracene. The preparation of 2,3-dimethyl-9,10-diethylanthracene is the first instance of the introduction of two *meso*-ethyl groups, by this process. As with the 1,2,9,10-tetramethylanthracene,[3] the intermediate iodoalkyl compounds of 2,3-dimethyl-9,10-diethylanthracene, 1,9,10-trimethylanthracene and 4,9-dimethyl-7,8-benzthiophanthrene were obtained in satisfactory yields by using a mixture of hydriodic and hydrobromic acids. Ether as a medium was also found to be superior to equal parts of benzene and ether. All attempts, so far, to convert 1,4-dimethyl-9,10-anthraquinone into the intermediate alkyl-iodoalkyl compound have been unsuccessful.

In a previous communication it has been shown that the cyclization of 2-α-thenoyl-1-naphthoic acid or 1-α-thenoyl-2-naphthoic acid does not give the expected quinone in either case, but always a mixture of the expected quinone and its isomer. This mixture is exceedingly difficult to separate into its components. However, pure 5,6-benz-4,9-thiophanthrenequinone, m. p. 167–168°, was obtained in 20% yield by the oxidation of 4-acetoxy-9-methyl-5,6-benzthiophanthrene, according to the procedure developed by Fieser.[1] It is interesting to note that the 2-[α-(α'-thienyl)-ethyl]-1-naphthoic acid which was required for the preparation of 4-acetoxy-9-methyl-5,6-benzthiophanthrene could not be obtained in a crystalline condition but only as an oil. Previous work[1] indicated no difficulty in obtaining this compound as a solid, m. p. 132–134°. However, the cyclization of the oily material with zinc chloride in acetic acid anhydride proceeded smoothly to give a very high yield of almost pure acetoxy compound. All attempts to prepare 7,8-benz-4,9-thiophanthrenequinone, starting with 1-α-thenoyl-2-naphthoic acid (I) according to the above method[1] were unsuccessful. We then sought to reduce 1-α-thenoyl-2-naphthoic acid according to Scholl and Neovius[4] and obtained an amorphous solid which could not be crystallized. The crude material (II) was therefore treated with zinc chloride and acetic acid anhydride to bring about a possible cyclization and again the result was an intractable solid. However, the latter (III) on oxidation with sodium dichromate afforded a 15–20% yield of pure 7,8-benz-4,9-thiophanthrenequinone (IV), m. p. 202–204°. As a check on the procedure we prepared by the same method pure



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(1) Sandin and Fieser, THIS JOURNAL, **62**, 3098 (1940).

(2) Hershberg and Fieser, *ibid.*, **63**, 2561 (1941).

(3) Sandin, Kitchen and Fieser, *ibid.*, **65**, 2018 (1943).

(4) Scholl and Neovius, *Ber.*, **44**, 1080 (1911).

TABLE I

9,10-DIALKYLANTHRACENES AND 4,9-DIALKYLBENZTHIOPHANTHRENES

No.	Compound	M. p., °C. (cor.)	Yield, % pure	Description	Formula	Analyses, % Calcd. C	H	Found C	H
I	9,10-Dimethylanthracene	178–179[a]	80	Yellow needles	.....		..		..
II	1,9,10-Trimethylanthracene	90– 92	50	Yellow needles from alcohol	$C_{17}H_{16}$	92.68	7.32	92.30	7.46[d]
III	2,9,10-Trimethylanthracene	93– 96[b]	55	Yellow needles	.....		..		...
IV	2,3,9,10-Tetramethylanthracene	138–140[c]	95	Yellow plates	.....		..		...
V	2,3-Dimethyl-9,10-diethylanthracene	113–114	20	Yellow needles from alcohol	$C_{20}H_{22}$	91.54	8.46	91.29	8.77[d]
VI	4,9-Dimethyl-5,6-benzthiophanthrene	158–159[e]	72	......	.....		..		...
VII	4,9-Dimethyl-7,8-benzthiophanthrene (V)	99–100	20	Pale yellow needles from dil. AcOH	$C_{18}H_{14}S$	82.40	5.38	82.55	5.25[f]

[a] Bachmann and Chemerda [*J. Org. Chem.*, **4**, 583 (1939)] report m. p. 180.5–181°. We characterized this compound and all other previously recorded ones by means of the picrates. [b] Bachmann and Chemerda, *ibid.*, report m. p. 95–96° when crystallized rapidly from alcohol. [c] Fieser and Webber [THIS JOURNAL, **62**, 1360 (1940)] report m. p. 139.4–140.2° [d] Semi-microanalysis by J. C. Nichol. [e] Sandin and Fieser [*ibid.*, **62**, 3098 (1940)] report m. p. 158–159°. [f] Microanalysis by Eleanor Werble.

TABLE II

PICRIC ACID AND TRINITROBENZENE DERIVATIVES

No.	Made from no.	M. p., °C. (cor.)	Description, from alcohol	Formula	Analyses, % Calcd. C	H	Found C	H
VIII	II and picric acid	142–144	Black needles	$C_{17}H_{16}\cdot C_6H_3O_7N_3$	61.44	4.26	61.00	4.32[a]
IX	V and picric acid	134–136	Black needles	$C_{20}H_{22}\cdot C_6H_3O_7N_3$	63.54	5.13	63.56	5.23[a]
X	VII and trinitrobenzene	165	Dark red needles	$C_{18}H_{14}S\cdot C_6H_3O_6N_3$	60.62	3.61	60.84	3.47[b]

[a] Semi-microanalysis by J. C. Nichol. [b] Microanalysis by Eleanor Werble.

TABLE III

INTERMEDIATE ALKYL-IODOALKYL COMPOUNDS

No.	Of no.	Yield, % crude	Description, yellow	Formula	Analysis, % on crude material Calcd. I	Found I
XI	I	85	Crystals	$C_{16}H_{13}I$	38.2	38.4 37.7[a]
XII	II	55	Amorphous solid	$C_{17}H_{15}I$	36.7	35.8 36.0[a]
XIII	III	60	Crystals	$C_{17}H_{15}I$	36.7	36.4 36.6[a]

[a] Macroanalysis by R. B. S.

5,6-benz-4,9-thiophanthrenequinone in an over-all yield of 15–20%, starting with 2-α-thenoyl-1-naphthoic acid. Again, as in the case of the isomeric compound, all of the intermediates were obtained as amorphous solids which could not be crystallized.

The results of these experiments are recorded in Tables I, II and III. The general directions for the preparation of the compounds are essentially the same as described by Sandin and Fieser,[1] and for that reason only a few typical experiments will be mentioned.

Experimental Part[5]

5,6-Benz-4,9-thiophanthrenequinone (a) from 4-Acetoxy-9-methyl-5,6-benzthiophanthrene.—A solution of 3.2 g. of 4-acetoxy-9-methyl-5,6-benzthiophanthrene in 70 cc. of glacial acetic acid was kept at the boiling point during the addition in small portions of 13 g. of powdered sodium dichromate. The solution was kept near the boiling point for one hour and then allowed to stand at about 60° for twelve hours. It was then poured into 500 cc. of water, heated in order to coagulate the precipitate and filtered, and the product was extracted with sodium hydroxide. The yield of crude material, m. p. 159–162°, was 1.5 g. Vacuum sublimation at 0.1–0.2 mm. and at 150–160° afforded 0.57 g. of pure quinone, m. p. 167–168°.

(b) From 2-α-Thenoyl-1-naphthoic Acid.—The reduction of 6.2 g. of 2-α-thenoyl-1-naphthoic acid was carried out according to the procedure of Scholl and Neovius.[4] After filtering and acidifying, there was obtained 5.5 g. of amorphous material, m. p. 95–130°, which could not be purified by crystallization. The cyclization process of Fieser and Hershberg[6] was therefore carried out on 4.3 g. of the amorphous substance, which afforded 4.2 g. of solid which again was intractable. The crude product was oxidized with sodium dichromate according to the procedure already described. One sublimation and one crystallization from glacial acetic acid gave 0.9 g. of pure 5,6-benz-4,9-thiophanthrenequinone, m. p. 167°.

4,9-Dimethyl-5,6-benzthiophanthrene.—To a solution of the Grignard reagent from 1.0 g. of magnesium and excess methyl iodide in 20 cc. of anhydrous ether and 20 cc. of benzene was added 0.95 g. of pure 5,6-benz-4,9-thiophanthrenequinone. The quinone went into solution at room temperature overnight. The reaction mixture was poured slowly into a solution (cooled to 0°) of 12 cc. of hydriodic acid (sp. gr. 1.7) in 40 cc. of methanol. Glacial acetic acid (40 cc.) was then added and the iodo compound

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(5) All melting points are corrected.

(6) Fieser and Hershberg, THIS JOURNAL, **59**, 1028 (1937).

which separated was reduced with stannous chloride in dioxane by the method of Sandin and Fieser.[1] This yield of almost pure 4,9-dimethyl-5,6-benzthiophanthrene, m. p. 158°, was 0.7 g. One crystallization from glacial acetic acid raised the m. p. to 158–159°.

7,8-Benz-4,9-thiophanthrenequinone (IV).—Following the procedure (b) detailed above, for the isomeric quinone, 3.5 g. of 1-α-thenoyl-2-naphthoic acid (I) afforded 0.67 g. of 7,8-benz-4,9-thiophanthrenequinone, m. p. 202–204°.

Anal. Calcd. for $C_{16}H_8O_2S$: S, 12.13. Found: S, 11.92, 11.94.[7] A mixture of equal parts of this preparation and a sample of the quinone (m. p. 203–204°, sublimed twice and recrystallized from glacial acetic acid eleven times to constant m. p.) made by the cyclization of 1-α-thenoyl-2-naphthoic acid[1] melted at 202.5–203.5°.

4,9-Dimethyl-7,8-benzthiophanthrene (V).—The procedure was essentially the same as described for 4,9-dimethyl-5,6-benzthiophanthrene, with the exception that ether was used for the preparation of the Grignard reagent and also that a mixture of equal parts of hydriodic and hydrobromic acids was used for the precipitation of the iodomethyl compound.

2,3-Dimethyl-9,10-diethylanthracene.—In this case 2,3-dimethylanthraquinone was added to the Grignard reagent made from ethyl iodide, ether and magnesium. It was found advantageous to use a mixture of hydrobromic acid (sp. gr. 1.4) and hydriodic acid (sp. gr. 1.7) as in the above instance. The reduction with stannous chloride in dioxane proceeded smoothly.

1,9,10-Trimethylanthracene.—The melting point of this compound changes on standing. One sample which had been kept for three weeks, melted unsharply at 210° The change is probably a dimerization. In the preparation of the compound it is essential that the reduction reaction mixture be worked up as rapidly as possible and that purification be made through the picrate.

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Summary

1. The preparation of five *meso*-alkylanthracenes is described.

2. 4,9-Dimethyl-7,8-benzthiophanthrene, an isomer of the active carcinogen 4,9-dimethyl-5,6-benzthiophanthrene, has been prepared.

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[7] Macroanalysis by R. K.

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The Identification of Aryl Iodides

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Many useful procedures have been described for making derivatives of aryl halides.[1,2] Recently Huntress and Carten[3] have used chlorosulfonic acid as a reagent for this purpose and found it to yield excellent results. Of thirty-two aryl halides studied, thirty afforded characteristic arylsulfonyl chlorides which were readily converted to the corresponding arylsulfonamides. However, Huntress and Carten obtained unsatisfactory results with certain iodo derivatives of aromatic hydrocarbons.

The authors of this paper report a study of some aryliodoso chlorides as applied to the characterization of a number of aryl iodides. Aryliodoso chlorides decompose on heating, usually into the iodo compounds and chlorine. There is also the "migration" of chlorine to ring carbon with the formation of hydrogen chloride and chlorine substitution compounds.[4] Phenyliodoso chloride, for example, decomposes at 120–121°, giving up chlorine and hydrogen chloride. There are a few instances in the chemical literature where this property has been used in the identification of aryl iodides. Leicester and Bergstrom,[5] working on the thermal decomposition of triphenylselenonium iodide characterized iodobenzene by conversion into phenyliodoso chloride, and further checked by a mixed melting point with a known sample of phenyliodoso chloride. Similarly Ganguly and Le Fèvre,[6] working on the iodo-*p*-cymene formed by the direct iodination of the hydrocarbon, characterized 2- and 3-iodocymene by converting them into the corresponding iodoso chlorides. Their melting points were found to be 97° and 85–87°, respectively, whereas an equal-part mixture melted at about 75°. C. Willgerodt[7] in his monograph lists approximately one hundred and twenty-five iodinated aromatic compounds which have been converted into solid iodosochlorides. Willgerodt's data should prove useful for identification work.

The authors of this paper have found that the iodoso chlorides of some aryl iodides are satisfactory derivatives in that they are prepared easily and quickly, and require no purification. The io-

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[1] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 159–161.

[2] Kamm, "Qualitative Organic Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1932, pp. 194–196.

[3] Huntress and Carten, THIS JOURNAL, **62**, 511 (1940).

[4] Ingold, Smith and Vass, *J. Chem. Soc.*, 1245 (1927). See also Brazier and McCombie, *ibid.*, **101**, 968 (1912); Buchan and McCombie, *ibid.*, 137 (1931); Matheson and McCombie, *ibid.*, 1103 (1931).

[5] Leicester and Bergstrom, THIS JOURNAL, **51**, 3587 (1929).

[6] Ganguly and Le Fèvre, *J. Chem. Soc.*, 1697 (1934).

[7] C. Willgerodt, "Die organischen Verbindungen mit mehrwertigem Jod," F. Enke, Stuttgart, 1914.