cis- and *trans*-hydroxy acids and of camphoric and isocamphoric acids.

2. Isomerization does not occur in the reduction of *allo*-methyl hydrogen camphorate under these conditions.

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The Synthesis of Symmetrical Diaryl Ethylenes*

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Trithiobenzaldehyde upon being heated above its melting point alone or with copper powder gives considerable stilbene.[1] The desirability of using this reaction as a method for preparing substituted stilbenes as well as their analogs in the naphthalene, anthracene, and phenanthrene series has been made the subject of this investigation.

The starting polymeric thioaldehydes are made in good yields by passing hydrogen chloride and hydrogen sulfide into solutions of the oxo-aldehydes. The thioaldehydes are then decomposed by heating in the presence of very finely divided copper powder. This method is applicable to unsubstituted or alkoxy substituted aryl thioaldehydes and although the yields in most cases are not especially good the method offers promise because of its simplicity and the ready availability of starting materials. When freshly reduced copper powder is not used in the pyrolysis of the thioaldehydes, sulfur-containing compounds in addition to the ethylene compounds result. For instance, trithiobenzaldehyde when heated alone forms tetraphenylthiophene as well as stilbene.

1,2-Di-(3-phenanthryl)-ethylene, 1,2-di-(2-methoxy-1-phenanthryl)-ethylene, and 1,2-di-(9-anthryl)-ethylene have not been heretofore prepared. The method followed in their preparation is indicative of their structure. Upon mild oxidation, the ethylene double bond is broken with the formation of known acids which were isolated to further substantiate the structure of these ethylene compounds. The dibromide was made of each known ethylene compound as a means of identification. The heretofore unknown dibromide of 1,2-di-(9-anthryl)-ethylene was also made. That the bromine added to the ethylene double bond was proved by oxidation to anthraquinone.

2-Methoxyphenanthrene-1-aldehyde was prepared by an adaptation of the method of Kalischer, Keller and Scheyer[2] in which the aldehyde group is introduced directly by phosphorus oxychloride and N-methylformanilide. An 80% yield was obtained.

Experimental

Preparation of the Ethylene Compounds.—The thioaldehyde was ground to a fine powder and then intimately mixed with 3 to 4 times the theoretical amount of freshly reduced copper powder. The mixture was heated for thirty minutes in a small flask by means of an oil-bath to the temperature indicated in Table I. After cooling and breaking up the fused mass, the ethylene compound was extracted with boiling benzene. 1,2-Di-(9-anthryl)-ethylene proved to be only slightly soluble in benzene and several extractions with large quantities of benzene were necessary in this case. The benzene solutions were then concentrated to bring about crystallization. Frequently, treatment with Norit was required to remove color from the ethylene compound and generally one to two recrystallizations from benzene (or alcohol in the case of the more soluble ones) were required to obtain a pure product. The yields in Table I are in terms of pure compound.

1,2-Di-(3-phenanthryl)-ethylene.—This compound crystallized from benzene as very small, light-yellow crystals, m. p. 289° (cor.), which exhibited a greenish-blue fluorescence in ultraviolet light.

Anal. Calcd. for $C_{30}H_{20}$: C, 94.70; H, 5.30; mol. wt., 380. Found: C, 94.52; H, 5.60; mol. wt. determination (Rast camphor method), 354 and 390.

The compound was oxidized with a slight excess of chromic anhydride in glacial acetic acid to the known phenanthraquinone-3-carboxylic acid.

1,2-Di-(2-methoxy-1-phenanthryl)-ethylene.—This compound crystallized from benzene as light-cream colored needles, m. p. 277° (cor.), which exhibited a greenish blue fluorescence in ultraviolet light.

Anal. Calcd. for $C_{32}H_{24}O_2$: C, 87.24; H, 5.49; mol. wt., 441; methoxyl, 2. Found: C, 87.16; H, 5.59; mol. wt. determination (Rast camphor method), 453 and 429; methoxy, 1.96.

Upon oxidation with excess 3% sodium hypochlorite at reflux temperature the known 2-methoxyphenanthroic-1-acid resulted.

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[1] H. Klinger, *Ber.*, **9**, 1893 (1876).

[2] G. Kalischer, K. Keller and H. Scheyer, U. S. Patent 1,807,693, June, 1931.

TABLE I

Sulfur compound	M. p., °C.	Pyrolysis temp., °C.	Diarylethylene obtained	Yield, %	M. p., °C.
Trithiobenzaldedyde[a]	225	230	Stilbene	45	124
Trithiosalicylaldehyde[b]	210	215	2,2′-Dihydroxystilbene	trace	197
Trithio-*p*-hydroxybenzaldehyde[b]	215	220	4,4′-Dihydroxystilbene	trace	284
Trithio-*o*-nitrobenzaldehyde[c]	164–175	160	2,2′-Dinitrostilbene	0	192
Trithiomethylvanillin[c]	223	235	3,4,3′,4′-Tetramethoxystilbene	25	155
Polythionaphthaldehyde-1	155–203	200	1,2-Di-(1-naphthyl)-ethylene	30	161
Polythionaphthaldehyde-2	170–177	230	1,2-Di-(2-naphthyl)-ethylene	22	255
Trithio-β-ethoxynaphthaldehyde[d]	233	290	1,2-Di-(2-ethoxy-1-naphthyl)-ethylene	62	215
Polythiophenanthrene-3-aldehyde	220	230	1,2-Di-(3-phenanthryl)-ethylene	27	287
Polythio-2-methoxyphenanthrene-1-aldehyde	271	275	1,2-Di-(2-methoxy-1-phenanthryl)-ethylene	71	277
Polythioanthracene-9-aldehyde[d]	260	270	1,2-Di-(9-anthryl)-ethylene	38	337

Prepared by method of: [a] E. Baumann and E. Fromn, *Ber.*, **22**, 2600 (1889). [b] K. Kopp, *Ann.*, **277**, 339 (1894). [c] E. Worner, Ber., **29**, 151 (1896). [d] J. H. Wood and R. W. Bost, THIS JOURNAL, **59**, 1721 (1937).

1,2-Di-(9-anthryl)-ethylene.—This compound forms small, yellow crystals from benzene in which it is only very slightly soluble. The compound softens at 330° and melts with decomposition at 338° (cor.). It fluoresces a green-yellow in ultraviolet light. Upon oxidation with excess chromic oxide in glacial acetic acid anthraquinone results.

Anal. Calcd. for $C_{30}H_{20}$: C, 94.70; H, 5.30; mol. wt., 380. Found: C, 94.17; H, 5.39; mol. wt., 379 and 352.

1,2-Dibromo-1,2-di-(9-anthryl)-ethane.—A partial solution of 0.4 g. of 1,2-di-(9-anthryl)-ethylene in 400 ml. of dry carbon tetrachloride was refluxed fifteen minutes with 0.49 g. of dry bromine. After evaporation to 100 ml., 0.21 g. of yellow needles separated. After recrystallizing twice from benzene, the compound melted at 268° (cor.).

Anal. Calcd. for $C_{30}H_{20}Br_2$: Br, 29.58. Found: Br, 29.23.

Oxidation in glacial acetic acid with chromic anhydride gave anthraquinone.

Polythionaphthaldehyde-1.—A solution of 6.9 g. of α-naphthaldehyde in 75 ml. of ethanol was saturated with hydrogen chloride. Then at 0° dry hydrogen sulfide and hydrogen chloride were passed in for two hours. The white precipitate thus formed was washed with three 25-ml. portions of ethanol. The yield of the polymer was 6.8 g. (90%) which melted over a range of 155° to 170°.

Anal. Calcd. for $(C_{10}H_7CHS)_x$: S, 18.60. Found: S, 18.41.

This polymer can be separated by recrystallization from ethyl acetate into fractions which differ considerably in melting points. This was found to be true also of the other thioaldehydes in the naphthalene, phenanthrene, and anthracene series which are discussed in this section.

Polythionaphthaldehyde-2.—A solution of 5.8 g. of β-naphthaldehyde and 25 ml. of ethanol and 25 ml. of benzene was treated as above. There resulted 4 g. (62.5%) of a white precipitate which melted at 170–177°.

Anal. Calcd. for $(C_{10}H_7CHS)_x$: S, 18.60. Found: S, 18.87.

Polythiophenanthrene-3-aldehyde.—The oxo-aldehyde was dissolved in the smallest possible quantity of absolute ethanol and this solution was then saturated with dry hydrogen chloride. The solution was cooled to 0° and hydrogen sulfide and hydrogen chloride were then bubbled in for several minutes until precipitation was complete. After recrystallizing from toluene a pure white product (82%) which melted at 221° was obtained.

Anal. Calcd. for $(C_{14}H_9CHS)_x$: S, 14.41. Found: S, 14.35.

Polythio-2-methoxyphenanthrene-1-aldehyde.—A solution of 5 g. of the oxo-aldehyde in 100 ml. each of benzene and ethyl acetate was completely saturated with dry hydrogen chloride. Hydrogen sulfide and hydrogen chloride were then passed in at room temperature until precipitation of the thioaldehyde was complete, which generally required about 30 minutes. The crude product which was light-gray (yield 95%) was recrystallized twice from hot toluene from which it separated as small, white crystals, m. p. 271°.

2-Methoxyphenanthrene-1-aldehyde.—A mixture of 8.5 g. of N-methylformanilide and 10.5 g. of phosphorus oxychloride was permitted to stand in a 100-ml. flask for thirty minutes. The flask was fitted with a tube to carry off hydrogen chloride vapor, the whole being protected from outside moisture. Five grams of 2-methoxyphenanthrene was then added and the temperature of the mixture was gradually raised to 80° where it was maintained for two hours. The contents of the flask was then poured slowly, with vigorous stirring, into 150 cc. of ice water. Lumps were carefully broken up and the flask was filled with water to decompose the compound adhering to the walls. The whole stood overnight. The yellow precipitate was filtered off and recrystallized from alcohol after being treated with Norit. An 80% yield (4.5 g.) of the pure aldehyde was obtained.

Summary

1. Procedures for the preparation of stilbene and stilbene homologs and analogs by heating the proper thioaldehyde are proposed. Yields run from a trace to 71%.

2. Several new thioaldehydes and diaryl substituted ethylenes are reported.

3. The direct introduction of an aldehyde group into 2-methoxyphenanthrene with $POCl_3$ and N-methylformanilide was accomplished with an 80% yield.

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