to conjugate systems have been reported.

2. Several reactions have been carried out to determine the stability of these products.

3. The methods used in separating the hydrogenolysis products of these compounds are being improved and further work in this field will be reported at an early date.

GAINESVILLE, FLORIDA RECEIVED JULY 2, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Sulfur Studies. XII. Thioaldehydes in the Naphthalene and Anthracene Series

BY J. H. WOOD AND R. W. BOST

In a previous paper[1] it was shown that thioaldehydes of the benzene series either polymerize or undergo the Cannizzaro reaction immediately upon formation. This work has been extended into the naphthalene and anthracene series with the idea that the increased molecular weight might retard polymerization reactions to the extent that the monomer could be isolated and studied.

α-Thionaphthaldehyde and β-ethoxythionaphthaldehyde are much more resistant to polymerization than thiobenzaldehyde and we have been able to keep dilute solutions of these thioaldehydes from twenty-four to thirty-six hours before complete polymerization occurred. They exhibit the condensation reactions characteristic of oxo-aldehydes such as the elimination of hydrogen sulfide with 2,4-dinitrophenylhydrazine with the formation of the hydrazone. They give color reactions with Grote's reagent and form precipitates with mercuric chloride. In the presence of much acid, immediate polymerization occurs with the formation of the cyclic trimer.

The cyclic trimer, β-ethoxytrithionaphthaldehyde, is formed in a quantitative yield upon passing hydrogen sulfide in solutions of the aldehyde which have been saturated previously with dry hydrogen chloride. Upon being vacuum distilled, the trimer is mainly decomposed into the new stilbene analog, *sym*-di-β-ethoxynaphthylethylene. This furnishes an excellent synthesis of *sym*-dinaphthyl substituted ethylenes. If the distillation is carried out in the presence of a few crops of concentrated sulfuric acid, some depolymerization also occurs and we have isolated from the distillate a few drops of monomeric β-ethoxythionaphthaldehyde as a red oil. Alcoholic solutions of the oil give the characteristic reactions mentioned above. Polymerization occurs in a few hours.

Thioanthracene-aldehyde-9 polymerizes immediately upon formation into linear polymers and we have been unable to prepare the cyclic trimer. This is no doubt due to the large anthranyl groups which prevent ring closure. Further evidence of this is the fact that both geometrical isomers of trithiobenzaldehyde are formed in the same reaction, but the *trans* form is produced in a much greater quantity. On the other hand, only one of the two possible geometrical isomers of β-ethoxytrithionaphthaldehyde is formed in the reaction similar to that by which the trithiobenzaldehydes are produced, and it is logical to assume that it is the *trans* form. That is, the β-ethoxynaphthyl group does not permit ring closure when all are on the same side of the ring and only the *trans* form is produced. With anthracene-thioaldehyde-9, ring closure is not possible even with two groups on one side and the other on the opposite side.

The aldehydes used in this investigation are not on the market and considerable time was consumed in finding satisfactory methods by which fairly large quantities could be made readily. The general syntheses of aldehydes which give fair yields in the benzene series were found to give none, or at best only poor yields in the naphthalene and anthracene series. The methods described below were found to be the most satisfactory of those tried for the preparation of the aldehydes used.

Experimental

α-Naphthaldehyde.—α-Naphthylcarbithioic acid was prepared by the method of Bost and Mattox.[2] The semicarbazone of the aldehyde was prepared from the carbithioic acid by the method of Wuyts, Berman and Lacourt.[3] Hydrolysis of the semicarbazone gave the aldehyde. Purification was accomplished by means of the bisulfite reaction followed by distillation.

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(1) J. H. Wood and R. W. Bost, THIS JOURNAL, **59**, 1011 (1937).

(2) R. W. Bost and W. J. Mattox, *ibid.*, **52**, 332 (1930).

(3) H. Wuyts, L. Berman and A. Lacourt, *Bull. soc. chim. Belg.*, **40**, 665 (1931).

β-Ethoxynaphthaldehyde and Anthracene-aldehyde-9.—These two aldehydes[4] were prepared with excellent yields by the action of formylmonomethylaniline and phosphorus oxychloride upon the corresponding β-ethoxynaphthalene and anthracene.

β-Ethoxynaphthaldehyde 2,4-Dinitrophenylhydrazone.—This compound has not been prepared previously and since it is the most suitable derivative by which the thio- or oxo-aldehyde is identified, its characterization was necessary. It was prepared in the usual manner by the action of a saturated solution of 2,4-dinitrophenylhydrazine upon a hot alcoholic solution of the aldehyde in the presence of a drop of concentrated hydrochloric acid. Upon cooling, precipitation was practically quantitative in the form of red needles. Ordinarily, purification was not necessary. However, when necessary, purification was accomplished by recrystallization from a 1:1 mixture of benzene–ethyl acetate; red needles, m. p. 258°, resulted.

Anal. Calcd. N, 14.66. Found: N, 14.42.

Anthracene-aldehyde-9 2,4-Dinitrophenylhydrazone.—This compound was prepared and purified by the method described above; red needles resulted, m. p. 265°.

Anal. Calcd. N, 14.51. Found: N, 14.38.

β-Ethoxythionaphthaldehyde.—Upon passing hydrogen sulfide for several hours into 125 cc. of an alcoholic solution of β-ethoxynaphthaldehyde which contained 0.3 cc. of concentrated sulfuric acid, a light pink precipitate formed which was a mixture of the cyclic thiotrimer with a small amount of the monomeric thioaldehyde. The precipitate was removed and washed with alcohol. Upon extracting the precipitate with 50 cc. of boiling ethyl acetate, the monomer passed into solution and the cyclic trimer was left as a white precipitate. The ethyl acetate solution gave a red precipitate with an ethyl acetate solution of mercuric chloride. This precipitate became yellow in about one minute. The 2,4-dinitrophenylhydrazone of the aldehyde was precipitated from the ethyl acetate solution upon adding the proper reagents. Upon standing or upon evaporation of the solvent, polymerized thioaldehydes separated from the ethyl acetate solution. After about thirty-six hours, the solution no longer gave tests characteristic of a thioaldehyde group.

β-Ethoxytrithionaphthaldehyde.—The trimer was formed in varying quantities along with other compounds when hydrogen sulfide was passed into solutions of the aldehyde. The speed of the reaction and the quantity of the trimer depended upon the acid concentration of the solution. A quantitative yield was obtained as follows: 12 g. of β-ethoxynaphthaldehyde was dissolved in a mixture of 125 cc. each of ethyl acetate and benzene. Dry hydrogen chloride was passed into this solution until it was completely saturated. The color of the solution changed to a dark green. Dry hydrogen sulfide was then bubbled in at 0° while the passage of hydrogen chloride was continued. A deep red color appeared but immediately faded with the appearance of a white, microcrystalline precipitate. The reaction was complete in thirty minutes, the solid filtered and washed with hot benzene. A snow-white product resulted which melted at 283°; provided the temperature was held at about 265° for a few minutes, the compound changed to a red liquid. A molecular weight determination by the melting point depression of naphthalene showed the compound to be the trimer. Tests with Grote's reagent and 2,4-dinitrophenylhydrazine showed the absence of a free thioaldehyde group. *Anal.* Calcd.: S, 14.83. Found: S, 14.57.

Pyrolysis of β-Ethoxytrithionaphthaldehyde.—Seven grams of the trimer and 4 drops of sulfuric acid were heated to about 300° at the pressure of 5 mm. in the apparatus described in a previous paper.[1] Mainly decomposition accompanied by slight depolymerization resulted. *sym*-Di-β-ethoxynaphthylethylene and sulfur were the products of the decomposition while β-ethoxythionaphthaldehyde resulted from the depolymerization. A small quantity of the oxo-aldehyde also was formed by oxidation. The last three compounds were in the distillate with a small portion of the ethylene derivative, but most of the ethylene compound remained in the residue. Purification of the residue was accomplished by recrystallization from hot benzene. *sym*-Di-β-ethoxynaphthylethylene was obtained as white needles, m. p. 213°, in a yield of about 70%. The distillate was purified by extracting with 20 cc. of hot absolute alcohol. The thioaldehyde went into solution and was obtained as a red oil upon evaporation of the alcohol. The alcohol insoluble portion of the distillate was recrystallized from benzene. Sulfur and small amounts of the ethylene derivative were obtained. Solutions of *sym*-di-β-ethoxynaphthylethylene fluoresce a bluish-green in visible light, while in ultraviolet light, the fluorescence is a brilliant white.

Anal. Calcd.: C, 84.74; H, 6.57. Found: C, 84.73; H, 6.68.

Polymerized Anthracene Thioaldehydes.—Hydrogen sulfide was passed into an alcoholic solution of anthracene aldehyde-9 and a yellow precipitate of m. p. 178° resulted. The same compound was obtained upon passing in small quantities of dry hydrogen chloride with the hydrogen sulfide, but the reaction was very much faster. *Anal.* Calcd. for monomer or cyclic polymer: S, 14.44. Found: S, 12.65.

A different substance was obtained by changing the conditions as follows: 15 g. of anthracene-aldehyde-9 was dissolved in a mixture of 100 cc. of ethyl acetate and 150 cc. of benzene. The solution was saturated with dry hydrogen chloride. The color changed to a deep red. Upon passing in dry hydrogen sulfide at 0°, a yellowish-green precipitate formed in a quantitative yield. The precipitate was filtered off, washed with benzene, then boiled with 300 cc. of benzene, cooled and refiltered; m. p. 266°; sulfur 12.42%.

Still a different compound was obtained by passing in hydrogen sulfide as above except that the temperature was 23° instead of 0°. A bluish-green polymer resulted which melted around 263°.

In the presence of 0.5% alcoholic potassium hydroxide, hydrogen sulfide reacted with the aldehyde to give a polymer which melted at 205°. When glacial acetic acid was used as the solvent, a polymer was obtained which melted around 203°. Extraction with hot benzene left a yellow residue which melted at 223°. Sulfur: 14.74%. Molecular weight determinations of the polymers were unsuccessful due to their insolubility in the usual solvents.

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(4) G. Kalischer, H. Scheyer and K. Keller, U. S. Patent 1,807,693, June 2, 1931.

Analyses for sulfur were either too low or too high for cyclic polymers. Also, a cyclic polymer would not possess a variable melting point since it would represent one molecular species. These facts indicate rather clearly that the above polymers are linear. The length of the chain and consequently the physical properties were determined by the conditions under which they were formed. If the terminal valence were satisfied by non-sulfur groups, the sulfur content was found to run low, and *vice versa*.

Vacuum distillations of the polymers in the anthracene series led to results entirely different from those obtained in the naphthalene and benzene series. The polymers, m. p. 266 and 263°, upon being heated above their melting points, gave tars from which nothing definite was isolated except 9-methylanthracene. Much hydrogen sulfide was evolved.

Summary

1. The 2,4-dinitrophenylhydrazones of anthracene-aldehyde-9 and β-ethoxynaphthaldehyde were characterized.

2. A monomeric thioaldehyde was isolated and its tendency to polymerize was studied.

3. An excellent synthesis for naphthyl substituted ethylenes was obtained.

4. Several new polymerized thioaldehydes were prepared.

5. The effect of group size upon ring closure was discussed.

CHAPEL HILL, N. C. RECEIVED JUNE 23, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Structure of Gossypol. I

BY K. N. CAMPBELL, R. C. MORRIS[1] AND ROGER ADAMS

Gossypol,[2] the yellow pigment present in cottonseed, was first isolated by Marchlewski.[3] Although it has been investigated in several laboratories,[4] no structural formula has as yet been suggested for it.

The principal difficulty thus far encountered in the study of gossypol has been due, primarily, to the lack of methods of preparation of more than a very limited number of pure crystalline derivatives or degradation products suitable for structural deductions. Gossypol is highly reactive chemically but is sensitive to oxidation, particularly in alkaline solution, and exhibits an especial tendency under the usual experimental conditions to yield amorphous or ill-defined crystalline compounds or mixtures extraordinarily resistant to purification.

The preliminary results in this investigation were similar and led to the conclusion that only by limiting the study to the preparation of those derivatives of definite, unquestioned purity, could important contributions to the knowledge of the chemistry of gossypol be accomplished. The extraction of gossypol, its purification, the explanation of its various melting points and its color reactions are described in this preliminary paper.

Many researches have been reported on the methods of isolation. The procedure found most satisfactory is that described by Carruth,[4d] who extracted the oil from the ground seed with petroleum ether and then extracted the gossypol with ether. The gossypol was isolated as gossypol-acetic acid.

A more rapid method of extraction described by Clark[5] also was investigated, but due to the large amount of oil present the separation of gossypol-acetic acid was found to be extremely slow. The method of Carruth was adopted in preference.

The gossypol-acetic acid was converted into gossypol by dissolving in ether, adding water and evaporating the ether from the mixture. A brownish product is thus obtained which is difficult to get perfectly pure by crystallization and which, even after purificaton, gives a reddish solution when dissolved in ether. The recorded observations that gossypol is oxidized readily and is not reduced by sulfur dioxide led us to a slight modification of the procedure which proved

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(1) A portion of a thesis submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

(2) The authors are indebted to the Buckeye Cotton Oil Company, subsidiary of The Proctor and Gamble Company, for a gift of the cottonseed meats from which the gossypol was extracted.

(3) Marchlewski, *J. prakt. Chem.*, **60**, 84 (1899).

(4) (a) Carruth and Winters, *J. Biol. Chem.*, **32**, 245 (1917); Schwartz and Alsberg, *J. Agr. Research*, **25**, 285 (1923); (b) Carruth and Winters, *ibid.*, **12**, 83 (1918); (c) Gallup, *J. Biol. Chem.*, **77**, 437 (1928); (d) Carruth, THIS JOURNAL, **40**, 647 (1918); (e) Clark, *J. Biol. Chem.*, **75**, 725 (1927); (f) *ibid.*, **76**, 229 (1928); (g) *ibid.*, **77**, 81 (1928); (h) *ibid.*, **78**, 159 (1928); (i) THIS JOURNAL, **51**, 1475, 1479 (1929); *Oil & Fat Industries*, **6**, July (1929); (j) Karrer and Tobler, *Helv. Chim. Acta*, **15**, 1204 (1932); (k) Schmid and Margulies, *Monatsh.*, **65**, 391 (1934); (l) Grünbaumówna and Marchlewski, *Biochem. Z.*, **286**, 295 (1936); (m) Podolskaja, *ibid.*, **284**, 401 (1936); *Fettchemische Umschau.*, **42**, 96 (1935).

(5) Clark, *Oil & Fat Industries*, **6**, 15 (1929)