densing hydantoin with benzaldehyde. Ruhemann and Stapleton's[1] hydantoin melting at 220° is the chief product of the reaction as generally observed in our previous experiments.

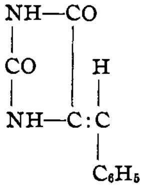
The isomeric modification (*trans*-benzalhydantoin) was identified in the alcoholic filtrates left after purification of the hydantoin melting at 220° (*cis*-benzalhydantoin). It deposited after concentration of these liquors, and was purified by a fractional crystallization from 95% alcohol. It separated from this solvent in burrs or aggregates of distorted prisms which melted at 246° to a clear oil. This modification is less soluble in alcohol than the isomer melting at 220°.

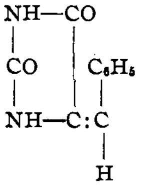
Calc. for $C_{10}H_8O_2N_2$, N = 14.89; found, N = 14.78.

The yield of this hydantoin melting at 246° is extremely small, being less than 1% of the theoretical. An attempt to prepare this modification by heating the isomer melting at 220° was unsuccessful. The latter was recovered unaltered after heating to the melting point of the higher modification (246°). In the case investigated by Johnson and Hadley[1] the higher melting modification of benzaldiphenylhydantoin (*trans*-form) was the chief product of the reaction. It is, therefore, a very interesting fact that benzaldehyde condenses with hydantoin in an anomalous manner, forming chiefly the lower melting modification of the hydantoin (*cis*-form melting at 220°).

Summary.

Benzalhydantoin (II) occurs in two modifications melting at 220° and 246°, respectively:





NEW HAVEN, CONN.

THE ACTION OF CHLORAL, BROMAL AND BENZALDEHYDE ON THE POLYCYCLIC HYDROCARBONS IN THE PRESENCE OF ALUMINIUM CHLORIDE.

[PART II.]

BY G. B. FRANKFORTER AND W. KRITCHEVSKY.

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As has already been shown by us[2] when chloral is brought in contact with benzene or one of its derivatives in the presence of anhydrous aluminium chloride at the ordinary temperature, a violent reaction takes place,

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[1] *Loc. cit.*

[2] *Bull.* 2, "Chemical Studies," University of Minnesota, also abstract, THIS JOURNAL, 26, 1511.

resulting in complete decomposition of both the chloral and the hydrocarbon; but when these substances are brought together at a low temperature, zero or below, an entirely different change takes place, resulting in most cases in a condensation reaction resembling very closely the so-called Baeyer reaction in which concentrated sulfuric acid is used as a condensation reagent.

Thus, when benzene or a derivative is treated at 0° with chloral in the presence of aluminium chloride, the following reaction takes place:

$$2C_6H_6 + OCH—CCl_3 + Al_3Cl_3 = (C_6H_5)_2CH—CCl_3 + H_2O + AlCl_3$$

or

$$2C_6H_5OH + OCH—CCl_3 + AlCl_3 = (C_6H_4OH)_2CH—CCl_3 + H_2O + AlCl_3$$

or

$$2C_6H_5OCH_3 + OCH—CCl_3 + AlCl_3 = (C_6H_4OCH_3)_2CH—CCl_3 + H_2O + AlCl_3$$

Condensation of Naphthalene with Chloral and Bromal by Means of Aluminium Chloride.—In order to determine whether or not the above condensation reaction could be extended to the more complex aromatic derivatives, experiments were begun on the polycyclic compounds. It was found, as will be shown in the following pages, that aluminium chloride acts in the same manner that it did with the aromatic compounds, forming analogous condensation products. The naphthalene reaction was unusually energetic; so much so, in fact, that great care was necessary in order to prevent total decomposition. In case the temperature was allowed to rise, decomposition began immediately; but if carefully controlled, at zero or below, the condensation reaction was almost quantitative.

α-Dinaphthyldichloroethylene, $(C_{10}H_7)_2=C=CCl_2$.—One molecule of naphthalene and one of chloral were brought together and treated with one molecule of aluminium chloride for several hours, care being taken to keep the temperature at zero or below. After the reaction was completed, the mass was treated with water and finally distilled with steam. The black residue left was removed, extracted with ether and finally distilled *in vacuo*. Excess of naphthalene first sublimed in the condenser at 100° and 60 mm. pressure. The temperature then rapidly rose to 300° at 55 mm. pressure. At 160°, decomposition began with liberation of hydrochloric acid. Finally a thick red oil distilled over at about 300° which later crystallized on the cool walls of the condenser. The residue in the flask completely decomposed at 340°.

The red crystalline mass was removed from the condenser and examined. Treated with hot alcohol, the red color immediately disappeared and a part of the substance dissolved. The part insoluble in alcohol was found to be soluble in benzene. The alcohol-soluble part was crystallized several times from alcohol, when it appeared as transparent needles, m. p. 147–

148°. The molten crystals again took on the characteristic red color already observed in preparation. An examination indicated that the compound was doubtless α-dinaphthyldichloroethylene, the same compound which Grabosky prepared by an entirely different method. As α-dinaphthyltrichloroethane has a melting point of 150°, within but two degrees of the dichloro derivative, analyses were made with the following results:

Calc., C = 75.86, H = 4.02, Cl = 20.12; found, C = 75.80, H = 4.10, Cl = 20.02

The above analyses leave no doubt as to the compound being the ethylene derivative.

β-Dinaphthyldichloroethylene, $(C_{10}H_7) = C = CCl_2$.—The part in the above experiment which was found to be insoluble in alcohol was dissolved in benzene and allowed to evaporate when the substance crystallized out as white glistening crystals. The last traces of benzene and also traces of the α-compound were removed by washing with alcohol. The substance thus purified had a melting point of 219°. This substance also corresponds to the β-dinaphthyldichloroethylene which Grabosky prepared by an entirely different method.

β-Dinaphthyldibromoethylene, $(C_{10}H_7)_2 = C = CBr_2$.—As has already been stated, when aluminium bromide is added to bromal in the presence of a hydrocarbon, no reaction takes place; but when aluminium chloride is substituted for the bromide, a vigorous reaction takes place, requiring a freezing temperature in order to prevent complete decomposition. Two molecules of naphthalene were treated with one and a half of bromal and one molecule of aluminium chloride added, care being taken to keep the temperature at 0°, as the reaction became violent liberating hydrochloric acid gas if the temperature was allowed to rise to 10°. After keeping the temperature at 0° for three days the reaction seemed to be complete. The whole mass was poured into water in order to remove the aluminium chloride and the excess of bromal. The residue was then subjected to steam distillation. The dark residue left after steam distillation was dissolved in ether and then washed with a little dilute caustic soda solution. The ether solution was then removed, the ether evaporated and the residue distilled *in vacuo*. The first part distilled over between 60° and 120° at 10 mm. pressure as a perfectly colorless liquid. It contained both bromal and naphthalene. Between 120° and 250° a small quantity of yellow oil passed over. It had a distinct phenol odor. Between 250° and 320° decomposition began with the liberation of hydrochloric acid, while a yellow liquid distilled over and solidified in the neck of the condenser. The residue left in the flask was completely decomposed at 320°.

The crystalline substance was removed from the condenser and treated with cold alcohol, in which it was found to be insoluble. It is slightly soluble in hot alcohol. The insoluble part from the hot alcohol was recrystallized several times from benzene. The purified substance had a melting point of 223–225°.

Analyses gave the following:

Calc. for $(C_{10}H_7)_2=C=CBr_2$: C = 60.27, H = 3.20, Br = 36.53; found, C = 60.20, H = 3.31, Br = 36.83 and 36.66

The substance which dissolved in alcohol was found to be a gummy mass on evaporating off the alcohol.

The Action of Chloral on Anthracene in the Presence of Aluminium Chloride.—The fact that chlor condensation products were obtained from naphthalene and its derivatives by treating with aluminium chloride led to preliminary experiments along the same line with anthracene.

Dianthracenedichloroethylene, $(C_{14}H_9)_2=C=CCl_2$.—Following out the method already described, one molecule of anthracene was suspended in ten volumes of petroleum ether, cooled to 0° and treated with one and a quarter molecules of chloral and, under vigorous stirring, one molecule of aluminium chloride was added. The temperature was not allowed to rise above 10° during the reaction. After the chloride had been added, the stirring was continued for several hours and the temperature allowed to gradually rise to room temperature. During the reaction large volumes of hydrochloric acid were liberated. After standing a day at room temperature the reaction seemed to be complete. The petroleum ether was distilled off and the residue treated with water in order to dissolve the chloride and the unchanged chloral. The black residue which remained was purified by steam distillation and treated with alcohol and ether in order to remove last traces of anthracene. The substance remaining was dissolved in benzene and precipitated out by means of alcohol. The precipitate thus obtained was a brownish yellow powder. It was found to be insoluble in acids and bases, slightly soluble in alcohol, ether and carbon disulfide but very soluble in chloroform, carbon tetrachloride and benzene. It refused to crystallize from any of the solvents. It did not have a sharp melting point but turned black and began to decompose at 340°. It was purified several times by dissolving in carbon tetrachloride and precipitating with alcohol and also by dissolving in benzene and precipitating with alcohol. From 40 g. of the impure substance, 25 g. were obtained in pure form by reprecipitation.

Calc. for $(C_{14}H_9)_2=C=CCl_2$, Cl = 15.84; found, Cl = 16.15, 16.18 and 16.45.

9,10-Anthracenedichloroethylene, $C_{14}H_8=C=CCl_2$.—It was found that when anthracene was treated with chloral and aluminium chloride in the presence of benzene, the reaction appeared to be different from the one already mentioned, in which petroleum ether was used as a solvent. Accordingly, one molecule of anthracene and five molecules of chloral were dissolved in ten times their volume of benzene and treated with one molecule of aluminium chloride at 0°. The reaction which took place resembled, in some respects, the one in which petroleum ether was used as the solvent. The yellow powder obtained was found to be insoluble in the inorganic solvents, namely, the acids and bases; slightly soluble in alcohol and ether but very soluble in benzene, chloroform and carbon tetrachloride. It refused to crystallize and did not have a sharp melting point. It decomposed at a very high temperature. Analyses of the purified substance gave numbers which correspond to the formula given above.

Calc. for $C_{14}H_8=C=CCl_2$, C = 70.84, H = 2.95, Cl = 26.12; found, C = 70.74, H = 3.19, Cl = 26.37.

From the analysis given above, it is evident that condensation took place with one molecule of anthracene instead of two as observed in the case of benzene, naphthalene and their derivatives.

In order to determine the position in which the chloral molecule entered the anthracene molecule, the substance was suspended in glacial acetic acid and oxidized with chromium trioxide, using the proportions of the substance acetic acid and chromium trioxide ordinarily given for the oxidation of anthracene to anthraquinone. The powder remained unchanged and no anthraquinone derivatives were formed. It is evident therefore, that the chloral had entered the gamma positions, thus preventing the formation of anthraquinone derivative. Duplicate oxidation experiments were made with pure anthracene, when anthraquinone was readily obtained.

From the above experiments it was evident that the solvent had something to do with the way in which the reaction goes. In order to test out more fully the solvent influence on the reaction, the above experiments were repeated using carbon disulfide as the solvent, when a different compound was obtained.

9,10-Anthracenetrichloroethane, $C_{14}H_8=CH—CCl_3$.—One molecule of anthracene was suspended in ten times its volume of carbon disulfide and treated with one and a half molecules of chloral and one of aluminium chloride. The temperaure was kept at 0°. A small amount of hydrochloric acid was liberated. At the end of five or six hours the reaction seemed to be complete. The substance was partially purified by steam distillation and by washing with alcohol. The residue was then treated with ether, in which it was found to be partially soluble. The soluble part was examined and found to be composed of two or more substances which could not be separated. The insoluble part was dissolved in benzene and precipitated by means of alcohol. Thus obtained, the substance appeared as a brown amorphous powder without a distinct melting point. Analyses of the substance indicated that it was not quite pure. The experiment was, therefore, repeated, modifying the process by removing all of the water-soluble substances before treating with alcohol and ether. By dissolving in benzene and precipitating with alcohol several times it was obtained in pure form. Thus obtained, it was a yellowish brown powder insoluble in all the common solvents except benzene, chloroform, carbon tetrachloride and acetone. It is unchanged by boiling alcoholic potash, concentrated nitric acid and bromine.

Analyses gave the following:

Calc. for $C_{14}H_8{=}CH{-}CCl_3$, C = 62.55, H = 2.93, Cl = 34.53; found, C = 63.05, H = 2.76, Cl = 32.50

Complete combustion of the substance was very difficult, owing to the fact that some of the carbon was deposited on the porcelain boat as graphite. This unusual stability may be due to the fact that the chloral radical is joined to the anthracene in the meso position, as was also indicated by the oxidation experiments.

The Action of Bromal on Anthracene in the Presence of Aluminium Chloride and Carbon Disulfide.—Bromal readily reacts with anthracene in the presence of aluminium chloride, especially when carbon disulfide is used as a solvent. As has already been stated, no reaction takes place if aluminium bromide is used instead of the chloride. Furthermore, the temperature must be kept near 0° in order to obtain satisfactory results.

9,10-Anthracenetribromoethane, $C_{14}H_8{=}CH{-}CBr_3$.—One molecule of anthracene and two of bromal were dissolved in ten volumes of carbon disulfide and one molecule of aluminium chloride added piece-meal. A very small amount of hydrochloric acid was liberated during the reaction. After the reaction was completed, the whole mass was washed with water until all of the water-soluble substances had been removed. The disulfide solution was separated from the water, treated with alcohol and shaken, when the substance was precipitated as a dark brown powder. It was filtered off, washed with alcohol, dissolved in benzene and reprecipitated with alcohol. By redissolving in benzene and reprecipitating several times, the substance changed to a chocolate-brown powder which did not melt at 360°. It proved to be insoluble in the acids and bases and in alcohol and ether. It is readily soluble, however, in chloroform, carbon tetrachloride and benzene. It is not changed by the ordinary oxidizing reagents; neither is it changed by bromine or alcoholic potash.

Analysis of the purified substance gave the following:

Calc. for $C_{14}H_8{=}CH{-}CBr_3$, C = 43.54, H = 2.04, Br = 54.43; found, C = 42.14, H = 2.30, Br = 52.82

Like the anthracene derivatives already mentioned, this substance is characterized by its unusual stability. This characteristic doubtless throws some light on the structure of the molecule, for it at least eliminates the aldol reaction which was observed in connection with the benzene reaction. Furthermore, the fact that no anthraquinone could be obtained by oxidation leads to the belief that chloral is joined to carbon atoms 9 and 10 in the anthracene molecule.

The Action of Chloral on Phenanthrene in the Presence of Aluminium Chloride and Carbon Disulfide.—Chloral reacts readily with phenanthrene in the presence of aluminium chloride. Best results were obtained, however, when carbon disulfide was used as a solvent.

9,10-Phenanthrenetrichloroethane, $C_{14}H_8 = CH - CCl_3$.—One molecule of phenanthrene was dissolved in two molecules of chloral, ten volumes of carbon disulfide and one molecule of aluminium chloride added. The reaction was violent and a large amount of hydrochloric acid liberated even though the temperature was kept at 0°. After the reaction was completed and the whole mass purified by means of water, alcohol and ether, it was finally obtained in pure form by dissolving in benzene and reprecipitating several times by means of alcohol. The substance thus obtained was a yellow powder without a definite melting point, but decomposing at a high temperature.

Calc. for $C_{14}H_8=CH-CCl_3$, C = 62.55, H = 2.93, Cl = 34.53; **found,** C = 62.59, H = 2.96, Cl = 34.76.

It was found to be insoluble in all of the common solvents except chloroform, carbon tetrachloride and benzene. It remains unchanged by treating with concentrated nitric acid and the common oxidizing and reducing reagents. It is evident again that the chloral has attached itself to the phenanthrene molecule in the meso position.

The Action of Bromal on Phenanthrene in the Presence of Aluminium Chloride and Carbon Disulfide.—Bromal does not combine with phenanthrene in the presence of aluminium bromide; however, when the chloride is substituted for the bromide, a vigorous reaction takes place even though the temperature is kept at 0°.

9,10-Phenanthrenetribromoethane, $C_{14}H_8 = CH - CBr_3$.—One molecule of phenanthrene was dissolved in two of bromal, ten volumes of carbon disulfide and one molecule of aluminium chloride added. A vigorous reaction began immediately and a large amount of hydrochloric acid was liberated. After the reaction was complete, the compound formed was purified with water and alcohol as previously stated and finally reprecipitated several times from benzene by the addition of alcohol. The compound thus obtained was a yellow powder like the one previously mentioned; neither could it be obtained from any of the solvents in crystalline form. Like the previous compound mentioned it is soluble only in chloroform, carbon tetrachloride and benzene. It does not change when heated at 300°.

Analyses of the purified substance gave the following:

Calc. for $C_{14}H_8=CH-CBr_3$, C = 43.54, H = 2.04, Br = 54.43; found, C = 43.89, H = 2.45, Br = 54.05.

Like its analogous compounds, it remains unchanged in the presence of the common oxidizing and reducing reagents.

The Action of Benzaldehyde on Phenanthrene in the Presence of Aluminium Chloride and Carbon Disulfide.—One molecule of phenanthrene was dissolved in one and a half of benzaldehyde and five volumes of carbon disulfide. One and a half molecules of aluminium chloride were then cautiously added. After the reaction was completed and the whole mass purified by means of water, alcohol and ether, it was further purified by dissolving in benzene and reprecipitating several times with alcohol. On adding about half of the necessary amount of alcohol to completely precipitate out the substance from the benzene, and filtering, the substance may be separated into two distinct compounds: the one precipitated out by the alcohol as a resin of unknown composition, and the other a brown powder obtained by evaporating off the alcohol and benzene.

Diphenanthrenephenylmethane, $(C_{14}H_9)_2 : CH.C_6H_5$.—The above-mentioned brown powder was redissolved and reprecipitated several times by means of excess of alcohol. Analysis of the substance gave the following:

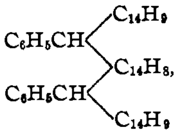
Calc. for $(C_{14}H_9)_2CHC_6H_5$, C = 94 59, H = 5.41; found, C = 94.19, H = 5.28

Molecular weight determination gave 445; calc. 444.

The purified substance was dark yellow powder melting and decomposing at 165°.

Dibenzalmesotriphenanthrene, $(C_6H_5CH)_2(C_{14}H_8)(C_{14}H_9)_2$.—The resinous substance above mentioned was purified several times by dissolving in benzene and reprecipitating by means of alcohol. The substance was finally obtained as a brown powder which melted at 195–197° with decomposition.

Calc. for



$$\begin{matrix} & & C_{14}H_9 \\ C_6H_5CH & & \\ & & C_{14}H_8 \\ C_6H_5CH & & \\ & & C_{14}H_9 \end{matrix}$$

C = 94.65, H = 5.35; found, C = 94.45, H = 5.48.

Molecular weight determination gave 705; calc. 710.

We were unable to obtain any of these complex compounds in crystalline form. However, by reprecipitating several times as has already been indicated, they were from all appearances in pure form. It is unusual that these hydrocarbons, some of them at least, have a distinct color. Some of these colored substances are under investigation at the present time.

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[From the Chemical Laboratory, U. S. Bureau of Mines.]

THE SEPARATION OF THE CONSTITUENTS IN A NATURAL GAS FROM WHICH GASOLINE IS CONDENSED.

By George A. Burrell and Frank M. Seibert.

Received December 7, 1914.

In a previous communication[1] to This Journal the authors showed

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[1] This Journal, 36, 1537 (1914).