alcohol and glacial acetic acid, and insoluble in benzene. It dissolves in alkaline solutions.

Anal. Calcd. for $C_{17}H_{16}O_4N_2$: N, 8.97. Found: 9.00, 9.1

3,5-Di(*p*-hydroxyphenyl)hydantoin, V.—This compound was obtained in an impure condition by heating the corresponding dimethyl ether with hydrobromic acid in glacial acetic acid solution. After completion of the reaction the excess of acetic acid was evaporated and the residue then diluted with water, when an oil separated which solidified on cooling. This showed a strong color reaction with Millon's reagent but was non-crystalline, and gave no sharp melting point; yield, 75%. The compound dissolved easily in alcohol, glacial acetic acid, acetone and dil. alkali solutions, but was insoluble in water and benzene. It was dried for several weeks in a desiccator over sulfuric acid, and the nitrogen determined by the Kjeldahl method.

Anal. Calcd. for $C_{15}H_{12}O_4N_2$: N, 9.87. Found: 8.21, 8.23.

Summary

1. The desirability of synthesizing phenol derivatives of hydantoin and investigating their antiseptic properties is emphasized.
2. Six of the seven theoretically possible mono- and diphenol derivatives (*para* compounds) of hydantoin have been described.
3. All of these compounds have been synthesized by application of methods already described in the chemical literature.
4. No phenol derivatives of hydantoin have hitherto been described.
5. The antiseptic properties of these various compounds will be reported in a later publication.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE JESSE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

THE REACTION BETWEEN BENZAL-ANILINE AND CARBON DISULFIDE AT HIGH TEMPERATURE AND PRESSURE

BY LUCIUS A. BIGELOW

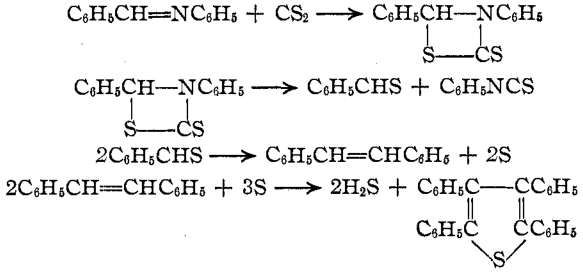
RECEIVED AUGUST 8, 1924 PUBLISHED JANUARY 8, 1925

The purpose of this investigation was to study the reaction between benzal-aniline, $C_6H_5CH{=}NC_6H_5$, and carbon disulfide; first, with the idea of finding a new method for entering the mustard oil series, and second, with the intention of throwing some light upon the action of carbon-disulfide upon the $>CH{=}N-$ linkage. The reaction expected is as follows: $C_6H_5CH{=}NC_6H_5 + SCS \longrightarrow C_6H_5CHS + C_6H_5NCS$. Preliminary experiments showed that the benzal-aniline, while it is extremely soluble in carbon disulfide, crystallizes from it unchanged. Also, mixtures heated in sealed tubes at 100° showed no evidences of interaction. Experiments were then carried out in sealed tubes at higher temperatures, but these proved unsatisfactory on account of the very considerable pressures developed, and the resulting frequent explosion of the tubes. It was certain, however, that a reaction did occur under these conditions, which yielded crystalline products other than the original anil. The odor of phenylmustard oil was quite noticeable and the mixture had become highly colored. Subsequently, the runs were made in a small iron autoclave, equipped with a thermometer well, pressure gage and safety valve.

Commercial carbon disulfide was placed in this apparatus and heated gradually and evenly, the temperature and pressure being read at intervals until the former had reached 255° uncorrected and the latter 66 atmospheres, according to the instruments at my disposal. The curve plotted from these data (See Fig. 1) was smooth and essentially a parabola. Upon repeating the experiment with a concentrated solution of benzal-aniline in carbon disulfide, very different results were observed. At lower temperatures the curve very nearly coincided with that for pure carbon disulfide. At about 170°, however, it began to diverge, and this change had become very considerable at 180°, the rate of pressure increase being much less than for carbon disulfide alone. At higher temperatures, the divergence was very great, indicating that a chemical change had occurred. It was later found that the reaction would just take place at 170° corresponding to a pressure at equilibrium of 19 atmospheres.

When the apparatus was cooled and opened, no pressure was evident nor was there any odor of hydrogen sulfide. The iron was not attacked appreciably. Upon evaporation of the carbon disulfide, both liquid and solid products were found to have been formed, as well as considerable tarry matter. These were separated and identified as far as possible by the usual methods of vacuum fractionation and crystallization. It was found that phenylmustard oil (C_6H_5NCS), stilbene ($C_6H_5CH{=}CHC_6H_5$), thiobenzanilide ($C_6H_5CS{-}NHC_6H_5$), thiocarbanilide ($CS(NHC_6H_5)_2$), thionessal (tetraphenyl-thiophene, ($(C_6H_5)_4C_4S$), and possibly small amounts of other products had been formed.

This indicates that the expected reaction had taken place, but that the original products had undergone several secondary changes due to the high temperature. The results seem to be well explained by the following reactions.



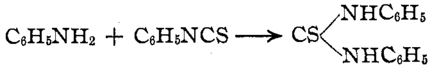
1. $C_6H_5CH{=}NC_6H_5 + CS_2 \longrightarrow \begin{array}{c} C_6H_5CH{-}NC_6H_5 \\ |\qquad| \\ S{-}{-}CS \end{array}$

2. $\begin{array}{c} C_6H_5CH{-}NC_6H_5 \\ |\qquad| \\ S{-}{-}CS \end{array} \longrightarrow C_6H_5CHS + C_6H_5NCS$

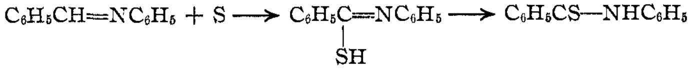
3. $2C_6H_5CHS \longrightarrow C_6H_5CH{=}CHC_6H_5 + 2S$

4. $2C_6H_5CH{=}CHC_6H_5 + 3S \longrightarrow 2H_2S + \begin{array}{c} C_6H_5C{-}{-}CC_6H_5 \\ \|\qquad\| \\ C_6H_5C\qquad CC_6H_5 \\ \diagdown S \diagup \end{array}$

5. $C_6H_5CH{=}NC_6H_5 + H_2S \longrightarrow C_6H_5CHS + C_6H_5NH_2$

6.


$$C_6H_5NH_2 + C_6H_5NCS \longrightarrow CS\begin{cases}NHC_6H_5\\NHC_6H_5\end{cases}$$

7.


$$C_6H_5CH{=}NC_6H_5 + S \longrightarrow \underset{\displaystyle SH}{\underset{|}{C_6H_5C}}{=}NC_6H_5 \longrightarrow C_6H_5CS{-}NHC_6H_5$$

Reaction 3 has long been known, as well as 4 and 6, while Reaction 5 seems probable on account of the easy hydrolysis of the anil. A reaction very similar to the last one above has been described by Wallach[1] in the reaction of sulfur on benzyl-aniline at 220°, hydrogen sulfide being evolved and thiobenzanilide produced.

With a reaction mixture such as is described above, quantitative data, either theoretical or practical, are not very easily obtained. Only the general results may be expressed readily. When the temperature is kept as low as possible the yield of mustard oil is approximately 25% of the amount called for in Reactions 1 and 2, allowing for the benzal-aniline which was recovered unchanged in the process. If the amount of mustard oil converted into thiocarbanilide be also allowed for, this value should be a little higher, nearly 30%.

Mustard oil, stilbene and tarry residue are formed in nearly equal quantities, while about half this amount of thiobenzanilide and thiocarbanilide is produced, along with approximately one-seventh as much thionessal. Over 20% of the anil may be recovered.

Experimental Part

The Benzal-aniline.—This was prepared by mixing equimolecular portions of benzaldehyde and aniline; yield, from alcohol, 77%; m. p., 52°; the value given in the literature[2] is 54°.

Preliminary Experiments.—A concentrated solution of the anil in carbon disulfide (1 g. per cc.) was heated in a bomb tube, ultimately for five hours at 265°. A reaction took place yielding, among other products, a crystalline substance which after purification melted at 149–150°. It had the properties of thiocarbanilide and, in an equal mixture with that substance, melted at 148–150°. The values reported are 151°[3] and 153°.[4]

The Autoclave.—After this, the runs were carried out in a small iron autoclave, of about 500cc. capacity. This was constructed from an iron pipe with an iron plug welded into one end and a heavy flange to the other. The inside chamber was 11.5 cm. deep by 9.4 cm. in diameter and the thickness of wall 6 mm. A graphite-asbestos gasket proved very satisfactory. The lid was secured with heavy bolts and had a thermometer tightly welded into it. It was also provided with openings for the safety valve and the pipe leading to the pressure gage. This pipe contained a deep U, kept filled with carbon disulfide to protect the gage from injury.

Reaction in the Autoclave.—A solution of 100 g. of anil in 100 cc. of carbon disulfide was placed in a beaker in this pressure apparatus, heated evenly with a gas flame to 230°,

---

[1] Wallach, *Ann.*, **259**, 301 (1890).

[2] Michaelis, *Ber.*, **24**, 750 (1891), Footnote 3.

[3] Lellmann, *Ann.*, **221**, 21 (1883). Losanitch, *Ber.*, **19**, 1821 (1886).

[4] Bamberger, *Ber.*, **14**, 2638 (1881), Footnote 3.

and the temperature maintained at this point for two hours. Pressure and temperature were read at intervals. The results are plotted in Fig. 1, which also shows the corresponding relations for carbon disulfide when heated alone.

As the curves indicate, the reaction took place at 180°, so this particular run was greatly overheated. The products were dark and tarry, having no odor of mustard oil and a very noticeable one of hydrogen sulfide.

A succession of similar runs was then made, the solution of anil in carbon disulfide being contained in a small Erlenmeyer flask standing in the autoclave. Some of the mixture left the flask during heating and was allowed to remain in the bottom of the autoclave. This residue did not increase much as subsequent runs were made. It was found that a two-hour period of heating, at a temperature of 170° corresponding to a pressure *at equilibrium* of 19 atmospheres, was just sufficient to cause the reaction to take place.

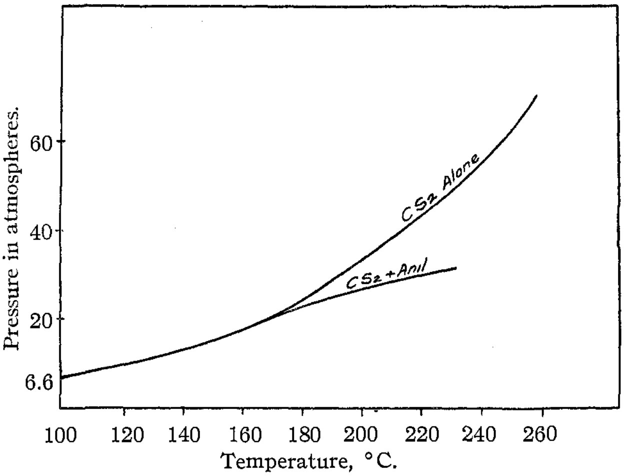


Fig. 1.—Pressure *vs.* temperature for carbon disulfide and carbon disulfide (100 cc.) plus benzal-aniline (100 g.).

Larger Scale Operations.—Exactly 500 g. of benzal-aniline dissolved in 500 cc. of carbon disulfide was heated, in portions, under the conditions mentioned above. The products were united and the carbon disulfide was removed at 70° under a pressure of 45–55 mm. of mercury. On cooling and standing for a long period, the oil became thick with crystals, and after filtration, 170 g. of crude crystals and 331 g. of crude dark oil were obtained.

The Liquid Products; First Vacuum Fractionation.—The mixture was subjected to fractional distillation at 4mm. pressure. Under 100° a clear oil distilled, followed by a mixture of oil and white crystals, which were separated by filtration. The distillation was interrupted at this point. The clear liquid, on fractionation, yielded pure phenyl-mustard oil, boiling at 218–222° (corr.). A 3.0g. sample of this, boiled with 10 cc. of 95% alcohol for five hours, gave 2.4 g. of crude phenyl-thio-urethan which, on crystallization, gave thick, white plates melting at 70–71°. The true melting point is given[5] as 71–72°. The solid substance distilling with the oil was pure white, melted at 152–153°, and was doubtless thiocarbanilide. The residual oil from the vacuum distillation, on cooling, yielded two crops of crystals, which will be considered later.

---

[5] Liebermann, *Ann.*, **207**, 145 (1881).

Second Vacuum Fractionation.—Further distillation of the residual oil at 3mm. pressure yielded a mixture of liquid and solid, boiling from 100° to 169° where decomposition began. A considerable portion of this distilled between 153° and 155°. This time, however, all the distillate solidified completely when entirely cold. This distillate was heated to 100°, at which temperature most of it melted and was filtered hot. The residue (m. p., 149–151°) was thiocarbanilide while the filtrate, which nearly solidified on cooling, was essentially identical with the original anil; m. p., 51–53° (after washing with alcohol).

The Non-volatile Residue.—The tarry residue from the distillation was mixed with alcohol and allowed to stand. Crystals separated, which were largely insoluble even in boiling alcohol. This portion, recrystallized from benzene, gave a nearly white crystalline powder, melting at 183–184°. The substance gave a test for sulfur but none for nitrogen, and on treatment with isatin and sulfuric acid gave a beautiful, dark green color (indophenin reaction). This corresponds exactly with the properties given[6] for thionessal.

The residue of tar after the removal of the thionessal did not yield further identifiable products.

The Solid Products; Fractionation from Benzene.—The mixed crystalline products, together with some obtained from the oil and mentioned above, amounted to 197 g. and were fractionally crystallized from benzene. At first there separated crusts, melting at 148–149°, which were composed of thiocarbanilide. After this, a fraction was obtained which on recrystallization from alcohol gave colorless tables; m. p., 123–124°. This was stilbene, whose melting point is given[7] as 124°. A sample of the substance, treated with a solution of bromine in carbon tetrachloride, gave a white bromo compound, which on crystallization from much alcohol gave when rapidly heated the correct[8] melting point of 237°. Also, 2.0 g. of the stilbene in 20 cc. of absolute alcohol, treated with 2.0 g. of sodium gave almost 2 g. of dibenzyl;[9] m. p., 50–53°. The dibenzyl when crystallized from alcohol gave white leaves melting at 51–53°, which is in accord with the value given in the literature.[7] Further fractionation from benzene did not give pure compounds.

Chemical Separation.—It was observed that a yellow substance accompanied the stilbene, which could be quantitatively separated from the latter by a cold solution of sodium hydroxide. The alkaline solution produced was nearly colorless and on acidification deposited a bright yellow, crystalline powder. This yielded yellow plates from alcohol, which softened at 95–97° and melted at 98°. They consisted of thiobenzanilide, whose melting point is given[10] as varying from 95° to 98°. A sample of the thiobenzanilide on boiling with concd. hydrochloric acid evolved hydrogen sulfide. The resulting liquid deposited benzoic acid (m. p., 121°) when cooled and when made alkaline gave the hypochlorite test for aniline, which is in accordance with the reaction, $C_6H_5CS—NHC_6H_5 + 2H_2O \longrightarrow C_6H_5COOH + C_6H_5NH_2 + H_2S$.

The residues from the various operations contained anil and tarry matter, but no considerable amount of any other compound appeared to be present in them.

Summary

The action of carbon disulfide upon benzal-aniline has been investigated and the following reaction products have been identified: phenyl-

---

[6] Baumann and Klett, *Ber.*, **24**, 3310 (1891).

[7] Michaelis and Lange, *Ber.*, **8**, 1314 (1875).

[8] Zincke, *Ann.*, **198**, 127 (1879).

[9] Klages, *Ber.*, **35**, 2647 (1902).

[10] Bernthsen, *Ann.*, **192**, 32 (1878).

mustard oil, thiocarbanilide, stilbene, thiobenzanilide and thionessal (tetraphenyl-thiophene). Reactions are given and a pressure-temperature curve for carbon disulfide is included.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE CONDENSATION OF CARBON TETRACHLORIDE AND PHENOL: AURIN

BY M. GOMBERG AND H. R. SNOW[1]

RECEIVED AUGUST 8, 1924 PUBLISHED JANUARY 8, 1925

Friedel,[2] in a note, states that aurin is formed when carbon tetrachloride is heated with an excess of phenol and zinc chloride. Heumann[3] patented a process for producing aurin by heating under pressure carbon tetrachloride and phenol with various condensing agents, such as aluminum chloride, stannic chloride or zinc chloride and he stated that without pressure, only a trace of aurin is produced.

We have investigated this reaction and find that Heumann's assertion is incorrect. Aurin is produced in quite as good yield when the condensation is carried on at ordinary pressure as when in an autoclave, namely, about 35%. We find also that many other products are formed simultaneously with aurin. The successful isolation of certain intermediate products, together with the identification of all the final products, has enabled us to give an interpretation as to the probable mechanism of this condensation reaction.

We have also studied the method for making aurin which has been commonly used in the past, namely, from phenol, oxalic acid and sulfuric acid, and we find that here, too, a mixture of various substances results, and that the technical product is far from pure aurin.

The Mechanism of the Condensation Reaction

1. The first stage in the reaction consists in the condensation of two molecules of phenol with one of carbon tetrachloride and diphenoxy-dichloromethane (I) is thus formed.[4] If the requisite amount of water be present in the mixture, this dichloride becomes hydrolyzed to diphenyl carbonate (II), which is stable and can undergo no further change under the conditions of the experiment. In fact, good yields of diphenyl carbonate can be obtained by this method.

---

[1] The material here presented is from the dissertation submitted by H. R. Snow to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1922.

[2] Friedel, *Bull. soc. chim.*, **50,** 2 (1888).

[3] Heumann, *Friedländer*, **3,** 103; Ger. pat., 68,976, **1893.**

[4] Gomberg and Jickling, THIS JOURNAL, **37,** 2580 (1915).