carrying out this work, and to Mr. J. R. Spies for the micro-combustions.

Summary

The physical and chemical characteristics of the fat extracted from the dried mycelium of *Penicillium javanicum* van Beijma have been determined. The fat is composed of palmitic, stearic, tetracosanic, oleic and α- and β-linoleic acids, in addition to glycerol and a small quantity of unsaponifiable matter.

Normal tetracosanic acid has for the first time been identified as a constituent of mold fat.

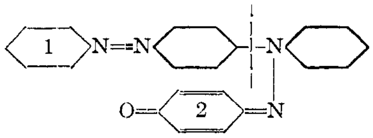
WASHINGTON, D. C. RECEIVED JANUARY 10, 1934

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Studies in the Di-aryl Acyl Hydrazine Series. III. The Oxidation of Acetylhydrazobenzene

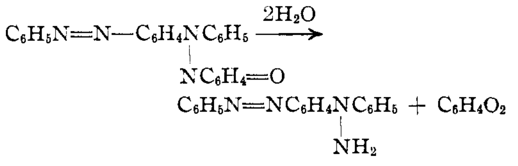
BY FRANK O. RITTER

In a previous communication in this series[1] the formation of a highly colored oxidation product on treatment of acetylhydrazobenzene with dichromate in glacial acetic acid solution was described. Further study of this product has proved it to have the structure shown.

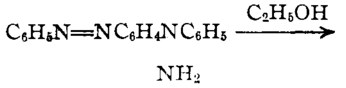
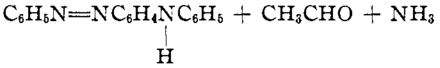


The correctness of this structure is established from the following considerations: (1) the molecular formula is $C_{24}H_{18}N_4O$, (2) the products of reduction are *p*-aminodiphenylamine, aniline and *p*-aminophenol, (3) titration with stannous chloride requires eight equivalents of hydrogen, (4) treatment with alcoholic potassium hydroxide forms *p*-phenylaminoazobenzene.

The latter substance was prepared by Witt[2] by coupling of the benzenediazonium salt with diphenylamine. The amount of this substance theoretically obtainable from our product is 72.2, while that actually isolated is 65 to 70%. Its formation from our product appears to involve hydrolysis and then reduction of the resulting secondary hydrazine as follows



$$C_6H_5N{=}N{-}C_6H_4\underset{\substack{|\\ NC_6H_4{=}O}}{N}C_6H_5 \xrightarrow{2H_2O} C_6H_5N{=}NC_6H_4\underset{\substack{|\\ NH_2}}{N}C_6H_5 + C_6H_4O_2 \quad (1)$$

$$C_6H_5N{=}NC_6H_4\underset{\substack{|\\ NH_2}}{N}C_6H_5 \xrightarrow{C_2H_5OH} C_6H_5N{=}NC_6H_4\underset{\substack{|\\ H}}{N}C_6H_5 + CH_3CHO + NH_3 \quad (2)$$

The latter point was corroborated by investigation of the action of alcoholic potassium hydroxide upon diphenylhydrazine, which was found to yield diphenylamine and ammonia This reaction probably involves oxidation of the alcohol to acetaldehyde. The isolation of benzoquinone in this reaction is not possible because it undergoes further reaction with alkali.

The structure of the oxidation products shows that its formation involves two molecules of the original acetylhydrazobenzene. If the nitrogen linkage of the original acetylhydrazobenzene is unbroken during the transformation to the oxidation product (the simplest assumption), one can readily trace the two original molecules in the structure of the final product. These have been indicated in the above structure by a dotted line.

It is also evident why only acetyl hydrazo compounds with an open para position[1] can yield these oxidation products. The open para position in one molecule is necessary to form a new bond, while the open para position in the second molecule is necessary to develop the quinonoid structure.

Furthermore, since the oxidation product contains a semidine nucleus, one is led to speculate whether the semidine transformation of hydrazo compounds does not also involve an analogous bimolecular compound, which, subsequently, by rejection of two phenyl nuclei (marked (1) and (2)) yields the semidine and the "bases of splitting." If we assume that this transitory union of the two molecules of the hydrazo compound can take place in only one sense because of the differ-

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(1) Ritter, THIS JOURNAL, **53**, 670 (1931).

(2) Witt, *Ber.*, **12**, 261 (1879).

ence in basic character of the nitrogen atoms in the hydrazo linkage[1] we can account for the "maintenance of the aryl combination"[3] which is always observed in the semidine transformation. These assumptions are also in harmony with the fact that the semidines are always formed in yields of about 50%.[4]

Experimental Part

***p*-Benzene-azoquinone Diphenylhydrazone.**—26.5 grams of acetylhydrazobenzene is added to 250 cc. of glacial acetic acid, and 23.1 g. of $Na_2Cr_2O_7 \cdot 2H_2O$ added during the ten minutes with frequent shaking. The mixture heats spontaneously to about 50°, and assumes a deep violet color. It is allowed to stand for two hours, with occasional shaking, and then slowly diluted with 1.5 liters of water. This brings about a partial precipitation of the oxidation product, which becomes practically complete after an additional ten or twelve hours. A partial purification of this product is effected by solution in 500 cc. of 95% alcohol and reprecipitation by the addition of 600 cc. of water during a two-hour period. After twelve hours, 16 g. of a red finely divided solid may be filtered from the alcohol–water mixture. This material is dried, ground in a mortar, and put in crystalline form by extraction in a Soxhlet extractor with 90–120° ligroin; 11.3 g. of a red crystalline solid is thus obtained after about fifteen hours of extraction. It is finally crystallized twice from 95% alcohol, yielding 8.5 g. of the pure material as dark red needles with bronze luster, m. p. 163° corr. It is soluble in chloroform, acetone, glacial acetic acid and hot alcohol, somewhat less so in cold alcohol and benzene, slightly soluble in ligroin.

Anal. Calcd. for $C_{24}H_{18}N_4O$: C, 76.19; H, 4.76; N, 14.81; mol. wt., 378. Found: C, 76.51; H, 4.51; N, 14.52; mol. wt. (cryoscopic in benzene), 413.

Reduction of the Hydrazone with Alcoholic Potassium Hydroxide.—One gram of the pure hydrazone is boiled for ten minutes with a solution of 0.2 g. of potassium hydroxide in 10 cc. of 95% alcohol. The evolution of ammonia may be detected by its odor and action on moist litmus paper. After cooling of the solution 15 cc. of water is added and the mixture allowed to stand overnight. Crystals of *p*-phenylaminoazobenzene separate, which on recrystallization from 40% alcohol melt at 86°; yield, 65%. A mixed melting point with an authentic sample shows no change. The nitroso derivative prepared according to Witt's[2] procedure melts at 120°.

Reduction with Zinc and Glacial Acetic Acid.—1.7 grams of the hydrazone is dissolved in 25 cc. of acetic anhydride and 6 g. of zinc dust added. Glacial acetic acid is then added dropwise, with constant shaking, until the red color of the solution is discharged (about 2 cc. is necessary). The mixture is then heated for fifteen minutes at 60–70° in warm water to ensure completeness of reduction and acetylation of the reduction products, and the solution then filtered from the excess of zinc dust. The excess acetic anhydride is hydrolyzed by adding 100 cc. of water, and the solution evaporated to dryness on the steam-bath. A solid residue remains, which is dissolved in a small quantity of 95% alcohol. On spontaneous evaporation of the alcohol crystals of acetyl-*p*-aminodiphenylamine are deposited. These are separated, washed with a benzene–alcohol mixture (1:1), and dried; m. p. 156° corr.; mixed melting point with authentic sample of acetyl-*p*-aminodiphenylamine remains unchanged. After the mother liquor deposits no more acetyl-*p*-aminodiphenylamine on spontaneous evaporation, the mother liquor is evaporated to dryness, leaving a solid residue. The residue on extraction with hot water dissolves, with the exception of a small amount of a dark colored oil, from which the aqueous extract is decanted. The latter, containing acetanilide and acetyl-*p*-aminophenol, is evaporated to dryness on the steam-bath, and the acetyl derivatives separated by extraction with boiling benzene, in which acetyl-*p*-aminophenol is practically insoluble. Cooling of the benzene extract causes the separation of crystals of quite pure acetanilide, m. p. 114°. The isolation of acetyl-*p*-aminophenol from the residue remaining after benzene extraction is effected by recrystallization from water by spontaneous partial evaporation. After one recrystallization from 50% alcohol it melts at 170°; mixed melting point with authentic sample of acetyl-*p*-aminophenol remains unchanged.

Reduction with Standard Stannous Chloride Solution.—The formation of aniline, *p*-aminophenol and diphenylamine by reduction, as outlined in the preceding paragraph, requires eight equivalents of hydrogen for each mole of hydrazone. On titration with standard stannous chloride solution, 0.0208 g. of the hydrazone was found to be equivalent to 0.0417 g. of stannous chloride (theoretical, 0.0418 g.). The following procedure was used: 20.8 cc. of a solution of the hydrazone in absolute alcohol (1.0000 g./l.) was heated to 60–70° on the water-bath, and stannous chloride solution (0.0189 *N*) added from a buret until the color of the solution was discharged; volume of stannous chloride solution used, 23.15 cc.

Reduction of Unsymmetrical Diphenylhydrazine with Alcoholic Potassium Hydroxide Solution.—Diphenylhydrazine hydrochloride (0.5 g.) is added to a solution of 0.5 g. of potassium hydroxide in 15 cc. of 95% alcohol, and the solution refluxed on the steam-bath for twenty minutes. The evolution of ammonia after a few minutes of boiling is detectable by its odor and also by its effect on a piece of moist litmus paper suspended in the condenser tube. Diphenylamine is isolated from the alcoholic solution by evaporation to dryness and extraction of the dry residue with petroleum ether. Spontaneous partial evaporation of the latter yields colorless crystals of diphenylamine of m. p. 53°.

Summary

1. The oxidation of acetylhydrazobenzene with sodium dichromate in glacial acetic acid solution is shown to produce *p*-benzene-azoquinone diphenylhydrazone.

2. It has been suggested that an analogous bimolecular compound may be an intermediate in the semidine rearrangement of hydrazo compounds.

NEW YORK CITY RECEIVED JANUARY 11, 1934

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(3) Jacobson, *Ann.*, **428**, 108 (1922).

(4) Willberg, *Ber.*, **35**, 955 (1902); Jacobson, *ibid.*, **29**, 2685 (1896); *Ann.*, **427**, 155 (1922); *ibid.*, **287**, 146 (1895).