TABLE II

PICRATES OF 2-METHYL AND 2-ETHYL-4-*p*-HALOGEN-PHENYLTHIAZOLES

Thiazole picrate	Formula	Appearance	M. p., °C. (corr.)	Analyses Kjeldahl–Gunning–Arnold method Calcd.	Found
2-Methyl-4-*p*-chlorophenyl	$C_{16}H_{11}O_7N_4SCl$	Yellow microcrystalline powder	163	12.77	12.80
2-Methyl-4-*p*-bromophenyl	$C_{16}H_{11}O_7N_4SBr$	Yellow glistening triclinic plates	160	11.60	11.70
2-Methyl-4-*p*-iodophenyl	$C_{16}H_{11}O_7N_4SI$	Yellow flat platelets	152	10.57	10.60
2-Ethyl-4-*p*-chlorophenyl	$C_{17}H_{13}O_7N_4SCl$	Yellow very fine acicular needles	143–144	12.38	12.21
2-Ethyl-4-*p*-bromophenyl	$C_{17}H_{13}O_7N_4SBr$	Yellow brilliant slender needles	143	11.27	11.25
2-Ethyl-4-*p*-iodophenyl	$C_{17}H_{13}O_7N_4SI$	Yellow shining microcrystalline plates	148	10.30	10.62

TABLE III

2-METHYL AND 2-ETHYL 4-*p*-HALOGEN-PHENYL THIAZOLE MERCURI-CHLORIDES

Thiazole mercuri-chloride	Formula	Appearance	M. p., °C. (corr.)	Analyses, % Kjeldahl–Gunning–Arnold method Calcd.	Found
2-Methyl-4-*p*-chlorophenyl	$C_{10}H_8NSCl \cdot HgCl_2$	Colorless brilliant microcrystalline prisms	202–203	2.91	2.85
2-Methyl-4-*p*-bromophenyl	$C_{10}H_8NSBr \cdot HgCl_2$	Colorless somewhat opaque needles	221	2.66	2.79
2-Methyl-4-*p*-iodophenyl	$C_{10}H_8NSI \cdot HgCl_2$	Colorless shining needles	235	2.45	2.57
2-Ethyl-4-*p*-chlorophenyl	$C_{11}H_{10}NSCl \cdot HgCl_2$	Colorless somewhat opaque long needles	164	2.83	3.12
2-Ethyl-4-*p*-bromophenyl	$C_{11}H_{10}NSBr \cdot HgCl_2$	Colorless chalky microcrystalline powder	177	2.60	2.57
2-Ethyl-4-*p*-iodophenyl	$C_{11}H_{10}NSI \cdot HgCl_2$	Colorless glistening needles	188	2.34	2.27

cc. of concd. hydrochloric acid, 100 cc. of water and 100 cc. of 95% alcohol. The crystals were washed with this solution, as water tended to precipitate salt from the mother liquor and rendered the crystals opaque. The physical properties are summarized in Table III.

Summary

Thioacetamide and thiopropioamide have been condensed with a series of *p*-halogen phenacyl chlorides to yield the corresponding 2-methyl and 2-ethyl-4-*p*-halogen-phenylthiazoles.

The thiazoles have been characterized by preparation of their picrates and mercuri-chlorides.

2819 MCGILL TERRACE
WASHINGTON, D. C.

RECEIVED JANUARY 8, 1934

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

Preparation of N-Benzoyl-*o*-aminobenzenesulfonamide. Condensation to Heterocyclic Compounds[1]

BY E. WERTHEIM

Previous work in this Laboratory has shown that diphenic sulfinide (diphensaccharin) (I) cannot be formed by the internal condensation of N-*o*-chlorobenzoyl-*o*-chlorobenzenesulfonamide.[2] In the present work the synthesis was attempted by the diazotization of N-benzoyl-*o*-aminobenzenesulfonamide (II), followed by various procedures to obtain the loss of nitrogen and ring closure. Difficulties were experienced in diazotizing due to the great tendency of (II) to lose water to form 3-phenyl-1,2,4-isobenzothiodiazine-1-dioxide (III). This occurred, for instance, when an alcoholic solution of (II) was saturated with hydrogen chloride.

With diazotization methods which avoided this difficulty ring closure produced not a seven- but a six-atom ring. The compound secured was an isomer of diphensaccharin, 3-phenyl-1,4,2-benzothioxazine-1-dioxide (IV). Analyses and molecular weight determinations confirm the proposed structure of (IV) as well as the following facts: the compound is insoluble in alkali and does not acetylate; mild hydrolysis yields a compound whose analysis agrees with that of the predicted

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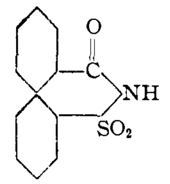
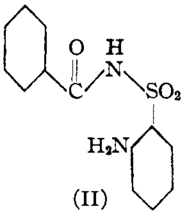
[1] Paper No. 340, Journal Series, University of Arkansas.

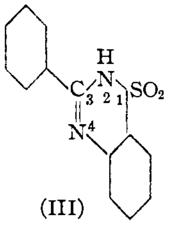
[2] Wertheim, THIS JOURNAL, **53**, 1172 (1931).



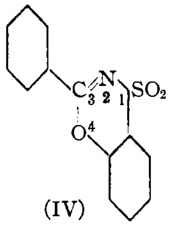
(I)



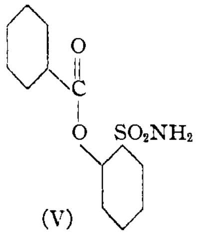
(II)



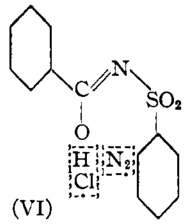
(III)



(IV)



(V)



(VI)

compound (V), while prolonged hydrolysis yields benzoic acid.

As compound (IV) could be produced from the diazonium chloride under strictly anhydrous conditions it seems evident that (II) reacts in the enol form as shown in (VI).

The formation of a five- or a six-atom ring by the method attempted here is normally a simple procedure. It is apparent from the results obtained that a seven-atom ring will form with far more difficulty. Further work on this problem will be carried on in this Laboratory.

Experimental Part

N-Benzoyl-*o*-nitrobenzenesulfonamide, $C_6H_5CONHSO_2C_6H_4NO_2$.—Twenty grams of *o*-nitrobenzenesulfonamide was heated to 170° with 16 g. of benzoyl chloride. After reaction had begun the mixture was heated to 175–180° for thirty minutes. After cooling, the solid mass was crushed and washed by decantation with warm ethanol. It was recrystallized from a mixture of acetone and ethanol as white microscopic squares and diamond-shaped plates of m. p. 197.5–198°.

Anal. Calcd. for $C_{13}H_{10}N_2O_5S$: C, 50.95; H, 3.29; N, 9.15; S, 10.47. Found: C, 51.30, 50.81; H, 2.88, 3.20; N, 9.21, 9.22; S, 10.59.

N-Benzoyl-*o*-aminobenzenesulfonamide, $C_6H_5CONHSO_2C_6H_4NH_2$.—A hot solution of 168 g. of ferrous sulfate in 300 cc. of water was added rapidly to a solution of 20 g. of the above nitro compound in 180 cc. of concd. ammonia water. As the last of the solution was added the precipitate in the flask changed from brown to black. The mixture was maintained nearly at the boiling point for two hours and then filtered. After saturation with hydrogen sulfide filtration was repeated, giving a colorless filtrate. This was cooled and acetic acid was added to secure the maximum precipitation of solid. About 80 cc. was required. The precipitated solid was recrystallized from dilute ethanol as white microscopic hexagonal or diamond-shaped thick plates of m. p. 198–198.5°.

Anal. Calcd. for $C_{13}H_{12}N_2O_3S$: C, 56.52; H, 4.35; N, 10.15; S, 11.59. Found: C, 56.64, 56.66; H, 4.14, 3.96; N, 10.29, 10.29; S, 11.45, 11.39.

Internal Condensation of (II). Production of (III).—A solution of 4 g. of (II) in 300 cc. of ethanol was saturated with hydrogen chloride, then warmed until all the precipitate again dissolved. Fifty cc. of water was added. The solution upon cooling deposited (III) in the form of short white needles of m. p. 302–303°.

Anal. Calcd. for $C_{13}H_{10}N_2O_2S$: C, 60.46; H, 3.88; N, 10.85; S, 12.40; mol. wt., 258. Found: C, 60.46, 60.43; H, 3.94, 3.81; N, 11.01, 10.66; S, 12.15, 12.23; mol. wt., 257.5, 251.5.

Compound (III) was also produced by heating (II) for a few minutes at 210°.

Compound (IV).—Two grams of (II) was dissolved in 15 cc. of water together with 10 cc. of *N* sodium hydroxide solution and 0.5 g. of sodium nitrite. The solution was cooled and added dropwise with mechanical stirring to a cold solution of 10 cc. of concd. hydrochloric acid and 90 cc. of water. Toward the close of this operation a precipitate appeared. Stirring was continued for twenty minutes, when the yellow sandy precipitate was separated and washed with water. The dry compound was light yellow; wt., about 1.7 g. It exploded violently when heated. With β-naphthol in alkali a deep red precipitate was obtained. Analytical results were unsatisfactory as the compound lost nitrogen on standing. That it contained the hydroxyl group seemed fairly certain since the identical substance was formed when sulfuric acid was used in the diazotization; moreover the addition of water to the diazonium chloride also gave the above compound.

Compound (IV) was obtained from the above precipitate by (1) warming it in kerosene (slowly from 75 to 110° until all nitrogen was released); (2) warming in water; (3) allowing it to stand over sulfuric acid (or water) for some weeks. Treatment of diazonium salt solutions with various catalysts also gave (IV) in many cases.

When (II) was diazotized in the absence of water (using a solution of acetic acid and acetyl chloride with hydrogen chloride and amyl nitrite), the diazonium chloride was obtained as a white flocculent precipitate upon the addition of ether. It was exceedingly hygroscopic. With water it changed at once to the yellow crystalline substance obtained in aqueous diazotizations. Heating of the acetic acid solution gave (IV). Compound (IV) crystallized from ethanol in short white needles of m. p. 176–177°.

Anal. Calcd. for $C_{13}H_9NO_3S$: C, 60.23; H, 3.48; N, 5.41; S, 12.35; mol. wt., 259. Found: C, 60.00, 59.90; H, 3.74, 3.0; N, 5.43, 5.46; S, 12.45; 12.40; mol. wt., 256.2, 258.5.

***o*-Benzoxybenzenesulfonamide,** $C_6H_5CO_2C_6H_4SO_2NH_2$ (V).—Compound (IV) dissolved almost completely in sodium hydroxide solution in about forty hours. Upon acidification (V) was obtained as a white precipitate. It was recrystallized from dilute acetic acid; m. p. 178–180°.

Anal. Calcd. for $C_{13}H_{11}NO_4S$: C, 56.31; H, 3.97; N, 5.05; S, 11.55. Found: C, 56.57, 56.41; H, 3.47, 3.11; N, 5.22; S, 11.73, 11.38.

When (IV) was heated for some time in hydrochloric acid solution benzoic acid was obtained. The remaining solution, after removal of sodium chloride, gave a deep purple color with ferric chloride.

Summary

Six-atom heterocyclic compounds formed by several condensation reactions of N-benzoyl-*o*-aminobenzenesulfonamide and its diazotization products are described. A seven-atom ring could not similarly be formed. A new ring system and five new compounds are reported.

FAYETTEVILLE, ARKANSAS RECEIVED JANUARY 9, 1934

[231ST CONTRIBUTION FROM THE COLOR AND FARM WASTE DIVISION, AND OIL, FAT AND WAX LABORATORY, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Chemical Composition of the Fat Produced by Penicillium Javanicum van Beijma[1]

BY GEORGE E. WARD AND GEORGE S. JAMIESON

Introduction

The presence of unusually large quantities of fatty substances in the mycelium of *Penicillium javanicum* van Beijma, as will be reported in a later communication, indicated the desirability of establishing the chemical composition of this material.

Relatively little information is available regarding the composition of fats produced by mold fungi. In 1906 Browne[2] described the chemical characteristics of a fat extracted from a Citromyces which had grown as a scum on the surface of molasses in the hot-room of a sugar factory. The fat, which comprised 27.50% of the air-dried scums, was similar to butterfat in saponification number, iodine number, Reichert–Meissl number, and melting point, and in the melting point and iodine number of the insoluble acids, but differed from fresh butterfat in the acid number and mean molecular weights of soluble and insoluble acids. No absolute identification of the fatty acid constituents was reported. Sullivan,[3] in 1913, found palmitic acid, oleic acid and two unidentified fatty acids in the dried mycelium of *Penicillium glaucum* which was grown on Raulin's solution. In 1927 and 1929 Barber[4] reported the production of fat by a species of Penicillium when it was grown on glycerol, xylose, glucose and sucrose solutions. The fat was composed of palmitic, stearic, oleic and α- and β-linoleic acids, and an x-ray analysis indicated the presence of a fatty acid containing nineteen carbon atoms. The hexabromide test showed the absence of linolenic acid. The fat had chemical characteristics lying within the following ranges, depending on variations in the culture media:

Saponification value	166–201
Iodine value of combined fatty acids	78–101
Melting point of saturated acids, °C.	54–55
Mean molecular weight of saturated acids	264–293
Percentage of saturated acids	16–29

Experimental Part

The fat described in this communication was produced by *Penicillium javanicum* van Beijma when it was cultured on 20% glucose solutions at 30° as will be described in a later paper. The fat was obtained by extracting 6240 g. of the dried mycelium with redistilled petroleum

TABLE I

PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE OIL FROM *Penicillium javanicum* VAN BEIJMA

Solidification point, °C.	6–7
Melting point, °C.	about 15
Specific gravity (25°/25°)	0.9145
Refractive index (25°)	1.4680
Acid value	10.6
Saponification value	191
Iodine value (Hanus)	84.0
Reichert-Meissl value	0.3
Acetyl value	10.7
Unsaponifiable matter,[5] %	2.00
Saturated acids (corrected),[6] %	30.8
Unsaturated acids (corrected),[6] %	60.8
Melting points of mixed saturated acids	52.5°
Mean molecular weight of saturated acids	272

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[1] Presented in part before the Section of Biological Chemistry of the American Chemical Society March 27–30, 1933, Washington, D. C.

[2] C. A. Browne, Jr., THIS JOURNAL, **28**, 465 (1906).

[3] M. X. Sullivan, *Science*, **38**, 678 (1913).

[4] H. H. Barber, *J. Soc. Chem. Ind.*, **46**, 200T (1927); *Biochem. J.*, **23**, 1158 (1929).

[5] Modified Kerr-Sorber method—R. Hertwig, G. S. Jamieson, W. F. Baughman and L. W. Bailey, *J. Assoc. Off. Agr. Chem.*, **8**, 439 (1925).

[6] Lead salt-ether method—"Methods of Analysis," Assoc. Official Agr. Chem., 3d ed., 324 (1930).