

TABLE II
 ACRIDINE THIO DERIVATIVES

No.	Compound	Form	Solvent	M. p., °C.
I	Acridyl-2-benzoylmercaptan ^a	Light yellow lustrous plates	Alcohol (70%)	178-179
II	Acridyl-2-mercaptan ^b	Greenish-yellow prisms	120-130
III	Diacridyl-2,2'-disulfide ^c	Light yellow lustrous plates	Ethyl acetate	245-246
IV	Dihydrochloride of III	Orange-yellow needles	HCl (2%)	255 (dec.)

No.	Solubility	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
I	Org. solv.	C ₂₀ H ₁₈ ONS	76.19	76.16	4.13	4.16
II	Org. solv. and in dil. NaOH	C ₁₈ H ₉ NS	73.93	72.85	4.27	4.13
III	C ₆ H ₆ , CHCl ₃ , difficultly in EtOH	C ₂₆ H ₁₆ N ₂ S ₂	74.29	74.33	3.81	3.95
IV	Hydrolyzes in water	C ₂₆ H ₁₆ N ₂ S ₂ ·2HCl	63.29	63.05	3.65	3.96

^a Yield, 74% of the theoretical. ^b Hydrolysis is effected by six hours of refluxing instead of one hour. This compound could not be obtained pure, for the ethereal solution of carefully dried material, on evaporation in a desiccator (vacuum) over sodium hydroxide gave a product which was altogether insoluble in dilute sodium hydroxide. ^c Yield, the theoretical.

The thioacridines listed in Table II are prepared according to the procedure described by Edinger for the preparation of thioquinoline.⁸

I hereby desire to thank Professor Hata for his interest in the work.

(8) Edinger, *Ber.*, **41**, 937 (1908).

Summary

Sulfuric acid acts upon phenylanthranilic acid to form acridone-2-sulfonic acid together with a small amount of acridone-4-sulfonic acid.

TOKYO, JAPAN

RECEIVED APRIL 15, 1935

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORIES OF THE UNIVERSITY OF FLORIDA]

The Preparation of Certain Acyl and Benzenesulfonyl Derivatives of *o*-Aminophenol

BY LAWRENCE H. AMUNDSEN AND C. B. POLLARD

In the purification of a sample of *o*-benzenesulfonaminophenyl benzenesulfonate¹ a small quantity of a different compound was isolated. From its composition it appeared to be the tribenzenesulfonyl derivative of *o*-aminophenol. This has been confirmed by synthesis. In view of the failure of attempts by Tingle and Williams² to obtain the corresponding tribenzoyl compound, we have reinvestigated the problem and have developed a satisfactory procedure for the purpose.

Experimental

N-Potassium Salt of *o*-Benzenesulfonaminophenyl Benzenesulfonate.—This salt crystallized while a hot solution of 75 g. of the free compound¹ in 500 cc. of 10% potassium hydroxide was allowed to cool. After several recrystallizations from 25 parts of alcohol the yield was 79%; m. p. 220° (not sharp and varies with rate of heating).

Anal. Calcd. for C₁₈H₁₄KNO₆S₂: N, 3.28; S, 15.00; K, 9.15. Found: N, 3.29; S, 14.65; K, 9.54.

It is soluble in hot water, ethyl alcohol, β -hydroxyethyl ether and dioxane; insoluble in ethyl ether, benzene and hexane.

(1) Pollard and Amundsen, *THIS JOURNAL*, **57**, 357 (1935).
 (2) Tingle and Williams, *Am. Chem. J.*, **37**, 51 (1907).

Acyl and benzyl derivatives were prepared by heating with the corresponding chlorides in dioxane. The data relating to these preparations are shown in Table I; the products are, in general, soluble in acetone, benzene, chloroform, dioxane and hot alcohol; insoluble in ether and hexane.

TABLE I

N-ACYL-*o*-BENZENESULFONAMINOPHENYL BENZENESULFONATES

Acyl, etc.	Hours heated	Yield, %	M. p., °C.	Analyses, %			
				Calcd.		Found	
			N	S	N	S	
Acetyl	5	74	115-116	3.25	14.87	3.23	14.83
Benzoyl	4.5	87	125.5-126	2.84	13.00	2.57	12.94
Benzenesulfonyl	1.5	89	164-164.5	2.65	18.17	2.66	17.80
Benzyl	16	52	144.5-145.5	2.92	13.38	2.90	13.23

***o*-Dibenzoylaminophenyl Benzoate.**—A solution of 15 g. of *o*-benzoylaminophenyl benzoate and 10 g. of benzoyl chloride in 30 cc. of nitrobenzene was boiled under reflux for twelve hours. The product crystallized on cooling. After recrystallization from either alcohol, acetone or toluene it melted at 170.5-171.5°. The yield was 43.5%. When amyl ether was employed as solvent the yield was 72.5%.

Anal. Calcd. for C₂₇H₁₉NO₄: N, 3.33. Found: N, 3.31.

In the course of the work three other new derivatives of *o*-aminophenol were prepared. Data relating to them are

supplied in Table II. The solubilities of the two diacyl compounds in organic liquids resemble those of the trisubstituted derivatives.

TABLE II
DERIVATIVES OF *o*-AMINOPHENOL

Product	<i>p</i> -Anisoyl- <i>o</i> -amino- phenol	<i>p</i> -Anisoyl- <i>o</i> -amino- phenylbenzene- sulfonate	<i>o</i> -Benzene- sulfonamino- phenylbenzo- ate
Method	Groenik ³	Schotten- Baumann	Schotten- Baumann
Yield, %	95	84	70.5
M. p., °C.	171.5-172	113.5-114.5	143.5-144.5
N, %	Calcd.	5.76	3.82
	Found	5.56	3.68
S, %	Calcd.	8.73	9.08
	Found	8.51	8.75

This occasion is taken to correct the melting point of *o*-

(3) Groenik, *Bull. soc. chim.*, [2], **25**, 177 (1876).

hydrocinnamylaminophenyl isovalerate, 92-93°, previously reported from this Laboratory.⁴ It has since been found that crystallization of this compound from dilute alcohol, the solvent used at that time, appears never to give a pure product. When crystallized several times from ether, the compound melts at 113.5-114.5°.

Summary

The N-potassium salt of *o*-benzenesulfonamino-phenyl benzenesulfonate has been prepared; on treatment with acyl chlorides and benzyl chloride the corresponding trisubstituted derivatives of *o*-aminophenol are formed. Some other new derivatives of *o*-aminophenol are also described.

(4) Pollard, Sparks and Moore, *THIS JOURNAL*, **54**, 3283 (1932).

GAINESVILLE, FLORIDA

RECEIVED JUNE 13, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Effect of Ammonium Chloride upon the Growth and Production of Acid by *Aspergillus niger*

BY ELLIS I. FULMER, L. M. CHRISTENSEN AND HERMANN SCHOPMEYER

In a previous communication by Schopmeyer and Fulmer¹ it was shown that various molds produce yeast growth stimulus when grown on synthetic media containing either glycerol or sucrose as substrate. In order to study this phenomenon more adequately, systematic investigations were made of the effect of the composition of the medium upon the growth of *Aspergillus niger*. In view of the growing importance of the use of molds in the production of chemicals, a subject which has been reviewed by May and Herrick,² the production of acid was also followed. The general literature on the production of chemicals by molds has been summarized by Buchanan and Fulmer³ and Fulmer and Werkman.⁴

The utilization of *Aspergillus niger* for the production of citric acid was stimulated by the well-known work of Currie.⁵ Pruess, Peterson, Steenbock and Fred⁶ studied the effect of the composition of the medium upon the yield of mycelium

by the above organism. Recently, Doelger and Prescott⁷ have presented data on the production of citric acid by a species of *Aspergillus niger* selected from eight species on the basis of ability to produce the acid.

There is considerable argument in the literature as to the nitrogen requirement of molds. *Aspergillus niger* is omnivorous in this respect. The standard media reported contain nitrate nitrogen; if ammonium salts alone are used, ammonium nitrate is indicated. Studies in these Laboratories have shown ammonium chloride to be an excellent sole source of nitrogen for the growth of yeast (Fulmer, Nelson and Sherwood,⁸ Fulmer, Sherwood and Nelson⁹ and Sherwood and Fulmer.¹⁰) It was found that for each temperature there are two optimal concentrations of the salt. These optimal concentrations, in grams of salt per 100 cc. of medium, are expressed by the relations

$$\begin{aligned} \text{1st optimum} &= 0.096 + 0.00306t^{\circ} & (1) \\ \text{2d optimum} &= 0.595 + 0.0223t^{\circ} & (2) \end{aligned}$$

(1) H. Schopmeyer and E. I. Fulmer, *J. Bact.*, **22**, 23 (1931).

(2) O. E. May and H. T. Herrick, U. S. Dept. Agr. Circ. 216 (1932).

(3) R. E. Buchanan and E. I. Fulmer, "Physiology and Biochemistry and Bacteria," Vol. III, Williams and Wilkins Co., Baltimore, Md.

(4) E. I. Fulmer and C. H. Werkman, "An Index to the Chemical Action of Microorganisms on the Non-Nitrogenous Organic Compounds," C. C. Thomas, Springfield, Ill.

(5) J. N. Currie, *J. Biol. Chem.*, **31**, 15 (1917).

(6) L. M. Pruess, W. H. Peterson, H. Steenbock and F. B. Fred, *ibid.*, **90**, 369 (1931).

(7) W. P. Doelger and S. C. Prescott, *Ind. Eng. Chem.*, **26**, 1142 (1934).

(8) E. I. Fulmer, V. E. Nelson and F. F. Sherwood, *THIS JOURNAL*, **43**, 191 (1921).

(9) E. I. Fulmer, F. F. Sherwood and V. E. Nelson, *Ind. Eng. Chem.*, **16**, 921 (1924).

(10) F. F. Sherwood and E. I. Fulmer, *J. Phys. Chem.*, **30**, 738 (1926).