and then allowed to come to room temperature. The orange-colored powder which separated was collected on a suction filter and washed with alcohol and ether. The product was dried in the air out of direct light. This dye was only slightly soluble in water, but in sodium bicarbonate solution it gave a deep purple solution. Mercury separated from this solution on standing for forty-eight hours.

Anal. Subs., 0.1500: Hg, 0.0217. Calcd. for $C_{36}H_{28}O_{16}N_6S_4Na_2Hg\cdot 5C_2H_5OH$: Hg, 14.24. Found: Hg, 14.4.

Tetrazotization of Acetoxymercuri-benzidine and Coupling with 2-Amino-8-naphthol-6-sulfonic Acid.—The tetrazotization was performed with the same amount of material as described before and the tetrazonium salt was coupled with 4.8 g. of 2-amino-8-naphthol-6-sulfonic acid. The dye separated as a reddish-purple powder which was washed with alcohol and ether and dried in the air out of direct light. It was only slightly soluble in water, but gave a deep purple solution in sodium bicarbonate solution. This solution deposited mercury on standing for forty-eight hours.

Anal. Subs., 0.1500: Hg, 0.0276. Calcd. for $C_{34}H_{26}O_{10}N_6S_2Hg\cdot 3C_2H_5OH$: Hg, 18.5. Found: Hg, 18.4.

Summary

1. Monoacetoxymercuri derivatives have been prepared by treating benzidine and *o*-tolidine in glacial acetic acid with mercuric acetate.
2. These acetoxymercuri derivatives can be tetrazotized and coupled with naphthalene derivatives to give azo dyes which are related in their structure to Trypan Red and Trypan Blue.
3. The mercurated dyes are not stable and readily lose mercury and are hence unsuitable for pharmacological testing.

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

ARYL SULFONE DERIVATIVES OF DIBASIC ACIDS[1]

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It was recently shown that phthalyl chloride reacts readily with sulfonamides to give phthalimide derivatives[2] when the materials are merely heated or are boiled in toluene solution. The following study develops this and other practical methods for the preparation of aryl sulfone derivatives of dibasic acids.

Whereas certain suggested methods such as heating phthalic anhydride with *p*-tolyl sulfonamide or with its sodium salt, or heating *p*-tolyl sulfonyl chloride with phthalimide, failed to yield the desired product, it was found that heating phthalic anhydride with *p*-tolyl sulfonamide in the presence of phosphorus oxychloride readily gave the phthalimide derivative in sub-

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[1] The material presented in this paper is from part of a thesis submitted by Theodore Evans, du Pont Fellow for 1929–1930, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, **1930**.

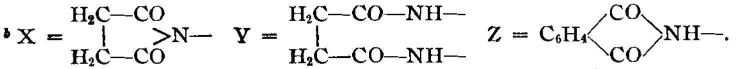
[2] Evans and Dehn, THIS JOURNAL, **51**, 3651 (1929).

TABLE I

RESULTS OF EXPERIMENTS

Acid derivative[a]	Used Sulfonamide, etc.	Method	Formula of compound[b]	M. p., °C.	Crystal form	Soluble in hot solvent	Sulfur, % Calcd.	Sulfur, % Found
SCl	Phenyl	I[c]	$X—SO_2·C_6H_5$	161	Prisms	Toluene	13.40	13.59
SCl	*p*-Bromphenyl	II	$X—SO_2·C_6H_4Br(p)$	181	Prisms	Toluene	10.08	10.16
SCl	*p*-Tolyl	II[d]	$S—SO_2·C_7H_7(p)$	184	Prisms	Alcohol	12.66	12.78
SA	*p*-Tolyl	III	$X—SO_2·C_7H_7(p)$	184	Prisms	Alcohol	12.66	12.74
SCl	*m*-Nitro-*p*-tolyl	II	$X—SO_2·C_7H_6NO_2$[d,f]	212–213	Prisms	Toluene	10.75	10.51
SCl	*o*-Tolyl	I, II	$X—SO_2C_7H_7(O)$	136	Prisms	Toluene	12.66	12.63
SCl	*β*-Naphthyl	I	$X—SO_2·C_{10}H_7$	175–176	Rectangles	Alcohol	11.08	10.97
SA	Phenyl	III	$Y{=}(SO_2C_6H_5)_2$	235–237	Prisms	MEK[g]	16.18	15.69
SA	*p*-Bromphenyl	III	$Y{=}(SO_2C_6H_4Br)_2$	231	Needles	Toluene	11.57	11.43
SA	*m*-Nitro-*p*-tolyl	III	$Y{=}(SO_2C_7H_6NO_2)_2$	236	Needles	Toluene	12.47	12.47
SA	*o*-Tolyl	IV	$Y{=}(SO_2C_7H_7)_2$	231–232	Needles	MEK[g]	15.11	14.96
SCl	*o*-Tolyl	II	$Y{=}(SO_2C_7H_7)_2$	231–232	Needles	Alcohol	15.11	
SA	*β*-Naphthyl	III	$Y{=}(SO_2C_{10}H_7)_2$	248	Prisms	Insoluble	12.92	12.46
PA	Phenyl	III[f]	$Z.SO_2C_6H_5$	205	Needles	Toluene	11.12	11.09
PA	*p*-Bromophenyl	III	$Z.SO_2C_6H_4Br$	246	Needles	Toluene	8.76	
PCl	*p*-Bromophenyl	II	$Z.SO_2C_6H_4Br$	246	Needles	Toluene	8.76	8.65
PA	*p*-Tolyl	III[f]	$Z.SO_2C_7H_7$	237[d]	Prisms	Toluene	10.59	10.42
PA	*m*-Nitro-*p*-tolyl	III[f]	$Z.SO_2C_7H_6NO_2$	247	Needles	Toluene	9.26	
PA	*o*-Tolyl	III[f]	$Z.SO_2C_7H_7$	182[d]	Prisms	Toluene	10.59	10.07
PCl	*β*-Naphthyl	I	$Z.SO_2·C_{10}H_7$	216	Prisms	Toluene	9.51	9.23
PA	*β*-Naphthyl	IV	$Z.SO_2.C_{10}H_7$	216	Prisms	Toluene	9.51	9.44
SCl	Benzamide	II[e]	$X—CO·C_6H_5$	130	Hexagons	EtOH		
Maleic acid	Phenyl	III	$C_4H_2O_2(NHSO_2C_6H_5)_2$	258	Prisms	Insoluble	16.26	15.75

[a] Abbreviations used: SA = succinic anhydride; SCl = succinyl chloride; PCl = phthalyl chloride; PA = phthalic anhydride.



[b] $X = \begin{array}{l} H_2C{—}CO \\ \mid \qquad >N{—} \\ H_2C{—}CO \end{array}$ $Y = \begin{array}{l} H_2C{—}CO{—}NH{—} \\ \mid \\ H_2C{—}CO{—}NH{—} \end{array}$ $Z = C_6H_4\begin{array}{c} CO \\ \\ CO \end{array}NH{—}.$ [c] Gerhardt and Chiozza, *Ann. chim.*, [3] **46**, 158 (1856), heated the materials to 160°; melting point given, 160°. [d] Walkowa, *J. Russ. Phys.-Chem. Soc.*, **2**, 244 (1870); no melting point given. [e] Titherley prepared this compound by the action of benzoyl chloride on succinimide; melting point given, 130°. [f] Evans and Dehn, THIS JOURNAL, **51**, 3651 (1929). [g] Methyl ethyl ketone.

stantially quantitative yield. This method was tried with various aryl sulfonamides and was found to be uniformly effective with phthalic anhydride. The same method applied to succinic and maleic anhydrides yielded compounds of the type $(H_2CCO\text{-}NHSO_2R)_2$, except that when R is *p*-tolyl the succinimide derivative results. However, with succinyl chloride the amides give succinimide derivatives. That the succinyl chloride does react in the normal form is evidenced by its reaction with benzamide to give benzoyl succinimide,[3] with *p*-tolyl sulfonamide to give the same product as the anhydride, and with *o*-tolyl sulfonamide to give in part the succinamide derivative.

It seems probable that with anhydrides and phosphorus oxychloride reactions take place in two steps, the first being the combination of one molecule of anhydride and one molecule of amide, $HOOCCH_2CH_2CONHSO_2R$. This then either forms the imide derivative or eliminates water with a second molecule of the amide to form the di-substituted diamide.

Methods of Preparation

I. The reacting materials were heated without a solvent in an oil-bath to 150–200°. The product was then recrystallized, usually from toluene.

II. The materials were refluxed in toluene for twelve to twenty-four hours. The solution was then concentrated, precipitated by the addition of ether, and the product filtered off and recrystallized.

III. The materials were heated to 100° in phosphorus oxychloride for several hours. Ether was then added, the product filtered off and washed well with ether and hot alcohol, and then recrystallized.

IV. The same as III except that the materials were heated to the boiling point of the phosphorus oxychloride.

Summary

1. Phthalyl and succinyl chlorides react with sulfonamides to give imide derivatives.

2. Phthalic anhydride reacts with sulfonamides in the presence of phosphorus oxychloride to give substituted phthalimides.

3. Succinic anhydride reacts with sulfonamides in the presence of phosphorus oxychloride to give derivatives of succinamide except in the case of *p*-tolyl sulfonamide.

4. Maleic anhydride and benzene sulfonamide in the presence of phosphorus oxychloride give the derivative of maleic amide.

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[3] Although benzoyl succinimide and benzamide melt within one degree of each other, there can be no doubt that our product is benzoyl succinimide, since it is insoluble in ether, whereas benzamide is very soluble, and, further, when cautiously hydrolyzed with sodium carbonate, it yields benzoyl succinamic acid, m. p. 180° [Titherley, *J. Chem. Soc.*, **85**, 1679 (1904)].