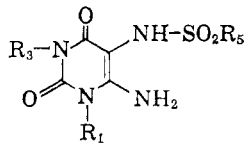
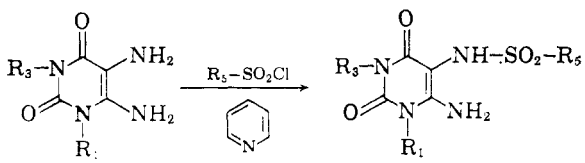
TABLE I

1,3-DISUBSTITUTED 5-SULFONAMIDO-6-AMINOURACILS



No.	R_5	Formula	M.P., °C.	Yield, %	Nitrogen Calcd.	Nitrogen Found	Sulfur Calcd.	Sulfur Found
		A. 1-(2-Methylallyl)-3-methyl-5-sulfonamido-6-aminouracils (R_1 = CH_2=C(CH_3)—CH_2—; R_3 = CH_3—)						
I	C_2H_5—	$C_{11}H_{18}N_4O_4S$	157–161	57.8	18.53	18.59	10.60	10.72
II	C_6H_5—	$C_{15}H_{18}N_4O_4S$	196–197.5	44.4	15.99	15.83	9.15	9.11
III	p-$CH_3C_6H_4$—	$C_{16}H_{20}N_4O_4S$	199–200	52.8	15.38	15.31	8.80	8.79
		B. 1-Allyl-3-ethyl-5-sulfonamido-6-aminouracils (R_1 = CH_2=CH—CH_2—; R_3 = C_2H_5—)						
IV	C_6H_5—	$C_{15}H_{18}N_4O_4S$	188.5–195	93.0	15.99	15.97	9.15	9.15
V	p-$CH_3C_6H_4$—	$C_{16}H_{20}N_4O_4S$	200–202.5	95.0	15.38	15.39	8.80	9.03

aminouracils were prepared using the method of Bredereck and co-workers.[2] The compounds were synthesized by reaction of a 1,3-disubstituted 5,6-diaminoracil[1] with a substituted sulfonyl chloride in pyridine as shown below. The compounds thus prepared are shown in Table I with their physical properties.



These compounds were devoid of diuretic activity but several were active as appetite inhibitors, both subcutaneously and orally.

EXPERIMENTAL

General procedure for the preparation of 1,3-disubstituted 5-sulfonamido-6-aminouracils. The appropriate 1,3-disubstituted 5,6-diaminouracil[1] (0.0238 mole) is dissolved in 50 ml. of pyridine and 0.024 mole of the desired aryl or alkyl sulfonyl chloride is added. When the exothermic reaction has subsided, the solution is heated on the steam bath, with stirring, for 1.5 hr. The pyridine is removed at reduced pressure and to the residue is added 50 ml. of water. The product, an oil, solidifies on standing and is filtered by suction. Recrystallization from absolute ethanol yields the desired sulfonamido derivative in pure form. All compounds in Table I were prepared in this manner.

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(2) H. Bredereck, I. Hennig, and O. Mueller, *Ber.*, **86**, 850 (1953).

Isomerization of 4-Biphenylyl Arenesulfonates

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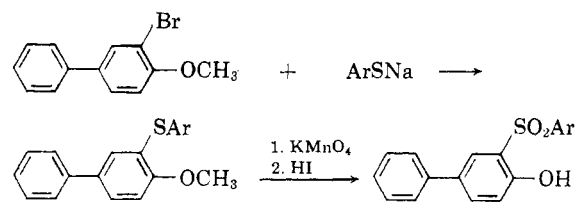
In a continuation of our studies on the Fries rearrangement of aryl arenesulfonates,[1] we report in this communication the behavior of some biphenylyl arenesulfonates. On heating with anhydrous aluminum chloride at 140–160°, the benzene- and p-toluenesulfonates of 4-hydroxybiphenyl underwent isomerization to o-hydroxy sulfones(I). The yields were, however, poor. No heteronuclear rearrangement was found to occur. The products were synthesized unambiguously by the following scheme:



(Ar = C_6H_5 or p-$CH_3C_6H_4$)

2-Biphenylyl arenesulfonates, when heated with aluminum chloride, gave alkali-soluble products but they could not be characterized. For example, 2-biphenylyl p-toluenesulfonate gave a pasty mass which solidified slowly. It could not be crystallized.

(1) V. Baliah and M. Uma, *Rec. trav. chim.*, **77**, 667 (1958); *Rec. trav. chim.*, **80**, 139(1961).

EXPERIMENTAL

The isomerization of 4-biphenylyl benzenesulfonate. A mixture of 5 g. (0.016 mole) of 4-biphenylyl benzenesulfonate and 7.2 g. (0.054 mole) of powdered anhydrous aluminum chloride was heated at 140–160° for 1 hr. After cooling, the product was decomposed with ice and hydrochloric acid. The resulting solid was filtered and extracted with dilute sodium hydroxide solution. The alkali extract was acidified, filtered, and extracted with ether. Evaporation of ether gave 0.15 g. (3%) of a product which, on repeated crystallization from ethanol, melted at 97–99°. The melting point was not depressed on admixture with *4-hydroxy-3-phenylsulfonylbiphenyl*, synthesized unambiguously.

Anal. Calcd. for $C_{18}H_{14}O_3S$: C, 69.65; H, 4.54. Found: C, 69.50; H, 4.42.

4-Methoxy-3-phenylthiobiphenyl. To a solution of sodium ethoxide (0.7 g. of sodium in 10 ml. of absolute ethanol) 3.3 g. (0.03 mole) of thiophenol was added and the alcohol was evaporated. The resulting phenyl sodium sulfide was mixed with 8 g. (0.03 mole) of 3-bromo-4-methoxybiphenyl[2] and 0.8 g. of copper powder and heated at 220–240° for 4.5 hr. After cooling, the product was treated with 3 g. of zinc dust and 100 ml. of dilute (2*N*) sulfuric acid and steam-distilled. Extraction of the residue with ether gave the *sulfide*. The yield was 8 g. (90%). It boiled at 220–223°/6 mm. and was obtained as a viscous liquid.

Anal. Calcd. for $C_{19}H_{16}OS$: C, 78.03; H, 5.52. Found: C, 78.30; H, 5.60.

4-Methoxy-3-phenylsulfonylbiphenyl. A solution of 3 g. of the foregoing sulfide in glacial acetic acid was treated with excess of saturated potassium permanganate solution and heated on a water bath for 15 min. The solution was then decolorized with sulfur dioxide, diluted with water, and the precipitated solid was filtered. Crystallization from ethanol gave 2.1 g. (63%) of the *sulfone;* m.p. 177–179°.

Anal. Calcd. for $C_{19}H_{16}O_3S$: C, 70.36; H, 4.97. Found: C, 70.41; H, 5.00.

4-Hydroxy-3-phenylsulfonylbiphenyl. A mixture of 1 g. of the above sulfone and 10 ml. of hydriodic acid (*d* 1.7) was heated at 160–170° for 5 hr. The product was poured into water, the precipitated solid was removed by filtration, washed with water and extracted with dilute sodium hydroxide solution. Acidification of the alkali extract gave an oil which solidified slowly. The yield was 0.6 g. (63%). The compound was crystallized from ethanol; m.p. 97–99°.

Anal. Calcd. for $C_{18}H_{14}O_3S$: C, 69.65; H, 4.54. Found: C, 69.39; H, 4.40.

Isomerization of 4-biphenylyl-p-toluenesulfonate. The procedure was the same as that described for the benzenesulfonate. The yield of the hydroxy sulfone was 8%. After recrystallizing from ethanol, it melted at 112–114°. There was no depression in the melting point on admixture with *4-hydroxy-3-p-tolylsulfonylbiphenyl*, synthesized unequivocally.

Anal. Calcd. for $C_{19}H_{16}O_3S$: C, 70.36; H, 4.97. Found: C, C, 70.57; H, 5.01.

4-Methoxy-3-p-tolylthiobiphenyl was obtained from 3-bromo-4-methoxydiphenyl and *p*-thiocresol in 79% yield. It boiled at 258–260°/9 mm.

Anal. Calcd. for $C_{20}H_{18}OS$: C, 78.39; H, 5.92. Found: C, 78.59; H, 5.99.

4-Methoxy-3-p-tolylsulfonylbiphenyl. Oxidation of the above sulfide with potassium permanganate solution gave this *sulfone* in 60% yield. It was crystallized from ethanol; m.p. 171–173°.

Anal. Calcd. for $C_{20}H_{18}O_3S$: C, 70.99; H, 5.36. Found: C, 71.01; H, 5.40.

4-Hydroxy-3-p-tolylsulfonylbiphenyl was obtained in 60% yield by demethylating the foregoing compound with hydriodic acid. After recrystallizing from ethanol, it melted at 112–114°.

Anal. Calcd. for $C_{19}H_{16}O_3S$: C, 70.36; H, 4.97. Found: C, 70.15; H, 4.79.

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(2) D. H. Hey and E. R. B. Jackson, *J. Chem. Soc.*, 802 (1936).

The Reactions of Thiolsulfonates and Thiolsulfinates with 1-Fluoro-2,4-dinitrobenzene

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Leandri and Tundo[1] have shown that 2,4-dinitrochlorobenzene reacts with aromatic thiolsulfonates to yield the corresponding 2,4-dinitrophenyl sulfones. We have studied this reaction employing the more reactive 1-fluoro-2,4-dinitrobenzene at room temperature in the attempt to develop methods for characterizing thiolsulfonates (RSO_2SR') and thiolsulfinates (RSO—SR') and mixtures of the two. Thiolsulfonates and thiolsulfinates reacted with excess fluorodinitrobenzene at 25° for forty to sixty hours in aqueous acetone–sodium bicarbonate suspension, aqueous tetrahydrofuran–sodium bicarbonate suspension, or in dimethylformamide–water–triethylamine solution and the products were separated by direct crystallization and by adsorption chromatography.

p-Tolyl *p*-toluenethiolsulfonate yielded, in addition to the expected 2,4-dinitrophenyl *p*-tolyl sulfone (65–89%), 2,4-dinitrophenyl *p*-tolyl sulfoxide (7–9%) and smaller yields of the corresponding sulfide.

The isolation of sulfoxide in these reactions is evidence that, in addition to reaction of the RSO_2 moiety with fluorodinitrobenzene to yield sulfone, the RS portion of the thiolsulfonate must yield the unstable intermediate sulfenic acid [RSOH] which reacts with fluorodinitrobenzene to give sulfoxide. The sulfenic acid may result either from a concerted reaction in which RS is eliminated as RSF which is hydrolyzed to sulfenic acid or from a direct reaction of hydroxyl ion on the positively polarized RS of the reacting molecule or on separated RS+.[2] More convincing evidence for this was obtained

(1) G. Leandri and A. Tundo, *Ann. Chim.* (*Rome*), **44**, 255, 264 (1954).

(2) The chemistry of the sulfenic acids has been summarized by Kharasch: N. Kharasch, S. J. Potempa, and H. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946); N. Kharasch, "The Sulfenic Acids and their Derivatives," in *Organic Sulfur Compounds*, Vol. I, Pergamon Press, London (1959).