able column packings to separate the peaks from IV and VI.

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Synthesis of Methylthiomethyl Isothiocyanate

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Considerable interest has been shown in methylthioalkyl isothiocyanates of the composition $CH_3S(CH_2)_nNCS$. These mustard oils contribute to the characteristic aroma of various *Cruciferae* species.[2] A number of these compounds (n = 2 to 9) were synthesized by Kjaer and Christensen,[2] but the first member of this series, methylthiomethyl isothiocyanate, has not been prepared. Recently, Bailey, *et al.*,[3] using gas chromatography and mass spectrometry for isolation and identification, have suggested that this isothiocyanate is an aroma component of fresh cabbage (*Brassica oleracea* var. *capitata alba*).

The synthesis of methylthiomethyl isothiocyanate was accomplished in good yields by refluxing chloromethyl methyl sulfide and potassium thiocyanate in petroleum ether, analogously to the preparation of methoxymethyl isothiocyanate.[4,5] The new mustard oil, which has a pleasing, pungent aroma, was characterized by conversion to the thiourea and isothiuronium picrate.[6]

Chloromethyl methyl sulfide was also found to react readily with thiourea to give the isothiuronium salt.

EXPERIMENTAL[7]

Chloromethyl methyl sulfide was prepared from dimethyl sulfide and sulfur chloride by the method of Richtzenhain and Alfredsson.[8]

Methylthiomethyl isothiocyanate. A mixture of 11.5 g. (0.12 mole) of dry, powdered potassium thiocyanate, 10 g. (0.10 mole) of chloromethyl methyl sulfide, and 40 ml. of petroleum ether (b.p. 35–75°) was stirred and refluxed for 6 hr. An additional 11 g. (0.11 mole) of powdered potassium thiocyanate was added during this period. After cooling overnight at 0–5°, the yellow oil that had separated as a lower layer was dissolved by adding methylene chloride. The solid present was filtered off, and the solvent was removed from the filtrate under reduced pressure. Distillation of the concentrate at 18 mm. yielded 9.88 g. (80%) of a light yellow liquid, b.p. 83–86°. Redistillation gave a mildly pungent, colorless liquid; b.p. 82–84° (17 mm.), n_D^{19} 1.5884.

Anal. Calcd. for $C_3H_5NS_2$: C, 30.23; H, 4.23; S, 53.79. Found: C, 30.40; H, 4.27; S, 54.16.

The infrared spectrum showed the typical strong isothiocyanate band at 4.97 μ.

N-(Methylthiomethyl)thiourea. A solution of 4 g. of methylthiomethyl isothiocyanate in 100 ml. of ammonia-saturated methanol was allowed to stand at room temperature for 16 hr. After removal of the methanol under reduced pressure, crystallization from hexane–ethyl acetate yielded 2.3 g. (50%) of white crystals, m.p. 96–101°. Several recrystallizations from hexane–ethyl acetate afforded glistening white leaflets, m.p. 102–104°. The absorption spectrum in ethanol showed a maximum at 247 mμ.

Anal. Calcd. for $C_3H_8N_2S_2$: C, 26.45; H, 5.92; N, 20.57. Found: C, 26.41; H, 5.96; N, 20.50.

S-Methyl-N-(methylthiomethyl)isothiuronium picrate was prepared by refluxing the thiourea in ethanol with a slight excess of methyl iodide and subsequent addition of ethanolic picric acid.[6] The picrate crystallized from ethanol as fine yellow leaflets, m.p. 153–155°.

Anal. Calcd. for $C_{10}H_{13}N_5O_7S_2$: C, 31.66; H, 3.45; S, 16.90. Found: C, 31.73; H, 3.56; S, 17.16.

S-(Methylthiomethyl)isothiouronium chloride. When a solution of 0.5 g. (0.0066 mole) of thiourea and 0.64 g. (0.0066 mole) of chloromethyl methyl sulfide in 17 ml. of acetone was allowed to stand at room temperature,[9] cloudiness began to appear in about 5 min. The mixture was cooled in ice after 1.5 hr. at room temperature, and the oil that had separated formed a white solid; 0.80 g. (70%), m.p. 126–129°. Two crystallizations from *n*-propyl alcohol gave colorless prismatic crystals, m.p. 131–133°.

Anal. Calcd. for $C_3H_9ClN_2S_2$: C, 20.86; H, 5.25; S, 37.13. Found: C, 21.10; H, 5.12; S, 37.40.

The picrate crystallized from ethanol as yellow needles, m.p. 158–160°.

Anal. Calcd. for $C_9H_{11}N_5O_7S_2$: C, 29.59; H, 3.04; S, 17.55. Found: C, 29.77; H, 3.22; S, 17.64.

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5-Sulfonamido-6-aminouracils

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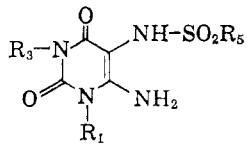
As part of a study of 5-substituted 6-aminouracils[1] as diuretics, a series of 5-sulfonamido-6-

(1) M. Kalm, *J. Org. Chem.*, in press.

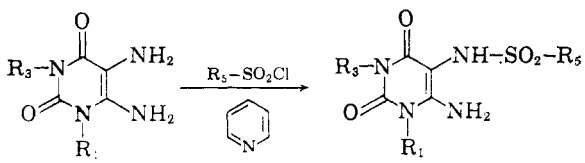
TABLE I

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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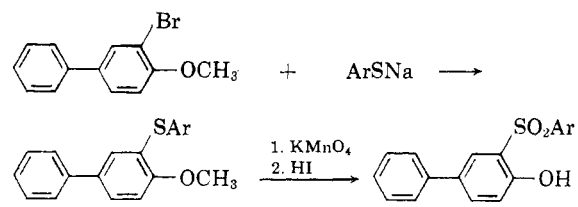
In a continuation of our studies on the Fries rearrangement of aryl arenesulfonates,[1] we report in this communication the behavior of some biphenylyl arenesulfonates. On heating with anhydrous aluminum chloride at 140–160°, the benzene- and p-toluenesulfonates of 4-hydroxybiphenyl underwent isomerization 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).