further small amount of pure product may be obtained by a third crystallization of the filtrate. Unreacted zinc salt and remaining glucuronide in the washings may be recovered by dissolving the sludge in hot acidified water, adding an excess of zinc acetate and recovering the insoluble salt by filtration.

Attempts to find some more suitable method for the hydrolysis of borneol glucuronide than the acid hydrolysis suggested by Quick for the preparation of glucuronic acid have not been successful. B-Emulsin will hydrolyze considerable quantities of glucuronide; however, the reaction rate is slow, the equilibrium poor for preparation purposes, and the high acidity produced by the free glucuronic acid destroys emulsin, necessitating continued addition of the enzyme. This last step therefore is the limiting one in the preparation of glucuronic acid by Quick's method.

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The Action of Methyl Isothiocyanate on Ethyl Acetonedicarboxylate

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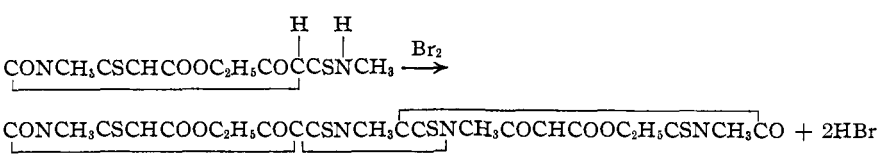
The highly substituted derivatives of piperidine obtained ultimately by the action of aryl isothiocyanates on the sodium enolate of ethyl acetonedicarboxylate undergo further cyclization, in the presence of bromine, into piperidyl benzothiazoles.[1] An examination of similar reactions with an alkyl isothiocyanate has shown that a piperidine is formed which also loses a molecule of hydrogen. Thiazole formation is impossible, therefore the assumption has been made that a spiro piperazine is obtained as the result of a bimolecular condensation.



(1) Worrall, THIS JOURNAL, **61**, 2967 (1939).

Abenius[2] found that a reaction of this type occurs with the bromoacetyl derivative of aniline.

Experimental

1 - Methyl - 2,4 - dioxo - 5 - carbethoxy - 6 - sulfopiperidine-3-thioformomethylamide.—Using the customary technique, 0.1 g. mole of the ester was changed into the disodium derivative and mixed with two equivalents of methyl isothiocyanate. The mixture, after the spontaneous reaction subsided, was heated for an hour and decomposed in the usual manner. The pasty product was extracted with cold alcohol and the residue crystallized from alcohol. Bright yellow platelets resulted, m. p. 98°, yield 4–5 g.

Anal. Calcd. for $C_{11}H_{14}N_2O_4S_2$: C, 43.7; H, 4.6. Found: C, 43.6; H, 4.5.

The substance, soluble in sodium carbonate solution is reprecipitated unchanged by a strong acid. Hot acid changes it into an intractable tar, while boiling with alcoholic potash produces methylamine, hydrogen sulfide and other decomposition products. The original material contained an insoluble portion (0.3 g.) that separated from a large volume of alcohol in slender pale yellow needles, m. p. 235–236°. An analysis indicated the formula $C_{18}H_{14}N_4O_5S_4$, but it was not identified.

1 - Methyl - 2,4 - dioxo - 5 - carbethoxy - 6 - sulfomethoxypiperidine-3-thioformomethylamide.—The product, obtained by heating 1 g. of the amide with methyl iodide–ethyl alcohol mixture for thirty minutes, separated on cooling as slender colorless needles, m. p. 110°.

Anal. Calcd. for $C_{12}H_{16}N_2O_4S_2$: C, 45.6; H, 5.1. Found: C, 45.3; H, 5.0.

Di - spiro - 3,3' - di - (1 - methyl - 2,4 - dioxo - 5 - carbethoxy - 6 - sulfopiperidine) - 3'',3''' - (1,4 - dimethyl - 2,5-disulfopiperazine).—Bromination of 1 g. of the amide in glacial acetic acid formed a precipitate that, after heating on a water-bath for a short time, was crystallized from alcohol. Cream colored needles separated, m. p. 180°.

Anal. Calcd. for $C_{11}H_{12}N_2O_4S_2$: C, 44.0; H, 4.0. Found: C, 43.6; H, 3.9.

It is dissolved by cold concd. sulfuric acid, forms a gelatinous substance with hot alcoholic potash (probably the corresponding carboxy derivative) and is only slightly attacked by long heating with concd. hydrochloric acid.

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(2) Abenius, *J. prakt. Chem.*, (2) **40**, 431 (1889).