154 (100%) (M^+), 126 (13), 98 (16), and 80 (27), compatible with II (7). Attempts to obtain an authentic sample of II for direct comparison were unsuccessful.

Reductive Acetylation of 3,6-Dihydroxy-2,5-toluquinone—The identification of 3,6-dihydroxy-2,5-toluquinone was further substantiated by its conversion to 2,3,5,6-tetraacetoxytoluene (III) by reductive acetylation (4, 6). Twenty milligrams of II was refluxed for 2 hr with 200 mg of powdered zinc and 5 ml of acetic anhydride. The mixture was cooled and filtered, and the filter was washed with 2 × 5 ml of hot acetic acid. The combined filtrate and washings were diluted to 30 ml with distilled water and extracted with 4 × 30 ml of chloroform. Evaporation of the pooled, dried chloroform extracts gave a white, crystalline residue (17 mg). Recrystallization of this residue from chloroform gave white needles of III, mp 197–198°, whose physical characteristics (melting point, mixed melting point, IR, NMR, and mass spectroscopy) were identical to those of an authentic sample.

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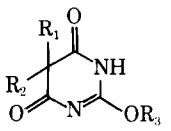
Synthesis of 5,5-Diethyl-2-ethoxytetrahydro-4,6-pyrimidinedione

R. BOUCHE

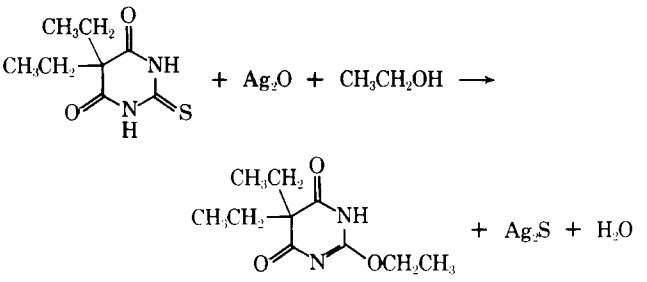
Abstract □ The original synthesis of 5,5-diethyl-2-ethoxytetrahydro-4,6-pyrimidinedione, a new pyrimidine derivative, is described. Evidence of its structure is given.

Keyphrases □ 5,5-Diethyl-2-ethoxytetrahydro-4,6-pyrimidinedione—synthesis, structure determination □ Pyrimidine derivatives—synthesis of 5,5-diethyl-2-ethoxytetrahydro-4,6-pyrimidinedione, structure determination

Alkoxy tetrahydro-4,6-pyrimidinediones (I), related to the family of barbituric acid derivatives, were prepared by a number of workers, starting from isourea alkyl ethers and condensing with substituted malonic esters or nitriles (1–3). They have also been obtained as by-products of the methylation of barbituric acid derivatives (4, 5). These synthesis methods reported require several steps. In the present paper, a new synthesis is reported for a one-step preparation in which silver oxide acts upon 5,5-diethyl-2-thiobarbituric acid in ethanol to give a new pyrimidine derivative, 5,5-diethyl-2-ethoxytetrahydro-4,6-pyrimidinedione



I



II

Scheme I

(II) (Scheme I). This reaction is similar to the general reaction of amides with silver oxide to form a salt (6) which is readily transformed into imidocarboxylic

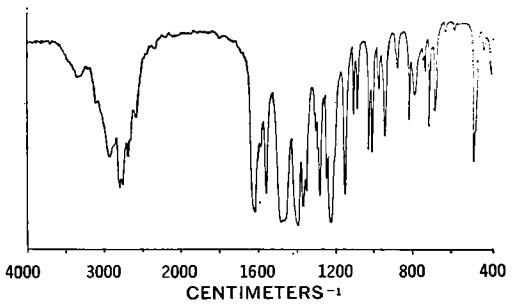


Figure 1—*IR spectrum of II.*

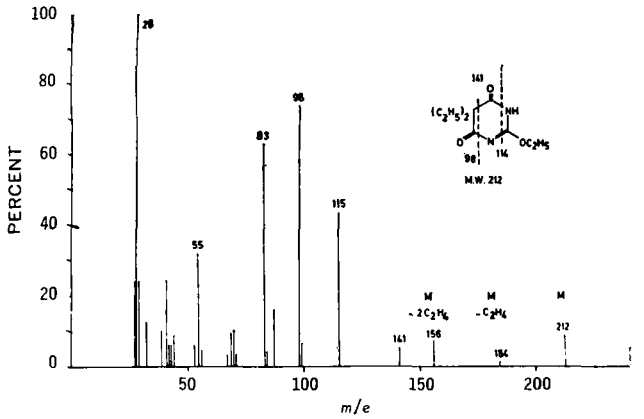


Figure 2—*Mass spectrum of II.*

acid derivatives by the action of a nucleophilic reagent.

A preliminary screening in mice using intraperitoneal administration suggested that the new compound produces skeletal muscle relaxation.

EXPERIMENTAL

To a solution of 1.84 g (0.01 mole) of 5,5-diethyl-2-thiobarbituric acid in 50 ml of absolute ethanol was added 2.6 g (0.03 mole) of silver oxide. The suspension was refluxed for 24 hr. After cooling and adding 2.5 g of talcum to adsorb excess silver oxide and silver sulfide, the mixture was filtered, the filtrate was evaporated to dryness, and the residue (1.9 g) was purified by TLC on silica gel with a solvent mixture of acetone–chloroform (1:9), R_f 0.37, corrected mp 77°.

The IR spectrum of II in chloroform showed two CO absorption bands at 1735 and 1700 cm^{-1} as well as a strong CN absorption at 1590 cm^{-1}. The spectrum taken in a KBr pellet is presented in Fig. 1. The NMR spectrum of II in deuterochloroform showed a badly resolved triplet of the NH proton at 1.02 ppm (τ); the quadruplets and the triplets of the ethoxy groups at 5.44 and 8.59 ppm, respectively; and the two ethyl groups at 7.98 and 9.16 ppm. In the mass spectrum (Fig. 2) were found the molecular ion peak at *m/e* 212 (calc. mol. wt. 212.26) and the usual pattern of fragmentation of the barbituric ring (7) with ion fragments resulting from the loss of a first ethylene molecule at *m/e* 156 and of an ethylisocyanate molecule at *m/e* 141.

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New Compounds: Unusual Chlorination of 2,3-Dimethyl-1,2,4-benzothiadiazine 1,1-Dioxide

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Abstract □ Chlorination of 2,3-dimethyl-1,2,4-benzothiadiazine 1,1-dioxide and its 6-chloro derivative with chlorine in dimethylformamide yielded a C-chlorinated end-product.

Keyphrases □ 2,3-Dimethyl-1,2,4-benzothiadiazine 1,1-dioxide—unusual chlorination in dimethylformamide yielding a C-chlorinated end-product □ Chlorination—2,3-dimethyl-1,2,4-benzothiadiazine 1,1-dioxide in dimethylformamide yielding a C-chlorinated end-product

The reported chlorination (1, 2) of 3-alkyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (I) yields the corresponding 7-chloro derivative (II). Similarly, 3-oxo-3,4-dihydro-1,2,4-benzothiadiazine 1,1-dioxide (III) yields a 7-chloro derivative (III*a*) or a 5,7-dichloro derivative (III*b*), depending on the reaction conditions.

This note reports the unexpected side-chain chlorination of 2,3-dimethyl-1,2,4-benzothiadiazine 1,1-dioxide (IV), which did not undergo ring chlorination but, in fact, yielded the corresponding 3-trichloromethyl derivative (IV*a*). Similarly, V yielded V*a*.

It was reported (2, 3) that a rearrangement due to the conversion of *N*-chloramines [the Orton reaction (4)] is possible with I and III. This yields a C-chlorinated end-product from the *N*-chloro intermediate.

Since such an intermediate is not possible in compounds of type IV, the present investigation suggests that the chlorination of these compounds in dimethylformamide undergoes a similar course of reaction as that of toluene or methylpyridine (5) when chlorinated with molecular chlorine.

EXPERIMENTAL

2-Methyl-3-trichloromethyl-1,2,4-benzothiadiazine 1,1-Dioxide (IV*a*)—Compound IV (6) (4 g) was dissolved in 14 ml of dimethylformamide. Chlorine was slowly added to the stirred solution at 45°. As soon as 4 g of chlorine was absorbed, the gas inlet