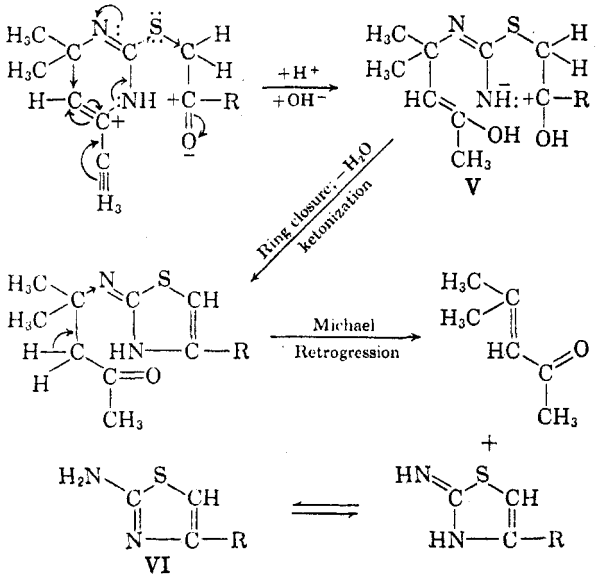
anism leading to the formation of 2-aminothiazoles (VI) could be shown below:

Hyperconjugation by CH_3 is opposed by the electron release by $(CH_3)_2C$; the former being stronger would leave a slight positive charge at the C-atom. It would appear that addition of a H at O and consequent demand at N of NH weakens the bond between it and the adjoining carbon and the breakage of this bond is followed by addition of OH resulting in the structure (V)



EXPERIMENTAL

Condensation of 2-mercapto-4,4,6-trimethyl-1,4-dihydropyrimidine with ω-bromoacetophenone: isolation of 2-amino-4-phenylthiazole and mesityl oxide. A mixture of 2-mercaptopyrimidine (A)(5.0 g.) and ω-bromoacetophenone (5.6 g.) was refluxed in ethanol (30 ml.) on a steam bath. After refluxing for about 1.5 hr., both components went into solution, whereafter a crystalline solid began to separate. After heating for 6 hr. the mixture was allowed to cool and the solid filtered and made basic with sodium bicarbonate. The base was collected by suction, washed with water, and crystallized from dilute ethanol, giving compound melting at 146°; the yield was 2.8 g. (50.2%).

Anal. Calcd. for $C_9H_8N_2S$: C, 61.3; H, 4.5. Found: C, 61.2; H, 4.6.

The analysis agrees with 2-amino-4-phenylthiazole. Moreover, the product did not depress the melting point on admixture with an authentic sample. The filtrate obtained after the separation of the solid was treated with 2,4-dinitrophenylhydrazine. The hydrazone so obtained melted at 199–200° and was identical with an authentic sample.

2-Mercaptopyrimidine (A) was similarly condensed with *p*-methoxy-ω-bromoacetophenone; the product on treatment with base of the solid crystallized from dilute ethanol; m.p. 205°. The yield was 36.8%.

Anal. Calcd. for $C_{10}H_{10}ON_2S$: C, 58.2; H, 4.8. Found: C, 58.5; H, 4.8%.

The product did not show a depression in melting point on admixture with an authentic sample of 2-amino-4(*p*-methoxyphenyl)thiazole.

Preparation of (III). A mixture of 2-mercaptopyrimidine (A) (5.0 g.) and ethylene dibromide (5.4 g.) was heated in an oil bath at 150° for 45 min. The orange yellow sirupy mass was cooled and treated with sodium bicarbonate. The solid so obtained was collected by suction, washed with water, and crystallized from dilute ethanol, giving a product melting at 180°; the yield being 4 g. (76%).

Anal. Calcd. for $C_9H_{14}N_2S$: C, 59.3; H, 7.6. Found: C, 58.9; H, 7.5.

Cyclization of 1-(β-hydroxyethyl)-2-mercapto-4,4,6-trimethylpyrimidine to (III). A 2.0-g. sample of 1-(β-hydroxyethyl)-2-mercapto-4,4,6-trimethylpyrimidine was treated in oil bath at 150° for 1.5 hr. The solid so obtained was crystallized from dilute ethanol, m.p. 180° and was confirmed to be III through its undepressed mixed melting point with the product obtained from the preceding experiment.

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Preparation of Substituted Thiamorpholine 1,1-Dioxides

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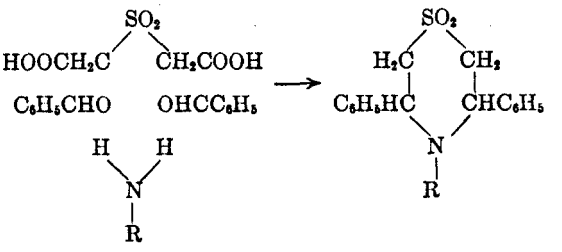
Received May 19, 1960

The work reported in this communication is a continuation of what has been published earlier by us.[1] Sulfonyldiacetic acid condensed with benzaldehyde and several aliphatic amines to give substituted thiamorpholine 1,1-dioxides.



The condensation proceeded as in the case of ammonia[1] but the yields are very much poorer with amines than with ammonia. The amines used were methylamine, ethylamine, allylamine, and benzylamine.

Diphenacyl sulfone also underwent condensations similar to diethyl sulfonyldiacetate[1] giving 2,6-dibenzoyl-3,5-diarylthiamorpholine 1,1-dioxides.

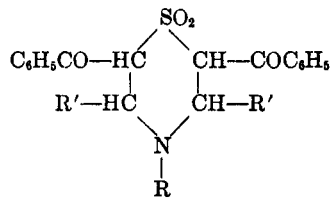
EXPERIMENTAL

3,5-Diphenyl-4-methylthiamorpholine 1,1-dioxide. A mixture of 2.73 g. (0.015 mole) of sulfonyldiacetic acid, 1.74 g. (0.015 mole) of a 25% aqueous solution of methylamine, 3.2 g. (0.03 mole) of benzaldehyde and 5 ml. of acetic acid was heated under reflux for 1.5 hr. After cooling, 50 ml. of ether was added to the product. The clear ethereal layer was separated, saturated with dry hydrogen chloride, and left overnight. The *hydrochloride* that separated was removed by filtration, washed with dry ether, and recrystallized from ethanol-ether, m.p. 255–257°. The yield was 0.7 g. (14%).

Anal. Calcd. for $C_{17}H_{20}ClNO_2S$: C, 60.42; H, 5.97. Found: C, 60.21; H, 5.93.

(1) V. Baliah and T. Rangarajan, *J. Chem. Soc.*, 3068 (1954).

TABLE I



No.[a]	R′	R	M.P.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1	C_6H_5	H	228–230	$C_{30}H_{25}NO_4S$	72.71	72.59	5.08	5.33
2	C_6H_5	C_2H_5	195–196	$C_{32}H_{29}NO_4S$	73.38	72.98	5.58	6.02
3	p-$CH_3OC_6H_4$	H	198–200 (dec.)	$C_{32}H_{29}NO_6S$	69.15	68.80	5.26	5.46
4	3,4-$CH_2O_2C_6H_4$	H	184–186 (dec.)	$C_{32}H_{25}NO_8S$	65.85	65.66	4.32	4.46
5	p-ClC_6H_4	H	200–203 (dec.)	$C_{30}H_{23}Cl_2NO_4S$	63.83	63.37	4.11	4.04

[a] Nos. 1 and 2 were recrystallized from ethanol and the rest from dioxane.

The *base* was liberated by dissolving the hydrochloride in ethanol, adding ammonia and diluting the solution with water. On recrystallization from ethanol it melted at 178–179°.

Anal. Calcd. for $C_{17}H_{19}NO_2S$: C, 67.72; H, 6.35. Found: C, 67.53; H, 6.55.

3,5-Diphenyl-4-ethylthiamorpholine 1,1-dioxide was prepared similarly to the foregoing compound. The ethereal solution, saturated with hydrogen chloride, gave only an oil on standing overnight in a refrigerator. The oil was taken up in ethanol and ammonia was added in slight excess. On dilution with water, the thiamorpholine derivative separated. The yield was only 0.05 g. (1%). After recrytallization from ethanol, it melted at 185–186°.

Anal. Calcd. for $C_{18}H_{21}NO_2S$: C, 68.55; H, 6.71. Found: C, 68.22; H, 6.64.

3,5-Diphenyl-4-allylthiamorpholine 1,1-dioxide. The reaction product from sulfonyldiacetic acid, benzaldehyde, and allylamine gave, on treatment with ether, distyryl sulfone in 23% yield. After removing it by filtration, the clear ethereal layer was worked up as in the previous case. 3,5-Diphenyl-4-allylthiamorpholine 1,1-dioxide was obtained in 13% yield. After recrystallization from ethanol, it melted at 192–195°.

Anal. Calcd. for $C_{19}H_{21}NO_2S$: C, 69.71; H, 6.47. Found: C, 69.74; H, 6.31.

3,5-Diphenyl-4-benzylthiamorpholine 1,1-dioxide hydrochloride. The condensation of sulfonyldiacetic acid, benzaldehyde, and benzylamine was effected as in the previous cases. The major product of the reaction was, however, distyryl sulfone (37% yield). The hydrochloride of the thiamorpholine derivative was obtained in only 3% yield. On recrystallization from ethanol-ether it melted at 222–223°.

Anal. Calcd. for $C_{23}H_{24}ClNO_2S$: C, 66.73; H, 5.84. Found: C, 66.48; H, 6.05.

The amount of the available hydrochloride being small, no attempt was made to get the base.

General procedure for the preparation of 2,6-dibenzoyl-3,5-diarylthiamorpholine 1,1-dioxides. Diphenacyl sulfone[2] (0.01 mole), the aromatic aldehyde (0.02 mole) and ammonium acetate or the amine (0.01 mole) were heated at reflux in 25 ml. of ethanol for 15 min. and the mixture was cooled. The separated solid was filtered and recrystallized from a suitable solvent. In all cases the yield was above 90%. Details regarding the individual compounds are given in Table I.

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(2) E. Fromm and J. Flaschen, *Ann.*, **394**, 312 (1912).

Synthesis of 3,5-Diaryl-1,4-thiazine 1,1-Dioxides

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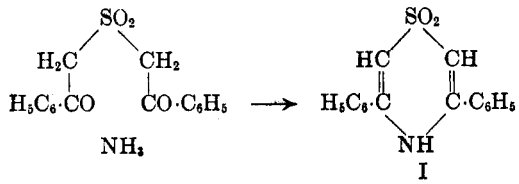
Received May 19, 1960

As a result of our interest in unsaturated cyclic sulfones we undertook the preparation of some substituted 1,4-thiazine 1,1-dioxides. Diphenacyl sulfone condensed with ammonia in glacial acetic acid, giving 3,5-diphenyl-1,4-thiazine 1,1-dioxide (I). There was no reaction when methylamine or ethylamine was used in place of ammonia. 3,5-Diphenyl-4-methyl-1,4-thiazine 1,1-dioxide was, however, obtained by methylating I with methyl iodide in acetone in the presence of potassium carbonate.



Di-*p*-bromophenacyl sulfone and di-*p*-chlorophenacyl sulfone condensed with ammonia in the same way as diphenacyl sulfone to give 3,5-di-*p*-bromophenyl-1,4-thiazine 1,1-dioxide and 3,5-di-*p*-chlorophenyl-1,4-thiazine 1,1-dioxide, respectively.

EXPERIMENTAL

3,5-Diphenyl-1,4-thiazine 1,1-dioxide. A mixture of 3 g. (0.01 mole) of diphenacyl sulfone[1] and 1.5 g. (0.02 mole) of ammonium acetate in 15 ml. of glacial acetic acid was heated under reflux for 2 hr. and cooled. The separated solid was removed by filtration and recrystallized from ethanol. The yield was 2.4 g. (85%). The compound melted at 270–272°.

Anal. Calcd. for $C_{16}H_{13}NO_2S$: C, 67.81; H, 4.62. Found: C, 68.00; H, 4.81.

3,5-Diphenyl-4-methyl-1,4-thiazine 1,1-dioxide. A solution of 1.4 g. (0.005 mole) of the foregoing compound in 60 ml.

(1) E. Fromm and J. Flaschen, *Ann.*, **394**, 312 (1912).