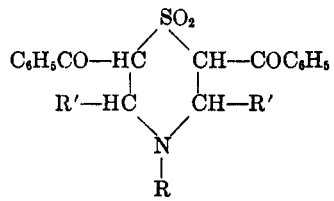
TABLE I



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

V. BALIAH AND T. RANGARAJAN

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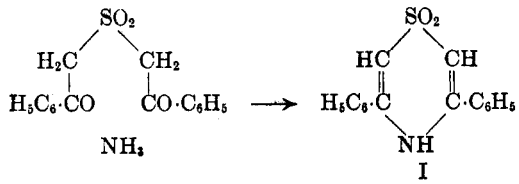
As a result of our interest in unsaturated cyclic sulfones we undertook the preparation of some substituted 1,4-thiazine 1,1-dioxides. Diphenacyl sulfone condensed with ammonia in glacial acetic acid, giving 3,5-diphenyl-1,4-thiazine 1,1-dioxide (I). There was no reaction when methylamine or ethylamine 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).

of dry acetone was treated with 4 g. (0.028 mole) of methyl iodide and 4 g. of anhydrous potassium carbonate and the mixture was heated under reflux for 8 hr. on a water bath. The acetone was then evaporated and water was added to the residue. The solid obtained was recrystallized from ethanol; yield, 0.8 g. (54%), m.p. 224–226°.

Anal. Calcd. for $C_{17}H_{15}NO_2S$: C, 68.64; H, 5.08. Found: C, 68.47; H, 5.15.

Di-p-bromophenacyl sulfone. A solution of 15 g. (0.035 mole) of di-*p*-bromophenacyl sulphide[2] in 50 ml. of glacial acetic acid was treated with 25 ml. of 30% hydrogen peroxide. The mixture was heated on a water bath for 2 hr. and cooled in ice water. The solid that separated was removed by filtration and washed with ethanol. After recrystallization from glacial acetic acid, the compound melted at 201–202°. The yield was 8.5 g. (53%).

Anal. Calcd. for $C_{16}H_{12}Br_2O_4S$: C, 41.75; H, 2.63. Found: C, 42.00; H, 2.50.

3,5-Di-p-bromophenyl-1,4-thiazine 1,1-dioxide. A mixture of 1.5 g. (0.00326 mole) of the above sulfone and 0.4 g. (0.0052 mole) of ammonium acetate in 4 ml. of glacial acetic acid was heated under reflux for 5 hr. The mixture was then cooled, the separated solid was filtered and washed with water. Recrystallization from glacial acetic acid gave colorless plates melting at 333° dec. The yield was 1.25 g. (87%).

Anal. Calcd. for $C_{16}H_{11}Br_2NO_2S$: C, 43.57; H, 2.51. Found: C, 43.54; H, 2.70.

Di-p-chlorophenacyl sulfone. Di-*p*-chlorophenacyl sulfide,[3] on oxidation with 30% hydrogen peroxide, gave this sulfone in 53% yield. On recrystallization from ethanol colorless needles melting at 182–183° were obtained.

Anal. Calcd. for $C_{16}H_{12}Cl_2O_4S$: C, 51.76; H, 3.26. Found: C, 51.44; H, 3.37.

3,5-Di-p-chlorophenyl-1,4-thiazine 1,1-dioxide was prepared similarly to 3,5-di-*p*-bromophenyl-1,4-thiazine 1,1-dioxide. The yield was 83%. The compound crystallized from glacial acetic acid as colorless plates and melted at 318–320° dec.

Anal. Calcd. for $C_{16}H_{11}Cl_2NO_2S$: C, 54.56; H, 3.15. Found: C, 54.46; H, 3.14.

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(2) A. Chrzaszczewska and S. Chwalinski, *Roczniki Chem.*, **8**, 432 (1928); *Chem. Abstr.*, **23**, 1629[8] (1929).

(3) A. Chrazaszczewska and S. Chwalinski, *Roczniki Chem.*, **7**, 6773 (1927); *Chem. Abstr.*, **22**, 1339[1] (1928).

Poly(methylene Sulfide)[1]

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Poly(methylene sulfide), also referred to as poly(thioformaldehyde), was synthesized in the course of investigating the relative influence of oxygen and sulfur on the properties of polymers having the repeat units polymethylene oxide and polymethylene sulfide.

EXPERIMENTAL

Synthesis. Into a three-necked 250-ml. flask fitted with a reflux condenser and a mechanical stirrer was added a solution of 43.2 g. (0.18 mole) of sodium sulfide nonahydrate in 80 ml. of water and 20 ml. of 95% ethyl alcohol. The solution was heated to a gentle reflux and 23.6 g. (0.18 mole) of freshly distilled bis(chloromethyl) sulfide,[2] n_D^{29} 1.5301, was gradually added in 15 min. The reaction mixture was refluxed for an additional 2 hr. The precipitated polymer was filtered from the hot reaction mixture, washed free of salts with warm water and finally washed with alcohol and hot benzene. The yield of the vacuum-dried, light yellow, powdery material was 4.9 g. (59.2%). It had a melting temperature[3] range of 220–245° (lit. m.p. 123–124,[4] 175–176).[5,6] These differences in the melting temperature may perhaps be due to differences in the molecular weights of the polymers.

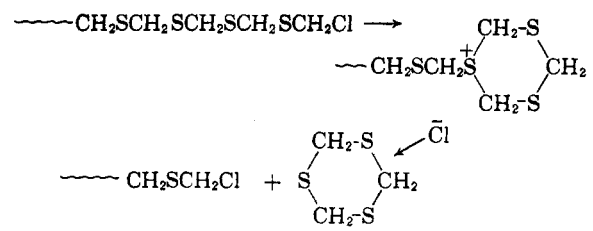
Anal. Calcd. for CH_2S: S, 69.56. Found: S, 68.7.

Properties. The polymer gave a crystalline x-ray diffraction pattern having *d* values of 4.37 (strong), 3.19 (weak), 3.00 (medium), 2.53 (weak), and 2.17A (weak).

It was insoluble in the boiling solvents: benzene, dioxane, *o*-dichlorobenzene, *N,N*-dimethylformamide, and nitromethane. Its reported solubility in alcohol and ether[4] or dimethylformamide[5] is contrary to our observations. The polymer was, however, soluble in *o*-phenylphenol and mixed tetrachlorobiphenyl (Monsanto's "Arachler 1254") at about 230°. On cooling these solutions, the polymer separated. In one experiment, the polymer gave an inherent viscosity of about 0.05 dl./g. at 230° in mixed tetrachlorobiphenyl. No attempt was made to stabilize the polymer against degradation during its dissolution and subsequent viscosity determination. No molecular weight determinations were made either by osmotic or light scattering method on account of the inherent difficulties of operation at the required high temperature.

When poly(methylene sulfide) was heated in a sublimator (bath temperature 190°) white needle-like crystals were slowly deposited on the cold finger. After two crystallizations from benzene, the sublimate gave an infrared spectrum and x-ray diffraction pattern, which were identical with those obtained from an authentic sample of *s*-trithiane. Molecular weight values of 154 and 161 were obtained for the sublimate and *s*-trithiane in benzene solution by the ebullioscopic method. These values are in fair agreement with each other, but are higher than the value 138 calculated for $C_3H_6S_3$.

The decomposition behavior of poly(methylene sulfide) to produce *s*-trithiane is believed to be due to the presence of some chloromethyl end groups of the polymer molecules. Presumbaly, the formation of the trithiane takes place *via* cyclic sulfonium salt formation:



Polymer molecules, which do not contain a halomethyl end group, cannot form the sulfonium salt and thus fail to give trithiane. Wohl's[6] polymer failed to sublime, because in

(1) Contribution No. 251 of the Goodyear Tire & Rubber Company.

(2) Sample kindly supplied by Stauffer Chemical Company.

(3) The heating rate during the melting range was 0.5° per minute or slower. The lower limit denotes the onset of liquefaction, while the upper limit represents the temperature for the complete disappearance of birefringence under the polarizing microscope.

(4) J. de Lattre, *Chem. Zentr.*, **83II**, 1192 (1912).

(5) F. Runge, Z. El-Hewehi, and D. Hempel, *J. Prakt. Chem.*, **8**, 1 (1959).

(6) A. Wohl, *Ber.*, **19**, 2344 (1886).