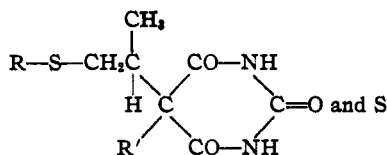


[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE MALTBIE CHEMICAL CO.]

Thioether Barbiturates. IV.  $\alpha$ -Methyl- $\beta$ -thioethyl DerivativesBY L. A. WALTER, L. H. GOODSON<sup>1</sup> AND RUSSEL J. FOSBINDER

This paper describes some barbituric and thio-barbituric acids of the structure



where R is *n*-butyl and ethyl and R' is ethyl and allyl. These compounds were prepared in the usual manner from the disubstituted malonic esters.

The barbituric acids were purified readily by crystallization from alcohol. The thiobarbituric acids were even more intractable than the iso-

$\beta$ -chloropropyl sulfides with sodio-malonic ester in toluene at 100° as described.<sup>2</sup> The mono-substituted malonic esters so obtained were purified by fractionation and alkylated with ethyl bromide and with allyl chloride in the usual manner with sodium ethylate in alcohol. All the compounds are listed in Table I.

## Experimental

**$\beta$ -Chloropropyl Ethyl Sulfide.**— $\beta$ -Hydroxypropyl ethyl sulfide, b. p. 70–73° at 35 mm., obtained in 90% yield from propylene chlorohydrin and sodium ethylmercaptide in absolute alcohol, was treated with thionyl chloride in chloroform as described.<sup>2</sup> The product, b. p. 52–55° at 12 mm., was obtained in 85% yield. Calcd. for C<sub>8</sub>H<sub>11</sub>ClS: Cl, 25.58. Found: Cl, 25.49.

TABLE I

BARBITURIC AND THIOBARBITURIC ACID

Malonic ester fraction used	B. p., °C.	Mm.	R	R'	M. p., °C., uncor.	Formula	Nitrogen, %		M. p., °C., uncor.	Formula	Nitrogen, %	
							Calcd.	Found			Calcd.	Found
112–114	1.3		Ethyl	Ethyl <sup>c</sup>	174–175	C <sub>11</sub> H <sub>15</sub> O <sub>2</sub> N <sub>2</sub> S	10.84	10.82	102–104	C <sub>11</sub> H <sub>15</sub> O <sub>2</sub> N <sub>2</sub> S <sub>2</sub>	10.29	10.27
118–120	1.3		Ethyl	Allyl <sup>c</sup>	138–139	C <sub>12</sub> H <sub>15</sub> O <sub>2</sub> N <sub>2</sub> S	10.37	10.57	78–86 <sup>a</sup>	C <sub>12</sub> H <sub>15</sub> O <sub>2</sub> N <sub>2</sub> S <sub>2</sub>	9.78	9.43
115–120	1		<i>n</i> -Butyl	Ethyl <sup>d</sup>	131.5–132.5	C <sub>12</sub> H <sub>17</sub> O <sub>2</sub> N <sub>2</sub> S	9.78	9.70		C <sub>12</sub> H <sub>17</sub> O <sub>2</sub> N <sub>2</sub> S <sub>2</sub> <sup>c</sup>	9.26	9.06
132–135	2		<i>n</i> -Butyl	Allyl <sup>d</sup>	84–86	C <sub>14</sub> H <sub>17</sub> O <sub>2</sub> N <sub>2</sub> S	9.38	9.48		C <sub>14</sub> H <sub>17</sub> O <sub>2</sub> N <sub>2</sub> S <sub>2</sub> Na <sup>b</sup>	8.32	8.18

<sup>a</sup> Wax-like. <sup>b</sup> Free acid not obtained as a solid. <sup>c</sup> The  $\alpha$ -methyl- $\beta$ -ethylthioethylmalonic ester used to prepare these compounds distilled at 106–108° at 1.3 mm. <sup>d</sup> The  $\alpha$ -methyl- $\beta$ -*n*-butylthioethylmalonic ester used to prepare these compounds distilled at 118–120° at 1.5 mm.

meric compounds described in paper III<sup>2</sup> and all were purified by crystallization of the sodium salts from absolute alcohol. These salts were solvates and when the alcohol was removed they were hygroscopic.

The intermediate malonic esters were prepared in 70–75% yields by the reaction of the alkyl

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(2) Walter, Goodson and Fosbinder, *THIS JOURNAL*, **67**, 659 (1945).

**$\beta$ -Chloropropyl *n*-Butyl Sulfide.**—This compound was prepared from  $\beta$ -hydroxypropyl *n*-butyl sulfide, b. p. 75° at 3.5 mm., and thionyl chloride as described above. Its b. p. was 52–55° at 1.5 mm. Calcd. for C<sub>7</sub>H<sub>15</sub>ClS: Cl, 21.27. Found: Cl, 21.21.

## Summary

Some 5-alkyl-5- $\alpha$ -methyl- $\beta$ -alkylthioethylbarbituric and thiobarbituric acids and the intermediates used in their preparation are described.

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