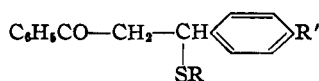


TABLE I



R	R'	Yield, %	M. p., °C.	Recryst. solvent	Formula	Analyses, %					
						Calcd.		Found			
						C	H	S	C	H	S
Methyl	H	98	47-48	Ethanol-water	C ₁₆ H ₁₆ OS	74.96	6.29	12.51	75.44	6.26	12.46
Ethyl	H	90	66-67	Hexane	C ₁₇ H ₁₈ OS	75.51	6.71	11.86	76.10	6.68	12.19
<i>n</i> -Dodecyl	H	95	52	Methanol	C ₂₇ H ₃₈ OS	78.97	9.32	7.81	79.06	9.41	7.93
Methyl	OCH ₃	90	54-56	Hexane	C ₁₇ H ₁₆ O ₂ S	71.30	6.33	11.20	71.13	6.16	10.99
<i>n</i> -Propyl	OCH ₃	94	65-66	Hexane	C ₁₉ H ₂₂ O ₂ S	72.57	7.05	10.20	72.82	7.05	10.37
<i>n</i> -Dodecyl	OCH ₃	91	41-41.5	Methanol	C ₂₈ H ₄₀ O ₂ S	76.31	9.15	7.28	75.98	9.32	7.53
Phenyl	OCH ₃	93	86.8	Methanol	C ₂₂ H ₂₀ O ₂ S	75.83	5.78	9.20	75.63	5.77	9.56
Benzyl	OCH ₃	96	58	Hexane	C ₂₃ H ₂₂ O ₂ S	76.21	6.12		76.35	5.96	
Pyridine-2-ethyl	OCH ₃	98	75-76	Methanol-water	C ₂₃ H ₂₃ NO ₂ S	43.18	6.14		72.99	6.06	

^a Analyses by Oakwold Laboratories, Alexandria, Va.

pounds reported here are new. The general method involved the treatment of an α,β -unsaturated ketone with the appropriate mercaptan in the presence of catalytic amounts of sodium ethoxide. Yields were excellent, ranging from 85 to 100%, and all the compounds studied were crystalline.

Experimental

β -Ketosulfides.—Directions are given for the preparation of one compound only. Others may be synthesized in a similar manner.

Benzylacetophenone β -*n*-Dodecylsulfide.—In a 125-ml. erlenmeyer flask were mixed 10.4 g. (0.05 mole) of benzylideneacetophenone, 10.1 g. (0.05 mole) of *n*-dodecyl mercaptan and 40 ml. of benzene. One-half ml. of 2 *N* sodium ethoxide was added and the mixture was vigorously shaken, a considerable amount of heat developing. After standing for twelve hours, glacial acetic acid was added dropwise until the solution was acid to phenolphthalein, and the solvent was removed under reduced pressure, leaving a crystalline residue which was recrystallized from methanol, giving a product melting at 52° in 95% yield. The properties and analyses of the new compounds are listed in Table I.

(3) All melting points were taken with a Fisher-Johns apparatus.

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2-Substituted-1,3-oxathiolanes

BY FRANK KIPNIS¹ AND JOHN ORNFELT

A search of the literature has indicated that surprisingly little information is available relating to the preparation and properties of 1,3-oxathiolanes. Sjöberg² discussed the preparation of 2,2,5-trimethyl-1,3-oxathiolane from acetone and 1-sulfhydryl-2-hydroxypropane in the presence of phosphorus pentoxide and sand. Other information³ has indicated the possibility of the formation of oxathiolanes from the interaction of aldehydes or ketones with 2-mercaptoethanol in the presence

(1) Present address: Oxford Products, Inc., Cleveland, Ohio.

(2) Sjöberg, *Ber.*, **75**, 13 (1942).

(3) Reference Form 5427A, Carbide and Carbon Chemicals Corporation, June 20, 1944.

of hydrochloric acid, but no specific data were given.

A method for the preparation of a number of hitherto unreported oxathiolanes is given here. These compounds are liquids with fresh, aromatic aromas, insoluble in water and soluble in most organic solvents, fairly stable to bases, but completely decomposed into the starting materials by very dilute acid. Table I summarizes the properties of three new oxathiolanes.

TABLE I

2-Substituent	2-SUBSTITUTED-1,3-OXATHIOLANES			
	Phenyl	<i>i</i> -Propyl	Methylene-3',4'-dioxiphenyl	
Yield, %	76.6	60.0	50.4	
B. p. { °C.	86-87	29	118	
{ mm.	5	2.5	1.5	
Empirical formula	C ₉ H ₁₀ OS	C ₉ H ₁₂ OS	C ₁₀ H ₁₀ O ₂ S	
Carbon, % {	Calcd.	65.02	54.50
	Found ^a	64.74	54.00
Hydrogen, % {	Calcd.	6.06	9.15
	Found ^a	5.97	9.26
Sulfur, % {	Calcd.	19.29	...	15.25
	Found ^a	18.89	...	15.64

^a Analyses by Oakwold Laboratories, Alexandria, Virginia.

Experimental

All the oxathiolanes were prepared by the same method. Directions are given for one compound only.

2-Isopropyl-1,3-oxathiolane.—In a 1000-ml. 3-neck interjoint flask fitted with a sealed Hershberg stirrer, dropping funnel and Dean-Stark adapter and condenser, was placed 39 g. (0.5 mole) of 2-mercaptoethanol, 36 g. (0.5 mole) of isobutyraldehyde and 250 ml. of dry benzene. The stirrer was started and a solution of 250 mg. of hydrogen chloride in 10 ml. of anhydrous ether was added from the dropping funnel during five minutes. A considerable amount of heat was produced and water was evolved. The mixture was refluxed for ninety minutes, and at the end of which time the theoretical amount of water (9 ml.) had been removed. The solution was cooled, washed thoroughly with 10% potassium carbonate, dried over calcium sulfate, filtered and the solvent stripped from the filtrate. The residue was fractionated at 29-31° (2.5 mm.) through a 35-cm. Vigreux column to give 39.6 g. (60%) of a colorless oil with a pleasant aroma.

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