tion of mercury(I) perchlorate, and (c) the solution containing mercury(II) perchlorate was added to a slurry of the freshly precipitated mercury(I) compound. Using mercury(I) sulfate precipitation, the procedure corresponding to (a) was the only type experiment performed.

The results of experiments of type a and b are reported in Table I. It is seen that the exchange is essentially complete even in experiments of type (b).

TABLE I

EXCHANGE OF MERCURY(I) AND MERCURY(II) IONS

Exp. type	Ppt.	Composition (moles/liter) (Hg^{++})	(Hg_2^{++})	(H^+)	Extent of exchange
a	Hg_2Cl_2	0.0031	0.0016$^{\otimes}$[a]	0.5[b]	94, 98
a	Hg_2Cl_2	$10^{-5}$$^{\otimes}$[a]	10^{-3}	0.5[b]	>98
b	Hg_2Cl_2	$10^{-5}$$^{\otimes}$[a]	10^{-3}	0.5[b]	97[c], 98[d]
b	Hg_2Cl_2	$10^{-5}$$^{\otimes}$[a]	10^{-3}	3	97–98[e]
a	Hg_2CrO_4[f]	0.0044	0.0069$^{\otimes}$[a]	0.1	94, 98
b	Hg_2CrO_4[f]	0.0048$^{\otimes}$[a]	0.0067	0.1	92, 102
a	Hg_2SO_4[g]	0.0093	0.0059$^{\otimes}$[a]	0.16[h]	~100%
a	Hg_2SO_4[g]	0.0136$^{\otimes}$[a]	0.0064	0.16[h]	

[a] ⊗ at concentration indicates activity started here. [b] Solutions also contain 3 *M* sodium perchlorate. [c] Two experiments. [d] Two experiments at 0°. [e] Three experiments; Cl^- concentration 0.04–0.06 *M*. [f] Composition of solid not established. [g] Precipitation incomplete; results of two experiments coupled lead to listed conclusion. [h] Not corrected for HSO_4^- formation.

The results of the experiments of type b involving mercury(I) chromate are consistent with a mechanism involving rapid homogeneous exchange and a rapid rate of recrystallization of the freshly precipitated solid. The concentration conditions in the chloride experiments are such that no conclusions may be drawn in this regard.

Experiments of type c are relevant to this question. The extent to which mercury(II) ion exchanges with precipitated mercury(I) chloride varies. The extent of exchange is approximately 30% if the mercury(II) is added within a few seconds after precipitation and then stirred with the precipitate for 2.5 minutes; it is 10% if the mercury(II) is added 7.5 minutes after precipitation and then stirred for 2.5 minutes. These represent extremes in the results of the seven experiments of this type performed. Contrasted with this are the results of this type experiment involving mercury(I) chromate. It was found that mercury(II), added in an amount comparable to the mercury(I), present as long as one minute after the precipitation of the mercury(I) chromate, exchanges completely with the precipitate upon stirring an additional two minutes. If, however, six minutes elapse between the time of precipitation and the addition of the mercury(II), essentially no exchange occurs upon stirring two minutes. This behavior, too, is consistent with a mechanism involving a rapid homogeneous exchange coupled with a relatively high recrystallization rate for freshly precipitated mercury(I) chromate and a much lower recrystallization rate for the coagulated solid. Visual observations reveal the change in the nature of the precipitate at times approximately one minute after precipitation. It was found that mercury(I) chromate precipitated under these conditions would dissolve completely in approximately thirty seconds upon treatment with excess iron(II) if only thirty seconds elapsed between the time of precipitation and addition of iron(II), while many minutes were required if this time interval was increased to three minutes.

This work doesn't discount the possibility that the exchange observed is in reality being induced during the precipitation. Under the conditions of these experiments it appears that the bond in dimeric mercury(I) is readily broken.

It has been shown that mercury(I) ion diffuses approximately 10% more rapidly than mercury(II) under certain concentration conditions. This observation is consistent with the relative diffusion coefficients determined by Kolthoff and Miller.[3] The condition under which this separation is achieved $((Hg_2^{++})_0/(Hg^{++})_0 = 0.5)$ is such that the counting rate of the diffusate would vary by only 5% depending upon whether the extent of exchange is 0% or 100%. The analytical and counting rate uncertainties are such that it does not appear worthwhile to use this technique in the exchange study.

Experimental

The radioactive mercury was prepared by the Hg(*n*, γ) reaction in the Oak Ridge pile and allocated by the United States Atomic Energy Commission. The work was all performed after the Hg^{197} had decayed; thus the mercury isotope present was $Hg^{205,203}$. Solutions of active mercury(II) perchlorate were prepared by dissolving active mercury(II) oxide in perchloric acid. Solutions of active mercury(I) perchlorate were prepared by allowing a solution of mercury(I) perchlorate to exchange for several days with a small amount of active mercury(II) perchlorate. Other reagents were all analytical reagent grade and all solutions were prepared using doubly distilled water.

The mercury(I) fraction was generally counted in the form precipitated while the mercury(II) was counted as the oxide or a basic salt. The samples were mounted for counting on filter paper by suction filtering.

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(3) Kolthoff and Miller, THIS JOURNAL, **63**, 2732 (1941).

DEPARTMENTS OF CHEMISTRY
OF HARVARD UNIVERSITY AND
THE UNIVERSITY OF WISCONSIN

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β-Ketosulfides

BY FRANK KIPNIS[1] AND JOHN ORNFELT

In the course of studies on certain sulfur-containing ketones, it became desirable to prepare a series of β-ketosulfides. This type of compound had been synthesized previously,[2] but those com-

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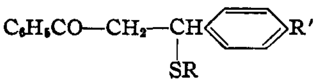
(1) Present address: Oxford Products, Inc., Cleveland, Ohio.

(2) Ruhemann, *J. Chem. Soc.*, **87**, 461 (1905); Posner, *Ber.*, **35**, 809 (1905); Nicolet, THIS JOURNAL, **53**, 3066 (1931); **54**, 1998 (1932); **57**, 1098 (1935); Nicolet, *J. Biol. Chem.*, **95**, 389 (1932); Morgan and Friedman, *Biochem. J.*, **32**, 733 (1938); Fromm and Hubert, *Ann.*, **394**, 301 (1912); Frank and Smith, THIS JOURNAL, **68**, 2104 (1946).

TABLE I



$C_6H_5CO—CH_2—CH(SR)—C_6H_4—R'$

R	R'	Yield, %	M. p., °C.	Recryst. solvent	Formula	Analyses,[a] % Calcd. C	H	S	Found 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
n-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	$C_{17}H_{18}O_2S$	71.30	6.33	11.20	71.13	6.16	10.99
n-Propyl	OCH_3	94	65–66	Hexane	$C_{19}H_{22}O_2S$	72.57	7.05	10.20	72.82	7.05	10.37
n-Dodecyl	OCH_3	91	41–41.5	Methanol	$C_{28}H_{40}O_2S$	76.31	9.15	7.28	75.98	9.32	7.53
Phenyl	OCH_3	93	86.8	Methanol	$C_{22}H_{20}O_2S$	75.83	5.78	9.20	75.63	5.77	9.56
Benzyl	OCH_3	96	58	Hexane	$C_{23}H_{22}O_2S$	76.21	6.12		76.35	5.96	
Pyridine-2-ethyl	OCH_3	98	75–76	Methanol–water	$C_{23}H_{23}NO_2S$	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°[3] in 95% yield. The properties and analyses of the new compounds are listed in Table I.

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

RESEARCH LABORATORIES
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RECEIVED MAY 26, 1949

2-Substituted-1,3-oxathiolanes

BY FRANK KIPNIS[1] 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. Sjoberg[2] 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 information[3] has indicated the possibility of the formation of oxathiolanes from the interaction of aldehydes or ketones with 2-mercaptoethanol in the presence 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-SUBSTITUTED-1,3-OXATHIOLANES

2-Substituent		Phenyl	*i*-Propyl	Methylene-3',4'-dioxyphenyl
Yield, %		76.6	60.0	50.4
B. p.	°C.	86–87	29	118
	Mm.	5	2.5	1.5
Empirical formula		$C_9H_{10}OS$	$C_6H_{12}OS$	$C_{10}H_{10}O_2S$
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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(1) Present address: Oxford Products, Inc., Cleveland, Ohio.

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

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