1, 2-DITHIOLIUM SALTS

I. 3-Alkylthio- and 3-Carboxymethylthio-1, 2-Dithiolium Iodides

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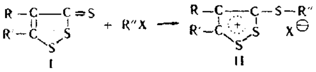
The reaction of aryl-1, 2-dithiol-3-thiones with alkyl iodides and with ICH_2COOH and $ICH_2COOC_2H_5$ has been studied. This gives 3-alkylithio-3-carboxymethylthio-, and 3-ethoxycarbonylmethylthio-1, 2-dithiolium iodides. Compounds of the first type are formed only with lower unbranched alkyl iodides (CH_3I, C_2H_5I, and n-C_3H_7I), and salts of the last two types were previously unknown.

1, 2-Dithiol-3-thiones (I) readily react with methyl iodide [1–6] and with dimethyl sulfate [5], forming 3-methylthio-1, 2-dithiolium salts (II), R" = CH_3).



I II

X = I, CH_3OSO_2; R" = $CH_3(CH_2)_n$ (n = 0-2), CH_2COOH, $CH_2COOC_2H_5$

However, 3-alkylthio-1, 2-dithiolium salts containing an alkyl group R" other than CH_3 have not been obtained previously, and the very possibility of their formation has not been studied. Salts of type II in which the substituents R" contains a functional group were unknown.

By the scheme given above we have synthesized new salts of type II with R" = C_2H_5, n-C_3H_7, CH_2COOH and $CH_2COOC_2H_5$ (see table). We were unable to obtain the analogous salts by the reaction of aryl-substituted 1, 2-dithiol-3-thiones with R" = i-C_3H_7I, n-C_4H_9I, C_6H_5I, CH_2I_2, CHI_3 and $HOCH_2CH_2I$.

The 3-carboxymethylthio-1, 2-dithiolium salts (R" = CH_2COOH) are of special interest. They are green or yellow-green crystalline substances, while the compounds of structure II with R" = C_nH_{2n+1} or $CH_2COOC_2H_5$ have colors from dark red to orange. They are insoluble in water and in the usual organic solvents but dissolve in aqueous solutions of Na_2CO_3 and NaOH (with a red-brown coloration) and in ethanolic KOH (forming a bright red solution). The results of a study of the physical and chemical properties of the 3-carboxymethylthio derivative of 1, 2-dithiolium salts will be published separately.

EXPERIMENTAL

Iodoacetic acid was obtained by the double decomposition of chloracetic acid and an aqueous solution of sodium iodide, mp 82° C [7].

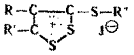
Ethyl iodoacetate was prepared by the esterification of the free acid with ethanol in the presence of H_2SO_4, bp 38–40° C (3 mm); n_D^{20} 1.4992.

Ethylene iodohydrin was obtained by the double decomposition of ethylene chlorohydrin with potassium iodide in ethanol, bp 55–57° C (10 mm); n_D^{20} 1.5310 [8].

3-Ethylthio-4-p-tolyl-1, 2-dithiolium iodide. A solution of 1.0 g (0.004 mole) of 4-p-tolyl-1, 2-dithiol-3-thione and 2.0 ml (3.8 g, 0.024 mole) of ethyl iodide in 50 ml of ethanol was heated to the boil until the separation of a precipitate of the salt II ceased. This was filtered off with suction, washed with benzene, and dried in vacuo. Yield 1.5 g (88.5%) mp 191° C.

3-n-Propylthio-4-p-tolyl-1, 2-dithiolium iodide. A solution of 1.0 g (0.004 mole) of 4-p-tolyl-1, 2-dithiol-3-thione and 2.0 ml (3.5 g, 0.02 mole) of n-propyl iodide in 30 ml of benzene was heated to the boil for 5–6 hr. On

3-Organothio-1,2-dithiolium Iodide



R	R′	R″	Mp, °C	Color and form of the crystals	Empirical formula	Found, %			Calculated, %		
						C	H	S	C	H	S
H	C_6H_5	C_2H_5	165	Lustrous orange-red plate	$C_{11}H_{11}S_3I$	36.60	3.08	26.32	36.07	3.28	26.26
H	p-$CH_3C_6H_4$	C_2H_5	191	Lustrous orange needles	$C_{12}H_{13}S_3I$	37.51	3.65	25.09	37.91	3.45	25.24
H	p-$CH_3OC_6H_4$	C_2H_5	171	Lustrous red-orange plates	$C_{12}H_{13}OS_3I$	36.75	3.15	24.21	36.37	3.31	24.27
H	p-$CH_3C_6H_4$	n-C_3H_7	158	Lustrous dark red plates	$C_{13}H_{15}S_3I$	39.46	4.03	24.92	39.60	3.84	24.39
H	p-$CH_3C_6H_4$	$CH_2COOC_2H_5$	133	Orange needles	$C_{14}H_{15}O_2S_3I$	38.21	3.58	21.61	38.39	3.45	21.94
H	p-$CH_3OC_6H_4$	$CH_2COOC_2H_5$	130	Yellow-orange needles	$C_{14}H_{15}O_3S_3I$	37.25	3.94	21.38	37.01	3.33	21.15
p-$CH_3OC_6H_4$	H	$CH_2COOC_2H_5$	123	Brown plates	$C_{14}H_{15}O_3S_3I$	37.68	3.30	21.54	37.01	3.33	21.15
H	C_6H_5	CH_2COOH	177	Yellow-brown	$C_{11}H_9O_2S_3I$	33.02	2.91	24.08	33.32	2.27	24.21
H	p-$CH_3C_6H_4$	CH_2COOH	167	Yellow-green	$C_{12}H_{11}O_2S_3I$	35.30	2.89	23.79	35.15	2.68	23.40
H	p-$CH_3OC_6H_4$	CH_2COOH	163	Green-yellow	$C_{12}H_{11}O_3S_3I$	34.16	2.71	22.42	33.81	2.59	22.56
p-$CH_3OC_6H_4$	H	CH_2COOH	168	Lustrous green plates	$C_{12}H_{11}O_3S_3I$	33.78	2.57	22.23	33.81	2.59	22.56

standing, crystals deposited, and these were filtered off with sunction, washed with benzene, and dried. Yield 0.65 g (37.2%), mp 158° C.

3-Carboxymethylthio-4-p-tolyl-1,2-dithiolium iodide. A solution of 1.0 g (0.004 mole) of 4-p-tolyl-1,2-dithiol-3-thione and 1.0 g (0.005 mole) of iodoacetic acid in 20 ml of benzene was heated to the boil for 2 hr. The precipitate that deposited was filtered off with suction, washed with ethanol and benzene, and dried in vacuo. Yield 1.2 g (65.7%), mp 167° C (decomp).

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