REACTION OF SULFOLENES WITH SILVER SALTS OF CARBOXYLIC ACIDS AND HALOGENS

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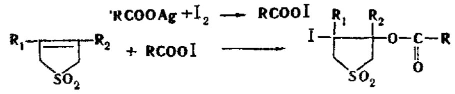
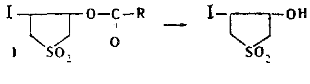
The reaction of sulfolenes with silver salts of carboxylic acids and iodine at a ratio of 1:1:1 has given the corresponding acylated iodohydrins. The partial deactivation of the double bond of 3-sulfolenes as compared with ordinary olefins has been shown.

It is known [1,2] that olefins react with silver salts of carboxylic acids and halogens in a molar ratio of 1:2:1 with the formation of acylated glycols. In studying the behavior of sulfolenes with silver benzoate and acetate in the presence of iodine, we obtained, in the case of silver benzoate, 3,4-dibenzoyloxysulfolane [3] and detected by means of analytical thin-layer chromatography the presence of a small amount of 3-benzoyloxy-4-iodosulfolane (I) in the reaction products. With silver acetate under similar conditions, the original 3-sulfolene was regenerated. Since it is assumed that the formation of acylated glycols takes place through acylated halohydrins [1], it appeared of interest to study the reaction of sulfolenes with silver acetate at an equimolar ratio of the reactants.

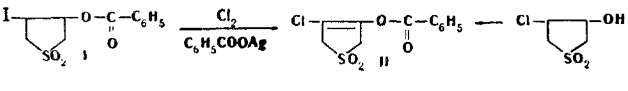
It was found that under these conditions silver acetate reacts with 3-sulfolene, 3-methyl-3-sulfolene, and 3,4-dimethyl-3-sulfolene in a similar manner to silver benzoate with the formation of the corresponding acylated iodohydrins, the difference between them consisting only in the lower yield of the acetyliodohydrins



On hydrolysis, the compounds obtained gave the trans-iodohydrin



With silver benzoate and chlorine, the iodine in I was replaced by chlorine



The product II formed gave no depression of the melting point in a mixture with the trans-3-benzoyloxy-4-chlorosulfolane obtained by the reaction of benzoyl chloride with trans-3-hydroxy-4-chlorosulfolane.

We were unable to obtain 3-acyloxy-4-chlorosulfolanes by the reaction of 3-sulfolene with silver salts and chlorine. With bromine under analogous conditions the initial 3-sulfolene was regenerated and trans-3,4-dibromosulfolane (III) was isolated in a yield of 35%.

Thus, in contrast to ordinary ethyleneic compounds, sulfolenes react selectively with silver salts of carboxylic acids and halogens. The features of their behavior are easily explained if it is assumed that the reaction with a ratio of the reactants of 1:2:1 takes place with the participation of the complex [4] $\mathrm{RCOOX \cdot RCOOAg \rightleftharpoons RCOOX + RCOOAg}$, the addition of which to the double bond is determined by its stability and the activity of the multiple bond. Since in the sulfolenes the double bond is partially deactivated under the influence of the sulfonyl group, only the most stable benzoyl hypoiodite can react with them. Under these conditions acetyl hypoiodite probably reacts with an excess of the salt without affecting the sulfolene. With equimolar amounts of the reactants, i.e., in the absence of an excess of the salt, the acetyl hypoiodite formed, like benzoyl hypoiodite, reacts with the sulfolenes giving acetoxyiodosulfolanes. However, since acetyl hypoiodite is thermally less stable [5], the yield of acetoxyiodosulfolanes is lower than that of the benzoyloxyiodosulfolanes and depends to a considerable extent on the presence of substituents on the double bond.

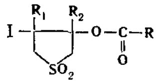
EXPERIMENTAL

3-Benzoyloxy-4-iodosulfolane (I). 5.9 g (0.05 mole) of 3-sulfolene was added to a mixture of 11.5 g (0.05 mole) of silver benzoate and 12.5 g (0.05 mole) of iodine in 250 ml of carbon tetrachloride heated to 60° C. The mixture was boiled for 30 hr. The precipitate of silver iodide was filtered off while hot. 4.6 g of I crystallized out of the cooled filtrate. After it had been separated off, the filtrate was washed successively with aqueous solutions of Na_2SO_3 and Na_2CO_3 to eliminate iodine and benzoic acid and then with water to neutrality. After the organic layer had been dried and the solvent had been distilled off, an additional 5.4 g of I was obtained together with 3.0 g of a residue which did not crystallize and contained (according to thin-layer chromatography) I, 3-sulfolene, iodobenzene, and biphenyl. The total yield of I was 10.0 g (54.6%), and after two recrystallizations from carbon tetrachloride it had mp 124°-125° C.

3-Acetoxy-4-iodosulfolane (VI) and the benzoyl- and acetyliodohydrins of 3-methyl-3-sulfolene (IV, VII) and of 3,4-dimethyl-3-sulfolene (V, VIII) were obtained similarly. The properties and yields of the compounds obtained are given in the table.

Reaction of 3-sulfolene with silver benzoate and bromine. With stirring, 8.0 g (0.05 mole) of bromine in 25 ml of chloroform was added to a mixture of 11.5 g (0.05 mole) of silver benzoate and 5.9 g (0.05 mole) of 3-sulfolene in 200 ml of chloroform cooled to 0° C. The mixture was boiled for 13 hr and was then treated in the manner described above. This gave 4.9 g (35.3%) of III with mp 143°-144° C. According to the literature [6], mp 144° C. Found, %: Br 57.50. Calculated for $C_4H_6Br_2O_2S$, %: Br 57.49.

3-Benzoyloxy-4-chlorosulfolane (II). a) 1.0 g of chlorine was passed into a cooled mixture of 3.0 g (0.008 mole) of I and 2.8 g (0.012 mole) of silver benzoate in 60 ml of chloroform, and then the mixture was stirred at 20°-25° C for 3 hr and at 60° C for 5 hr. This gave: 1) 0.3 g (14%) of II with mp 135°-136° C. Found, %: C 48.38; H 4.12; S 11.21; Cl 12.48. Calculated for $C_{11}H_{11}ClO_4S$, %:



R₁	R₂	R	Mp, ° C	Empirical formula	Found, %				Calculated, %				Yield, %
					C	H	S	I	C	H	S	I	
H	H	C_6H_5	124—125	$C_{11}H_{11}IO_4S$	35.95	3.14	8.64	34.62	36.08	3.03	8.76	34.62	54.6
H	H	CH_3	91— 92.5	$C_6H_9IO_4S$	—	—	—	41.78	—	—	—	41.73	23.0
H	CH_3	C_6H_5	130—131	$C_{12}H_{13}IO_4S$	37.92	3.60	8.80	33.30	37.90	3.45	8.48	33.37	55.7
H	CH_3	CH_3	120—121.5	$C_7H_{11}IO_4S$	—	—	—	39.82	—	—	—	39.89	5.7
CH_3	CH_3	C_6H_5	156—157.5	$C_{13}H_{15}IO_4S$	40.03	3.94	7.89	31.83	39.60	3.84	8.13	32.18	22.4
CH_3	CH_3	CH_3	130—131.5 (decomp.)	$C_8H_{13}IO_4S$	—	—	—	38.02	—	—	—	38.20	3.0

C 48.05; H 4.04; S 11.67; Cl 12.90; and 2] 0.2 g (7%) of 3,4-dibenzoyloxysulfolane with mp 179°-180° C. Found, %: S 8.87. Calculated for $C_{18}H_{16}O_6S$, %: S 8.90.

b) 6.4 g (0.045 mole) of benzoyl chloride was added to 2.5 g (0.015 mole) of 4-chloro-3-hydroxysulfolane in 50 ml of dry chloroform. The mixture was boiled in a current of dry nitrogen saturated with HCl until the solid matter had dissolved completely. This gave 3.5 g (84.6%) of II. After recrystallization from chloroform, the product melted at 135.5°-136.5° C.

Hydrolysis of 3-acetoxy-4-iodosulfolane (VI). 3.0 g (0.01 mole) of VI was boiled in 50 ml of distilled water for 8 hr and then the solution was evaporated at a pressure of 10 mm Hg with periodic removal by filtration of the precipitate of 3-hydroxy-4-iodosulfolane formed. Yield 1.9 g (72.5%). After recrystallization from methanol, the product melted with decomposition at 180.5°-181° C. According to the literature [7], mp 180°-181° C.

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