REACTION OF β-MERCAPTOETHANOL WITH α-BROMOACETYLENIC KETONES

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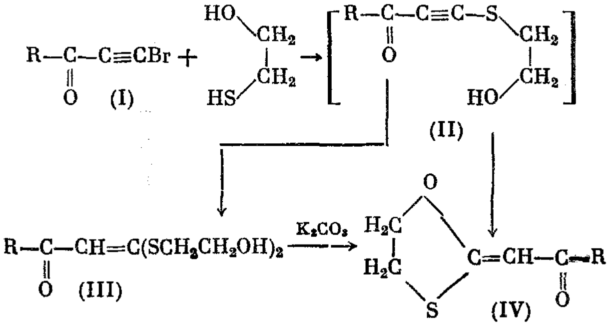
As a continuation of studying the reaction of acetylenic ketones with functional derivatives of thiols [1-4] we studied the reaction of α-bromoacetylenic ketones (Ia-c) with β-mercaptoethanol.

2-(Acylmethylene)-1,3-oxathiolanes (IVa-c) were obtained by the reaction of (Ia-c) with β-mercaptoethanol in the presence of K_2CO_3 as the catalyst (method A). The reaction evidently proceeds via the intermediate step of forming the corresponding acylethynyl sulfides (II) and cyclization of the latter to 1,3-oxathiolanes.

The reaction of (Ia, b) with β-mercaptoethanol in the presence of triethylamine (method B) leads to a mixture of 2-acylmethylene-1,3-oxathiolanes (IVa, b) and the corresponding α-ketoketene mercaptals (IIIa, b) in an ~5:1 ratio:



R=C_6H_5 (a), C_4H_3S (b), 2-$C_2H_5C_4H_2S$ (c)

Only the α-ketoketene mercaptals (IIIa, b) are formed in a respective yield of 42 and 58% when compounds (Ia, b) are reacted under these conditions with a two-fold or more excess of β-mercaptoethanol. When heated in $CHCl_3$ in the presence of K_2CO_3, (IIIa) is converted to 2-benzoylmethylene-1,3-oxathiolane (IVa) (Table 1).

The structure of the synthesized compounds was confirmed by the IR and PMR spectra. The IR spectra of compounds (IIIa, b) have the following absorption bands (ν, cm^{-1}): 1610-1640 (C=O). 1580-1595 (C=C), 690-705 (C—S), 3350-3400 (associated OH group). In the IR spectra of compounds (IVa-c) the C=O group absorbs at 1610-1630 cm^{-1}, the C=C bond has an absorption band in the 1570-1580 cm^{-1} region, and the C—S and C—O bonds of the 1,3-oxathiolane ring are depicted by intense bands at 705 and 1280 cm^{-1}. The parameters of the PMR spectra of compounds (IIIa, b) and (IVa-c) are given in Table 1.

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrometer as KBr pellets, while the PMR spectra were obtained on a Tesla BS-480 C spectrometer (80 MHz) in CCl_4 solution and using HMDS as the internal standard.

2-(Benzoylmethylene)-1,3-oxathiolane (IVa). Method A. With stirring, to a solution of 2.09 g of (Ia) and 0.78 g of β-mercaptoethanol in 30 ml of dry $CHCl_3$ at ~20° was added 2 g of K_2CO_3, and the stirred mixture was refluxed for 2 h. The solution was cooled, filtered, the filtrate was partially evaporated in vacuo, and the residue was chromatographed on Al_2O_3 in a 3:1 benzene—ether mixture to give 1.57 g (76%) of (IVa), mp 99-101° (from ethanol).

Method B. With stirring, to a solution of 2.09 g of (Ia) in 15 ml of ethanol at ~20° was added a solution of 0.78 g of β-mercaptoethanol and 1.01 g of triethylamine in 20 ml of

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TABLE 1

Compound	Yield, %		mp, °C	Found/Calculated, %			Empirical formula	PMR spectrum (δ, ppm)		
	method A	method B		C	H	S		CH=	S—CH$_2$	O—CH$_2$
(IIIa)	–	42	104–105	55,25/55,12	5,35/5,30	22,31/22,61	$C_{13}H_{16}O_3S_2$	6,16 s	–	–
(IIIb)	–	58	122–124	45,86/45,52	5,03/4,82	33,46/33,13	$C_{11}H_{14}O_3S_3$	6,22 s	–	–
(IVa)	76	68	99–101	63,88/64,07	4,83/4,86	15,44/15,53	$C_{11}H_{10}O_2S$	6,61 s	3,06 m	4,33 m
(IVb)	45	14	148–149	50,81/50,94	3,65/3,77	29,97/30,18	$C_9H_8O_2S_2$	6,50 s	3,10 m	4,40 m
(IVc)	64	–	80–82	55,62/55,94	4,85/5,00	26,71/26,67	$C_{11}H_{12}O_2S_2$	6,50 s	3,10 m	4,30 m

ethanol, and the mixture was stirred for 2 h. The alcohol was partially evaporated in vacuo and the ammonium salt was precipitated with ether. The precipitate was filtered, the filtrate was partially evaporated in vacuo, and the residue was chromatographed on Al_2O_3 in a 3:1 benzene—ether mixture to give 1.4 g (68%) of (IVa), mp 99-101° (from ethanol), and 0.34 g (12%) of (IIIa), mp 104-105° (from ethanol).

2-(Thenoylmethylene)-1,3-oxathiolane (IVb). Obtained the same as (IVa) from 2.15 g of (Ib) and 0.78 g of β-mercaptoethanol. Yield of (IVb) 0.95 g (45%) (method A). By method B the yield of (IVb) was 0.29 g (14%).

2-(5-Ethylthenoylmethylene)-1,3-oxathiolane (IVc). Obtained the same as (IVa) from 2.43 g of (Ic) and 0.78 of β-mercaptoethanol by method A; yield 1.49 g (64%).

1-Phenyl-3,3-bis(β-ethanolthio)-2-propen-1-one (IIIa). With vigorous stirring, to a solution of 2.09 g of (Ia) in 50 ml of ethanol were added in drops a solution of 1.56 g of β-mercaptoethanol in 10 ml of ethanol and then 0.5 g of triethylamine, and the mixture was stirred for 1 h at ~20°. The solution was cooled to 0°, and the obtained precipitate was filtered and washed with chilled ethanol to give 1.19 g (42%) of (IIIa), mp 104-105° (from ethanol).

1-(2-Thienyl)-3,3-bis(β-ethanolthio)-2-propen-1-one (IIIb). Obtained the same as (IIIa) from 2.15 g of (Ib) and 1.56 g of β-mercaptoethanol; yield 1.68 g (58%).

Preparation of 2-benzoylmethylene-1,3-oxathiolane (IVa) from 1-Phenyl-3,3-bis(ethanol-B thio)-2-propen-1-one (IIIa). With vigorous stirring, to 1.42 g of (IIIa) in 30 ml of dry $CHCl_3$ was added 1 g of K_2CO_3 and the stirred mixture was refluxed for 2 h. The solution was cooled to 20°, filtered, the filtrate was partially evaporated in vacuo, cooled to 0°, and the precipitate was filtered to give 0.74 g (72%) of (IVa), mp 99-101° (from alcohol).

CONCLUSIONS

A method was developed for obtaining 2-benzoylmethylene-1,3-dithiolanes, which is based on the reaction of α-acetylenic ketones with β-mercaptoethanol.

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