A NEW METHOD OF SYNTHESIZING α,β-UNSATURATED SULFIDES

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One of the most general methods of synthesizing α,β-unsaturated sulfides is nucleophilic addition of thiols to acetylenes [1, 2]. However, this method cannot always be used, since it is connected with using free mercaptans, which are unstable in a number of cases and cannot be isolated. Besides this, the addition of thiols to acetylenes is complicated by a secondary process – free-radical reaction of the thiol with the unsaturated sulfide, which leads to formation of a dithioether; and this lowers the yield of the desired product. It is known that esters of thiol acids form thiols in high yield on hydrolysis [3]. The thiol esters themselves can be prepared simply and in quantitative yields by various methods [3]. Most often thiol acids are used for this purpose; they easily add to various unsaturated compounds [4, 5].

In the present work we report a method of synthesizing α,β-unsaturated sulfides directly from thiolacetates [6]. To do this, the latter compounds are treated with an excess of acetylene in alkaline medium, without isolating the free thiols. Various conditions for carrying out this process were studied in the case of n-heptyl thiolacetate (see below, Table 1). The highest yields of vinyl sulfides were obtained when the reaction was carried out in the temperature range 70-90°, in the presence of 1-1.3 moles of KOH per mole of starting thiolacetate, using dioxane as solvent. In this process the alkali fills a double role: on one hand it causes alcoholysis of the starting thiolacetates to the thiols; on the other, it catalyzes addition of the thiolate ion to acetylene. Using alkyl or cyclohexyl thiolacetates (I-III), and also β-alkoxyethyl thiolacetate (IV) (which were obtained by addition of thiolacetic acid to 1-alkenes [7], cyclohexene [8], or vinyl ether [9], respectively), we succeeded in isolating vinyl sulfides V-VIII in rather high yields

$$\underset{\text{(I)—(IV)}}{RSCOCH_3} \xrightarrow[KOH]{CH_3OH} [RSK] + CH{\equiv}CH \rightarrow \underset{\text{(V)—(VIII)}}{RSCH{=}CH_2}$$

$$R = n\text{-}C_6H_{13}\ \text{(I), (V)},\ n\text{-}C_7H_{15}\ \text{(II), (VI)},\ \text{cyclohexyl}\ \text{(III), (VII)},\ n\text{-}C_6H_{13}O(CH_2)_2\ \text{(IV), (VIII)}$$

An attempt to accomplish a similar reaction with α-alkoxyethyl thiolacetates ended unsuccessfully, apparently because of the instability of the intermediately formed α-alkoxyethanethiols in the alkaline medium [10]. If one uses as starting materials compounds which have several thiolacetate groups in the molecule (for example, 1,2-diacetylthioethane (IX), which is easily formed from vinyl thiolacetate and thiolacetic acid [11]), it is possible to synthesize compounds with several sulfide groups, for example (X)

$$\underset{\text{(IX)}}{CH_3COSCH_2CH_2SCOCH_3} + 2CH{\equiv}CH \xrightarrow[KOH]{CH_3OH} \underset{\text{(X)}}{CH_2{=}CHS(CH_2)_2SCH{=}CH_2}$$

This method was also used to prepare divinyl sulfide derivatives, by taking account of the possibility of the existence of vinyl thiols [12], stabilized in the form of thiolates, as intermediate compounds. Actually, the mixture of cis- and trans-styryl thiolacetates (XI) which is formed on reaction of thiolacetic acid with phenylacetylene [13] gave a mixture of cis- and trans-styryl vinyl sulfides (XII).

$$\underset{\text{(XI)}}{C_6H_5CH{=}CHSCOCH_3} \xrightarrow[KOH]{CH_3OH} [C_6H_5CH{=}CHSK] + CH{\equiv}CH \rightarrow \underset{\text{(XII)}}{C_6H_5CH{=}CHSCH{=}CH_2}$$

It was of interest to extend this method to the synthesis of more complex vinyl sulfides. For example, using a mixture of endo- and exo-epimers of norbornenyl thiolacetates (XIII) [14], we isolated a mixture of the endo- and exo-epimers of vinyl norbornenyl sulfide (XIV). These compounds could not be obtained previously in the Diels-Alder reaction of divinyl sulfide with cyclopentadiene [15].

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TABLE 2

Compound: No.	Compound: Name	Yield, %	bp, °C (p, mm Hg)	d_4^{20}	n_D^{20}	Found, %: C	Found, %: H	Found, %: S	Empirical formula	Calculated, %: C	Calculated, %: H	Calculated, %: S	Infrared spectral data, cm^{-1}: $\nu_{C=C}$	Infrared spectral data, cm^{-1}: $\nu_{SO_2, SO}$
V	Vinyl hexyl sulfide	71	52—53 (4)	—	1,4740	66,42	11,25	21,90	$C_8H_{16}S$	66,58	11,18	22,22	1588	—
VI	Vinyl heptyl sulfide	69	67—68 (4)	0,8668	1,4752	67,95	11,17	20,11	$C_9H_{18}S$	68,30	11,45	20,25	1588	—
VIII	Vinyl hexyloxyethyl sulfide	84	98,5—99,5 (5)	0,9136	1,4715	63,53	10,70	16,89	$C_{10}H_{20}OS$	63,77	10,70	17,02	1590	—
VII	Vinyl cyclohexyl sulfide*	66	50—51 (3)	—	—	—	—	—						
X	1,2-Divinylthioethane	54	63—63,5 (3)	—	1,5662	49,08	6,86	44,07	$C_6H_{10}S_2$	49,27	6,69	43,87	1588	—
XII	Vinyl styryl sulfide	50	107—107,5 (3)	—	1,6395	73,14	6,27	19,89	$C_{10}H_{10}S$	73,03	6,21	19,76	1592	—
XIV	2-Vinylthiobicyclo[2.2.1] heptene-5	59	61,5—62,5 (3)	1,6366	1,5418	70,66	7,95	21,12	$C_9H_{12}S$	70,96	7,94	21,06	1582	—
XV	Vinyl hexyl sulfoxide	80—85	67—68 (0,03)	—	1,4789	—	—	19,70	$C_8H_{16}OS$	—	—	20,00	—	1053, 1070
XVI	Vinyl hexyl sulfone		72—74 (0,02)	—	1,4638	—	—	18,40	$C_8H_{16}O_2S$	—	—	18,21	—	1335, 1140
XVII	Vinyl heptyl sulfoxide		76—78 (0,02)	—	1,4771	—	—	18,59	$C_9H_{18}OS$	—	—	18,39	—	1045, 1070
XVIII	Vinyl cyclohexyl sulfone		80—82 (0,02) mp 52—53	—	—	54,88	8,05	—	$C_8H_{14}O_2S$	55,10	8,10	—	—	1340, 1135

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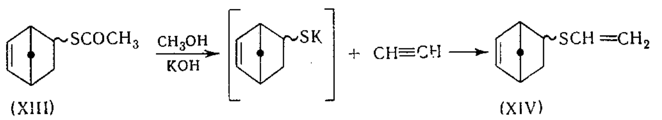
*Literature [16]: bp 69-71° (9 mm); n_D^{25} 1.5094.

TABLE 1. (Heating time in all experiments, 4 h)

Amount, moles: 1-heptyl thiolacetate	Amount, moles: acetylene	Amount, moles: KOH	T., °C	Yield of VI, %
0,03	0,6	0,036	80—90	66
0,03	0,6	0,036	70—72	60
0,03	0,6	0,036	50—60	40
0,05	0,6	0,05	90—95	69
0,03	0,7	0,015	90—95	48



The structure of the compounds synthesized was confirmed by their infrared spectra, and, for some of them, by oxidation to sulfoxides and sulfones.

EXPERIMENTAL

All experiments on synthesis of vinyl sulfides were carried out in a rocking autoclave with addition of hydroquinone.

Vinyl Heptyl Sulfide (VI). Heptyl thiolacetate (II) (8.7 g), 2.8 g of KOH in 15 ml of CH_3OH and 50 ml of dioxane were heated for 4 h with 16 g of acetylene at 90°. The reaction mixture was filtered from precipitated salts and most of the solvents was evaporated; the residue was diluted with ether, washed with water, and dried over Na_2SO_4. The yield of (VI) was 5 g (69%). Yields of (VI) under other conditions are given in Table 1.

All the α,β-unsaturated sulfides (Table 2) were prepared with small deviations from the method described above, starting from the corresponding thiolacetates. Oxidation to sulfoxides or sulfones was carried out by the usual method with concentrated peracetic acid in ether at reduced temperature, using 1 or 2 moles of oxidatant per mole of the unsaturated sulfide as appropriate.

CONCLUSIONS

1. A new method of synthesizing α,β-unsaturated sulfides has been developed, which consists of alkaline cleavage of thiolacetates in the presence of acetylene.

2. Wide applicability of this method has been demonstrated.

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