METHOD FOR SYNTHESIS OF ALKYL VINYL SULFIDES BY THE DIRECT VINYLATION OF THIOLS IN APROTIC DIPOLAR SOLVENTS

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One of the simplest methods for the synthesis of vinyl sulfides is the nucleophilic addition of thiols to acetylene [1-3]. The reaction in accomplished without a solvent or else in dioxane medium at 70-130°C in an autoclave under pressure. Under these conditions the process is complicated by the side reaction of the free-radical addition of the thiol to the unsaturated sulfide, which lowers the yield of the main product. In the present paper is reported a method for the synthesis of aliphatic vinyl sulfides by the vinylation of alkylthiols in active dipolar aprotic solvents like hexamethylphosphoric triamide (HMPT) or dimethyl sulfoxide (DMSO)

$$RSH + CH \equiv CH \rightarrow RSCH=CH_2$$

R = C_2H_5, n-C_4H_9, n-C_8H_{17}, n-$C_{12}H_{25}$, t-C_4H_9; i-C_3H_7.

It is known that such solvents substantially accelerate many nucleophilic processes [4-5]. However, up to now they were not used to accelerate the nucleophilic addition of thiols to acetylene.* It was shown in [7] that the use of these solvents leads to a reduction in the temperature of the reaction for the vinylation of thiols by ~70-80°, which should correspond to an increase of at least 2 orders of magnitude in the reaction rate. Due to the high solubility of acetylene in HMPT and DMSO the possibility is created of running the process at a minimum temperature and pressure not only in a steel autoclave, but also in a glass apparatus at atmospheric pressure. The optimum reaction conditions depend on the nucleophilicity of the employed thiols. Thus, primary thiols give quite high yields of the vinyl sulfides at temperatures of 10-20°, while secondary and tertiary thiols react with acetylene only at temperatures of the order of 30-40°. As a catalyst for primary thiols can be used KOH, NaOH, or the thiolates of the corresponding thiols, in an amount of 10-20 mole %. Secondary and tertiary thiols add smoothly to acetylene only in the presence of the previously prepared thiolates of the employed thiols (Table 1). The side processes of forming 1,2-dithio ethers are practically not observed when the reaction is run in HMPT or DMSO. Besides this, the vinyl sulfides do not form azeotropic mixtures with the indicated solvents, and consequently the low-boiling members of this series can be isolated directly from the reaction mixtures by distillation.

As a result, the use of aprotic dipolar solvents greatly simplifies the synthesis of alkyl vinyl sulfides and makes it easy to run the process under laboratory conditions. However, the attempt to effect the vinylation of thiolacetic acid in either HMPT or DMSO solution, the same as previously [8] and under other conditions, ended in failure. Thiolacetic acid fails to add to acetylene at low temperature (–10, 0°), while instead of vinyl thiolacetate a mixture of tarry products is formed at higher temperature (40-50°).

EXPERIMENTAL

All of the thiols were freshly distilled prior to use. The constants of the obtained vinyl sulfides (see Table 1) agreed with the literature data. The purity of the vinyl sulfides was checked by GLC using a

* To be sure, it is known [6] that replacing ethanol by N,N-dimethylformamide causes an acceleration of the reaction for the addition of p-thiocresol to phenylacetylene by approximately 15 times.

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TABLE 1

Expt. No.	Thiols	Taken, M			T, °C	Solvent, ml		Yield, %
		thiol	KOH	sodium thiolate		HMPT	DMSO	
1	Ethanethiol*	1,00	0,200	—	20	200	—	85,0
2	Butanethiol†	0,09	—	0,009	10—20	40	—	90,0
3	"	0,05	0,005	—	10—20	—	40	68,0
4	"	0,07	0,007 (NaOH)	—	20	—	40	74,0
5	"	0,10	0,005	—	20	50	—	60,0
6	n-Octanethiol*	0,10	0,010	—	10—20	50	—	70,0
7	n-Dodecanethiol†	0,05	—	0,005	10—20	50	—	68,0
8	2-Propanethiol*	0,10	—	0,010	40	40	—	66,0
9	2-Methyl-2-propanethiol	0,07	—	0,007	30	54	—	78,0

*Expt. 1 was run in a 1-liter flask, and Expts. 4-5 in 8.9-0.5-liter [sic] flasks.
†The experiments were run in a glass flask.

KhT-63 chromatograph 10% poly(neopentylglycol succinate) deposited on Chromosorb W (80-100 mesh) as the stationary phase, and temperatures of 80-150°.

With stirring, a solution of 0.005-0.01 mole of the catalyst in 40-50 ml of either HMPT or DMSO in a flask was saturated with acetylene at 10-20°, and then, without stopping the acetylene addition, a solution of 0.05-0.1 mole of the thiol in 10-15 ml of the solvent was added in drops. The stirring and acetylene addition were continued for 1 h. The low-boiling vinyl sulfides were separated by direct distillation from the reaction mixture. In order to obtain the high-boiling vinyl sulfides the reaction mixture was diluted with ether, washed with water, dried over Na_2SO_4, and distilled.

In a rotated steel autoclave were placed 0.05-1 mole of the thiol, 0.005-0.2 mole of the catalyst, and 40-200 ml of either HMPT or DMSO. The mixture was repeatedly saturated with acetylene at room temperature until a constant pressure of at least 10-12 gauge was retained. At the end of saturation the stirring at room temperature, or at 30-40°, was continued for 1 h. The vinyl sulfides were isolated as described above.

CONCLUSIONS

A method was developed for the synthesis of vinyl alkyl sulfides by the nucleophilic addition of thiols to acetylene in aprotic dipolar solvents, like hexamethylphosphoric triamide and dimethyl sulfoxide.

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