ADDITION OF HYDROGEN SULFIDE AND MERCAPTANS TO β,β-DIMETHYLVINYL VINYL KETONE

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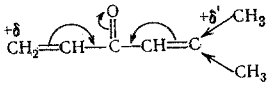
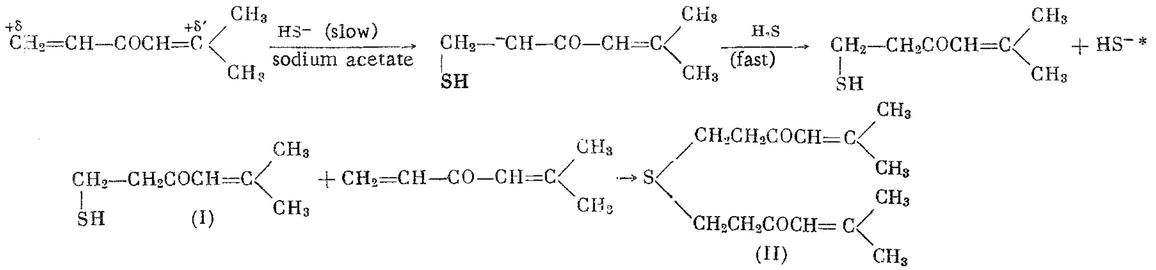
The question of the manner in which H_2S and mercaptans add to β,β-dialkylvinyl vinyl ketones has theoretical importance for the synthesis of substituted bicyclic sulfides by the addition of hydrogen sulfide to ketodienes, having double bonds that are conjugated with the carbonyl group.

On the basis of theoretical considerations, a careful analysis of the experimental data obtained in the study by Nazarov and Kuznetsova [1], and our experiments, we came to the conclusion that the direction indicated by the authors of [1] for the addition of hydrogen sulfide and mercaptans to β,β-dimethylvinyl vinyl ketone is incorrect. Nucleophilic attack of the double bond, the electron density of which is low due to conjugation with the CO group, occurs in the presence of alkaline catalysts (sodium acetate). The electron density of the double bond in the substituted vinyl group is high due to the +I-effect of the two methyl groups (i.e., $+\delta > +\delta'$). Consequently, the addition of KOH, HOH, HCN, etc., should take place at the unsubstituted vinyl group, where attack by the RO^-, OH^-, or CN^- anion is made easier, which was observed by Nazarov and co-workers [2-8].



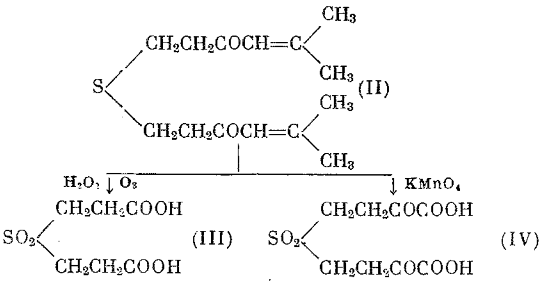
The nucleophilic addition of hydrogen sulfide or mercaptans to β,β-dimethylvinyl vinyl ketone should go in the same manner as the addition of water and alcohols to the unsubstituted vinyl group.



$$\overset{+\delta}{C}H_2{=}CH{-}COCH{=}\overset{+\delta'}{C}(CH_3)_2 \xrightarrow[\text{sodium acetate}]{HS^-\ (\text{slow})} \underset{SH}{CH_2}{-}{}^{-}CH{-}CO{-}CH{=}C(CH_3)_2 \xrightarrow[(\text{fast})]{H_2S} \underset{SH}{CH_2}{-}CH_2COCH{=}C(CH_3)_2 + HS^{-}\,{}^{*}$$

$$\underset{SH}{CH_2}{-}CH_2COCH{=}C(CH_3)_2\ (\text{I}) + CH_2{=}CH{-}CO{-}CH{=}C(CH_3)_2 \rightarrow S[CH_2CH_2COCH{=}C(CH_3)_2]_2\ (\text{II})$$

The oxidation of sulfide (II) can be expected to yield the following compounds.



$$S[CH_2CH_2COCH{=}C(CH_3)_2]_2\ (\text{II}) \xrightarrow{H_2O_2,\ O_3} SO_2(CH_2CH_2COOH)_2\ (\text{III});\qquad \xrightarrow{KMnO_4} SO_2(CH_2CH_2COCOOH)_2\ (\text{IV})$$

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* According to [9], the nucleophilic addition of mercaptans has an anionic-chain character, for example:

$$CH_2{=}CH{-}COOCH_3 + RS^- \xrightarrow[\text{catalyst}]{\text{alkaline}} RSCH_2\bar{C}HCOOCH_3$$

$$RSCH_2\bar{C}HCOOCH_3 + RSH \rightarrow RSCH_2CH_2COOCH_3 + RS^-$$

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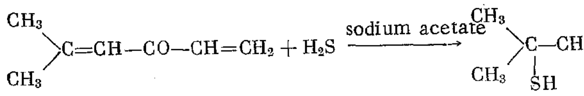
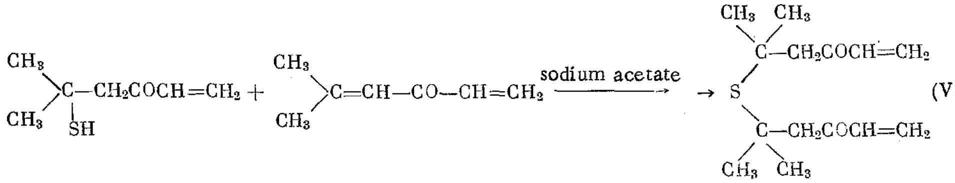
The dibasic β,β'-sulfonyldipropionic acid (III) of composition $C_6H_{10}O_6S$ is known; according to [10-11], it melts at 224° and can be recrystallized from water.

It was shown in [1] that the addition of hydrogen sulfide to β,β-dimethylvinyl vinyl ketone (at 0°, in the presence of sodium acetate) goes exclusively at the substituted vinyl group.



$$(CH_3)_2C{=}CH{-}CO{-}CH{=}CH_2 + H_2S \xrightarrow{\text{sodium acetate}} (CH_3)_2C(SH){-}CH_2COCH{=}CH_2 \quad \text{(V)}$$

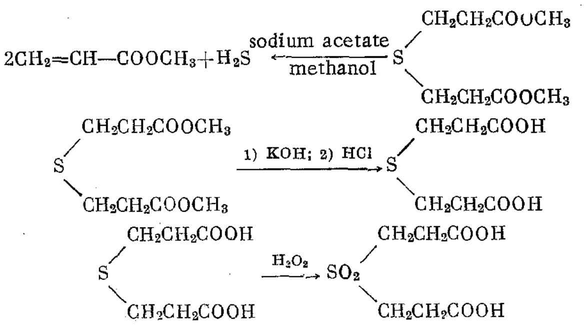
The formed mercaptan (V) can react with a second molecule of β,β-dimethylvinyl vinyl ketone, giving sulfide (VI).



$$(CH_3)_2C(SH){-}CH_2COCH{=}CH_2 + (CH_3)_2C{=}CH{-}CO{-}CH{=}CH_2 \xrightarrow{\text{sodium acetate}} S[C(CH_3)_2{-}CH_2COCH{=}CH_2]_2 \quad \text{(VI)}$$

The authors of [1] proved the manner in which hydrogen sulfide and mercaptans add by the destructive oxidation of the sulfide. The conclusion that the unsubstituted vinyl group was present in the investigated sulfide was based mainly on the detection of formic acid (when the sulfide was ozonized) and the absence of acetone when the sulfide was oxidized with potassium permanganate [1]. The authors of [1] indicate the detection of β,β-dimethylvinyl vinyl ketone in the ozonization products of the sulfide. This testifies to the decomposition of the investigated sulfide with the liberation of the starting ketone. Consequently, the formic acid could have formed from the β,β-dimethylvinyl vinyl ketone and a conclusion regarding the structure of sulfide (VI) cannot be made on the basis of the yield of HCOOH. The material balance in the oxidation experiment with potassium permanganate was unsatisfactory, for which reason a small amount of acetone could have remained undetected. When the authors of [1] oxidized the sulfide with hydrogen peroxide they isolated a dibasic acid of composition $C_6H_{10}O_6S$ (48% of theory), which after recrystallization from alcohol melted at 222-223°. This compound was assumed to be α-keto-γ-sulfoisocaproic acid (VII) (previously unknown). However, based on its chemical nature this acid should not be capable of recrystallization from alcohol, and even more so have such a high melting point.* We do not know of any cases where dialkyl sulfides are oxidized to sulfonic acids using H_2O_2. Actually, the authors of [1] obtained the above mentioned β,β'-sulfonyldipropionic acid (III). This conclusion was verified by us experimentally.

An oil, from which a crystalline product cannot be isolated, is formed when hydrogen sulfide is passed for 10 h into a refluxing acetone solution of β,β-dimethylvinyl vinyl ketone, containing a small amount of sodium acetate (under the conditions indicated in [1]). However, when hydrogen sulfide is passed in for 8 min the reaction goes normally and leads to the crystalline sulfide in good yield. The oxidation of this substance with hydrogen peroxide in acetic acid solution gives β,β'-sulfonyldipropionic acid, which melts at 221-222°, and does not depress the mixed melting point with authentic β,β'-sulfonyldipropionic acid. The latter was obtained by us from methyl acrylate by the scheme:



$$2CH_2{=}CH{-}COOCH_3 + H_2S \xrightarrow[\text{methanol}]{\text{sodium acetate}} S(CH_2CH_2COOCH_3)_2$$

$$S(CH_2CH_2COOCH_3)_2 \xrightarrow{\text{1) KOH; 2) HCl}} S(CH_2CH_2COOH)_2$$

$$S(CH_2CH_2COOH)_2 \xrightarrow{H_2O_2} SO_2(CH_2CH_2COOH)_2$$

The addition of hydrogen sulfide goes quite completely in the presence of a catalytic amount of sodium acetate when hydrogen sulfide is passed into a refluxing methanol solution of methyl acrylate for 30 min; the addition of a large amount of sodium acetate (100 g per 150 g of methyl acrylate) and the passage of

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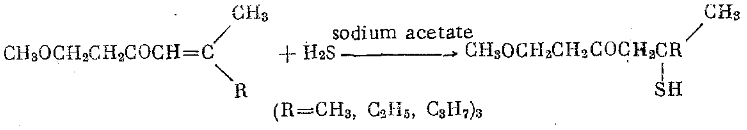
* For example, decanesulfonic acid $C_{10}H_{21}SO_3H$ melts at 46° [12].

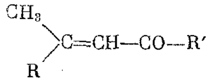
hydrogen sulfide for 25 h, as is suggested in [13], are completely needless. What has been said above indisputably proves the structure of sulfide (II) and the manner in which H_2S adds to the unsubstituted vinyl group of β,β-dimethylvinyl vinyl ketone. According to [14], the addition of H_2S to β,β-dialkylvinyl β'-methoxyethyl ketones, not having an unsubstituted vinyl group, goes with much greater difficulty than to β,β-dimethylvinyl vinyl ketone.



$$\mathrm{CH_3OCH_2CH_2COCH{=}C(CH_3)R + H_2S \xrightarrow{\text{sodium acetate}} CH_3OCH_2CH_2COCH_2CR(CH_3)(SH)}$$

$(R{=}CH_3,\ C_2H_5,\ C_3H_7)_3$

The authors of [14] indicate that the unsubstituted vinyl group in β,β-dialkylvinyl vinyl ketones accelerates addition to the substituted vinyl group. Actually, the low reactivity of compounds of the type



$$\mathrm{(CH_3)(R)C{=}CH{-}CO{-}R'}$$

toward the nucleophilic addition of H_2S or mercaptans (and even more so, secondary and tertiary mercaptans) is explained simply by the presence of the substituted vinyl group, with a high electron density of the double bond, making attack by HS^- or RS^- difficult.

EXPERIMENTAL

Preparation of β,β-Dimethylvinyl Vinyl Ketone.* A mixture of 62 g of dimethylamine hydrochloride, 18 g of paraform, 49 g of mesityl oxide, 50 ml of ethanol, 1 g of hydroquinone and 0.5 ml of concentrated HCl solution was heated under reflux for 15 min in a flask fitted with a stirrer. The reaction mixture became completely clear; then the reflux condenser was replaced by a descending condenser and most of the ethanol was vacuum-distilled (30 mm), with heating on the water bath (85°). The residue was treated with 30 ml of water, and the obtained solution of the salt of the Mannich base was added quite rapidly (in 30 min), in drops, with vigorous stirring, to 80 ml of dibutyl phthalate, heated in vacuo (10 mm) at 160-170° (the thermometer was immersed in the liquid).

The receiver was cooled in a mixture of ice and salt. To the distillate was added anhydrous sodium acetate, and the upper organic layer was separated; the sodium sulfate precipitate was rinsed several times with ether and the ether extracts were added to the main substance. 0.5 ml of acetic acid and 0.5 g of hydroquinone were added to the ether solution, and the ether was distilled under a slight vacuum, with heating on the water bath (60-65°). The residue was vacuum-distilled. We obtained 24 g (43.7% of theory) of β,β-dimethylvinyl vinyl ketone as a greenish liquid, bp 57-61° (20 mm). Redistillation gave a product with bp 56-57° (20 mm); n_D^{20} 1.4833; d_4^{20} 0.8869. Literature data [16]: bp 57° (20 mm); n_D^{15} 1.4823; [15]: bp 60-61° (22 mm); n_D^{20} 1.4750; d_4^{20} 0.9050.

Preparation of bis-(5-Methyl-4-hexen-3-one) Sulfide (II). To a solution of 9.5 g of β,β-dimethylvinyl vinyl ketone in 60 ml of acetone was added a solution of 0.2 g of sodium acetate in 2 ml of water, and then hydrogen sulfide was passed into the refluxing solution for 8 min. The end of reaction was determined by the solution losing its yellow color. The acetone was distilled off, the residue was diluted with ether, a small amount of anhydrous sodium sulfate was added, the mixture was filtered, and the ether was vacuum-distilled (3 mm) from the filtrate, with heating on the water bath. We obtained 9.7 g of a light-colored oil; the substance crystallized completely when cooled in ice. The material was rubbed well with hexane, cooled in ice, and the snow-white crystals were filtered. We obtained 6.7 g (61% of theory) of sulfide (IV), mp 37-38°. Found %: S 12.64. $C_{14}H_{22}O_2S$. Calculated %: S 12.61. Literature data [1]: mp 39.5-40°.

Oxidation of bis-(5-Methyl-4-hexen-3-one) Sulfide (II) with Hydrogen Peroxide. To a solution of 2.0 g of sulfide (II) in 10 ml of acetic acid was added 10 ml of perhydrol (29%). After seven days the mixture was cooled in ice, and the white crystalline precipitate was filtered and washed on the filter with ethanol and then hexane. We obtained 0.74 g (44.8% of theory) of β,β'-sulfonyldipropionic acid, mp 221-223°. After recrystallization from ethanol the substance melted at 221-222° and did not depress the mixed melting point with authentic β,β'-sulfonyldipropionic acid. Found %: S 15.02. $C_6H_{10}O_6S$. Calculated %: S 15.26. Literature data [10, 11]: mp 224°.

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* By a modification of the method given in [15].

Preparation of Dimethyl Ester of β,β'-Thiodipropionic Acid. To a solution of 18.4 g of methyl acrylate in 80 ml of methanol was added a solution of 1 g of sodium acetate in 1 ml of water, and then hydrogen sulfide was passed into the refluxing solution for 30 min. After this the methanol was distilled off (at the end — under vacuum), the residue was diluted with ether, a small amount of anhydrous sodium sulfate was added, the mixture was filtered, the ether was distilled off, and the residue was vacuum-distilled. We obtained 16.9 g (77% of theory) of the dimethyl ester of β,β'-thiodipropionic acid as a colorless oil, bp 107° (1 mm); (5 mm); n_D^{20} 1.4750; d_4^{20} 1.1569. Found %: S 15.64; MR 50.19. $C_8H_{14}O_4S$. Calculated %: S 15.55; MR 50.21. Literature data [13]: bp 138-139° (6 mm); n_D^{25} 1.4713; [17]: n_D^{20} 1.4750; d_{20}^{20} 1.156.

Preparation of β,β'-Thiodipropionic Acid. 24.3 g of the dimethyl ester of β,β'-thiodipropionic acid was heated under reflux with a solution of 14 g of KOH in 100 ml of methanol for 2 h. The methanol was vacuum-distilled, with heating on the water bath, and the residue was treated with 50 ml of water and then acidified with concentrated HCl solution (about 25 ml). The water was vacuum-distilled, with heating on the water bath, and the residue was extracted 4 times with hot toluene. Crystals deposited when the toluene was cooled, which were filtered and washed with hexane. We obtained 12.0 g (57% of theory) of β,β'-thiodipropionic acid, mp 125-127°. After recrystallization from toluene the substance melted at 126-128°. Found %: S 17.48. $C_6H_{10}O_4S$. Calculated %: S 17.99. Literature data [18]: mp 130-131°.

Preparation of β,β'-Sulfonyldipropionic Acid. 1.8 g of β,β'-thiodipropionic acid was dissolved in 10 ml of hot acetic acid, the solution was cooled somewhat, and then 9 ml of perhydrol (29%) was added to the warm solution. The next day the bulky crystalline precipitate was filtered and washed on the filter with acetic acid, then with benzene, and dried in the air. We obtained 1.7 g (81% of theory) of β,β'-sulfonyldipropionic acid, mp 218-220°. After recrystallization from alcohol the substance melted at 219-220°. Found %: S 15.09. $C_6H_{10}O_6S$. Calculated %: S 15.23. Literature data [10, 11]: mp 224°.

CONCLUSIONS

The nucleophilic addition of hydrogen sulfide or mercaptans to the unsubstituted vinyl group takes place when β,β-dimethylvinyl vinyl ketone is reacted with hydrogen sulfide or mercaptans.

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