HYDROGENATION OF 1-ALKYL(ARYL)THIO-1-BUTEN-3-YNES OVER PALLADIUM CATALYST

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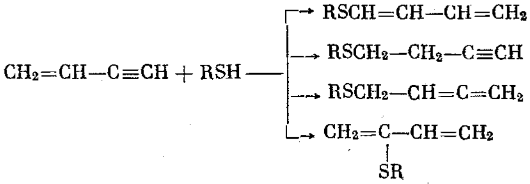
The nucleophilic addition of thiols to vinylacetylene under mild conditions (50-60° in alcohol) leads mainly to the formation of 1-alkyl(aryl)thio-1,3-butadienes and a small amount of other compounds [1]



The separation of these mixtures is quite difficult. A more convenient method for the preparation of the cis-1-alkyl(aryl)thio-1,3-butadienes could be the selective hydrogenation of cis-1-alkyl(aryl)thio-1-buten-3-ynes, which are easily obtained by the stereospecific nucleophilic trans-addition of thiols to diacetylene in alcohol medium [2]

$$RSCH{=}CH{-}C{\equiv}CH \xrightarrow{H_2} RSCH{=}CH{-}CH{=}CH_2$$

In connection with this we investigated the possibility of the selective hydrogenation of the methyl-, tert-butyl- and phenyl-1-buten-3-ynes. At the same time, this synthesis route could be regarded as being a counter synthesis, which corroborates the cis-structure of the alkyl(aryl)thiobutadienes that are formed by the nucleophilic thiylation of vinylacetylene in protonic solvents [1]. For the selective reduction of the acetylenic bond before the double bond it is customary to use either Lindlar catalyst [3] or Raney nickel [4, 5] in the presence of amines. As was shown by Marvell and Tashiro [6], unsaturated compounds in their ease of hydrogenation can be arranged in the following order: $R-C\equiv CH > R-C\equiv C-R > R-C=CH_2 > R-CH=CH-R$. The same authors [6], and also Crombie and co-workers [7], employed selective semireduction of the acetylene bond for the preparation of certain dienes and trienes from the corresponding enyne and dienyne compounds. There is little information in the literature on the catalytic hydrogenation of unsaturated sulfides [8, 9].

By means of preliminary experiments it was established that the hydrogenation of alkylthiobutenynes over Lindlar catalyst proceeds at an extremely slow rate (in the presence of 200 mg of catalyst, a total of only 0.4 mole of hydrogen, when based on one bond, is absorbed in 6 h). The more active and stable palladium catalyst, obtained by the reduction of palladium chloride with sodium borohydride as described in [10], proved to be especially suitable. Although the catalyst is poisoned and the reduction rate of repetitive samples of the alkylthiobutenyne decreases when 1-alkylthiobutenynes are hydrogenated completely to the sulfides, this poisoning has a reversible character. After washing the catalyst several times with methanol the rate of hydrogenation on it, for example, of cyclohexene (as a standard) gradually reaches nearly its initial value. The hydrogenation was run at room temperature and atmospheric pressure in methanol solution. The course of the reaction was followed via the GLC analysis of individual samples, which were taken

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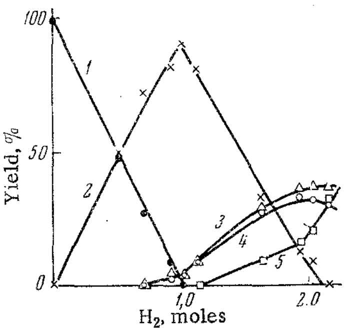

Fig.1

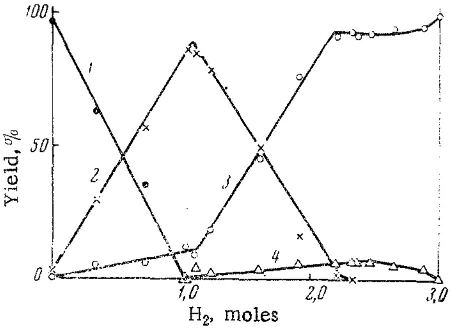

Fig.2

Fig.1. Composition of catalyzate during the hydrogenation of cis-1-methylthio-1-buten-3-yne: 1) cis-1-methylthio-1-buten-3-yne; 2) cis-1-methylthio-1,3-butadiene; 3) and 4) cis-trans-1-methylthio-1-butene; 5) methyl butyl sulfide.

Fig.2. Composition of catalyzate during the hydrogenation of cis-1-tert-butylthio-1-buten-3-yne: 1) cis-1-tert-butylthio-1-buten-3-yne; 2) 1-tert-butylthio-1,3-butadiene; 3) 1-tert-butylthio-1-butene and butyl tert-butyl sulfide.

during the hydrogenation process. Curves were constructed on the basis of the obtained data, which characterized the change in the composition of the catalyzate as a function of the amount of added hydrogen.

As can be seen from Figs.1 and 2, the hydrogenation of the triple bond in the cis-methyl- and cis-tert-butylthiobutenynes proceeds quite selectively. After the absorption of 1 mole of H_2 per mole of starting butenyne the reaction mixture contains 85-90% of the diene sulfide, 5-6% of the products of further reduction, and the same amount of the starting compound. However, for the preparative isolation of the 1-alkylthio-1,3-butadienes it is best to stop the hydrogenation after the absorption of 0.85-0.9 mole of hydrogen, where the reaction mixture contains 80-85% of the diene, 3-4% of alkylthiobutenes, and 12-17% of the starting butenyne. The latter compounds can be easily removed by treating the catalyzate with ammoniacal silver complex. The structure of the 1-alkylthio-1,3-butadienes is confirmed by the data of the IR spectra, in which intense bands at 1577 and 1625 cm^{-1} correspond to the conjugated diene grouping; the bands of the deformation vibrations of the cis-thiovinyl hydrogens are also present at 760 cm^{-1}. Based on the GLC data, these compounds are completely identical with the cis-1,3-diene adducts that are obtained under the conditions of the nucleophilic reaction of thiols with vinylacetylene in alcohol medium [1].

Under analogous conditions, from the trans-1-methylthio-1-buten-3-yne that was obtained via the preparative gas-chromatographic partition of a mixture of the cis- and trans-1-methylthiobutenynes [11], was isolated a product that contained 50% of the trans-diene; the other 50% represented the products of the further hydrogenation of the diene. Apparently, the selectivity of reduction of the trans-butenynes is lower than that of the cis-isomers. In the IR spectrum of the obtained mixture the doublet of bands at 1570 and 1620 cm^{-1} corresponds to the 1,3-diene grouping.

The results of the reduction of the pure isomers of the methylthiobutenynes testify to the fact that their hydrogenation is not accompanied by noticeable cis–trans isomerization with respect to the double bond. This is also corroborated by means of special experiments that were run on keeping a mixture of the cis–trans methylthiobutenynes over a hydrogen-saturated Pd – B catalyst in a nitrogen atmosphere. Neither hydrogenation of the triple bond due to the hydrogen of the catalyst nor cis–trans isomerization is observed under these conditions. Analysis of the compounds containing the tert-butylthio group is somewhat difficult, since as yet we have been unable to select the proper GLC conditions for effecting a separation of the corresponding cis- and trans-compounds and the saturated sulfide.

The hydrogenation of cis-1-phenylthio-1-buten-3-yne apparently proceeds in the same manner as in the case of its alkylthio derivatives. Not making a preparative isolation of the products, it was shown by us that the absorption of 1 mole of hydrogen leads to a compound that is chromatographically identical with the cis-1-phenylthio-1,3-butadiene formed during the nucleophilic thiylation of vinylacetylene by thiophenol in alcohol medium [1]. As by-products we also detected compounds that are formed by the further reduction of cis-1-phenylthio-1-buten-3-yne.

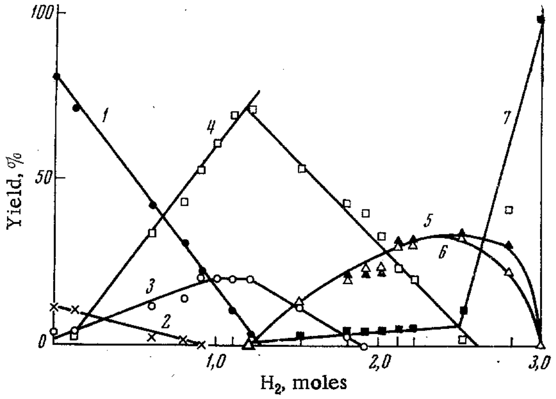

Fig. 3. Composition of catalyzate during the hydrogenation of cis-trans-1-methylthio-1-buten-3-ynes: 1) and 2) cis- and trans-1-methylthio-1-buten-3-ynes; 3) and 4) cis- and trans-1-methylthio-1,3-butadienes; 5) and 6) cis and trans-1-methylthio-1-butenes; 7) methyl butyl sulfide.

As a result, the hydrogenation of the stereoisomeric alkylthiobutenynes over Pd – B catalyst can be considered to be a fairly reliable method for the synthesis of the corresponding stereoisomeric butadiene compounds. The addition of the next molecule of hydrogen to the formed alkylthiobutadienes can lead to the formation of five possible isomers

$$RSCH{=}CH{-}CH{=}CH_2 + H_2 \longrightarrow$$

$\rightarrow RSCH{=}CH{-}CH_2{-}CH_3$ cis- and trans-

$\rightarrow RSCH_2{-}CH{=}CH{-}CH_3$ cis- and trans-

$\rightarrow RSCH_2{-}CH_2{-}CH{=}CH_2$

In the IR spectrum of the products, obtained in the hydrogenation of the cis-butenynes with 2 moles of hydrogen, is absent the doublet of bands in the 3090-3100 cm^{-1} region that is characteristic for the $=CH_2$ group, which excludes the presence of the 1-alkylthio-3-butene in the reaction mixture. We also failed to detect the 1-alkylthio-2-butene (C = C frequency in the IR spectrum at 1670 cm^{-1}) in the reaction mixtures, which was synthesized by us for chromatographic comparison both by the procedure given in [12]:

$$CH_2{=}CH{-}CH{=}CH_2 + RSH \xrightarrow{h\nu} RSCH_2{-}CH{=}CH{-}CH_3$$

and by the reduction of the 1-alkylthio-2-butyne [13] over Pd – B catalyst

$$RSCH_2{-}C{\equiv}C{-}CH_3 \xrightarrow{H_2} RSCH_2{-}CH{=}CH{-}CH_3$$
$$R{=}CH_3,\ t\text{-}C_4H_9$$

Both spectroscopically and chromatographically, the hydrogenated mixture proved to be identical with the 1-alkylthio-1-butene that was obtained by counter synthesis from butyraldehyde using the procedure given in [14]

$$CH_3{-}CH_2CH_2CHO + 2RSH \rightarrow CH_3CH_2CH_2CH\,(S_2R) \xrightarrow{-HSR} CH_3CH_2{-}CH{=}CHSR$$
$$R{=}CH_3,\ t\text{-}C_4H_9$$

In the IR spectrum of the 1-alkylthio-1-butene the intense frequency characteristic for the C = C bond had dropped to 1608-1615 cm^{-1}, which is evidently explained by the presence of a sulfur atom in direct proximity to the double bond. As a result, practically only the terminal double bond of the alkylthiobutadienes undergoes reduction under the investigation conditions, while the C = C bond, found attached to the sulfur atom, apparently remains completely untouched. Analogous observations were made in [8] during the hydrogenation of dienes that simultaneously contain RS and Cl attached to one of the double bonds.

From what has been said it follows that when compounds of the type of 1-alkylthio-1-buten-3-ynes are hydrogenated over palladium–boride catalyst the ease of reduction of the multiple bonds decreases in the order: $-C \equiv CH > -CH = CH_2 > -CH = CH - SR$.

Apparently, both in the hydrogenation process (3) and when preparation is by the counter synthesis route (6), approximately equimolar mixtures of the cis- and trans-1-alkylthio-1-butenes are formed, since the chromatograms of the 1-methylthio-1-butene obtained by the two methods each have two peaks of approximately the same magnitude. These same two compounds, but now in different ratios, are formed when trans-1-methylthio-1-buten-3-yne is reduced (2). As a result, it is possible to assume that cis– trans isomerization occurs at the step of hydrogenating the 1-alkylthio-1,3-butadienes to the olefin sulfides, which proceeds more profoundly when the cis-product is hydrogenated. A similar phenomenon during the hydrogenation of the trans-alkoxybutadienes was also observed by the authors of [15].

The exhaustive hydrogenation to the saturated sulfides was not studied in detail by us. However, from Figs. 1-3 it is quite obvious that the saturated compounds already appear in the mixture after the absorption of 1 mole of hydrogen.

EXPERIMENTAL

The IR spectra were taken on a UR-10 instrument in a cell with a thickness of 0.026 mm. The liquid reaction products were chromatographed on an LKhM-5 instrument using a 2-meter column, which was filled with poly(ethylene glycol adipate) deposited on Chromosorb W; the carrier gas was helium. The NMR spectra were taken on an RS-60 instrument in CCl_4 solution, using tetramethylsilane as the internal standard. The preparative partition of the cis – trans 1-methylthio-1-buten-3-yne was run on the chromatograph described in [16].

The cis-1-alkyl(aryl)thiobutenynes were obtained by the method indicated in [2, 17].

Catalytic Hydrogenation of 1-Alkylthio-1-buten-3-ynes. A solution of 1.0-1.5 g of the 1-alkylthio-1-buten-3-yne in 20-30 ml of methanol was hydrogenated over 0.15-0.20 g of Pd – B catalyst in a rocking hydrogenation vessel (700 turns per minute) via the addition of hydrogen from a calibrated buret. The quantitative composition of the catalyzate was determined by the GLC method, employing a syringe to remove samples during the course of hydrogenation. The characteristic diagrams, obtained in the hydrogenation of the methyl- and tert-butylthiobutenynes, are shown in Figs. 1-3.

Hydrogenation of Mixed cis – trans-Methylbutenynes in a Nitrogen Atmosphere. The Pd – B catalyst (100 mg) was first saturated with hydrogen for 1 h, after which the hydrogenation vessel was purged with nitrogen and then a solution of 0.71 g of the mixture, having a cis : trans ratio of 9 : 1, in 20 ml of methanol was added. After shaking for 1.5 h in a nitrogen atmosphere the composition of the mixture, on the basis of the chromatographic analysis data, did not change.

Preparative Synthesis of 1-Alkylthio-1,3-butadienes. A solution of 1.5 g of cis-1-methylthio-1-buten-3-yne in 20 ml of methanol, in the presence of 0.15-0.20 g of the catalyst, was saturated with hydrogen until 0.85-0.9 mole per mole of starting compound had been absorbed. Then the reaction was stopped and to the obtained mixture was added 1.0 g of $AgNO_3$ in aqueous ammonia solution. The solution was separated from the precipitate and poured into water; the product was extracted with ether; yield 0.5 g (30%); n_D^{20} 1.5490; d_D^{20} 0.9057. Found: C 59.72; 59.81; H 7.98; 7.99; S 31.69; 31.81%. C_5H_8S. Calculated: C 59.92; H 8.05; S 32.02%.

Under analogous conditions, the diene was obtained from 3.5 g of cis-1-tert-butylthio-1-buten-3-yne; yield 1.1 g (29%); bp 55.5-56° (14 mm); n_D^{20} 1.5125; d_4^{20} 0.8620. Found: C 67.34; 67.45; H 9.86; 9.95; S 22.20; 22.22%. $C_8H_{14}S$. Calculated: C 67.52; H 9.93; S 22.59%.

Butyraldehyde Dimethyl Thioacetal. A mixture of 9.8 g of methyl mercaptan, 7.2 g of freshly distilled butyraldehyde and 0.2 g of p-toluenesulfonic acid was placed in a flask, equipped with a magnetic stirrer and a reflux condenser, cooled with a mixture of dry ice and acetone. The mixture was slowly heated in such a manner that the evaporating methyl mercaptan descended from the reflux condenser in drops. The process was continued until the temperature of the reaction mixture reached 64°.. The upper layer was poured into cold caustic solution and extracted with ether. After drying and distilling off the solvent the product was vacuum-distilled; yield 10.2 g (72%); bp 84-84.5° (13 mm); n_D^{20} 1.5080; d_4^{20} 0.9733. Found: C 47.91; 47.78; H 9.43; 9.34; S 42.29; 42.38%. $C_6H_{14}S_2$. Calculated: C 48.00; H 9.33; S 42.66%.

1-Methylthio-1-butene. A mixture of 8.8 g of butyraldehyde dimethyl thioacetal and a catalytic amount of phosphoric acid was heated in a distillation flask in such a manner that the formed 1-methylthio-1-butene slowly collected in the receiver. The crude product was washed with 0.5 M NaOH solution, then with water, and dried over $MgSO_4$; yield 4.5 g (75%); bp 122-124°; n_D^{20} 1.4812; d_4^{20} 0.8702. Found: C 58.47; 58.61; H 9.90; 9.64; S 30.81; 30.74%. $C_5H_{10}S$. Calculated: C 58.82; H 9.80; S 31.37%. An absorption band at 1610 cm^{-1} is present in the IR spectrum, which is characteristic for a double bond.

Butyraldehyde Di-tert-butyl Thioacetal. The reaction between 21 g of butyraldehyde and 52.5 g of tert-butyl mercaptan in the presence of 0.4 g of p-toluenesulfonic acid was run in the same manner as in the case of the synthesis of the dimethyl thioacetal, but an ordinary reflux condenser was used. The temperature of the reaction mixture was 84°; the yield was 16 g (23%); bp 98.5-100.5° (3 mm); n_D^{20} 1.4830; d_4^{20} 0.9007. Found: C 61.70; 61.74; H 10.98; 11.12; S 26.90; 27.13%. $C_{12}H_{26}S_2$. Calculated: C 61.45; H 11.14; S 27.36%.

1-tert-Butylthio-1-butene. The di-tert-butyl thioacetal of butyraldehyde was treated under the same conditions as in the preparation of 1-methylthio-1-butene. The yield of 1-tert-butylthio-1-butene was 3.1 g (50%); bp 60.5-61° (15 mm); n_D^{20} 1.4670. Found: C 66.99; 67.04; H 11.07; 11.15; S 21.58; 21.67%. $C_8H_{10}S$. Calculated: C 66.58; H 11.18; S 22.23%. An absorption band at 1610 cm^{-1} was detected in the IR spectrum.

1-Methylthio-2-butene. The synthesis was run as described in [12]. Bp 122-123°; n_D^{20} 1.4785. In the IR spectrum, in the absorption region of the double bond, was detected a doublet of bands at 1645 and 1670 cm^{-1}. From [12]: bp 67-68° (100 mm); n_D^{20} 1.4790; in the IR spectrum the double bond is depicted by absorption bands at 1625 and 1655 cm^{-1}.

1-tert-Butylthio-2-butene. The sysnthesis was run as described in [12]. From 13.5 g of tert-butyl mercaptan and 8.1 g of 1,3-butadiene was obtained 2.24 g (11%) of product; bp 66-67° (19 mm); n_D^{25} 1.4650. Found: C 66.74; 66.95; H 11.05; 11.35; S 21.71; 21.78%. $C_8H_{16}S$. Calculated: C 66.66; H 11.11; S 22.22%. In the IR spectrum was detected a weak absorption band of the double bond at 1670 cm^{-1}.

CONCLUSIONS

1. A method was developed for the catalytic hydrogenation of the triple bond in 1-alkyl(aryl)thio-1-buten-3-ynes in order to obtain 1-alkylthio-1,3-butadienes.

2. The most suitable catalyst for the reduction of di-unsaturated sulfides is the Pd – B catalyst.

3. The addition of hydrogen to 1-alkyl(aryl)thio-1,3-butadienes goes in the 3,4 position with the formation of 1-alkyl(aryl)thio-1-butenes.

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