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CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY

# Methods for the Synthesis of γ-Acetopropyl Alcohol

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**Abstract**—The methods for the synthesis of γ-acetopropyl alcohol (APA) used for the production of vitamin $B_1$, antimalarial drugs, and polymers are analyzed. Promising APS synthesis methods are the hydrogenation–hydration of sylvane, the hydrogenation of furfural, and syntheses based on allyl acetate, sodium acetoacetic ester, and γ-butyrolactone.

**Keywords:** γ-acetopropyl alcohol, sylvane, furfural, allyl acetate, preparation methods

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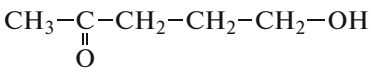
## INTRODUCTION

γ-Acetopropanol (5-hydroxypentan-2-one, 4-ketopentanol, 4-oxopentanol, acetopropanol, APA, (**I**)) is used to obtain thiamine (vitamin $B_1$) and synthesize the aliphatic part of such antimalarial drugs as chloroquine [1, 2], acryquine (mepacrine), plasmoquine, and quinocide [3, 4]. The antimalarial drug chloroquine and derivatives of it have been studied as drugs for treating COVID-19 since 2020 [5, 6].



(**I**)

APA is used to synthesize polymerization initiators in the production of synthetic rubber [7–10], insect pheromones [11], and Laurencion (5-hydroxy-2,3-pentanedione), a red seaweed metabolite [12].

Compound (**I**) was produced at the Salavat Petrochemical Plant (Republic of Bashkortostan) [13], the Belgorod Vitamin Plant [14], and the Akrikhin Pharmaceutical Plant (Staraya Kupavna) in the Soviet Union [15]. APA is now mainly produced in China, not Russia, and this hinders the development of modern pharmaceutical and polymer technologies. The aim of this work was to analyze the procedures and technologies for producing acetopropyl alcohol.

APS synthesis methods can be classified into two groups:

(1) Synthesis from renewable raw materials:

(a) One-stage hydrogenation-hydration of sylvane (α-methylfuran, (**II**)) using a variety of catalysts.

(b) Hydrogenation of furfural to sylvane with subsequent hydrogenation–hydration of the latter according to 1a.

(c) Other possibilities of the catalytic conversion of furfural.

(2) Syntheses from petrochemical raw materials:

(a) Based on allyl acetate.

(b) Based on ethyl acetate.

(c) From γ-butyrolactone.

(d) Other possibilities of obtaining APA from petrochemical raw materials.

## 1. SYNTHESIS FROM RENEWABLE RAW MATERIALS

### *(a) One-Pot Hydrogenation–Hydration of Sylvane*

The hydrogenation–hydration of sylvane in APA according to K.S. Topichev and L.N. Pavlov has been known since the 1930s. It began on an industrial scale at the Salavatsk Petrochemical and Belgorod Vitamin combines in 1972 [13, 14, 19, 20]. The reaction proceeds over 1–5 C–O bonds of sylvane (Fig. 1) through the formation of 2-methyl-4,5-dihydrofuran (dihydrofuran, **III**) [21–24], which in an acid–aqueous medium produces the cyclic form of APA, 2-oxy-2-methyltetrahydrofuran (**IV**) [14, 25–30]:

Subsequent hydrogenation reaction **III** proceeds in anhydrous medium to form a by-product, tetrahydrosylvane (**V**, Fig. 2), the process of complete hydrogenation [26–31].

Acetopropyl alcohol can be synthesized from sylvane in one step. Hydrogenation–hydration is done in enameled batch autoclaves using palladium as a cata-

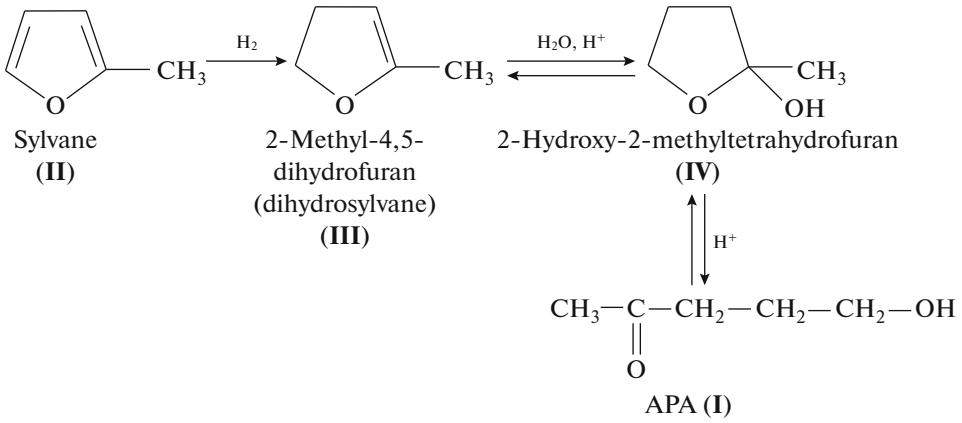



**Fig. 1.** Hydrogenation–hydration of sylvane into APA.

lyst (palladium is introduced into the reactor as palladium(II) chloride in 15–20% aqueous hydrochloric acid solution) at temperatures of 50–60°C. After the autoclave is purged with nitrogen, hydrogen is supplied to the system at a pressure of 5–6 atm. The process takes 9–12 h. The yield of product after neutralization and purification is 40–54 wt %, based on sylvane. After the reaction is compelete, metallic palladium is reduced by hydrogen precipitates, simplifying the regeneration of the expensive metal [13, 19, 20].

Under the conditions of today, technology based on homogeneous catalysts cannot compete with similar ways of producing APA on heterogeneous catalysts, but many of its details could be used to develop modern technology.

Heterogeneous bifunctional catalysts have been proposed for obtaining APA from (**II**), particularly palladium deposited on an acid support. Such catalysts allow us to reduce the acidity and aggressiveness of the medium, facilitate regeneration of the catalyst, and increase the number of cycles of its use [13, 14, 32–40]. A variety of organic solvents have also been introduced into the system to accelerate the dissolution of sylvane.

Table 1 presents data on preparing (**I**) from (**II**) on solid catalysts and organic solvents.

Table 1 shows the maximum yields of (**I**) (75–85 wt %) on solid catalysts are obtained on palladium supported by activated carbon. Palladium catalyst on alumina has greater mechanical strength than carbon catalysts. It is not consumed by the reaction medium, but it does give lower yields of (**I**).

More modern solid acidic carriers (e.g., cesium salts of heteropolyacids or sulfated zirconium oxide) were not used to prepare (**I**) from (**II**).

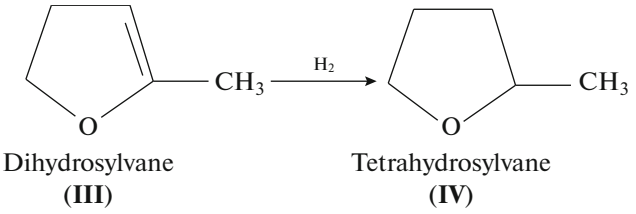



**Fig. 2.** Formation of tetrahydrosylvane as a by-product.

*(b) Hydrogenation of Furfural to Sylvane*

Furfural (**VI**) is a product of the processing of pentosan-containing plant raw materials; it is catalytically hydrogenated through furfuryl alcohol (**VII**) into (**II**) on copper–chromium catalysts at 175–200°C and pressures of 10–20 MPa (Fig. 3) [21, 41, 42].

Technical furfural based on woodworking waste is now being produced at the Kirov Biochemical Plant [43]. Furfural is almost the only raw material to produce sylvane. Different catalysts of hydrogenation are use for its synthesis. Compound (**II**) was synthesized with a yield of 82 wt % on a nickel–chromium catalyst at 210°C [44]; 80–94 wt % of the target product was obtained on copper chromite at the same temperature [24, 45–48], but this catalyst loses its activity and mechanical strength upon overheating. Up to 94–95 wt % of compound (**II**) forms at 250°C from furfural during vapor phase hydrogenation on a copper–chromium–aluminum catalyst (NTK-4) [49].

Zolotarev et al. studied the hydrogenation of (**VI**) into (**II**) in a continuous laboratory plant at 200–250°C on copper–aluminum, copper–aluminum–zinc, and copper–chromium catalysts. The maximum yield (65 wt %) was obtained on copper–aluminum catalyst, and promoting it with zinc and chromium did not result in high yields [14]. Yields of up to 80 wt % sylvane, however, was obtained on copper–aluminum–zinc catalyst during the vapor phase hydrogenation of (**VI**) at 225°C [50].

High yields of (**II**) have been obtained in foreign works during the vapor-phase or liquid-phase hydrogenation of (**VI**). As much as 95 wt % of (**I**) was

**Table 1.** Solid catalysts and organic solvents in synthesis of APA from sylvane

| Catalyst | Conditions | Solvent for sylvane and water | Yield of APA, wt % | Ref. |
|---|---|---|---|---|
| Pd black | 50°C | — | 53 | [17] |
| Pd/C in hydrochloric acid | 40–65°C, 3–7 atm | — | 75 | [32, 33] |
| Pd/C in hydrochloric acid | 25°C, 1.7–2.5 atm, flow reactor | Acetone | 65–75 | [14, 34–36] |
| Pd/C in hydrochloric acid | 25–30 °C, 2.8 atm, pH 6–7 | — | 85 | [37] |
| Pd/C | 25°C, 1.7–2.5 atm, citrate buffer system | — | 73 | [38] |
| Pd/C | 20°C, 0.05–15% of thiazole | — | 61 | [39] |
| Pd/KU-2 | 50–60°C, 0.6 MPa | Acetone | 58 | [40] |
| $Pd/Al_2O_3$(IK-7-1) | 50–60°C, 0.6 MPa | Acetone | 63 | [40] |
| $Pd/Al_2O_3$(IK-7-1) | 60–70°C, 0.2–0.6 MPa, flow reactor | Isopropanol | 70 | [27] |
| Ni–Cr, Ni–Al, Ni–zeolite | Formic acid, 150°C, 75 atm, flow reactor | Dioxane | 30–40 | [14] |
| Ni–kieselgur | Formic acid, 160°C, 11 MPa | Methanol | 34 | [25] |

obtained during the vapor-phase hydrogenation of furfural at 200–250°C on copper chromite [51, 52]; 99.5 wt % was obtained on copper chromite deposited on coal [51–53]; and 98 wt % was obtained on Cu–$Fe/SiO_2$ catalyst [51–54]. The main problem that arises during the operation of such catalysts is their coking, so they must be regenerated.

Liquid-phase hydrogenation of (**VI**) was studied to solve the problem of catalyst coking, but it gives lower yields of a target product than the vapor-phase process. Up to 93 wt % (**II**) was achieved even on ruthenium supported on cobalt oxide in THF [55], while Cu–Fe catalyst allows us to obtain only 51 wt % of a target product in *n*-octane [56].

A variety of heterogeneous mono- and bimetallic catalysts were studied recently to produce (**II**) from (**VI**) via hydrogen transfer catalytic hydrogenation. Similar catalysts include ruthenium [57–60], copper–aluminum [61, 62], copper–nickel [63], copper–palladium [64], and iron–magnesium [65, 66]. The hydrogenation of (**II**) on ruthenium catalysts proceeds at temperatures around 100°C and up to 380°C on less active catalysts. Aliphatic alcohols (methanol, isopropanol, and isobutanol) [57–66] and formic acid [67] were used as hydrogen donors. This avoided having to use explosive hydrogen gas. At the same time, alcohols act as solvents in such systems. A maximum yield of (**II**) (around 94 wt %, calculated according to (**VI**)) was achieved on copper–aluminum catalyst in methanol [61].

### *(c) Other Possibilities for the Catalytic Conversion of Furfural*

An important product of the processing of (**VI**) is pentanediol-1,4. It is widely used as a solvent to produce cosmetics [68], as a monomer to produce elastic polymers similar to spandex, and as a hydrophilic component to synthesize biosurfactants [69]. The hydrogenation–hydration of furfural to pentanediol-1,4 in one stage on ruthenium deposited on mesoporous carbon (Ru-SMK-3) was shown to be possible in [70]. The process is a cascade of hydrogenation and hydration reactions at 80°C that forms (**VII**) and then 1,4-pentanediol with a yield of around 90%. (**I**) forms (41 wt %) when the temperature is reduced to 60°C. It is assumed that (**I**) is an intermediate compound when obtaining pentanediol-1,4 from (**VI**) or (**II**) [70].

A process for converting 1,4-pentanediol to APA on a conventional dehydrogenation catalyst (copper chromite) was patented in [71, 72]. The maximum yield of (**I**) was 63 wt %. There is also the question of the selectivity of dehydrogenation (i.e., the possible ratio of the yields of APA and 4-hydroxypentanal (**VIII**)). The thermodynamic limitations of such a ratio are determined by the equilibrium (Fig. 4).

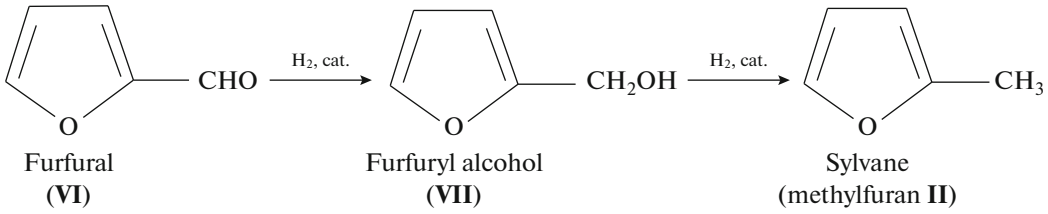



**Fig. 3.** Hydrogenation of furfural to sylvane.

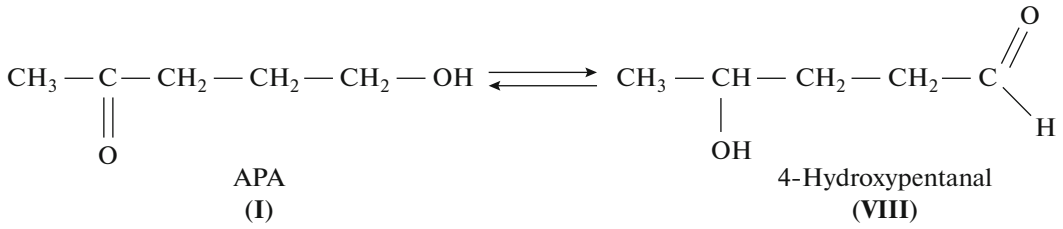



**Fig. 4.** Equilibrium of acetopropyl alcohol and 4-hydroxypentanal.

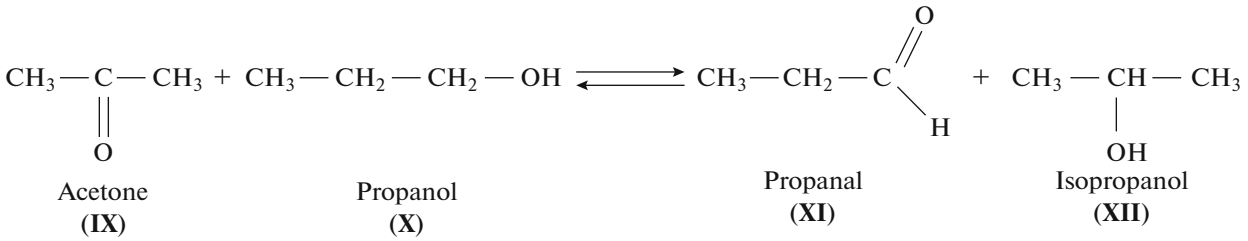



**Fig. 5.** Model reaction for equilibrium (**I**) and (**VIII**).

It can be modeled in the simplest approximation using the reaction in Fig. 5, for which $\Delta G = +9.7$ kJ/mol, which corresponds to equilibrium constant $K \approx 0.02$; i.e., (**I**) is thermodynamically more stable than (**VIII**).

Up to 20 wt % of (**I**) was also obtained in the hydrogenation of (VI) on palladium deposited on nanostructured carbon materials (nanoglobules and nanotubes) at 150°C in an aqueous medium [28–30]. The low yield of APA was probably because of side hydrogenation reactions of the furan ring up to tetrahydrosylvane (**V**) in water and the formation of cyclopentanone (Fig. 6) [28–30] via Piancatelli's rearrangement [73].

Recent study of the kinetics of furfural hydrogenation [74] showed that (**I**) forms from both (**VII**) and (**II**). Similar palladium catalyst on monolithic active carbon gives up to 10 wt % of (I) in water at 180°C [75].

The authors were able to achieve a 98% yield of (**I**) in the reduction of furfural in water at 90°C on 5%Pd–1%Au/$SiO_2$ catalyst, but only in a mixture with products (**III**) and (**IV**) of its cyclization [76].

Ruthenium supported on H-beta zeolite made allowed us to obtain 81% of a target product via hydrogenation of (**VI**) in aqueous solution at 80°C [77].

Table 2 compares the efficiency of hydrogenation processes in water. The results show that (**I**) forms in low yields in the direct one-stage processing of (**VI**) on bifunctional catalysts, and this way of preparing it was described in [70]. Implementing such a single-stage production technology and a three-stage process is difficult, due probably to several factors:

(1) The last stage of hydrolysis of a dihydrofuran ring in (**I**) requires strong acid catalysts, while (**VI**) and (**VII**) are inclined toward side acid–catalytic condensation processes and the formation of levulinic acid.

**Table 2.** Yields of APA in direct hydrogenation of furfural in water

| Catalyst | Conditions | Yield of APA, wt % | Ref. |
|---|---|---|---|
| (Ru-SMK-3) | 60°C | 41 | [70] |
| Pd/C | 150°C, 2.5 MPa $H_2$ | 20 | [28–30] |
| Pd–$TiO_2$ | 180°C, 2.1 MPa $H_2$ | 39% selectivity | [74] |
| Pd/ASM | 180°C | 10% | [75] |
| 5% Pd–1%Au/$SiO_2$ | 90°C, 2.0 MPa $H_2$ | 98% (with tautomer) | [76] |
| Ru/H-beta | 80°C, 1 MPa $H_2$ | 81% selectivity | [77] |

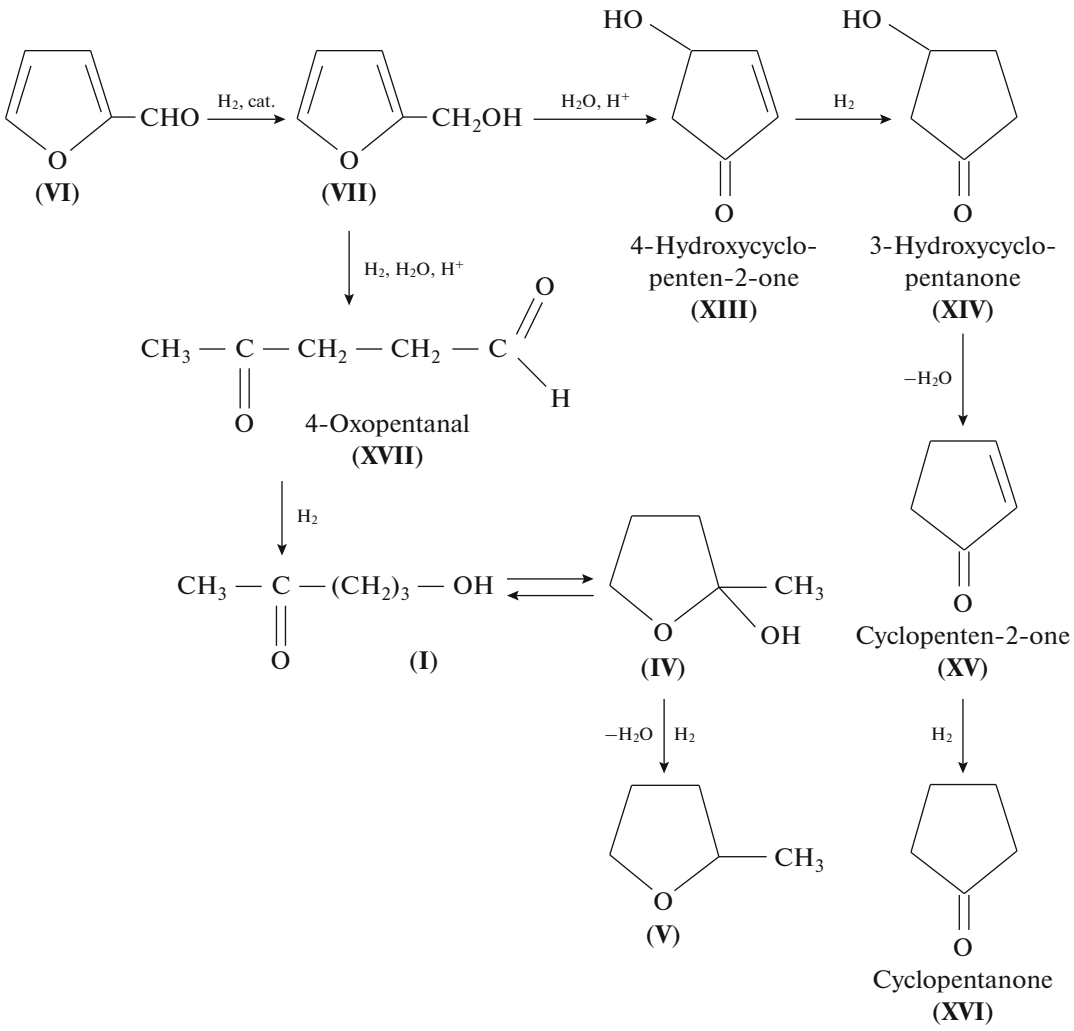



**Fig. 6.** Hydrogenation of furfural in water at 150°C [29].

(2) Industrial processes of the hydrogenation of **(VI)** into **(VII)** and the conversion of the latter into **(I)** proceed at different temperatures: 200 and 60°C, respectively.

(3) Only one double bond of a furan ring should be hydrogenated, and the carbonyl group must undergo hydrogenolysis to form a methyl group and obtain a one-stage process.

(4) It should be noted that the ratio of activities of acidic and hydrogenation components and the selectivity of the latter in the hydrogenation of a ring and a substituent can change during the operation and poisoning of a catalyst in such a process.

(5) A drop in the yields of **(I)** during the hydrogenation of **(VI)** in water is probably caused by the possible cyclization of a target product when using an acid catalyst in **(XVI)** [28–30], and by the formation of an APA tautomer, 2-hydroxy-2-methyltetrahydrofuran **(IV)**.

While these obstacles are serious, they are gradually being overcome. The first obstacle was overcome in converting **(VI)** to 1,4-pentanediol obtained in yields of up to 90% on bifunctional ruthenium catalysts [70]. The second obstacle is mainly due to the industrial hydrogenation of **(VI)** proceeding on low-activity catalysts (e.g., copper–chromium), while conversion is done on much more active palladium catalysts. Ruthenium and palladium catalysts for the hydrogenation of **(VI)** allow us to reduce the temperatures of these processes to the 60–100°C typical of conversion of sylvane [70, 78–80]. The third obstacle has been overcome in many works. For example, oxidized forms of palladium catalyze the hydrogenolysis of oxygen-containing substituents in the hydrogenation of furan compounds, while reduced forms catalyze the hydrogenation of furan rings [78–80].

These obstacles were largely overcome in [70, 76, 77]. Considerable success was achieved in the direct hydrogenation of furfural to acetopropyl alcohol and products **(III)** and **(IV)** of its cyclization (the yields of the mixture were up to 98% at 100% conversion) on

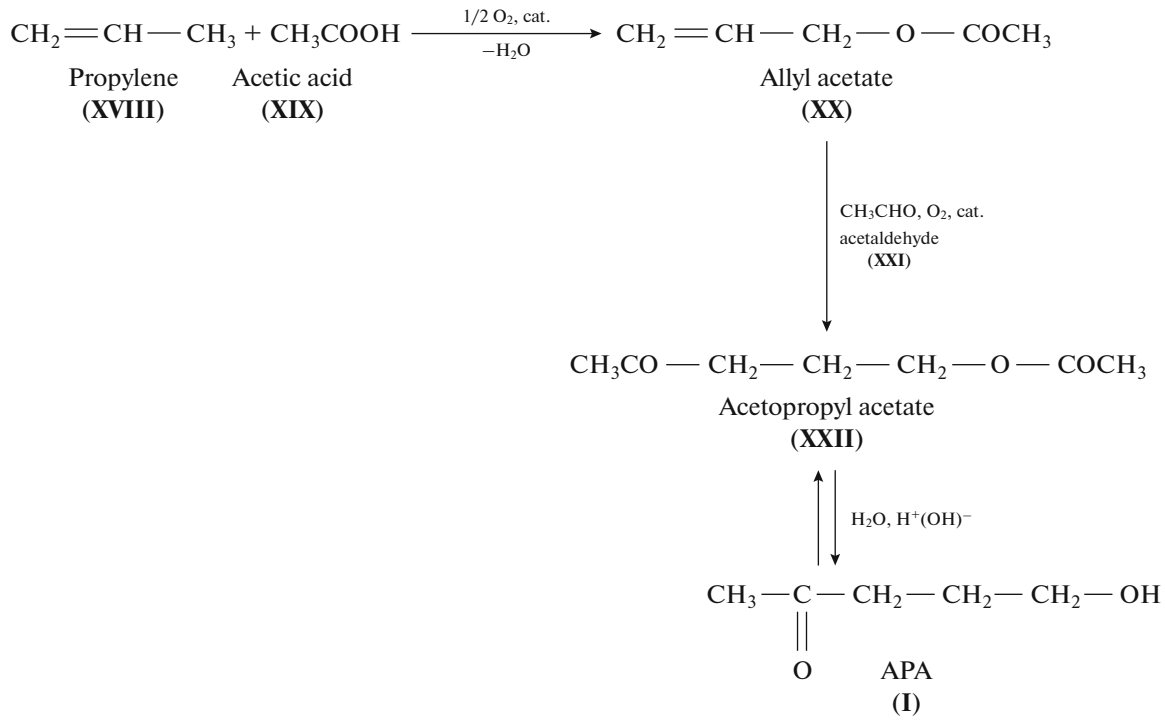



**Fig. 7.** Synthesis of APA from propylene, acetic acid, and acetaldehyde.

5%Pd–1%Au/$SiO_2$ catalyst [76]. High selectivity (81%) of the direct hydrogenation of (**VI**) in water was obtained on a Ru/H-beta catalyst [77], and 40% selectivity of APA was achieved in the hydrogenation of furfural on Pd/$TiO_2$ catalyst [74].

The above results show that processes for the direct processing of furfural into (**I**) have been developed. Over the last 2–3 years, the yields and selectivities of such processes reached values characteristic of the conversion of sylvane.

## 2. SYNTHESIS FROM PETROCHEMICAL RAW MATERIALS

### *(a) Synthesis Based on Allyl Acetate*

The preparation of (**I**) based on allyl ester of acetic acid was developed by Grigoriev et al. [81–83]. A scheme was proposed for preparing (**I**) from petrochemical raw materials (propylene, acetic acid, and acetaldehyde; Fig. 7) with yields of up to 54 wt % of acetopropyl acetate (1-acetoxypentanone-4, **XXII**) per allyl acetate (**XX**). The possibility of one-step synthesis of (**XX**) from high-tonnage products, propylene (**XVIII**) and acetic acid (**XIX**), is well known [84–86].

The free radical acylation of (**XX**) with acetaldehyde to form (**XXII**) (yields of up to 55 wt %) was studied thoroughly by Vinogradov and Nikishina [87–89]. Acylation proceeds at room temperature when using catalytic amounts of cobalt acetate (Fig. 8).

The subsequent conversion of (**XXII**) to (**I**) can proceed via acid or alkaline hydrolysis. Aqueous acid hydrolysis is performed at 80–100°C to form a large amount of wastewater contaminated with salts and organic pollutants. The acid that is used also corrodes the equipment. KU-2-8 sulfonic cationite was therefore proposed as a catalyst for hydrolysis [5]. The yield of APA under these conditions is 47 wt % per (**XX**).

A way of preparing APA via the transesterification of (**XXII**) with $C_8$–$C_{10}$ linear fatty alcohols or diethylene glycol catalyzed by tetrabutoxytitanate or mono-Na-diethylene glycolate was described in the Soviet Union in [90]. APA is produced at 170–205°C, atmospheric pressure, and with nitrogen introduced into the liquid layer of a reactor. The yield of the target product is 85 wt %. The separation of (**I**) from fatty alcohol acetates was not discussed in the patent in [90].

Direct interaction between acetaldehyde and allyl alcohol to form (**I**) is possible [91–93]. The patented process that proceeds at 80–100°C in a sealed glass ampoule when using atmospheric oxygen allowed 96% of a target product to be obtained, but it was not developed further [91].

The authors noted that (**I**) forms in a mixture with 2-methyl-2-(4oxopentyloxy)tetrahydrofuran (**XXV**) and 7-hydroxy-4-hydroxymethylheptanone-2 (**XXVI**) as by-products (Fig. 9) during the photochemical reaction between allyl alcohol (**XXIV**) and acetaldehyde (**XXI**) at −70°C [92, 93].

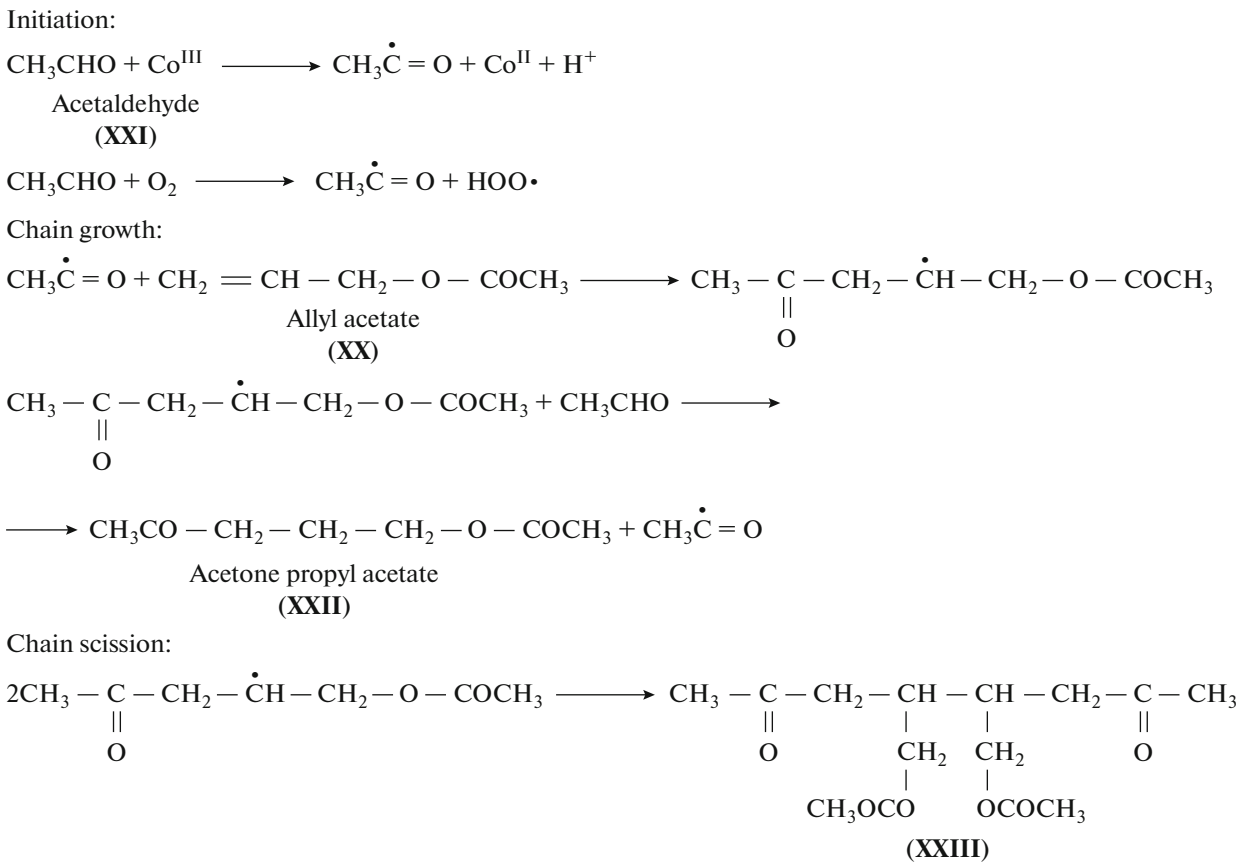



**Fig. 8.** Free radical acylation of allyl acetate.

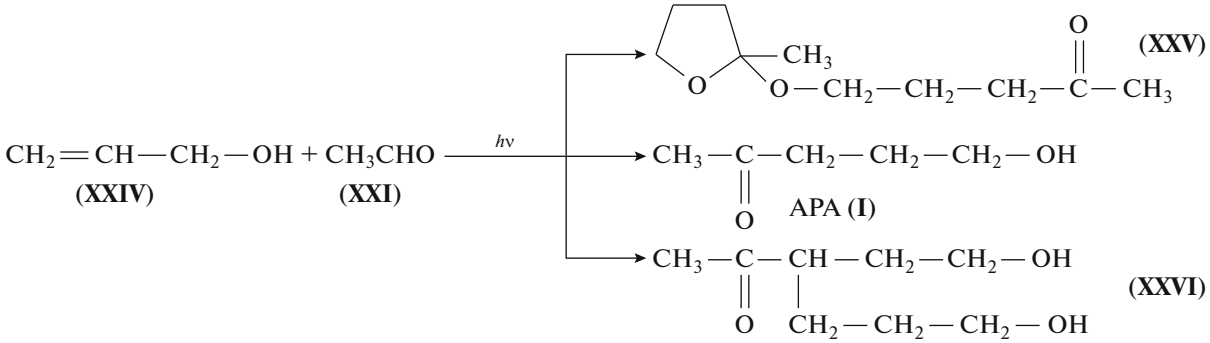



**Fig. 9.** Synthesis of APA from allyl alcohol and acetaldehyde.

The hydroacylation of (**XXIV**) with (**XXI**) was performed in a glass reactor at 60°C in an argon atmosphere [94]. Iron phthalocyanine complex was used as a catalyst. The selectivity of this process was 76% at 62% conversion of (**XXIV**).

The procedure for synthesizing (**I**) from allyl alcohol is very attractive and requires further development to increase the yield of the target product.

Difficulties in the direct synthesis of (**I**) from (**XXIV**) and (**XX**) could be due to possible side reactions of the reagents and intermediates:

(1) The hydrogen atom of the acetaldehyde molecule can detach from two positions of the methyl and carbonyl groups.

(2) A carbonyl radical can be attached at two atoms of a double bond.

(3) When oxygen is used, radicals can join its molecule to form peroxide radicals and other by-products.

(4) By-products form during chain termination through the interaction of radicals, and this contribu-

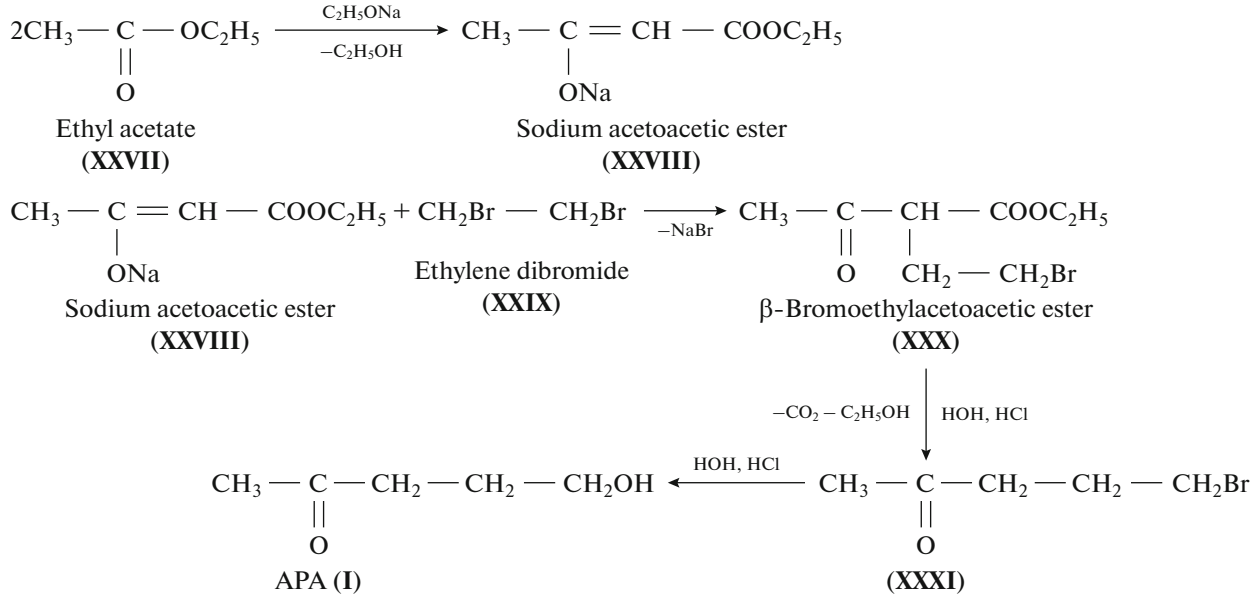



**Fig. 10.** Synthesis of APA based on ethyl acetate.

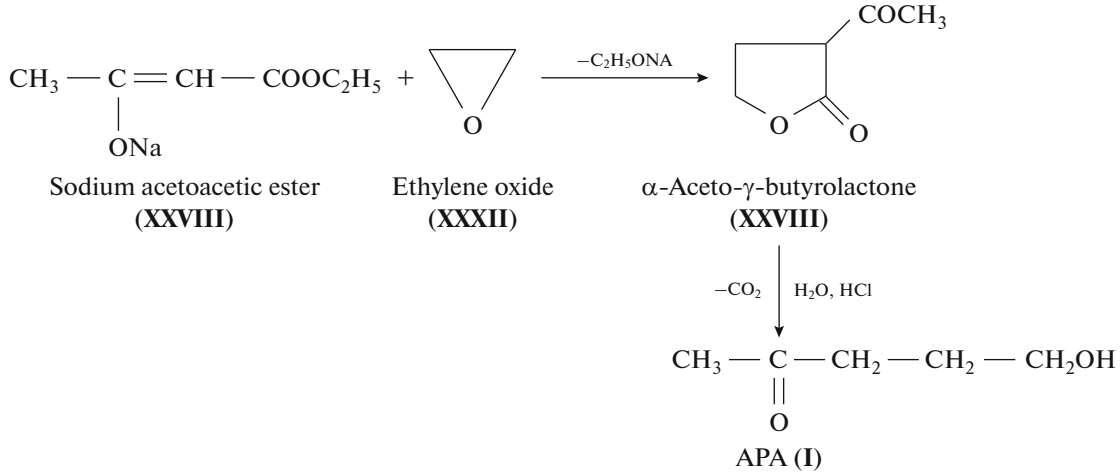



**Fig. 11.** Synthesis of APA based on sodium acetoacetic ester.

tion can be substantial when using short-chain processes.

It is reliably known that C–H bond of a carbonyl carbon is weaker than that of the methyl group only in (1): a $CH_3C•O$ radical is 32–50 kJ/mol stabler than a $•CH_2CHO$ radical [95, 96].

### *(b) Synthesis Based on Ethyl Acetate*

The procedure for obtaining APA through the bromo derivative of acetopropyl acetate (Fig. 10) has been known since the late 1800s and was described by Lipp and Colman [97, 98]. It is based on the action of ethylene dibromide (1,2-dibromoethane, **XXIX**) over 7–8 h at 100°C in absolute ethanol on sodium acetoacetic ester (**XXVIII**) obtained from ethyl acetate via Claisen ester condensation with subsequent hydrolysis of the resulting β-bromoethylacetoacetic ester (**XXX**) using diluted hydrochloric acid.

The yield of the target product is low (no more than 20 wt %), based on (**XXVIII**). This way of obtaining APA has only laboratory applications.

Knunyants et al. proposed a way of preparing (**I**) by treating (**XXVIII**) with ethylene oxide in absolute ethanol for 24 h at 0°C (Fig. 11) [99]. The reaction product (alcoholate) condenses intramolecularly to form the substituted β-hydroxyethylacetoacetic acid lactone (Knunyants lactone, **XXXIII**).

The hydrochloric acid hydrolysis of (**XXXIII**) results in ring opening and decarboxylation of the resulting β-keto acid to form (**I**). This was done on an industrial scale in the 1930s at the Akrikhin plant

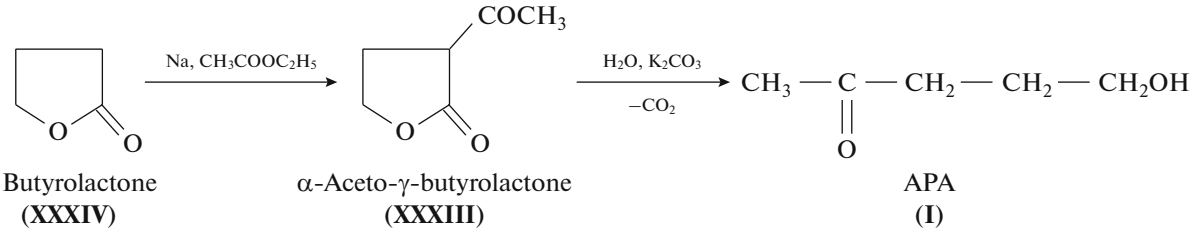



**Fig. 12.** Synthesis of APA from γ-butyrolactone.

(Staraya Kupavna) to synthesize the aliphatic chain of an antimalarial drug of the same name [15, 20]. The yield of APA is low (55 wt %, calculated per (**XXVIII**)), so this technology may not be able to compete with modern means of the catalytic hydrogenation of furfural [76, 77].

### *(c) Synthesis from γ-Butyrolactone*

Another way of preparing (**I**) using Knunyants lactone (**XXVIII**) is based on the condensation of γ-butyrolactone (**XXXIV**) with alkyl acetate when using metallic sodium (Fig. 12) [100]. The resulting (**XXXIII**) is hydrolyzed and decarboxylated in a potassium carbonate solution to form the target product. Compound (**XXXIV**) is prepared via the hydrogenation of maleic anhydride or the dehydrogenation of 1,4-butanediol [101–104]. The yield of (**I**) during the condensation of (**XXXIV**) is 82 wt %.

Sodium alcoholate can be used instead of flammable sodium [105], which reduces the yield of APA to 56 wt %. The authors proposed conducting the condensation of (**XXXIV**) with $C_1$–$C_4$ alkyl acetates and acetic acid at 340–380°C on alumina impregnated with a sodium hydroxide solution, followed by calcination to exclude metallic sodium [106, 107]. The yields of the target product were up to 87 wt % [106].

The condensation of (**XXXIV**) with acetic acid was studied under similar conditions [107]. The selectivity for (**I**) was 71–80% at 60–64% conversion of (**XXXIV**). A disadvantage of the process is the complex distillation

**Table 3.** Preparing APA from petrochemical raw materials

| Starting compounds | Catalyst and conditions | Yield of APA, wt % | Ref. |
|---|---|---|---|
| Allyl acetate | $Co(CH_3COO)_2$ | 47 | [81–83] |
| Allyl alcohol | | | |
| (a) | $O_2$, 80–100°C | 96* | [91] |
| (b) | Irradiation, −70°C | No data | [92, 93] |
| (c) | $Fe_2$[N-b-t-tert-ButPhtc], argon, 60°C | 76 select. | [94] |
| Ethyl acetate | | | |
| (a) Lipp | 100°C, absolute ethanol | 20 | [97, 98] |
| (b) Knunyants | 0°C, absolute ethanol | 55 | [99] |
| γ-Butyrolactone | | | |
| (a) | Na, 50°C | 82 | [100] |
| (b) | $C_2H_5ONa$, 50°C | 56 | [105] |
| (c) | $Al_2O_3$ impregnated with NaOH, 340–380°C | 87* | [106] |
| | $Al_2O_3$ impregnated with MeOH, 390°C | 71–80 select. | [107] |
| Alkynes | $NHC_1$-Au-OTs or $Na[PtCl_2(dmso)(NHC_2)]$ water, 50–80°C | 43 | [108, 109] |
| Carboxylic acids | *Pyrococcus furiosus*, 40°C, 5 barr $H_2$ | 51 | [111] |
| Butanediol-1,4 | $SiW_9A_{l3}$, $H_2O_2$, 90°C | 62 select. | [112, 113] |

* Patent data.
[N-b-t-*tert*-ButPhtc] is N-bridged tetra-*tert*-butyl phthalocyanine.
Me = Na, K, Rb, and Li.
$NHC_1$ = (1,3-bis(2,6-diisopropylphenyl)-imidazolylidene-2.
Ts = tosyl.
$NHC_2$ = *N*-heterocyclic carbene.

**Table 4.** Comparison of ways of obtaining APA

| Raw material | Number of stages | Maximum yields of APA, % | Disadvantages |
|---|---|---|---|
| Sylvane | 1 | 53–85 | Formation of tetrahydrosylvan |
| Furfural | 1 | 40–98 | Formation of furfural condensation products |
| Acetic acid, propylene, and acetaldehyde | 3 | 47 | Multi-stage and complex product isolation |
| Ethyl acetate | | | |
| (a) through bromo derivative | 4 | 20 | Multi-stage and use of Na |
| (b) through natracetoacetic ether and ethylene oxide | 4 | 55 | |
| γ-Butyrolactone, acetic acid | 2 | 40–50 | Complex product isolation |

purification of (**I**) ($T_b$ = 209°C) by removing close-boiling impurities (**XXXIV**) ($T_b$ = 204–206°C) and (**XXII**) ($T_b$ = 211°C). For this reason, (**I**) was dehydrated to (**III**), isolated, and then hydrolyzed to the target product [107]. This disadvantage is observed in other processes to obtain (**I**) through (**XXII**).

### *(d) Other Methods of APA Synthesis from Petrochemical Raw Material*

Methods for the synthesis of (**I**) via the hydration of alkynes [108–110] and carboxylic acids [111] or the oxidation of 1,4-butanediol [112, 113] are also known. However, these are less efficient than the ways described above because of low yields (40–60%) and the difficulty of separating the product from the homogeneous catalysts that are used.

Table 3 shows the possibilities of synthesizing APA from petrochemical raw materials.

## CONCLUSIONS

Table 4 compares the methods for the synthesis of (**I**).

The most attractive methods for the synthesis of (**I**) are the hydrogenation–hydration of sylvane and furfural and syntheses based on allyl acetate and γ-butyrolactone. Other ways are less promising, for a number of reasons.

Allyl acetate and γ-butyrolactone are products of fine organic synthesis. Syntheses of (**I**) on the basis of these compounds are therefore ultimately multi-step and may not be competitive. It should be noted that it is difficult to purify a target product of impurities of (**XXII**), an intermediate product of these processes.

The raw materials for APA synthesis from sylvane are furfural and ultimately renewable plant materials. APA is synthesized in two stages in the furfural–sylvan–APA technological chain. In our opinion, the most promising way of developing the production technology of (**I**) is to combine its two stages into a single-stage hydrogenation–hydration process for the target product. High efficiency was achieved for this approach (yields of products up to 98%) in [74–77]. This approach opens up new possibilities for processing pentosan-containing plant materials into acetopropyl alcohol with high yields.

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