NEW SYNTHESIS OF 1,3,5-HEXATRIENE FROM PIPERYLENE AND FORMALDEHYDE

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4-Propenyl-1,3-dioxane (I), the condensation product of piperylene and formaldehyde [1], can be used to synthesize interesting and practically useful compounds. It was shown previously that the thermocatalytic decomposition of (I) yields methylcyclopentadienes (MCPD) [2]. The conversion of (I) to 1,3,5-hexatriene (II) was studied in the present paper.

EXPERIMENTAL

The reaction products were analyzed by GLC on an LKhM-7M instrument using a programmed temperature in the range 70-230°C, a 300 × 0.4 cm column packed with 13% Silicone E-301 deposited on Chromaton N-AW, and H_2 as the carrier gas.

4-Propenyl-1,3-dioxane (I) (bp 177.5°, n_D^{20} 1.4520, d_4^{20} 0.9837), 4-hexene-1,3-diol (III) (bp 84-85° (4 mm), n_D^{20} 1.4510, d_4^{20} 0.9770), and 2,4-hexadien-1-ol (IV) (bp 67-68° (11 mm), n_D^{20} 1.4950) were synthesized as described in [1, 3, 4] and were 98-99% pure (based on the GLC data).

The thermocatalytic decomposition experiments were run in a 400 × 18 mm reactor of the flow type (catalyst volume = 10 ml), which was placed in an electric furnace. The reaction products were collected in a receiver, cooled with a mixture of ice and NaCl, and after neutralization, drying, and the addition of hydroquinone, were subjected to fractional distillation using a column with an efficiency of 16 theoretical plates. Here we isolated 1,3,5-hexatriene (II) (96% pure, the remainder was MCPD), bp 80°, n_D^{20} 1.5080, d_4^{20} 0.7910, and 2-methyl-5,6-dihydro-(2H)-pyran (V), (99.2% pure), bp 102.5°, n_D^{20} 1.4328, d_4^{20} 0.8794.

The fraction with bp up to 80° was refluxed for 30 h, the undimerized products (mainly piperylene) were distilled off up to 50° (40 mm), and the residue was decomposed by heating up to 170°. Here we isolated a mixture of 63% of 1-methyl- and 37% of 2-methylcyclopentadiene (based on the GLC data), bp 69-75°, n_D^{20} 1.4598, d_4^{20} 0.8180; the adduct with maleic anhydride had mp 50-52°.

It was also established by GLC that the reaction mixture contains a small amount of 2,4-hexadien-1-ol (IV).

DISCUSSION OF RESULTS

The thermocatalytic decomposition of 1,3-dioxanes, containing a methyl, methylene or methine group in the 4 position, leads to acyclic 1,3-dienes. MCPD are formed predominantly when propenyldioxane (I) is passed as a mixture with steam over H_3PO_4, deposited on silica gel [2]. As it proved, on other catalysts (Table 1) (I) forms mainly triene (II), together with MCPD and (V), and also small amounts of (IV) and piperylene.

A possible primary reaction product is diol (III), since its dehydration actually proceeds with the formation of the same compounds as in the thermocatalytic decomposition of (I) (see Table 1). However, we were unable to detect (III) in the conversion products of (I). In addition, triene (II) is formed in lower yield (53.7%) in the dehydration of (III) than in the decomposition of (I) (70.7%). Consequently, dienol (IV) and dihydropyran (V) are more probable primary reaction products. The conversion of (IV) to (II) on dehydration catalysts is known [5]. According to the results obtained by us, (V) when passed together with steam over calcium phosphates forms triene (II) in up to 75% yield, although it reacts with more difficulty than dioxane (I) (see Table 1).

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TABLE 1. Transformation Results of (I), (III), and (V) on Various Catalysts

Catalyst	T, °C	Space velocity h^{-1}	Conversion, %	Yield, % of theory*		
				(II)	MCPD	(V)
4-Propenyl-1,3-dioxane (I)						
KF-70	200	0,42	95,0	69,9	–	3,5
»	250	0,42	97,5	70,7	–	3,2
»	300	0,42	97,4	33,8	12,7	5,0
»	350	0,42	100,0	31,7	16,8	1,1
KDV-15	300	0,42	91,5	62,2	–	2,9
»	350	0,42	96,3	58,7	11,4	1,9
»	400	0,42	100,0	36,3	16,8	0,8
Al_2O_3	250	0,39	85,0	24,4	–	6,8
Aluminosilicate	250	0,42	68,1	25,4	4,1	9,9
Silica gel	300	0,42	73,0	43,1	–	9,1
4-Hexene-1,3-diol (III)						
KF-70	200	1,00	–	33,1	5,7	39,2
»	250	0,45	–	47,3	9,2	25,4
»	250	1,00	–	53,7	8,3	27,3
2-Methyl-5,6-dihydro-(2H)-pyran (V)						
»	250	0,36	49,2	75,0	10,1	–
»	300	0,36	81,0	44,4	19,0	–

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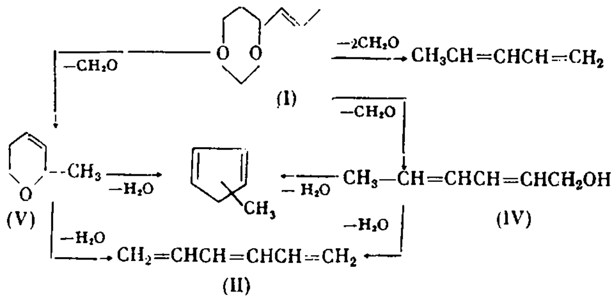
* Based on converted starting product (I), (V) and on taken (III).

The presence of piperylene in the reaction products is evidently the result of the partial cracking of (I).

In view of the obtained data a probable scheme for the thermocatalytic decomposition of (I) is the following:



The thermocatalytic decomposition of (I) on calcium phosphates (KF-70 and KVD-15) gives (II) in up to 70% yield (see Table 1). Compound (II) is formed in lower yield on the other catalysts tested by us, since a substantial part of (I) undergoes cracking.

CONCLUSIONS

1. The thermocatalytic decomposition of 4-propenyl-1,3-dioxane, which supposedly proceeds via the intermediate formation of 2,4-hexadien-1-ol and 2-methyl-5,6-dihydro-(2H)-pyran, leads to 1,3,5-hexatriene and methylcyclopentadienes.

2. The nature of the catalyst exerts the determining effect on the direction of the conversion of 4-propenyl-1,3-dioxane; in particular, when calcium phosphates are used the main reaction product is 1,3,5-hexatriene.

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SULFOOXIDATION OF SATURATED HYDROCARBONS, INITIATED BY OZONE AND HYDROGEN PEROXIDE

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The sulfooxidation of saturated hydrocarbons is the most promising method for the preparation of alkylsulfonic acids.

$$RH + SO_2 + {}^1/_2O_2 \rightarrow RSO_3H$$

The radical-chain character of the reaction stipulates the use of either UV or γ radiation as initiators, and also chemical initiators (Cl_2, O_3, organic peroxides, etc.).

The initiation of the reaction with the ozone—hydrogen peroxide system was studied in the present paper, which system was practically not used previously to initiate chain processes.

The reaction of O_3 with H_2O_2 proceeds with the intermediate formation of free radicals [1].

$$H_2O_2 + O_3 \rightarrow H\dot{O} + H\dot{O}_2 + O_2 \qquad (1)$$

$$H\dot{O}_2 + O_3 \rightarrow H\dot{O} + 2O_2 \qquad (2)$$

$$H\dot{O} + O_3 \rightarrow H\dot{O}_2 + O_2 \qquad (3)$$

$$H\dot{O} + H_2O_2 \rightarrow H\dot{O}_2 + H_2O \qquad (4)$$

The $\dot{O}H$ radicals quickly cleave a H atom from the hydrocarbon ($k_5 \sim 10^9$ liters/mole) [2]

$$RH + \dot{O}H \rightarrow \dot{R} + H_2O \qquad (5)$$

The formed alkyl radical $\dot{R}$ adds SO_2, and then the sulfooxidation goes by the known scheme [3].

In the absence of H_2O_2 the initiation rate is determined by the reaction:

$$RH + O_3 \rightarrow \dot{R} + H\dot{O} + O_2 \qquad (6)$$

When $[RH] \simeq 5$ mole/liter, $k_6 \sim 1 \cdot 10^{-2}$ liter/mole·sec [4], $O_3 \approx 1 \cdot 10^{-4}$ mole/liter in the gas mixture, and $W_i \sim 5 \cdot 10^{-6}$ mole/liter·sec.

The addition of H_2O_2 changes the initiating step, and W_i' in this case is determined by reaction (1), since reaction (5) proceeds with a high rate constant. Assuming k_1 is equal to the rate constant (reaction of ozone with methyl hydroperoxide is 10 liters/mole·sec [5]), $H_2O_2 \approx 1 \cdot 10^{-1}$ mole/liter, we obtain $W_i' \sim 10^{-4}$ mole/liter·sec. As a result, the addition of H_2O_2 to the reaction, with the other conditions kept constant, increases W_i' by ~10 times when $k_5 \cdot [RH] \gg k_3 \cdot [O_3] + k_4 \cdot [H_2O_2]$. The sulfooxidation rate should also increase by the same factor, since the chains are terminated linearly under the experimental conditions [6].

A study of the sulfooxidation rate as a function of the temperature and composition of the gas mixture disclosed that the optimum reaction temperature is 40°C, and the optimum $SO_2:O_2$ ratio = 2. It should be mentioned that clear reaction products are formed in the presence of H_2O_2.

The experimental data, given in Table 1, permit making the following conclusions. Aqueous H_2O_2 solution (without O_3) initiates the sulfooxidation inefficiently (Expts. 3 and 4). In the presence of O_3 the reaction rate depends on the $[H_2O_2]$ in solution, and the optimum amount of H_2O_2 is 0.5- 1 vol.% of the hydrocarbon

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