CATALYTIC REDUCTION OF UNSATURATED KETONES IN A CONTINUOUS REACTOR.

II. HYDROGENATION OF 6,10-DIMETHYL-3,5,9-UNDECATRIEN-2-ONE ON RANEY NICKEL

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UDC 615.356:[577.161.3+
577.161.5].012.1.002.62

The catalytic hydrogenation of three C=C bonds in pseudoionone [6,10-dimethyl-3,5,9-undecatrien-2-one (I)] gave hexahydropseudoionone (II), which is an intermediate product in the synthesis of vitamins E and K_1. The principal mechanisms for carrying out this reaction under batchwise conditions are given in [1-3]. Among the hydrogenation products 5,6-dihydropseudoionone (III), 3,4-dihydropseudoionone (IV), 3,4,5,6-tetrahydropseudoionone (V), and the product from saturation of the carbonyl group, viz. 6,10-dimethylundecan-2-ol (VI) have been determined in addition to (II). In practice the hydrogenation of compounds of this class uses catalysts based on palladium [4] and nickel [5]. Palladium catalysts possess high selectivity for saturating C=C bonds, stability in operation, and good regenerability. The qualities of nickel catalysts are their cheapness, mechanical stability, and the possibility of increasing their selectivity by introducing modifying additives [6-9].

Catalytic reduction of (I) was carried out in liquid phase both at room temperature and above, and at atmospheric or at increased hydrogen pressure. Alcohols C_2–C_5 of normal or iso structure are usually used as solvents.

The sequence of saturating the C=C bonds of pseudoionone depends on the nature of the catalyst and on the conditions of carrying out the reaction. As a rule the 5,6 bond being the last in the chain of a conjugated diene system is saturated first then reduction of the 3,4 bond is saturated last and with great difficulty. Frequently hydrogenation of the carbonyl group accompanies this process. Modifying additives may change the energy state of the catalyst surface and the sequence of saturating the 3,4 and 5,6 bonds [6, 9].

$$\underset{\text{I}}{RC(CH_3)=CHCH=CHCOCH_3} \qquad \underset{\text{III}}{RCH(CH_3)CH_2CH=CHCOCH_3}$$

$$RC(CH_3)=CHCH_2CH_2COCH_3 \qquad \underset{\text{II, V}}{RCH(CH_3)(CH_2)_3COCH_3}$$

$$\text{I, III, IV, V}: R=(CH_2)_2CH=C(CH_3)_2;$$

$$\text{II}: R=(CH_2)_3CH(CH_3)_2.$$

The authors of [6] considered that the addition of cadmium to the catalyst increased the affinity of the carbonyl group for the nickel surface which led to the preferential hydrogenation of the 3,4 bond.

A study of the hydrogenation of (I) was carried out in the proposed work in a continuous reactor on changing temperatures, partial hydrogen pressure, and volume supply rate of (I). A 10% solution of (I) in isopropyl alcohol was hydrogenated with constant bubbling of hydrogen equal to 0.15 liter/min. With the aim of increasing the selectivity of catalyst operation halides of group VIII metals were introduced into the solution in amounts 0.2% of the mass of (I). Additives probably act in two ways, they change the energy of the catalyst surface and protect the carbonyl group by a donor–acceptor mechanism. A description of the equipment, the method of selecting test samples, and the analysis of the obtained hydrogenation products was given in [11]. The obtained results are given in Fig. 1.

The influence of temperature was investigated in the range 30-70°C at a pressure of 2.0 MPa and a volume supply rate of solution of 0.45 h^{-1} (see Fig. 1b). Up to 45-55°C the relative content of (II) rapidly grew and reached a maximum value (87.2-88.3%) then gradually fell as a result of the accumulation of (VI) and at 70°C was 82.3%. Under these conditions (I), (III), and (IV) were absent from the reaction product. The overall curve for

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Kalinin Polytechnic Institute. All-Union Scientific-Research Institute for Vitamins, Moscow. Translated from Khimiko-farmatsevticheskii Zhurnal, Vol. 17, No. 2, pp. 197-199, February, 1983. Original article submitted May 3, 1982.

0091-150X/83/1702-0141$07.50

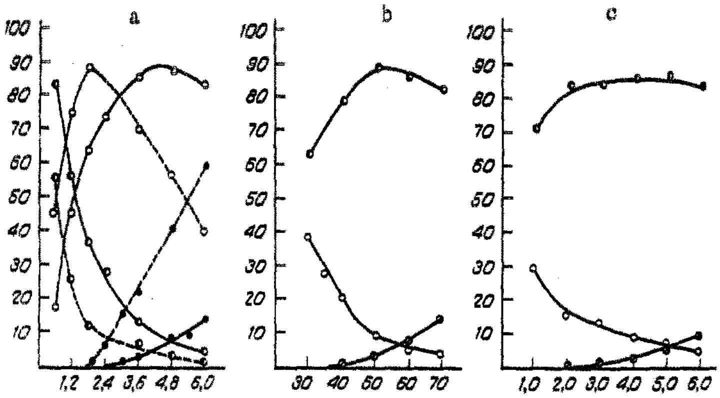

Fig. 1. Hydrogenation of 6,10-dimethyl-3,5,9-undecatrien-2-one (pseudoionone) (I) on Raney nickel in a continuous reactor. Relationship of catalysate composition to the parameters of carrying out the process. On the abscissa: a) supply rate (h^{-1}); b) temperature (°C); c) hydrogen pressure (MPa); on the ordinate is the composition of the reaction product (%): ● , I; ○, V; ◐ , II; ◦◦, VI.

the content of (II) has a clearly expressed maximum in the temperature region 50-60°C which indicates the appreciable influence of temperature on the process of reducing (I).

The influence of the partial pressure of hydrogen was studied in the range 1.0-6.0 MPa at a temperature of 50°C and a volume flow rate 0.45 h^{-1} (see Fig. 1c). The content of (II) had a maximum at a hydrogen pressure 4.0-5.0 MPa (88.4-89.2%) which was less marked than in the previous case. Compound (I) was absent over all the studied pressure range. Accumulation of (VI) occurred under these conditions beginning from 2.0 MPa (1.2%) and at 6.0 MPa reached 9.8%.

The volume supply rate of (I) in relation to the ratio of hydrogenation products was studied in the range 0.45-6.0 h^{-1} at a pressure of 2.0 MPa and a temperature of 50°C (see Fig. 1a, continuous line). The relative content of (II) rapidly fell with the growth in volume flow rate. Simultaneously a rapid accumulation of (V) occurred, the content of (V) reached a maximum (83.6-84.7%) at a volume flow rate of 3.6-4.2 h^{-1}, and after this gradually fell as a result of the accumulation of unreacted (I). The appearance of (I) in the reaction product occurred at a volume flow rate of 2.4 h^{-1} and its content reached 17.5% at a supply rate of 6.0 h^{-1}. As in the variants of conducting the process considered previously, (III) and (IV) were absent from the reaction products.

Similar work on the determination of the composition of the hydrogenation products as a function of the volume flow rate was carried out at a temperature of 30°C and a pressure of 2.0 MPa (see Fig. 1a, broken lines).

Consideration of the results obtained at all the studied values of process parameters showed first of all the absence of (III) and (IV), the products of saturating the 5,6 and 3,4 bonds of pseudoionone (I). This fall in selectivity according to intermediate products is evidently the result of difficulty in transporting reaction participants to the catalyst surface [12]. This conclusion is confirmed by the results of hydrogenating (I) in a batchwise regime with vigorous stirring, under conditions excluding difficulties in the transport of reacting substances (compound being hydrogenated, hydrogen, and hydrogenation products) [2]. In this case products were detected in the catalysate corresponding to each stage of saturation of (I) including (III) and (IV) and the composition of the catalysate was determined by the kinetic constants of the corresponding conversions. In our case in a reactor of the column type the absence of (III) and (IV) evidently indicated that the stage (I) → (III) (I → IV) is controlled by transport of the reagents. An analogous conclusion was drawn for stage (III) → (V) (IV → V).

The other intermediate product of the hydrogenation of (I), tetrahydropseudoionone (V), was contained in catalyzates in large quantities. The rate of conversion of (V) → (II) is probably determined by activation of the 9,10 C=C bond of compound (V) since the conditions determining the transport of reagents at this stage and at the stages considered above are approximately the same.

Comparison of the rates of saturation of two C=C bonds, which with the carbonyl group constitute the dienone system of pseudoionone (I) and of 6,10,14-trimethylpentadeca-3,5-diene-2-one (VII) [11], showed the lower activity of (I). Thus in the case of (VII) the extent of conversion at this bond at a supply rate of 2.1 h^{-1} was 96.8%. Under these conditions (I) had a degree of conversion to (V) equal to 84.8% (temperature 30°C, pressure 2.0 MPa in both cases). A drop in the rate of diffusion of molecules of (I) in comparison with molecules of (VII) on hydrogenation on Raney nickel took place in spite of the fact that the hydrocarbon radical of (I) is five carbon atoms smaller. An explanation of this phenomenon should evidently be sought in the higher rigidity of the radical of (I) as a result of the 9,10 bond. The molecule of (I) has a lower mobility of chain segments.

Thus the kinetics of the hydrogenation of (I) has a complex character in a continuous reactor of column type. Initially in stages (I) → (V) it is seemingly determined by the transport of reactants to the surface of the catalyst, then at stages (V) → (II) by the activation of the 9,10 bond of the intermediate product (V).

On the basis of the carried out experiment the following optimum conditions may be proposed for carrying out the process with the aim of obtaining a maximum yield of (II): temperature 50°C, partial pressure of hydrogen 2.0 MPa, volume flow rate of supply of 10% isopropanol solution of (I) 0.75 h^{-1}.

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