EPIMERIZATION OF ENDO- AND EXO-BORNEOLS IN THE PRESENCE OF AMMONIA AND/OR HYDROGEN ON A FUSED IRON CATALYST

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Epimerization of borneols was noted upon their reaction with ammonia and/or hydrogen on a fused iron catalyst. Borneols are hydroaminated to give bornylamines with predominance of the endo isomer.

The catalytic epimerization (configurational isomerization) of alcohols has not been studied extensively [1]. Interest in the catalytic epimerization is related both to the development of new stereoselective methods for the preparation of various oxygen- and nitrogen-containing compounds and the question of the mechanism of this reaction.

The epimerization of endo- and exo-borneols on nickel or copper in the liquid phase has been described [1].

(1)

In this case, it has been postulated that reaction (1) proceeds through the intermediate dehydrogenation of borneols to camphor [1]. However, there is no information in the literature on the possibility of such a reaction in the gas phase and in the presence of iron catalysts.

We have already established the unusual stereoselectivity of the gas-phase hydrogenation or hydroamination of camphor on a reduced promoted fused iron catalyst (RPFIC) with the predominant formation of the endo isomers of borneols or bornylamines [1]. One of the reasons for such stereoselectivity besides that examined in our previous work [2] may be the epimerization of the borneols or bornylamines obtained.

Thus, in the present work, we studied the possibility of the gas-phase epimerization of borneols upon their reaction with H_2 or $H_2 + NH_3$ in the presence of RPFIC.

EXPERIMENTAL

The reaction of borneols with H_2 or NH_3–H_2 was carried out in a flow system with a stationary bed of RPFIC, which contained 5 mass % V_2O_5. The remainder was Fe_3O_4 (for the nonreduced catalyst). A layer of stainless steel packing was placed over the catalyst. Evaporation of the borneols and their mixing with H_2 and NH_3–H_2 was carried out on the packing. The starting reagents were synthetic exo- and endo-borneol (from pine oil), which were repeatedly crystallized from ethanol, benzene, and toluene. The purity of the starting alcohols was ≥99.5% with the complete absence of camphor. The borneols were introduced into the reactor using a doser as ~30% solutions in benzene (endo-borneol) or toluene (exo-borneol).

The chromatographic analysis of the products obtained was carried out on quartz capillary columns as described in our previous work [2]. The error in the determination of the reaction products was 10 rel. %.

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TABLE 1. Conversion of Endo- and Exo-Borneols upon Reaction with H_2 or H_2-NH_3 on a Fused Iron Catalyst (the H_2 volumetric rate was 8000 h^{-1})

Experiment No.	T, °C	p_{H_2}	p_{NH_3}	H_2/alcohol mole ratio	Rate of alcohol inlet, g/h·liter$_{cat}$	Starting alcohol	Composition of product, %					
		MPa					conversion, %	endo-borneol*	exo-borneol*	camphor	camphane	unidentified products
1	200	1.8	–	40	1300	exo-Borneol	83	43	17	34	6	0
2	140	1.8	–	50	1100	»	46	40	54	6	0	0
3	140	0.1	–	50	1100	»	70	18	30	52	0	0
4	140	0.1	–	40	1200	endo-Borneol	25	75	7	18	0	0
5	100	0.1	–	50	1200	»	14	86	12	2	0	0
6	140	1.7	–	40	1500	»	34	66	28	6	0	0
7	200	1.7	–	40	1500	»	54	46	22	26	6	0
8	250	1.9	1	90	500	»	98	$\frac{2}{20}$	$\frac{0.4}{1.0}$	0.1	31	45.5
9	230	1.9	1	100	440	exo-Borneol	99	$\frac{1.4}{40}$	$\frac{1.0}{33}$	0.1	12	12.5

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*The percentage content of bornylamines relative to the endo and exo isomers is given in the denominator.

RESULTS AND DISCUSSION

Table 1 gives the results of the reaction of borneols with hydrogen and hydrogen–ammonia on an RPFIC, indicating that borneols undergo epimerization at 100-200°C with a large excess of H_2 (conditions conducive for the selective hydrogenation of camphor to borneols [2]). However, we were unable to find conditions for this reaction, under which the products of the conversion of the alcohols did not contain camphor. As indicated by a calculation of the equilibrium mixture of borneol, hydrogen, and camphor using the method of Van Krevelen and Chermin [3], the products of the conversion of the alcohols in the range of conditions selected should contain camphor. The amount of camphor decreases with increasing hydrogen pressure and decreasing temperature. We note that the data in Table 1 are in satisfactory accord with the calculated results (the greatest deviation is 30 rel. %). This indicates that the epimerization of borneols on RPFIC is related to hydrogen–dehydrogenation processes according to the scheme:

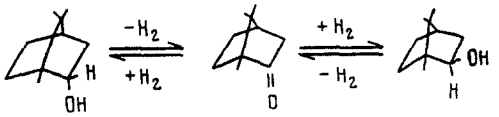

Table 1 also indicates that under comparable conditions, exo-borneol, upon reaction with H_2, undergoes greater conversion in comparison with endo-borneol (compare experiments 3 and 4). Apparently, this discrepancy arises from the steric control of the dehydrogenation reaction of the starting alcohol on RPFIC. In this regard, we cannot exclude that the enhanced yield of endo-borneol, which was observed previously in the hydrogenation of camphor on RPFIC [2] is partially due to the more rapid epimerization of exo-borneol. We note that these results, in principle, may be used for practical purposes for the interconversion of borneols or in the preparation of one of the isomers from their mixture.

If the mechanism for the epimerization is indeed related to dehydrogenation of borneols, then, the epimerization process should be slowed or completely stopped upon binding of intermediate camphor partially or completely in a compound excluding the possibility of its reversible hydrogenation to the alcohol. This hypothesis may be tested experimentally, for example, by studying the reaction of borneols with hydrogen–ammonia, i.e., upon their hydroamination. Since the rate-limiting step in the hydroamination of alcohols on RPFIC is their dehydrogenation to the corresponding carbonyl compounds [4], the concentration of camphor in this case should be close to zero. This should be seen in a change in the isomeric composition of the alcohols within the reaction product. From this viewpoint, let us examine the results of experiments 8 and 9 (see Table 1) obtained under conditions optimal for the hydroamination of camphor.

Let us first note the presence of traces of camphor (up to 0.1%) in all the products of the conversion of borneols, which does not permit us entirely to exclude a mechanism for the epimerization of borneols involving camphor. Apparently, this may account for the presence of the exo and endo isomers of the starting alcohols in the amination products of endo- and exo-borneols. We note that the corresponding carbonyl compounds (aldehydes or ketones) were not detected in the reaction products previously in the hydroamination of various alcohols on RPFIC [4].

We should note the possibility of the predominant preparation of endo-bornylamine by the hydroamination of both endo- and exo-borneols. Such stereoselectivity may be related to imine–enamine tautomerism on RPFIC in the step involving the reaction of intermediate camphor with ammonia [2]. The contribution to the observed composition of the bornylamines to their epimerization remains unclear and requires special study.

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