

An economical and convenient synthesis of 7-oxabicyclo[2.2.1]heptane

D. J. Sikkema and P. Hoogland

Enka Research Institute Arnhem, Velperweg 76, Arnhem, The Netherlands

and J. Bik and P. 't Lam

Akzo Research, Corporate Research Department, Velperweg 76, Arnhem, The Netherlands

(Received 10 October 1985; revised 17 December 1985)

A high-yield process for converting hydroquinone into 7-oxabicyclo[2.2.1]heptane by hydrogenation over Rh/Al₂O₃, isomerizing the *cis*-*trans* mixture of 1,4-cyclohexanediols into all-*trans* by treatment with sodium, and ring closure over A4 zeolites was demonstrated on mini-plant scale. Long-term continuous operation of the ring closure reactor gave no problems. The rhodium catalyst is poisoned after short use. Regeneration by mild oxidative treatment was demonstrated for Rh/C catalysts.

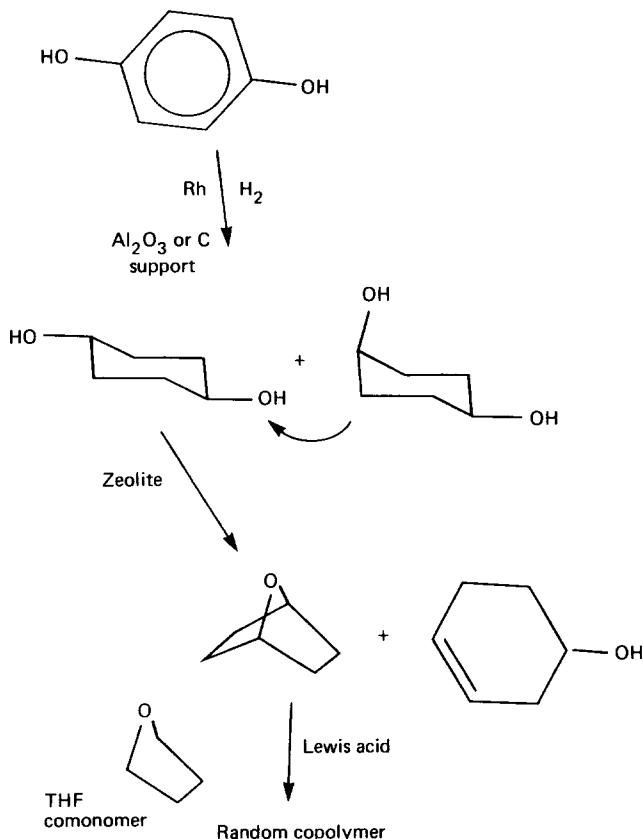
(Keywords: hydrogenation; alcohol epimerization; continuous alcohol-to-ether conversion; complex mixture distillation)

INTRODUCTION

In connection with our work on polymers¹ based on 7-oxabicyclo[2.2.1]heptane (OBCH) we required fairly large amounts of this relatively exotic monomer. A conceptually attractive route via Diels-Alder reaction of furan with maleic anhydride, followed by hydrogenation of the double bond and electrolysis of the dicarboxylic

acid² could not be effected, since the substrate proved to resist electrolytic oxidation at reasonable potentials. Ring closure of 1,4-cyclohexanediol (CHDL) to OBCH is described in the literature as a low-yield³ process featuring fast catalyst deactivation⁴. We discovered a high-yield process utilizing A4 molecular sieves.

RESULTS



Hydrogenation

We hydrogenated hydroquinone over supported rhodium in ethanol or methanol⁵. A fast deactivation of Rh/C was noted, presumably by polymerization of partly hydrogenated hydroquinone⁵. Stirring the inactivated catalyst in hot, dilute nitric acid regenerated the highly active form; the catalyst could thus be recycled many times before decreased selectivity suggested reconstitution type recycling. Alumina-supported rhodium⁶ showed higher selectivity for CHDL production, but even faster deactivation⁷. Nitric acid regeneration proved ineffective. Aged catalysts tend to produce more cyclohexanol, and significant amounts of the intermediate 4-hydroxycyclohexanone—over 10% may be found in excessively aged systems. Typical results are presented in Table 1.

Isomerization

cis-1,4-Cyclohexanediol can be converted into OBCH only inasmuch as it is isomerized to the *trans* isomer—a reaction occurring to some extent under ring closure conditions; a *cis*-*trans* equilibrium should contain 80% of *trans* isomer. 1,4-CHDL can be equilibrated by melting with a small amount of sodium, at 140°C (ref. 8). The reaction mixture solidifies because of the high *trans* isomer content and the formation of CHDL-sodium salt.

Simple flash distillation of the neutralized and filtered solution yields almost pure CHDL containing 80–82% of

Table 1 Typical product composition (wt%) after hydrogenation of hydroquinone in ethanol (40 wt%) over 20 g of catalyst (5% of Rh on support) per kilogram of substrate (i.e. 1 g of Rh per kilogram of hydroquinone) at 30 bar of hydrogen, 60°C, 0.5 kW m⁻³ of stirring power for 2 h (carbon) or 2.5 h (alumina)

	Rh/C	Rh/Al ₂ O ₃
Cyclohexane	2.0	0
Cyclohexanol	20.9	1.8
Cyclohexanone	0	1.0
<i>trans</i> -1,4-CHDL ^a	30.3	36.6
<i>cis</i> -1,4-CHDL	46.8	59.5
4-Hydroxycyclohexanone	0	0
Hydroquinone	0	0.8
Space velocity CHDL (kg m ⁻³ h ⁻¹)	150	120

^aCHDL = cyclohexanediol**Table 2** Isomerization results with and without recycled *cis*-1,4-cyclohexanediol

	Fresh diol	With recycle
Sodium (wt%)	10.0	9.3
<i>trans</i> content (%)	38	36
<i>trans</i> content of equilibrated product (%)	78	84
Reaction yield (%)	96	96
Reaction starting temp. (°C)	115	117
Maximum temp. (°C)	200	195

trans isomer. The *cis* isomer can easily be removed by extraction with a moderate amount of acetone: 1 kg of diol, containing 83% of *trans* isomer, treated with 1.6 kg of acetone yields 770 g of 99% pure *trans* isomer; 170 g of *cis* and 60 g of *trans* isomer are extracted. After removal of the acetone this *cis*-rich product can be recycled to the isomerization step (Table 2).

Ring closure

In the classical route to OBCH^{3,4}, roughly equal masses of CHDL and alumina are heated, producing 2:3 mixtures of OBCH and 3-cyclohexene-1-ol (CHEL) in poor yield at 240°C. Among silica, alumina, germania, titania, Sb₂O₃, CaO, CaCl₂, and A3, A4, Na-Y and Na-H-Y zeolites, only alumina, titania and A zeolites showed appreciable OBCH production in screening gas-phase reactions. Among these, the zeolites performed best.

The literature catalysts last for no more than a few hours^{3,4}. After a year of continuous operation, the A4 zeolite catalyst bed continued to perform satisfactorily, at a production rate of 20 g OBCH per kilogram of catalyst per hour.

Fresh A4 zeolite gives mainly cracking reactions; it must be penetrated as follows. Saturate with water from the ambient air and then pack in the reactor (a vertical electrically heated tube). Nitrogen is passed over the catalyst and in two days the temperature is raised to 225°C. Then 96% alcohol is passed over the catalyst: it is converted to ethyl ether in over 50% conversion; after 14 days the other content of the effluent alcohol has declined to about 3% and the catalyst is now ready for use. A solution of 30–40% of *trans*-1,4-cyclohexanediol in ethanol or methanol is passed over the catalyst (no preheater or evaporator necessary). In contrast with earlier work, we experienced no difference between methanol and ethanol. The reactor starts to produce OBCH at once. The temperature has to be set as low as possible, to just 98% CHDL conversion for optimum selectivity: the lowest temperature recorded was 215°C.

Table 3 Analysis of reaction products (wt%) using 55/45 *trans/cis* vs. pure *trans*-1,4-cyclohexanediol over pretreated A4 molecular sieves at 225°C, at a concentration of 25.6 wt% in 96% ethanol. When methanol is used as the solvent, no solvent-derived ether is found

	55% <i>trans</i>	100% <i>trans</i>
Cracking gases (2 comp., equal concentration)	1.5	1.0
Ether	4.6	2.3
Ethanol	64.4	66.7
Water	7.0	7.0
OBCH	12.4	17.4
Cyclohexenol	9.0	5.6
<i>trans</i> -1,4-CHDL	0.13	0
<i>cis</i> -1,4-CHDL	0.9	0
Conversion	94.5	100.0
Selectivity OBCH on total CHDL	52.4	70.7

In the course of a year the temperature had to be raised gradually from 220 to 245°C to maintain 98% conversion of starting material. Typical results for two feed types are presented in Table 3. They suggest that some *cis*-*trans* equilibrium occurs in the ring closure reactor: pure *trans* isomer yields 71% of OBCH; 55% *trans* yields 52% of OBCH on total CHDL intake, i.e. 95% on *trans* diol.

The OBCH/cyclohexenol ratio, which ultimately determines the reaction selectivity, can perhaps be improved by working under increased pressure⁷.

ISOLATION AND PURIFICATION

Only distillation operations are necessary for production of 99.95% pure PBCH with a water content below 100 ppm. Water forms an azeotrope with OBCH boiling at 88°C: 75/25 (wt) OBCH/water; at room temperature the mutual solubilities are 4% water in OBCH, 12% OBCH in water. At elevated temperatures the solubility of OBCH in water is considerably less. Apart from the water, the components behave more or less ideally and can be removed according to their boiling points. The distillation process comprises the following steps:

- (1) Flashing off 80% of the solvent alcohol, together with the main part of the cracking products.
- (2) Topping off the last alcohol and cracking products from the concentrated OBCH solution.
- (3) Azeotropic distillation of water and traces of alcohol; recovery of the 12% OBCH in the water by side stripping.
- (4) Distillative drying of the remaining product.
- (5) Collection of pure OBCH.
- (6) Collection of 5-hexenal, cyclohexenol and cyclohexanol.
- (7) Vacuum recovery of unreacted cyclohexanediols.

REFERENCES

- 1 Sikkema, D. J. and Hoogland, P. *Polymer* 1986, **27**, 1443
- 2 Radlick, P., Klem, R., Spurlock, S. and Sims, J. J. *Tetrahedron Lett.* 1968, 5117; Westberg, H. H. and Dauben, H. J., Jr. *ibid.* 5123
- 3 Olberg, R. C., Pines, H. and Ipatieff, V. N. *J. Am. Chem. Soc.* 1944, **66**, 1096; Wittbecker, E. L., Hall, H. K. and Campbell, T. W. *ibid.* 1960, **82**, 1218
- 4 Manassen, J. and Pines, H., Proc. 3rd. Int. Congr. Catalysis, Amsterdam, 1964, Vol. 2, pp. 845, 854
- 5 Rylander, P. N. 'Catalytic Hydrogenation in Organic Synthesis', Academic Press, New York, 1979
- 6 Rosenblatt, E. F., US Patent 2675390, 1954
- 7 Pines, H. and Kobylinski, T. P. *J. Catal.* 1970, **17**, 394
- 8 Batzer, H. and Fritz, G. *Makromol. Chem.* 1954, **14**, 179