PREPARATION OF 5-INDANOL

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Derivatives of 5-indanol are widely applied both in plant-protecting and in pharmaceutical industry.

The various compounds of 5-indanol have fungicidal [1], bacteriostatic [2] as well as insecticidal [3, 4] effects. Several papers have been published on the production of 5-indanol so far.

PARANJPE and co-workers [5] report on two ways of producing 5-indanol. One of them is the condensation of 2-formyl-cyclopentanone and aceton catalyzed by base for a reaction time of 21 days, the other one applies ethyl--cyclopentilidene-acetate as starting material and yields 5-indanol by a complicated method.

The starting materials of the most frequently and generally used syntheses are indan and indan derivatives, respectively. The requested product is obtained either by fusing indan-5-sulfonic acid K-salt [6], by diazotating 5-amino-indan, then evaporating the diazonium salt [7], or by oxidizing then hydrolyzing 5-acetyl-indan [8].

Production of indan involves the greatest problem usually solved in the following way: indene is catalytically hydrogenized at high pressure [9], toluol and ethylene are reacted under pressure [10], n-propylbenzol or 1-chlor--4-phenyl-butane is catalytically cycled [11, 12], 1-chlor-3-phenyl-propane is cycloalkylized [13] and finally 1-indanon is reduced [14].

In the method elaborated by us cinnamic acid has been used as starting material.

The cinnamic acid was transformed in basic media into β-phenyl-propionic acid in the presence of active carbon palladium.

Instead of the reducing agent suggested by PIETRA [15] an activated carbon palladium catalyst specially prepared in potassium solution of relatively high concentration has been used in our experiments [16]. Thus, the amount of catalyst could considerably be decreased even at an invariably good yield.

In the second reaction step the β-phenyl-propionic acid was cycled to 1-indanon at a temperature of 70—80 °C in polyphosphoric acid containing $ZnCl_2$.

At the boiling point of the solvent the compound obtained was reduced in diethylene-glycol with the modified Huang-Minlon method. After two hours of reaction and distillation of hydrazine-water mixture, indan was obtained in a good yield. In the following step indan was sulfonated with concentrated sulfuric acid. Indan-5-sulfonic acid trihydrate was obtained from the reaction mixture without salting out which was then transformed into indan--5-sulfonic acid K-salt with equimolar quantity of potassium hydroxide.

Potassium salt was fused in the mixture of potassium hydroxide and sodium acetate at a temperature of 275—285 °C.

5-indanol was obtained after acidification, solvent extraction and purification by vacuum distillation.

By this multistep method 5-indanol is relatively simple to produce in a good yield. This method does not require operation under high pressure. Production can safely and economically be realized with substances relatively well available.

Experimental

1. *Preparation of β-phenyl propionic acid*

To the mixture of 29.6 g (0.2 mol) cinnamic acid, 11.8 g (0.21 mol) potassium hydroxide and 400 cm^3 water, 1.0 g of 3% activated carbon palladium was added and heated to 100 °C under stirring. Afterwards 5.3 g (0.11 mol) hydrazine hydrate of 85% concentration were dropped in small portions to the previous mixture and stirring was kept on for about two hours, until ammonia ceased to produce. The hot reaction mixture was filtered and the filtrate acidified with high concentration hydrochloric acid. The β-phenyl propionic acid precipitating as oil solidified in cooling.

The white crystalline material was filtered, washed with water and dried.

The amount of the product obtained was 28.5 g, its melting point being 45—46 °C and the yield was 94.9%.

2. *Preparation of 1-indanon*

300 g polyphosphoric acid and 0.5 g ($3.67\ 10^{-3}$ mol) $ZnCl_2$ were added to 30.0 g (0.2 mol) β-phenyl propionic acid. The reaction mixture was heated to 70—80 °C under stirring and kept at this temperature for two hours.

Having poured it on ice, the separating crystals are filtered, neutralized by water and dried in vacuum. 24.9 g of raw material is obtained and the efficiency of the yield is as high as 94.3%.

The raw product is distilled in vacuum resulting in 21.1 g 1-indanon boiling at 120—122 °C/2000 Pa and melting at 37—39 °C. The yield of this process amounts to 80%.

3. *Preparation of indan*

The mixture of 26.4 g (0.2 mol) 1-indanon, 28.9 g (0.6 mol) hydrazine hydrate of 85% concentration, 44.8 g (0.8 mol) pulverized KOH and 200 cm^3 diethylene glycol is boiled for two hours, then the hydrazine-water mixture is distilled. Distillation is continued until no more nitrogen gas is produced.

A part of the indan produced in the course of the reaction is also distilled together with the hydrazine-water mixture. The residue is diluted with water of similar volume and its pH is adjusted to 7 with concentrated hydrochloric acid. The solution obtained is further distilled in vacuum. The distillates are combined and extracted with 3×200 cm^3 chloroform. The organic phase is then washed with 3×100 cm^3 water and dried by $MgSO_4$. After filtration the solvent is distilled. 17.6 g of indan result as pale yellow oil. $n_D^{25} = 1.5387$ A yield of 74.5% is achieved.

4. *Preparation of indan-5-sulfonic acid*

12.0 g (0.12 mol) conc. sulfuric acid are dropped to 11.8 g (0.1 mol) indan under mixing at room temperature. The mixture is gradually heated up to 100 °C, then cooled down to 10 °C. 5 cm^3 water are added and the precipitate is kept at a temperature 0—5 °C for a day.

Afterwards the separated product is filtered and dried. Finally 18.1 g of indan-5-sulfonic acid trihydrate are obtained at an efficiency of 71.7%. Melting point of the product is 86—91 °C.

5. *Preparation of 5-indanol*

The mixture of 50 g potassium hydroxide, 7.5 g sodium acetate and 1.5 cm^3 water is heated up to 275 °C and 23.6 g (0.1 mol) indan-5-sulfonic acid K-salt — obtained from the solution of 25.2 g (0.1 mol) indan-5-sulfonic acid trihydrate and of 100 cm^3 potassium hydroxide of 1 mol concentration after water distillation — are added in small portions.

The temperature is kept between 275—285 °C until the mixture thickens.

After cooling, the solidified substance is dissolved in 500 cm^3 water and its pH is adjusted to 5—6 with concentrated hydrochloric acid.

The aqueous phase is extracted with 3×200 cm^3 ether. The combined ether extracts are washed first with Na_2CO_3 of 10% concentration, then

neutralized with water and dried at Na_2SO_4. After the drying agent had been filtrated, the solvent was distilled. Thus 11.5 g raw 5-indanol are obtained in the form of a pale yellow oil giving a yield of 85.7%.

This substance is purified by vacuum distillation, resulting in 10.7 g product.

Boiling point: 115 °C/633 Pa
Melting point: 54—55 °C
Efficiency of production: 80%.

Summary

A multi-step synthesis has been elaborated using cinnamic acid as starting material for producing 5-indanol.

The process does not require operation under pressure and can safely be realized in simple industrial plants.

The product was obtained from relatively easily available starting materials in a good yield.

References

1. Coles, G. V.—Martin, J. T.—Byrde, R. J. W.: Ann. Rept. Agr. Hort. Research. Sta., Long Ashton, Bristol 101 (1956)
2. Shapiro, S. L.—Freedman, L.: Arch. intern. pharmacodynamie **120**, 25 (1959)
3. American patent 3 035 969 (1962)
4. German patent 2 365 555 (1975)
5. Paranjpe, K.—Phalnikar, N. L.—Nargund, K. S.: J. Univ. Bombay 12A, Pt. **3**, 66 (1943)
6. German patent 2 208 253 (1973)
7. Neunhoeffer, O.: Ber. 68B, 1774 (1935)
8. German patent 2 457 440 (1975)
9. Kazanskij, B. A.—Plate, A. F.—Terent'eva, E. M.: Akad. Nauk. S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenij, Sbornik **2**, 70 (1952)
10. American patent 3 082 267 (1963)
11. Liberman, A. L.—Bragin, O. V.—Kazanskij, B. A.: Doklady Akad. Nauk. S.S.S.R. **111**, 1039 (1956)
12. Baddeley, G.—Williamson, R.: J. Chem. Soc. **1956**, 4647.
13. Khalaf, A. A.—Roberts, R. M.: J. Org. Chem. **31** (1), 89 (1966)
14. Aziz-ur, R.—Nilda, F. N.: An. Asoc. Quim. Argent **57** (2), 117 (1969)
15. Pietra, S.: Ann. Chim. **46**, 477 (1956)
16. Hungarian patent 169 667 (1974)

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