Chemistry of Heterocyclic Compounds, Vol. 42, No. 8, 2006

CATALYTIC SYNTHESIS OF INDOLE FROM TETRAHYDROINDOLE ON Pd- AND Cr-CONTAINING CATALYSTS

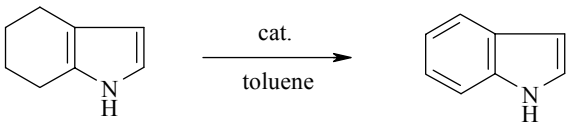
M. A. Ryashentseva

In the presence of Pd- and Cr-containing catalysts applied to γ-Al_2O_3 or sibunite 4,5,6,7-tetrahydroindole is converted into indole. Indole was obtained in quantitative yield on sulfided 0.15-0.5% Pd/γ-Al_2O_3 catalyst at 360°C and on catalysts containing 5% Cr_2O_3, 5% La_2O_3 (or 5% polirit), 1% K_2O/89% γ-Al_2O_3 at 475-480°C.

Keywords: indole, applied palladium-containing and chromium and lanthanum oxide-, polyrit-, and potassium-containing catalysts, 4,5,6,7-tetrahydroindole, toluene, dehydrogenation, carriers: γ-Al_2O_3, sibunite.

The conversion was studied previously of 1-vinyl-4,5,6,7-tetrahydroindole and mixtures of it with 4,5,6,7-tetrahydroindole (**1**) in benzene or toluene on applied Pd- and Cr-containing catalysts. On 1 and 1.5% Pd/γ-Al_2O_3 catalysts treated with hydrogen sulfide 1-ethyltetrahydroindole, 2-ethylindole, and indole **2** were formed, the yield of indole being 7% (300°C, volume rate of supply V_{wt} = 0.9 h^{-1}, duration of experiment τ = 20 min). On Cr oxide catalyst (500-525°C, V = 0.3-1.5 h^{-1}, τ = 30 min) mainly indole **2** is formed in 80% yield. With the aim of developing a method for obtaining pure indole we studied the dehydrogenation of tetrahydroindole **1**. Compound **1** is available and is obtained by the Trofimov reaction [2, 3] from cyclohexanone oxime and acetylene.

In the present work the conversion of tetrahydroindole **1** on Pd- and Cr-containing catalysts applied to a carrier has been studied and optimal conditions were found for the catalytic synthesis of indole **2** by the dehydrogenation of compound **1** in toluene on processed sulfided catalysts containing 0.15, 0.25, and 0.5% Pd on γ-Al_2O_3, and an industrial sample of 0.15% Pd on sibunite (carbon carrier). The catalyst consisted of 0.15% Pd, 99.85% γ-Al_2O_3 treated with H_2S, processed for 8 h periodically (experiment, heating in a stream of hydrogen on various days), while not reducing its high activity. The analogous catalyst on sibunite possesses the same activity, but is not as stable.



1 **2**

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 119991; e-mail: secretary@ioc.ac.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1176-1178, August, 2006. Original article submitted September 23, 2005.

 0009-3122/06/4208-1018

TABLE 1. Conversion in Toluene of Tetrahydroindole on Pd- and Cr-Containing Catalysts

Catalyst composition, wt.%	Toluene content, wt.%	Experimental conditions*			Yield of liquid catalyzate, wt.%	Composition of catalyzate, wt.%	
		T, °C	V_{wt}, h^{-1}	τ, min		**1**	**2**
0.15% Pd/γ-Al_2O_3,	84.4	300	0.5	30	100	14.2	85.8
treated with H_2S	84.4	355	0.5	20	100	1.7	98.3
	86.7	360	0.5	38	98		100
	86.8	360	0.47	39	100		100
	82.8	360	0.6	30	97.9		100
	85.0	360	0.5	30	99.1		100
0.25% Pd/γ-Al_2O_3,	85.5	350	0.5	30	97.5		100
treated with H_2S	85.5	370	0.5	20	100		100
	82.3	300	0.6	30	100		100
		350	0.6	25	100		100
	79.2	375	0.7	30	100		100
		400	0.5	25	100		100
0.5% Pd/γ-Al_2O_3,	79.5	370	1.0	30	97.5		100
treated with H_2S		400	1.4	30	87.2		100
0.15% Pd/sibunite	84.4	300	0.5	30	100	14.2	85.8
	84.4	355	0.5	20	100	1.66	98.3
	86.7	360	0.5	38	98.0		100
	86.8	360	0.47	39	100		100
	82.8	360	0.6	30	97.9		100
	85.0	360	0.5	30	99.1		100
5% Cr_2O_3, 5% La_2O_3,	83.0	474	0.3	45	90.0		100
1% K_2O, 89% γ-Al_2O_3	83.0	473	0.3	35	89.4	trace	100
	83.0	477	0.3	47	91.7	trace	100
	83.2	480	0.3	49	94.0		
	84.0	480	0.25	37	91.0	1.1	98.9
5% Cr_2O_3,	79.6	475	0.36	26	95.9		100
5% polirit,	83.5	476	0.3	26	89.7	2.9	97.1
1% K_2O, 89% γ-Al_2O_3	83.6	483	0.3	30	99.2	3.0	97.0

* Hydrogen supply rate 2.6 l/h.

It was shown that the activity of the catalysts was reduced at >380°C, on heating to 600°C the catalyst activity was reduced by half. At a catalyst composition of 0.25% Pd, 99.75% γ-Al_2O_3, H_2S (350°C, V = 0.5-0.6 h^{-1}) and Cr-oxide catalyst of composition 5% Cr_2O_3, 5% La_2O_3 (or 5% Polirit: 27% CeO_2, 1.3% La_2O_3, 0.75% Nd_2O_3, 0.25% Pr_2O_3), 1% K_2O, 89% γ-Al_2O_3, obtained as in [6], (475-480°C, V = 0.3-0.4 h^{-1}) tetrahydroindole **1** (14% solution in toluene) is converted into indole **2** in ~100% yield.

Efficient Pd- and Cr-containing catalysts on carriers and conditions have been found for the synthesis of indole **2** by the dehydrogenation of tetrahydroindole **1**.

EXPERIMENTAL

Tetrahydroindole, given by B. A. Trofimov and his coworkers, synthesized by the method of [4], was used in the work. The author is most grateful for this. The sample of 0.15% Pd/sibunite catalyst (in the form of pellets of diameter 2-3 mm, poured weight 0.6 g·cm^{-3}, specific surface measured by nitrogen absorption 680 $m^2 \cdot g^{-1}$, and by phenol absorption 230 $m^2 \cdot g^{-1}$) was obtained from V. A. Semikolenov [5], for which the author is grateful.

The conversion of tetrahydroindole **1** in toluene was carried out in a flow-through installation at atmospheric pressure, 300-480°C, V_{wt} = 0.3-1.4 h^{-1}, and duration 0.5-0.8 h. Palladium on aluminum catalysts containing 0.15, 0.25, and 0.5% Pd on an industrial sample of γ-Al_2O_3 (specific surface 200-220 $m^2.g^{-1}$, particle size 2 × 3 mm) as carrier. Catalysts were prepared by soaking. Reduction was effected with hydrogen at 350°C, sulfidation with hydrogen sulfide at 120°C. The preparation of Cr oxide catalyst of composition 5% Cr_2O_3, 5% La_2O_3, (or 5% Polirit: 27% CeO_2, 1.3% La_2O_3, 0.75% Nd_2O_3, 0.25% Pr_2O_3), 1% K_2O, 89% γ-Al_2O_3 was described in [6]. The reaction products were analyzed on a LKhM 8MD gas-liquid chromatograph (catharometer, temperature programing in the range 110-250°C, rate 12 deg/min), column 2000 × 3 mm, 3% OV 225 on chromaton N-Super (0.125-0.161 mm) and 1500 × 3 mm, 2% OV 225 on chromosorb G (0.147-0.175 mm) at 190°C, carrier gas was helium.

Indole **2** was isolated from the catalyzate by vacuum distillation. Bp 130°C (35 mm Hg) and mp 52.5°C correspond to the data of [7]. The results obtained are given in Table 1.

A sample of indole **2** was sent for testing in the All-Union Research Institute for Synthetic and Natural Perfume Substances and obtained a high assessment.

REFERENCES

1. M. A. Ryashentseva, Yu. B. Vol'kenshtein, V. M. Polosin, A. I. Mikhaleva, and R. N. Nesterenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1417 (1991).
2. B. A. Trofimov and A. I, Mikhaleva, *N-Vinylpyrroles* [in Russian], Nauka, Novosibirsk (1984), 260 pp.
3. B. A. Trofimov, *Usp. Khim.*, **58**, 1703 (1989).
4. B. A. Trofimov and A. I. Mikhaleva, *Khim. Geterotsikl. Soedin.*, 1299 (1980). [*Chem. Heterocycl. Comp.*, **16**, 979 (1980)].
5. V. A. Semikolenov, *Usp. Khim.*, **61**, 320 (1992).
6. M. A. Ryashentseva, E. P. Belanova, and Kh. M. Minachev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2756 (1978).
7. Beilstein, **20**, 304.