

REDUCTION OF TOLAN TO STILBENE BY SODIUM BOROHYDRIDE CATALYZED  
BY RHODIUM COMPLEXES

G. B. Shul'pin and G. V. Nizova

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$\text{NaBH}_4$  is a relative weak reducing agent. It has recently been shown that  $\text{NaBH}_4$  in combination with transition metal compounds is capable of reducing the  $\text{C}=\text{O}$  group to  $\text{CH}_2$  [1], hydrogenate the benzene ring [2] and reduce multiple bonds to  $\text{C}-\text{C}$  bonds [3, 4]. Thus, the reduction of tolan (I) in the presence of  $(\text{PPh}_3)_2\text{CoCl}$  gives dibenzyl in addition to cis- and trans-stilbenes (II).

We have found that rhodium complexes  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  (III) and  $\text{HRh}(\text{PPh}_3)_4$  (IV) catalyze the reduction of (I) by  $\text{NaBH}_4$ . We note that tolan is not reduced by  $\text{NaBH}_4$  in the absence of complexes (III) or (IV). The reaction in the presence of (III) or (IV) proceeds at  $20^\circ\text{C}$  in 1:1 benzene-ethanol to completion in a few hours (the disappearance of starting (I) was monitored by thin-layer chromatography on Silufol plates).

The use of (III) as a catalyst leads to the formation of a 5:1 mixture of trans- and cis-(II). The reaction catalyzed by (IV) gives almost pure trans-(II) (the amount of cis isomer is less than 1.5%).

We propose the following scheme for this catalytic reaction. Rhodium hydride (the chlorocarbonyl derivative is converted to the hydride by the action of  $\text{NaBH}_4$ ) adds to the triple bond with the formation of a  $\text{Rh}(\text{I})$   $\sigma$ -vinyl complex [5]. This complex adds hydride ions and converts to an  $\text{Rh}(\text{III})$  vinylhydride derivative, which decomposes into (II) and the starting  $\text{Rh}(\text{I})$  hydride complex.

#### EXPERIMENTAL

Complexes  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  (III) [6] and  $\text{HRh}(\text{PPh}_3)_4$  (IV) [7] were obtained as described in the literature. All the reactions were carried out in the air with magnetic stirring.

Reaction of Tolane (I) Catalyzed by (III). A solution of 200 mg (1.1 mmole) (I), 19 mg (0.03 mmole) (III) and 130 mg (3.4 mmoles)  $\text{NaBH}_4$  in 5 ml ethanol and 5 ml benzene was stirred for 2.5 h at  $20^\circ\text{C}$ . The solvent was evaporated in vacuum and the residue was separated on silica gel plates using hexane as eluent to give 16 mg cis- and 82 mg trans-(II) (49% total yield).

Reduction of (I) Catalyzed by (IV). A solution of 200 mg (I), 32 mg (0.03 mmole) (IV) and 130 mg  $\text{NaBH}_4$  in 5 ml ethanol and 5 ml benzene was stirred at  $20^\circ\text{C}$  for 4 h. Analogous work-up gave 125 mg (63%) trans-(II).

#### CONCLUSIONS

$\text{NaBH}_4$  in the presence of catalytic amounts of  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  or  $\text{HRh}(\text{PPh}_3)_4$  reduces tolan to stilbene. High trans steric selectivity of the reduction is observed in the presence of  $\text{HRh}(\text{PPh}_3)_4$ .

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