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REDUCTION OF TOLAN TO STILBENE BY SODIUM BOROHYDRIDE CATALYZED

BY RHODIUM COMPLEXES

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NaBH₄ is a relative weak reducing agent. It has recently been shown that NaBH₄ in combination with transition metal compounds is capable of reducing the C=O group to CH₂ [1], hydrogenate the benzene ring [2] and reduce multiple bonds to C-C bonds [3, 4]. Thus, the reduction of tolan (I) in the presence of $(PPh_3)_3CoCl$ gives dibenzyl in addition to cisand trans-stilbenes (II).

We have found that rhodium complexes RhCl(CO)(PPh₃)₃ (III) and HRh(PPh₃)₄ (IV) catalyze the reduction of (I) by NaBH₄. We note that tolan is not reduced by NaBH₄ in the absence of complexes (III) or (IV). The reaction in the presence of (III) or (IV) proceeds at 20°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 NaBH₄) adds to the triple bond with the formation of a Rh(I) σ -vinyl complex [5]. This complex adds hydride ions and converts to an Rh(III) vinylhydride derivative, which decomposes into (II) and the starting Rh(I) hydride complex.

EXPERIMENTAL

Complexes $RhCl(CO)(PPh_3)_2$ (III) [6] and $HRh(PPh_3)_4$ (IV) [7] were obtained as described in the literature. All the reactions were carried out in the air with magnetic stirring.

<u>Reaction of Tolan (I) Catalyzed by (III)</u>. A solution of 200 mg (1.1 mmole) (I), 19 mg (0.03 mmole) (III) and 130 mg (3.4 mmoles) NaBH₄ in 5 ml ethanol and 5 ml benzene was stirred for 2.5 h at 20°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 NaBH4 in 5 ml ethanol and 5 ml benzene was stirred at 20°C for 4 h. Analogous work-up gave 125 mg (63%) trans-(II).

CONCLUSIONS

NaBH₄ in the presence of catalytic amounts of $RhCl(CO)(PPh_3)_2$ or $HRh(PPh_3)_4$ reduces tolan to stilbene. High trans steric selectivity of the reduction is observed in the presence of $HRh(PPh_3)_4$.

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ISOMERIC COMPOSITION OF DITOLYLS FORMED UPON THE THERMAL DECOMPOSITION OF AN ANIONIC Pt(IV) σ -TOLYL CHLORIDE COMPLEX

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Heating a solution of $PtCl_6^{2-}$ ion (chloroplatinic acid or its sodium salt) and an aromatic compound ArH in aqueous CF_3CO_2H or in acetic acid leads to the formation a Pt(IV) σ aryl complex which may be separated by chromatography on silica gel containing NH₃ as a salt of [ArPtCl_4NH₃]⁻ [1, 2]. Upon more prolonged heating of the solution, the σ -complex decomposes with the formation of diaryls [1]. The removal of the free arene from the reaction solution leads to a marked decrease in the rate of decomposition of the σ -complex, indicating that one of decomposition pathways involves the reaction of the complex with the free arene [3, 4].

In the present work, we studied the isomeric composition of ditolyls formed upon the decomposition of the Pt(IV) σ -tolyl complex (I). The reaction was carried out in 4.5:1 CF₃CO₂H-H₂O at 90°C. Reaction (1) was followed relative to the loss of starting PtCl₆²⁻ ion over time by electronic spectroscopy and the accumulation of (I) by electronic spectroscopy and isomeric ditolyls by gas-liquid chromatography. In addition, PMR spectroscopy was used to determine the ratio of the m- and p-isomers of (I) formed in the platination of toluene (the o-isomer is not formed due to steric factors). A large excess of toluene was employed.

$$C_{6}H_{5}CH_{3} + PtCl_{6}^{2-} \xrightarrow{90^{\circ}} CH_{3}C_{6}H_{4}PtCl_{5}^{2-} \xrightarrow{90^{\circ}} CF_{3}COOH-H_{2}O} M, p-(I) \longrightarrow 3,3'-, 4,4'-, 3,4'-, 2,3'-, 2,4'-isomers of CH_{3}C_{6}H_{4}C_{6}H_{4}CH_{3} (1) (11)$$

The kinetic data are illustrated in Fig. 1. All the $PtCl_6^{2-}$ ion is virtually completely consumed after 3 h. At this time, the concentration of (I) reaches a maximum (the yield of (I) is 69%) and then (I) begins to decompose rapidly. While the fraction of the p-isomer of (I) formed at the onset Y^d is about 0.9, its relative content in the mixture drops to about 0.3. Isomers of (II) begin to form even in the initial stage of the reaction but an induction period in their accumulation is noted. The inflection on the kinetic curves for the accumulation of isomers (II) approximately corresponds to the maximum on the kinetic curve for the formation and decomposition of complex (I).

Gas-liquid chromatography revealed five isomers of (II) in the reaction mixture, namely, the 3,3'-, 4,4'-, 3,4'-, 2,4'-, and 2,3'-isomers. The 3,3'-isomer is formed in the least amounts at any moment in time. In the initial period (lh after the reaction onset), the concentration of 4,4'-(II) exceeds the concentration of any other isomer but after 2 h, the amount of 3,4'-(II) exceeds that of 4,4'-(II). Isomers of (II) containing the methyl group

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