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REDUCTION OF AROMATIC HALIDES WITH SODIUM BOROHYDRIDE CATALYSED BY TITANIUM COMPLEXES. UNEXPECTED ROLE OF AIR

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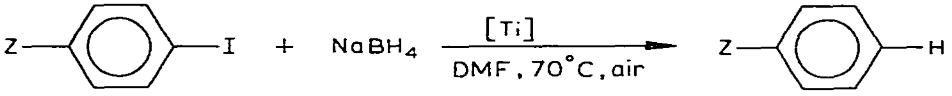
Summary

Aromatic halide are reduced in high yield by reaction with $NaBH_4$ activated by a catalytic amount of Cp_2TiCl_2 or $CpTiCl_3$ in DMF in the presence of air; the reduction does not occur under a rigorously inert atmosphere.

The readily available titanium complex Cp_2TiCl_2 has been successfully used for the catalytic activation of Grignard reagents [1], trialkylalanes [2] or aluminium hydrides [3]. We are interested at present in continuing a stable, easy to handle, and inexpensive hydride such as $NaBH_4$ with a good precursor for catalytic reactions such as Cp_2TiCl_2. In recent work devoted to the catalytic activation of $NaBH_4$, the reactions have to be carried out under an inert atmosphere [4]. We now report the selective reduction of aromatic halides (I) by $NaBH_4$ catalysed by $CpTiCl_2$ or $CpTiCl_3$ in the presence of air.



(I, Z = H, Cl, Br, CH_3O)

The results are summarized in Table 2 and were obtained by the following procedure: to 10 mmol of $NaBH_4$, 2.5 mmol of the aromatic halide (liquid halides are injected after the addition of solvent) and 0.25 mmol of Cp_2TiCl_2 or $CpTiCl_3$ contained in a tube equipped with a magnetic stirring bar and a condenser, were added at room temperature 10 ml of dimethylformamide (DMF) *

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* Commercial DMF without a drying procedure can be employed in these reductions.

TABLE 1

REDUCTION OF I WITH $NaBH_4$ AND TITANIUM COMPLEXES [a]

Z	Yield (%)	
	with Cp_2TiCl_2	with $CpTiCl_3$
H	98 (9)	95 (24)
Cl	99 (24)	93 (24)
Br [b]	85 (24)	75 (24)
CH_3O	80 (24)	98 (24)

[a] The yields were determined by GLC by use of internal standards, and reaction times (hours) are given in parentheses. Only 2—4% of the products were obtained from reactions without catalyst. [b] In this case 12% of benzene is also observed with Cp_2TiCl_2 and 10% with $CpTiCl_3$.

in the presence of air. All the reactions were carried out at 70°C. After quenching with water the products were extracted with ether. The reductions are nearly complete within 24 hours.

The reactions do not take place under a rigorously inert atmosphere (argon or nitrogen). In a run under argon with 1-chloro-4-iodobenzene and $CpTiCl_3$, only 13% of chlorobenzene was formed after 24 hours at 70°C (85% of unreacted starting material) and after an extra 24 hours at the same temperature in air 90% of chlorobenzene was recovered. The same observation was made for Cp_2TiCl_2. All these reductions seem to be initiated by molecular oxygen.

The reaction provides a method for a selective reduction of polyhalogenated aromatic hydrocarbons. Chlorides are not affected, and the low reactivity of bromides in comparison with iodides leads to the monoreduced molecules with a good yield. Further investigations are in progress to throw light on the exact course of the reactions and particularly to elucidate the role of oxygen, the influence of the solvent and that of the nature of the ligands in the titanium precursors. (The reductions are not catalysed by $Ti(On\text{-}Bu)_4$, for example.)

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