

Reductive Cleavage of Aryl-O- and Aryl-Cl-Bonds by C₈K: a Potential Method for the Degradation of Dioxins

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Potassium Graphite Intercalate, Reductive
Cleavage of Aryl Halides and Aryl Ethers

Potassium graphite intercalate in THF is a reagent for the reduction of aryl halides and the reductive cleavage of aryl ethers.

Much effort has been dedicated to processes that enable the reductive cleavage of chlorinated aromatic hydrocarbons and of aryl ethers. One of the various applications of such reactions could be the degradation of the highly toxic halogenated dibenzodioxins for which an effective laboratory procedure is missing.

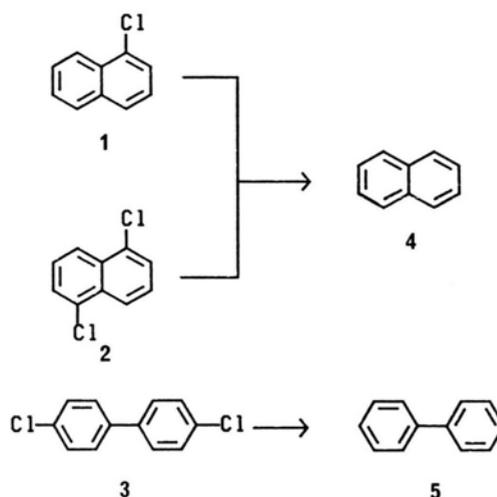
Published procedures for those reductions carried out with alkali metals require the use of liquid ammonia as solvent [1]. In other solvents the reactions occurs at higher temperature, resulting in the formation of undesired by-products [2]. The disadvantage of reaction at room temperature is the longer reaction time (up to 10 days) which make the process not useful [3].

Potassium graphite intercalate, C₈K, has been shown to be a useful and efficient reducing agent [4]. Its highly ordered structure, combined with high reactivity enables selective high yield reductive processes, *e.g.* reductive dimerization of diketones [5] and stereospecific debromination [6].

We wish to report here the application of this reagent for the reactions mentioned above. We found that the reductive cleavage of aryl-Cl and aryl-O bonds occur in short time at room temperature with THF as solvent. The cleavage of C–Cl and C–O bonds is further demonstrated on compounds chosen as model systems for chlorinated dibenzodioxins. It can be concluded from the results that the use of C₈K could lead to a simple and convenient laboratory

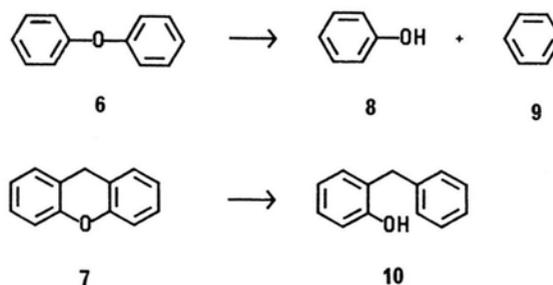
procedure for the degradation of these polluting compounds.

Reaction of C₈K with 1-chloronaphthalene (**1**), 1,8-dichloronaphthalene (**2**), or 4,4-dichlorobiphenyl (**3**) at R.T. resulted in a complete reduction to the corresponding hydrocarbons in less than 15 minutes. Work-up gave 93% and 82% of naphthalene (**4**), respectively, and 86% biphenyl (**5**) from reduction of the corresponding dichloro derivative.



Cleavage of the aryl-O-bond was investigated with diphenylether (**6**) and xanthene (**7**) and was detected by gas chromatography. After 4 h at room temperature only phenol (**8**) could be detected after reacting **6** with C₈K. Reaction of the reagent with **7** resulted in the formation of **10**. Work-up gave **8** or **10** in 78% and 73% yield.

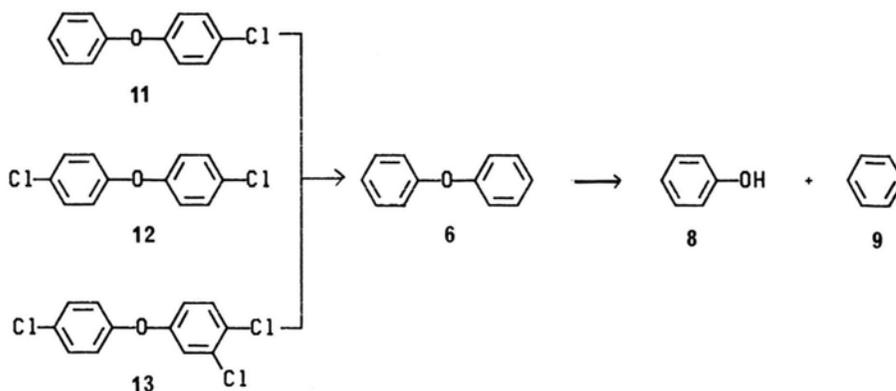
The simultaneous cleavage of aryl-O and aryl-Cl bonds is of importance for the degradation of chlorinated dioxins. We examined the reductions with chlorinated diphenyl ethers **11**, **12**, **13** as model compounds for the dioxins.



Analysis of the reaction mixture with GC showed after a few minutes diphenyl ether **6** as the sole pro-

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duct. Additional stirring at room temperature for 8 h completed the reaction and only phenol **8** was detectable by GC, and benzene **9** was identified by HPLC.

Experimental

General procedure: 1.2 g graphite and 0.5 potassium were stirred under an argon atmosphere and heated to 150 °C. After 15 min at this temperature

the brown graphite potassium intercalate was formed. At room temperature a solution of 564 mg (3 mmol) xanthene **7** in 50 ml dry THF was then added. For work-up the mixture was treated with 1 ml isopropanol and then with 1 ml diluted HCl. Filtration and evaporation of the filtrate gave 402 mg of a yellow oil which was pure by TLC. Crystallization gave 2-hydroxydiphenylmethane (**10**), m.p. 50 °C (lit. [7] m.p. 52 °C). Phenyl urethane m.p. 116 °C (lit. [7] m.p. 117.5 – 118 °C).

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