

PROPERTIES OF SODIUM BIS(2-METHOXYETHOXY)ALUMINIUM HYDRIDE. XIII.*

DECHLORINATION OF SUBSTITUTED CHLOROBENZENES

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Received August 13th, 1971

Employing the competition method, the kinetics of dehalogenation of chlorobenzene and its derivatives by sodium bis(2-methoxyethoxy)aluminium hydride at 145°C have been investigated. It has been found that methyl groups on the aromatic ring suppress the reactivity whereas a fluorine atom enhances it. The relative rate constants could be well correlated by the Hammett equation.

Čapka and Chvalovský¹ have shown that the strong reducing power of sodium bis(2-methoxyethoxy)aluminium hydride, $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$, can be utilized even for dehalogenation of aromatic compounds. After 1 h at 110°C the conversions of bromobenzene and chlorobenzene to benzene were 28% and 2%, respectively. Fluorobenzene was practically stable. In studying the dehalogenation of substituted chlorobenzenes by catalytic hydrogenation on palladium² we wanted to compare the structural effects on reactivity in the homogeneous and the heterogeneous reactions. For this purpose it seemed useful to investigate the dechlorination by the given complex hydride; the results are described in the present paper.

EXPERIMENTAL AND RESULTS

The reactivity of chlorobenzene and its derivatives was investigated by the competition method. On the basis of preliminary experiments we prepared a series of suitable mixtures of two compounds, of which one was chlorobenzene (except the experiments with *m*-fluorochlorobenzene, whose reaction was investigated in a mixture with *m*-chlorotoluene); the ratios of the two constituents were so chosen that the contents of the dechlorinated compounds in the reacted mixtures were comparable. This means that the content of the less reactive compound in the starting mixture was five to twenty times greater than that of the other one. Sodium bis(2-methoxyethoxy)aluminium hydride was added in a tenfold excess as a solution in *p*-cymene (1.6 mol/mol). The reaction mixture was sealed in a glass ampoule and heated to $145 \pm 0.1^\circ\text{C}$ for 4 h. Then it was allowed to cool down and hydrolysed by a small amount of 2M-HCl. The hydrocarbon layer was separated, dried and analysed by gas chromatography. The relative reaction rates were

* Part XII: This Journal 36, 2400 (1971).

determined from the ratio of peaks of the dechlorinated products on the basis of a preceding calibration. The total conversion of the more reactive chloro derivative was about 50%. The chloro derivatives employed (laboratory stores) were redistilled and dried with a molecular sieve. The *p*-cymene solution of sodium bis(2-methoxyethoxy)aluminium hydride was prepared from a commercial solution of this hydride in benzene: the solvent was distilled off *in vacuo*, *p*-cymene was added and the mixture was distilled again for some time to remove the last traces of benzene. The solution was then diluted with *p*-cymene to the required concentration of the hydride. The relative reaction rates of chlorobenzenes determined by the competition method (averages from 2 to 4 experiments) were:

Substituent	3-F	H	2-CH ₃	3-CH ₃	4-CH ₃	3-4-(CH ₃) ₂
k_{rel}	9.9	1	0.10	0.14	0.12	0.052

These data clearly show the decrease in reactivity of the chlorine atom with the increase in density of electrons in the aromatic ring, and accord with the conception of a nucleophilic action of complex hydrides^{3,4}. Their correlation by means of the Hammett equation (excluding *o*-chlorotoluene) was successful with the following parameters: the reaction constant ρ 4.0, the correlation coefficient r 0.974, the root-mean-square deviation 0.242.

Acknowledgement for technical assistance is due to Mr Z. Žitný.

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Translated by J. Salák.