DEHALOGENATION OF 4,4′-DICHLOROBIPHENYL WITH SODIUM DIHYDRIDOBIS(2-METHOXYETHOXO)ALUMINATE

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4,4′-Dichlorobiphenyl was reduced to biphenyl with sodium dihydridobis(2-methoxyethoxo)aluminate in toluene at 70–110 °C. The reaction course was described by two consecutive dehalogenation steps of the first order in the substrate. The dehalogenation was accelerated by catalytic amounts of Co(II) and Ni(II) l,3-pentanedionates. Dependence of dehalogenation steps on temperature and metal pentanedionate is reported, and rate data are compared with those obtained for 4-chlorobiphenyl, dichlorobenzene, and chlorobenzene.

Dehalogenation of noxious chlorinated organic compounds is widely used for their detoxification. Polychlorinated biphenyls (PCBs) are of special interest because of their previous extensive technical and industrial application. The most frequent, legally accepted way of their disposal is their incineration. However, alternative methods nondestroying the batch could be of advantage for reclaimable wastes with low PCB contamination[1,2].

Besides catalytic high-pressure hydrodechlorination on heterogeneous hydrorefining catalysts[3], the reductive cleavage of PCB C–Cl bonds has been effected also with metal hydrides (NaH (ref.[4]), CaH_2 (ref.[4]), $LiAlH_4$ (refs[4–6]), $NaBH_4/NiCl_2$ 1 : 1, ref.[7]), $NaBH_4$-induced photodehalogenation[8,9], and $NaBH_2(OCH_2CH_2OCH_3)_2/NiCl_2$ (1 : 1, ref.[10])). However, the reducing agent in large excess[5,6], drastic reaction conditions[4–6], photocatalysts[9], metal salts in stoichiometric amounts[7,10] or polar solvents[9,10] has made this route less perspective.

The efficiency of dihydridobis(2-methoxyethoxo)aluminate (SDMA) in the reductive dehalogenation of polychlorobenzenes[11,12] has lead us to extend its use also to PCB dehalogenation. As the complete dechlorination is determined by the reactivity of the least chlorinated PCB congeners, we chose 4,4′-dichlorobiphenyl and 4-chlorobiphenyl as model compounds.

EXPERIMENTAL

Chemicals

Sodium dihydridobis(2-methoxyethoxo)aluminate (70% solution in toluene, Synthesia Kolín) was used as obtained, after the actual hydride concentration had been determined iodometrically[13]. Toluene (analytical grade, Lachema Brno) was dried over $NaAlH_4$ and distilled. $Ni(acac)_2$ and $Co(acac)_2$ were commercial samples (Fluka, Buchs) and were used as obtained. 4,4′-Dichlorobiphenyl was prepared by the Sandmayer reaction[14]. The product was isolated in 98% purity by steam distillation. 4-Chlorobiphenyl was obtained in 95% purity by the procedure used[15] to synthesize 4-bromobiphenyl.

General Dehalogenation Procedure

To a thermostatted 50 ml-reaction vessel equipped with a thermometer, a reflux condenser and a magnetic stirrer, toluene solution (13 ml) of 4,4′-dichlorobiphenyl or 4-chlorobiphenyl (2 mmol each) and eventually toluene solution (2 ml) of Ni(II) or Co(II) l,3-pentanedionate (0.11 mmol) were added. Then, the reaction mixture was heated with stirring to the reaction temperature (70–110 °C) at which SDMA solution was added in one portion. Unless stated otherwise, SDMA was taken in threefold molar excess with respect to the chlorine of the substrate to be reduced. At fixed time intervals, samples of the reaction mixture were withdrawn and the unreacted hydride was destroyed by acidification[12]. After phase separation, the organic layer was analyzed gas chromatographically[11].

Kinetics of Dehalogenation

The dehalogenation of both chlorinated biphenyls was assumed to be first order in the substrate. The reaction of 4,4′-dichlorobiphenyl was treated as two consecutive dehalogenation steps (Eq. (*A*)).

$$4,4'\text{-}ClC_6H_4C_6H_4Cl \xrightarrow{k_1} 4\text{-}ClC_6H_4C_6H_5 \xrightarrow{k_2} C_6H_5C_6H_5 \qquad (A)$$

The rate constants for uncatalyzed dehalogenation were calculated as described earlier[11]. In the case of catalyzed reactions, due to their generally high reaction rates, the term for catalyst deactivation[12] was neglected. As the constants so obtained included the term for hydride concentration, the latter was excluded by dividing the constants by $[SDMA]^{0.5}$ for the uncatalyzed reduction[11] and by [SDMA] for the catalyzed one[12].

RESULTS AND DISCUSSION

Data presented in Table I demonstrate that the reduction of 4,4′-dichlorobiphenyl with SDMA to the mono derivative proceeds at both temperatures faster (entry 1) than an analogous reduction of 1,4-dichlorobenzene to chlorobenzene (entry 3). This reactivity difference is documented also by the rate constants for the reduction of an equimolar mixture of both compounds (entry 5).

The reverse order is found for the second step, the consecutive reduction of the monochloro derivatives to the corresponding hydrocarbons, in harmony with the lower reactivity of 4-chlorobiphenyl (entry 2) compared to chlorobenzene (entry 4).

The higher rate constant for the second step of the reduction of 4,4′-dichlorobiphenyl (to give biphenyl) compared to that obtained for the reduction of the expected intermediate, 4-chlorobiphenyl, as such (e.g. $0.9 \cdot 10^{-3}$ $l^{0.5}$ $mol^{-0.5}$ min^{-1} (entry 1, 70 °C) vs $0.19 \cdot 10^{-3}$ $l^{0.5}$ $mol^{-0.5}$ min^{-1} (entry 2, 70 °C)) is noteworthy. A similar discrepancy has been recently reported for the reduction of isomeric dichlorobenzenes[11] (illustrated in the present work by data for 1,4-dichlorobenzene, entry 3 vs entry 4). The most likely reason is the more complicated reaction course not fully described by the model of two consecutive reactions used by us for data treatment (Eq. (*A*), for more detailed discussion see ref.[11]).

However, even with SDMA in excess and in refluxing solvent, the SDMA reduction of low chlorinated biphenyls is of little preparative value (e.g. ca 10 mole % yield of 4-chlorobiphenyl was obtained by 1 h-reduction of 4,4′-dichlorobiphenyl at 110 °C).

Promising results have been obtained when the reduction was carried out in the presence of transition metal compounds, of which the best ones turned out to be $Ni(acac)_2$ and $Co(acac)_2$ (cf. ref.[12]). Relevant data are collected in Table II. They show

TABLE I

Dehalogenation of chlorobiphenyls and chlorobenzenes (2 mmol) with SDMA (3 : 1 Cl molar ratio) in toluene (15 ml). For procedure see Experimental

Entry	Compound	Temperature, °C	$k \cdot 10^3$ $l^{0.5}$ $mol^{-0.5}$ min^{-1}	Product
1	4,4′-$(ClC_6H_4)_2$	70	1.7	4-$ClC_6H_4C_6H_5$
			0.9	$C_6H_5C_6H_5$
		110	2.1	4-$ClC_6H_4C_6H_5$
			1.3	$C_6H_5C_6H_5$
2	4-$ClC_6H_4C_6H_5$	70	0.19	$C_6H_5C_6H_5$
		110	0.65	$C_6H_5C_6H_5$
3	1,4-$Cl_2C_6H_4$	70[a]	1.2	ClC_6H_5
			1.5	C_6H_6
		110	1.8	ClC_6H_5
			2.9	C_6H_6
4	ClC_6H_5	70[a]	0.81	C_6H_6
		110	2.3	C_6H_6
	4,4′-$(ClC_6H_4)_2$[b]	70	2.3	4-$ClC_6H_4C_6H_5$
	+ 1,4-$Cl_2C_6H_4$		1.1	ClC_6H_5

[a] Ref.[11]. [b] 2 mmol each.

that already catalytic amounts of the pentanedionates accelerate the first step of the reduction of 4,4′-dichlorobiphenyl by ca two orders of magnitude, and less so also the second step (Eq. (*A*)), compared to the uncatalyzed reaction. Another specific feature of

TABLE II
Dehalogenation of chlorobiphenyls and chlorobenzenes (2 mmol) with SDMA (3 : 1 Cl molar ratio) catalyzed by $Ni(acac)_2$ and $Co(acac)_2$ (0.11 mmol) in toluene (15 ml). For procedure see Experimental

Entry	Compound	Temperature, °C	$k \cdot 10^{2,a}$ l mol^{-1} min^{-1}	Product	Yield[b] mole %
			$Ni(acac)_2$		
1	4,4′-$(ClC_6H_4)_2$	70	15	4-$ClC_6H_4C_6H_5$	94
			0.2	$C_6H_5C_6H_5$	4.2
		110	200[c]	4-$ClC_6H_4C_6H_5$	7.0
			9.7[c]	$C_6H_5C_6H_5$	93[d]
2	1,4-$Cl_2C_6H_4$[e]	70[f]	0.84	ClC_6H_5	37
			0.14	C_6H_6	1.7
		110	1.4	ClC_6H_5	53
			0.19	C_6H_6	5.6
			$Co(acac)_2$		
3	4,4′-$(ClC_6H_4)_2$	70	160[g]	4-$ClC_6H_4C_6H_5$	16
			7[g]	$C_6H_5C_6H_5$	84
		110	190[h]	4-$ClC_6H_4C_6H_5$	0
			21[h]	$C_6H_5C_6H_5$	99.7[i]
4	1,4-$Cl_2C_6H_4$[e]	70[f]	0.49	ClC_6H_5	24
			0.09	C_6H_6	0.7
		110	2.4	ClC_6H_5	64
			0.15	C_6H_6	2.8
5	4-$ClC_6H_4C_6H_5$	70	2.0	$C_6H_5C_6H_5$	3.7
6	ClC_6H_5[e]	70[f]	0.18	C_6H_6	11
		110	1.2	C_6H_6	48

[a] First-order rate constants of Eq. (*A*). [b] GLC yield obtained after 1 h-reaction (for details see Experimental). [c] Reused catalyst: $k = 5 \cdot 10^{-2}$ and $1 \cdot 10^{-2}$ l mol^{-1} min^{-1}, respectively. [d] 99.9 % after 1.5 h. [e] 0.3 mmol catalyst. [f] Ref.[12]. [g] Reused catalyst: $k = 6 \cdot 10^{-2}$ and $2 \cdot 10^{-2}$ l mol^{-1} min^{-1}, respectively. [h] Reused catalyst: $k = 0.9$ and $5 \cdot 10^{-2}$ l mol^{-1} min^{-1}, respectively. [i] 96 mole % already after 30 min.

interest is much greater structure sensitivity of the reduction. This manifests itself both in the reduction of similar substrates (compare *k*'s e.g. in entries 1 and 2, and entries 3 and 4) and in the rate difference between consecutive reduction steps (compare *k*'s in each entry). The latter reflects in the selectivity of 1,4-dichlorobiphenyl reduction which, due to different rates of two reduction steps (Eq. (*A*)) can – with Ni(acac)$_2$ as the catalyst – be directed either to the monochlorinated derivative (cf. entry 1, 70 °C) or to the hydrocarbon (entry 1, 110 °C). By one order of magnitude higher efficiency of Co(acac)$_2$ favours this catalyst for the total dechlorination. When reused, the catalysts showed both lower activity and selectivity (cf. notes [c,g,h] in Table II).

High yields of the dechlorinated product obtained under mild conditions with SDMA in reasonable molar excess and Ni(II) or Co(II) pentanedionates in catalytic amounts makes this route a useful alternative to the so far most efficient stoichiometric hydride–transition metal reducing agents such as a recently reported[10] NaBH$_2$(alkoxy)$_2$–NiCl$_2$ in THF.

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