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

DEHALOGENATION IN THE PRESENCE OF PALLADIUM COMPLEXES

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Dehalogenation of aliphatic and aromatic halogeno derivatives with $NaAlH_2(OC_2H_4OCH_3)_2$ is accelerated by catalytic amounts of palladium complexes. The strongest effect was observed in the aromatic series, where even fluorobenzene was reduced. The effects of the amount of the catalyst and the nature of halogen were studied.

Reduction by complex hydrides in the presence of transition metals or their compounds[1-6] was used especially to facilitate the reaction of nitro compounds. In most cases the metal catalyst was added directly to the reaction mixture or the metal was first reduced from its salts before introducing the substrate, so that we deal here essentially with catalytic hydrogenation[1-4]. By contrast, Olah[5] has assumed that on appropriate mixing the components, unstable mixed hydride is transiently formed, which is the proper reducing agent. Vlček and Rusina[6] found that pyridine cobalt complexes act in the reduction of nitro compounds by sodium borohydride as homogeneous catalysts.

In connection with a study of reducing properties of sodium bis(2-methoxyethoxy)-aluminium hydride, especially in dehalogenations[7,8], and of catalytic properties of palladium[9], we were interested in catalytic effect of the metal or its compounds in the reduction of halogeno derivatives. As $NaAlH_2(OC_2H_4OCH_3)_2$ is mostly applied in aromatic solvents, we had to use a palladium compound soluble in this medium. For this purpose we have chosen nitrile complexes of the type $(RCN)_2.PdCl_2$, where R is phenyl or benzyl group. Their catalytic action was always tested by parallel experiments with uncatalysed reduction.

EXPERIMENTAL

Bis(phenylcyano)palladium dichloride and *bis(benzylcyano)palladium dichloride* were prepared by heating $PdCl_2$ with appropriate nitrile in excess (50 ml per 5 g of the chloride) in water bath for 20 min. The mixture was filtered while hot, the filtrate was cooled and diluted with ether

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to give yellow crystals of the complex, which were washed with ether and dried *in vacuo*. The so far unreported bis(benzylcyano)palladium dichloride melted at 93°C (decomposition) and its solubility in benzene was 0·99 g/100 ml. For $C_{16}H_{14}Cl_2NPd$ (411·7) calculated: 25·9% Pd, 6·8% N; found: 26·6% Pd, 6·4% N.

Reaction of bis(benzylcyano)palladium dichloride with the hydride. To 4 ml of 2M solution of sodium bis-(2-methoxyethoxy)-alumiumhydride in benzene, placed in a temperature controlled flask equipped with a stirrer and connected with volumetric burette, 2 ml of benzene palladium complex solutions of varying concentrations were added. In all cases the colour of the reaction mixture turned to brown-to-black; however, when the Pd concentration in the resulting solution was below c. $5 . 10^{-3}$ mol/l, no hydrogen evolution was observed. With the higher concentrations of the complex, the hydride was slowly decomposed, and brown to black precipitates were formed.

TABLE I

Survey of Conditions and Conversions Obtained in Dehalogenation by means of $NaAlH_2.(OC_2H_4OCH_3)_3$ in the Presence and in the Absence of Palladium Complexes

Halogeno derivative	mmol	Complex[a] mmol	Hydride mmol	Volume of the mixture ml	Temperature °C	Time h	Conversion %	Conversion without the catalyst %
1-Chlorooctane	10	A 0·10	10·5	13·2	22	22	8	7
	10	A 0·10	10·6	13·2	22	46	13	8
	10	A 0·10	10·5	13·2	50	5	23	13
Fluorobenzene	10	A 0·10	12·0	16·0	70	4	12	0
Chlorobenzene	5	B 0·06	5·3	6·8	70	2	26	10
	5	B 0·06	5·3	6·8	70	4·5	52	24
Bromobenzene	5	B 0·06	5·3	6·7	70	0·33	68	52
	5	B 0·06	5·3	6·7	70	1	99	54
	5	B 0·06	5·3	6·7	70	2	100	67
1-Chloronaphthalene	10	A 0·14	10·5	12·9	22	2	32	0·5
	10	A 0·14	10·5	12·9	22	5	57	6
	10	A 0·14	10·5	12·9	70	0·33	40	3
	10	A 0·14	10·5	12·9	70	1·25	47	6
	10	A 0·14	21	10·4	70	4	100	21
4-Bromoanisole	10	B 0·16	10·5	12·8	22	2·5	31	15
	10	A 0·14	10·5	12·8	70	0·28	50	20

[a] A denotes $(C_6H_5CN)_2PdCl_2$, B denotes $(C_6H_5CH_2CN)_2PdCl_2$.

Compounds used. 1-Chlorooctane, fluorobenzene, chlorobenzene, bromobenzene, 4-bromoanisole, and 1-chloronaphthalene were from laboratory stock and were distilled prior to use, dried over a molecular sieve, and their purity was checked by gas chromatography. Sodium-bis-(2-methoxyethoxy)aluminiumhydride (70% benzene solution) was supplied by the Institute of Inorganic Syntheses of Czechoslovak Academy of Sciences and its solutions in cumene and *p*-cymene were prepared by removing the benzene *in vacuo*, diluting the residue in the above solvent and evaporating the solvent, followed by dilution by this solvent to the required concentration. Fresh solutions of palladium complexes were always used, since it was found that they undergo decomposition on standing. Different solvents were used for purposes of chromatographic determination, *e.g.* in cases where the product was benzene.

Analysis. The course of the reaction and the purity of the compounds were followed on an instrument equipped with thermal-conductivity detector, using hydrogen as carrier gas and Apiezon L or poly(ethylene glycol monomethyl ether) as stationary phases. The proportion of the reaction products was determined from the heights of chromatographic peaks on the basis of calibration.

Reduction. To a substrate, a solution of a palladium complex in benzene, cumene, or *p*-cymene, was first added and then a solution of the hydride in these solvents. The flask was topped with calcium chloride drying tube and heated to the required temperature for fixed time. The mixture was then hydrolysed with 10% HCl, filtered, the non-aqueous layer was separated and analysed. In blank experiment the solution of the complex was replaced by the same volume of the solvent.

RESULTS

The conversions obtained in the reduction of various halogeno derivatives are recorded in Table I. The effect of the addition of the catalyst on dechlorination of 1-chlorooctane is quite small. Contrarily, a substantial rate acceleration was observed in the aromatic series. Remarkable result is particularly at least partial reduction of fluorobenzene, which cannot be effected in the absence of the catalyst, and also complete reduction of 1-chloronaphthalene.

In Fig. 1 is shown time-dependence of the reduction of 4-bromoanisole with and without the catalyst. It shows both distinct accelerating effect of the palladium complex, and unusual form of the non-catalytic curve, which after steep initial phase goes up very slowly. Similar dependence was also observed by us for other substrates, the position of the flat portion of the curve with respect to the ordinate was found to depend on the excess of the reducing agent. This indicates that practically obtainable yield in preparative reductions depend above all on the ratio of the reactants and to a lesser extent on the reaction time.

Preliminary experiments showed that there is no difference in catalytic action of the two palladium complexes employed. Fig. 2 illustrates distinct effect of the amount of the complex on the conversion of 1-chloronaphthalene. From the form of the curve, which speaks for saturation of the system by the complex, it is apparent that we do not deal here with a simple homogeneously catalytic scheme. A similar curve may be expected when the reduction proper is preceded by the equilibrium between the catalyst and one of the reactants. The same dependence could also be observed, however, if the palladium metal were catalytically active and it would agglomerate to bulkier particles with smaller specific surface. We have therefore made the attempt to ascertain the nature of the mixtures of palladium complex and hydride solutions. These experiments, in which we measured the volume of the gas evolved after mixing, yielded irreproducible results. Under otherwise identical conditions the amount of the hydrogen greatly varied (from zero to 10 mol H_2 per 1 mol Pd) and also the appearance of the reaction mixture underwent changes. It seems likely that the results were mainly influenced by the mode of mixing, *i.e.* by the efficiency of stirring during the addition of the complex to the hydride and by the rate of the addition. We have always observed the formation of dark coloured mixtures, from which in most cases a precipitate set down. This precipitate did not appear and no hydrogen (after subtraction of the blank experiment, the value of which was given by residual moisture) was observed, when the resulting concentration of the palladium complex was below $5 . 10^{-3}$ mol/l. As shown in Table I, the complex concentration in reaction mixture used by us were slightly above this limit. We have not succeeded in finding whether the dark coloured mixtures of the complex and the hydride are true or colloid solutions in respect to palladium moieties.

In conclusion it can be said that the course of the dehalogenation by sodium bis(2--methoxyethoxy)alumiumhydride is kinetically complex, both without (Fig. 1), and with the catalyst, the mode of the action of which is still unclear. It can, however,

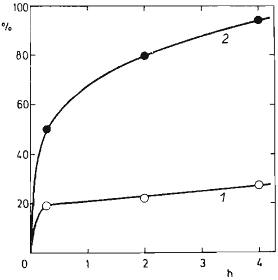

FIG. 1

Time-Dependence of Dehalogenation of 4-Bromoanisole at 70°C

The volume of the mixture was 12·8 ml, 10 mmol of the substrate, 10·5 mmol of the hydride, 1 without catalyst, 2 with 0·14 mmol of $(C_6H_5CN)_2PdCl_2$.

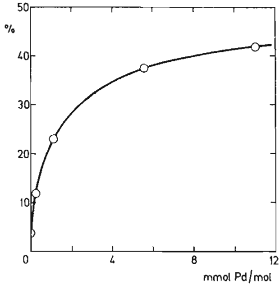

FIG. 2

Effect of the Amount of the Catalyst on the Conversion of 1-Chloronaphthalene at 70°C and Reaction Time of 0·5 h

The volume of the mixture was 9·9 ml, 10 mmol of the substrate, 10·5 mmol of the hydride, $(C_6H_5CH_2CN)_2PdCl_2$ was used as catalyst.

be reasonably assumed that the catalyst acts as hydrogen-carrier, and that either by forming a complex palladium hydride, or by decomposing to finely dispersed palladium (presumably deposited on voluminous hydride decomposition products) which transiently binds hydrogen on its surface.

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