April, 1981] © *1981 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *54*, *1265—1266 (1981)* 1265

The Transition-metal Catalyzed Dehalogenation of Aromatic Halides by NaOH-Alcohols. A Facile Method of Destroying Aromatic Polyhalides

Tadashi OKAMOTO* and Shinzaburo OKA
Institute for Chemical Research, Kyoto University, Uji 611

(Received July 25, 1980)

Synopsis. Aromatic halides are dehalogenated by heating with NaOH in alcoholic solvents in the presence of transition metal salts, such as rhodium(III) chloride or palladium(II) acetate and triphenylphosphine. Bis(pentabromophenyl) ether was converted into diphenyl ether in 2-propanol when treated for 5 h at 355 K with a catalytic cycle of more than 80.

Lately transition metal catalysts have been found to be useful for the substitution of aromatic halides.[1] Dehalogenation is the simplest type of these reactions, and many reports on the catalysis of palladium, rhodium, or nickel complexes using borohydride, formate, alkoxide, or secondary alcohols as the hydrogen source have been published.[2] These methods in the literature usually require low-valent metal complexes or powerful reducing agents such as borohydride. There has been one report on a dehalogenation catalyzed by rhodium(III) chloride using Na_2CO_3 in ethanol, but the substrate is limited to such activated halides as α-keto halides or benzyl halide.[3] In this report we wish to present a facile and inexpensive method of dehalogenation. Aromatic halides were heated with sodium hydroxide in alcoholic solvents in the presence of transition metal salts and triphenylphosphine to give dehalogenated aromatic compounds in moderate to excellent yields. No previous preparation of a low-valent catalyst or alkoxide was necessary.

TABLE 1. RHODIUM(III)-CATALYZED DEHALOGENATION OF AROMATIC HALIDES[a]

Substrate	Solvent	Yield of[b] arenes/%
Bromobenzene	MeOH	30
Bromobenzene	EtOH	78
4-Bromoanisole	EtOH	65[c]
4-Bromoanisole	*i*-PrOH	69
4-Bromoanisole	EtOH	27[d]
β-Bromostyrene	EtOH	65
3-Bromopyridine	EtOH	64
4-Bromoacetophenone	EtOH	15[e]
4-Bromoacetophenone	EtOH	25[f]
4-Bromobenzoicacid	EtOH	44[g]
4-Chlorobenzoic acid	EtOH	0[g]
1-Chloro-1-phenylethane	EtOH	h

a) Reactions were carried out at 335 K for 16 h with a substrate/catalyst of 50 and a NaOH/substrate of 1.5. Catalyst: $RhCl_3$–$2P(C_6H_5)_3$. b) Determined by gas chromatography based on the amount of substrate used. c) The reaction temperature was 351 K. d) Na_2CO_3 was used instead of NaOH; 73 h. e) Accompanied by 1-phenylethanol (7%). f) Accompanied by diphenylmethanol (*ca.* 25%). g) The NaOH/substrate was 2.5. h) The products were ethylbenzene and styrene, with the relative ratio being around 1. The yields were not determined.

Results and Discussion

The results for various substrates are listed in Table 1. The reactivity of bromide is higher than that of chloride, and electron-releasing substituents on the aromatic ring retard the reaction, as in the case of the oxidative-addition reaction of aryl halides with low-valent transition-metal complexes.[4] Palladium acetate–$2P(C_6H_5)_3$ was a better catalyst than $RhCl_3$ hydrate–$2P(C_6H_5)_3$. $NiBr_2[P(C_6H_5)_3]_2$ or $CoCl_2$ hydrate–$2P(C_6H_5)_3$ was ineffective for the reaction. This trend of reactivity is in accordance with that of the reduction potential (E_0) of metal salts.[5] These observations suggest that a low-valent metal complex is generated *in situ* and reacts with aromatic halides to give oxidative-addition products, which are then reduced by the alkoxide ion (or alcohol) according to the scheme shown by Eqs. 1—3, where X represents an anion such as a halide or acetate ion:

$$M^{n+}X_n \xrightarrow{R'_2CHO^- \text{ (or } R'_2CHOH)} M^{(n-2)+}X_{n-2} \tag{1}$$

$$M^{(n-2)+}X_{n-2} + ArY \longrightarrow M^{n+}(Ar)X_{n-2}Y \tag{2}$$

$$M^{n+}(Ar)X_{n-2}Y + R'_2CHO^- \text{ (or } R'_2CHOH) \xrightarrow{-Y^- \text{ (or HY)}} M^{(n-2)+}X_{n-2} + R'_2CO + ArH \tag{3}$$

There is a substantial difference in the reactivity of alcohols, MeOH<EtOH<*i*-PrOH. The slower reaction with Na_2CO_3 compared with NaOH suggests that NaOH is effective not only in neutralizing the hydrogen halide generated, but also in facilitating the reduction of metal complexes in some way.[6]

As may be seen from Table 1, the reaction is applicable to pyridine derivatives and also to vinyl halides. An aliphatic saturated halide such as 1-chloro-1-phenylethane was dehalogenated to give ethylbenzene, but it was accompanied by a substantial amount of styrene, the elimination product. The reduction of the carbonyl group is another side reaction; 4-bromobenzophenone gave almost equimolar amount of diphenylmethanol and the normal dehalogenation product of benzophenone.

Polyhalogenated aromatic compounds are dehalogenated by this system easily. The results are summarized in Table 2. Bis(pentabromophenyl) ether was converted to diphenyl ether (92% yield) by the catalysis of palladium acetate–$2P(C_6H_5)_3$ over a 5 h period at 355 K with a catalytic cycle of more than 80. Although polychlorinated biphenyl (Kanechlor) was dehalogenated more sluggishly than the bromide, the present reaction is suitable for the purpose of destroying

TABLE 2. DEHALOGENATION OF POLYHALOGENATED AROMATIC COMPOUNDSa)

Substrate (mmol)	Catalyst	Time/h	Dehalogenation (%)b)
Bis(pentabromophenyl) ether (1.9)	$Pd(OAc)_2$–$2P(C_6H_5)_3$	5	100
	$Pd(OAc)_2$–2Pyridine	56	94
	$RhCl_3$–$2P(C_6H_5)_3$	21	74
	$RhCl_3$–2DPEc)	56	87
Kanechlor 600 (4.3)	$Pd(OAc)_2$–$2P(C_6H_5)_3$	45	50
	$RhCl_3$–$2P(C_6H_5)_3$	19	33

a) The reaction was carried out at 355 K with a 20% excess of NaOH and 0.20 mmol of the catalyst in 10 ml of 2-propanol. b) Determined by the elemetal analysis of the product (mixture). c) Ethylenebis(diphenylphosphine).

environment-contaminating aromatic polychlorides, because highly chlorinated compounds, which are known to be difficult to destroy, were dehalogenated preferentially, as is illustrated in Fig. 1 for the dehalogenation of 2,3,4,5,6-pentachloroanisole. The figure further suggests the step-by-step mechanism of the dehalogenation reaction. There is no indication of a benzyne intermediate with a simultaneous elimination of two halogen atoms.

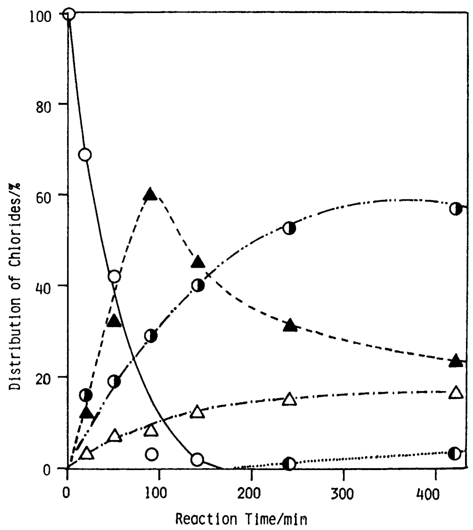

Fig. 1. Dehalogenation of 2,3,4,5,6-Pentachloroanisole. ○ Pentachloride, ▲ Tetrachloride, ◑ Trichloride, △ Dichloride, and ◐ Monochloride. $Pd(OAc)_2$, 0.27 mol; triphenylphosphine, 0.39 mmol; NaOH, 22.75 mol; substrate, 2.30 mmol in 10 ml of 2-propanol at 355 K. Product distribution was determined by gas chromatography.

Experimental

The palladium acetate was prepared by the method of Wilkinson.7) The other reagents were analytical-grade.

Dehalogenation of Aromatic Monohalides by $RhCl_3 \cdot 6H_2O$ and Triphenylphosphine. $RhCl_3 \cdot 6H_2O$ (20 mg), triphenylphosphine (40 mg), and NaOH (300 mg) were placed in a flask and deaerated. Into the flask we then added 5 mmoles of a substrate and 10 ml of a solvent, subsequently the mixture was stirred at 335 K for a specified period. The yields were determined by gas chromatography.

Dehalogenation of Bis(pentabromophenyl) Ether. Bis(pentabromophenyl) ether 1.78 g (1.9 mmol), NaOH 0.91 g (22.8 mmol), and the catalyst (0.2 mmol) were placed in a flask, and the mixture was flushed with nitrogen. Deaerated 2-propanol (10 ml) was then added to the flask, and the solution was refluxed for the specified period under stirring. The reaction mixture was then diluted with a 10-ml portion of H_2O and extracted by means of three 10-ml portions of hexane. The extract was concentrated and subsequently purified on a silica-gel column (hexane) from the base-promoted condensation products of acetone. The hexane effluent, which contained diphenyl ether and/or partly brominated diphenyl ethers, was concentrated and weighed. The average extent of dehalogenation was determined by the elemental analysis of the residue. The material balance of the reaction, as determined from the weight and the extent of dehalogenation of the residue, was generally good.8)

The dehalogenation of Kanechlor was carried out in a similar manner except for the amounts of the substrate and NaOH.

References

1) R. Cramer and D. R. Coulson, *J. Org. Chem.*, **40**, 2267 (1975); K. Takagi, T. Okamoto, Y. Sakakibara, A. Ohno, S. Oka, and N. Hayama, *Bull. Chem. Soc. Jpn.*, **48**, 3298 (1975).

2) N. A. Cortese and R. F. Heck, *J. Org. Chem.*, **42**, 3491 (1977): A. Zask and P. Helquist, *ibid.*, **43**, 1619 (1978): S.-T. Lin and J. A. Roth, *ibid.*, **44**, 309 (1979): Y. Tamaru, Y. Yamamoto, Y. Yamada, and Z. Yoshida, *Tetrahedron Lett.*, **1970**, 1401.

3) R. Grigg, T. R. B. Mitchell, and S. Sutthivayakit, *Tetrahedron Lett.*, **1979**, 1067.

4) T. T. Tson and J. K. Kochi, *J. Am. Chem. Soc.*, **101**, 6319 (1979), and the references cited therein.

5) J. P. Jesson and E. L. Muetterties, "Chemist's Guide," Marcel Dekker, New York (1969), p. 7.

6) The contribution of bases to the oxidation-reduction of transition-metal complexes was known, but the mechanisms were not clearly understood. See, for example, J. A. Switzer and J. F. Endicott, *J. Am. Chem. Soc.*, **102**, 1181 (1980), and the references cited therein.

7) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. R. Heff, and G. Wilkinson, *J. Chem. Soc.*, **1965**, 3632.

8) The material balance was 90—100% except for the reaction catalyzed by $RhCl_3$–2DPE (85%).