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The Dehalogenation of Organic Halides by Means of Iron(II) Chloride in Dimethyl Sulfoxide

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A recent publication[1] recorded a Wurtz-type condensation effected by iron(II) chloride-diamine complexes in ethanol. This has prompted us to publish our independent findings on the title reaction,[2] which has been examined in continuation of a previous investigation of the reactions of organic halides with copper(I) chloride in dimethyl sulfoxide (DMSO).[3] The observed results summarized in Table 1 are partly parallel to those of diamine complex,[1] but we wish to point out that the present reaction does furnish a practical, simple method for preparing tetraphenylethylene and *trans*-stilbene.

Iron(II) chloride tetrahydrate dissolves in DMSO to give a reddish-brown clear solution upon stirring in a nitrogen atmosphere for several minutes.[4] Benzylic and allylic halides were allowed to react in this 1M solution of the iron(II) salt. Dichlorodiphenylmethane, under the controlled conditions shown in Table 1, gave 1,2-dichloro-1,1,2,2-tetraphenylethane as the sole condensation product; this product was then further dehalogenated to tetraphenylethylene. In contrast, the dehalogenation by means of copper(I) chloride in DMSO gave tetraphenylethylene exclusively.[3] No 1,2-dichloro-1,1,2,2-tetraphenylethane was isolated in the latter reaction under any of the conditions examined.

Such step-by-step reduction was also observed in the case of benzotrichloride, which afforded α,α,α′,α′-tetrachlorobibenzyl or a mixture of *cis*- and *trans*-α,α′-dichlorostilbene, under the controlled conditions. Benzal bromide gave a good yield of *trans*-stilbene, whereas benzal chloride did not give any condensation products, but benzaldehyde only. Benzyl chloride also failed to give even a trace of bibenzyl. The sole product isolated was found to be benzyl alcohol. When the reaction was performed in a mixture of DMSO-ethanol, the resulting product was benzyl ethyl ether. These products may be explained by assuming the following schemes:

$$\begin{tikzcd}
R\text{-}X + Fe^{II}L_m(SH)_n \arrow[r] & R\text{-}XFe^{II}L_{m'}(SH)_{n'} \arrow[d] \arrow[dl] \\
HX + R\text{-}S + Fe^{II}L_m(SH)_n & R\cdot + Fe^{III}XL_{m-1}(SH)_n
\end{tikzcd}$$

L: DMSO, H_2O, halide ion
SH: protic solvent (EtOH)

TABLE 1. WURTZ-TYPE CONDENSATION INDUCED BY 1 M $Fe(II)Cl_2\cdot 4H_2O$/DMSO SOLUTION[a]

Substrate	Reaction temp (°C)	time (hr)	Product yield in %[b]
Ph_2CCl_2(Fe/X=2.5)	90	27	$Ph_2C=CPh_2$ (82)[c]
(Fe/X=0.5)	20—30	16	$Ph_2CClCClPh_2$ (65)[c]
$PhCCl_3$ (Fe/X=0.4)	60	27	$PhCCl_2CCl_2Ph$ (85)
$PhCCl_2CCl_2Ph$	90	17	PhCCl=CClPh (*cis* 76, *trans* 18)
$PhCHBr_2$	80	21	PhCH=CHPh (*trans* 83)[d]
PhCHBrCHBrPh (*meso*)	80	24	PhCH=CHPh (*trans* 95)
PhCOCHBrCHBrPh	r.t.	24	PhCOCH=CHPh (90)
$PhCHCl_2$	80	20	PhCHO (90)
$PhCH_2Cl$	80—90	20	$PhCH_2OH$ (69)
$PhCH=CHCH_2Cl$ (*trans*)	70—80	20	$PhCH=CHCH_2CH_2CH=CHPh$ (*trans* 34) $PhCH=CHCH_2OH$ (*trans* 33)

a) Unless otherwise stated the ratio of organic halides and iron(II) chloride was taken so as the atomic ratio of Fe: halogen to be 2.5:1.
b) Recovery was not considered in calculation of yields.
c) Benzophenone was obtained as solvolysis product.
d) Benzaldehyde was a minor product.

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1) K. Onuma, J. Yamashita and H. Hashimoto, This Bulletin, **43**, 836 (1970). See also R. S. Wade, R. Havlin and C. E. Castro, *J. Amer. Chem. Soc.*, **91**, 7530 (1969).

2) A part of this work was presented at the 23rd Annual Meeting of Chemical Society of Japan, Tokyo, April 3, 1970 (No. 16332) and the 160th National Meeting of ACS, Chicago, Ill., Sept 17, 1970 (No. ORGN 139).

3) H. Nozaki, T. Shirafuji, and Y. Yamamoto, *Tetrahedron*, **25**, 3461 (1969).

4) The iron(II) iodide-DMSO complex was isolated and characterized.[5] Attempts at isolating iron(II) chloride-DMSO complex similarly did not succeed.

5) F. A. Cotton, R. Francis, and W. D. Horrocks, *J. Phys. Chem.*, **64**, 1534 (1960).

Cinnamyl chloride gave the Wurtz product in addition to the hydrolysate, cinnamyl alcohol. All these observations may tentatively be explained as follows. The halide-iron salt complex undergoes a one-electron transfer, thus affording the R· radicals, whose recombination gives the coupling products, R–R. The driving force toward this direction is probably the susceptibility of C–X bond cleavage and the stability of R·. The alternative path is the S_N reaction in the coordination sphere of the iron(II) ion. The ligand-ligand reaction gives the observed solvolysis products, such as benzaldehyde, benzyl alcohol, and cinnamyl alcohol.

Finally, it should be added that the present reagent is effective in inducing vicinal dehalogenation; this is exemplified by the reaction of stilbene dihalides as well as by that of benzalacetophenone dibromide.

Experimental

All the melting points are uncorrected. The mass spectra were determined on a Hitachi RMU-6L spectrometer, and the NMR spectra, on a JEOL C-60-H spectrometer, in $CDCl_3$ or CCl_4 solution at 60 MHz. The microanalyses were performed at the Elemental Analyses Center of Kyoto University.

General Procedure of Reactions of Organic Halides with Iron(II) Chloride Tetrahydrate in DMSO. Iron(II) chloride was dissolved in freshly-distilled (over CaH_2) DMSO under a nitrogen atmosphere so as to give a *ca.* 1 M solution upon heating with stirring at 60—70°C for 30 min; then the solution was maintained at an appropriate reaction temperature (20—80°C). A solution (*ca.* 0.4 M) of an organic halide in DMSO was then added to this drop by drop. The atomic ratio of halogen: Fe(II) was taken to be 1:2.5 unless otherwise stated. Heating and stirring were continued until TLC indicated the absence of the halide. The mixture was then treated with water and extracted with ether or benzene. The extract was washed with water, dried (Na_2SO_4), and concentrated *in vacuo*. The products were separated and identified as usual. The following description refers to cases which cannot be covered sufficiently by Table 1.

Dechlorination of Dichlorodiphenylmethane. Dichlorodiphenylmethane (1.18 g, 0.005 mol) was treated with a solution of iron(II) chloride (1.00 g, 0.005 mol) in DMSO (30 m*l*) at 20—30°C for 16 hr. The reaction products were washed with MeOH. The recrystallization of the resulting crystalline product from benzene - EtOH (1:1) gave 1,2-dichloro-1,1,2,2-tetraphenylethane (0.65 g, 65%), mp (decomp.) 175—178°C (lit,[6] 184—186°C), which was identified by elemental analyses and by comparison with an authentic sample (IR, MS). The further dehalogenation of the dichloride with iron(II) chloride in DMSO yielded tetraphenylethylene. The concentration of the filtrate gave benzophenone (0.20 g, 22%). In another run, dichlorodiphenylmethane (2.50 g, 0.011 mol) was treated with a solution of iron(II) chloride (10.6 g, 0.053 mol) in DMSO (50 m*l*). The crude product was washed with MeOH and recrystallized from benzene - EtOH (1:1) to afford tetraphenylethylene (1.43 g, 82%), mp 220—222°C (lit,[7] 222—224°C).

Dechlorination of Benzotrichloride. Benzotrichloride (2.00 g, 0.010 mol) was treated with a solution of iron(II) chloride (2.48 g, 0.012 mol) in DMSO (20 m*l*) at 60°C for 27 hr. A work-up gave $\alpha,\alpha,\alpha',\alpha'$-tetrachlorobibenzyl (1.40 g, 85%), mp and mixed mp 159—160°C (EtOH) (lit,[8] 160—161°C), which was identified by means of its IR spectra. Tetrachlorobibenzyl (1.50 g, 0.005 mol) was treated with a solution of iron(II) chloride (10.0 g, 0.050 mol) in DMSO (50 m*l*) at 90°C for 17 hr. Chromatography on a short alumina column, followed by recrystallization (EtOH), afforded a mixture (1.17 g, 94%) of *cis*- and *trans*-α,α'-dichlorostilbene. Hand-sorting and recrystallizations gave pure constituents, the *cis* isomer as prisms, mp and mixed mp 60—62°C (lit,[9] 62—63°C), and the *trans* isomer as powdery microcrystals, mp and mixed mp 137—138°C (lit,[9] 142°C). The yields (*cis* 76%, *trans* 18%) were calculated on the basis of the product ratio determined by GLC (Apiezon L 30%).

Hydrolysis of Benzyl Chloride. Benzyl chloride (1.27 g, 0.010 mol) was treated with a solution of iron(II) chloride (4.98 g, 0.025 mol) in DMSO (30 m*l*) at 80—90°C for 20 hr, when TLC indicated the absence of benzyl chloride. The work-up of the mixture gave benzyl alcohol (0.75 g, 69%). However, the treatment of benzyl chloride (1.27 g, 0.010 mol) with EtOH (6 m*l*) and iron(II) chloride (1.99 g, 0.010 mol) in DMSO (30 m*l*) at 80—90°C, followed by a further usual work-up, gave benzyl ethyl ether (0.96 g, 70%). The treatment of benzyl chloride at 20°C gave no products but the starting material.

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6) M. S. Kharasch and H. C. Brown, *J. Amer. Chem. Soc.*, **61**, 3432 (1939).

7) "Org. Syntheses," Coll. Vol. 4. p. 914. (1963).

8) D. C. Sayles and M. S. Kharasch, *J. Org. Chem.*, **26**, 4210 (1961).

9) H. Staudinger, *Ber.*, **49**, 1969 (1916).