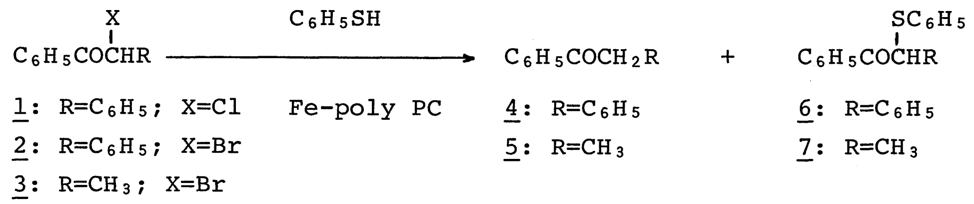
CHEMISTRY LETTERS, pp. 1241-1244, 1975. Published by the Chemical Society of Japan

# REDUCTIVE DEHALOGENATION OF α-HALO KETONES WITH BENZENETHIOL CATALYZED BY IRON-POLYPHTHALOCYANINE

Hiroo INOUE, Hiroyuki HATA, and Eiji IMOTO
Department of Applied Chemistry, College of Engineering, University
of Osaka Prefecture, Sakai-shi, Osaka 591

It is found that α-halo ketones are reduced with benzenethiol in the presence of iron-polyphthalocyanine to the parent ketones, although they are not reduced in the absence of iron-polyphthalocyanine. The iron-polyphthalocyanine appears to serve as an electron-transfer catalyst for the reductive dehalogenation.

Recently we reported the catalytic action of iron-polyphthalocyanine (Fe-poly PC) on the reduction of α-chlorodeoxybenzoin (1) with 1-benzyl-1,4-dihydronicotinamide to deoxybenzoin (4).[1] In such a reduction system, Fe-poly PC was shown to function as an electron-transfer carrier between 1-benzyl-1,4-dihydronicotinamide and 1. We have now extended this study to include the use of benzenethiol as a reducing agent, and found that Fe-poly PC catalyzes the reductive dehalogenation of α-halo ketones (1-3) with benzenethiol in dry benzene or 80 vol% aqueous methanol.



$$\overset{X}{C_6H_5COCHR} \xrightarrow[\text{Fe-poly PC}]{C_6H_5SH} C_6H_5COCH_2R + \overset{SC_6H_5}{C_6H_5COCHR}$$

1: $R=C_6H_5$; $X=Cl$
2: $R=C_6H_5$; $X=Br$
3: $R=CH_3$; $X=Br$
4: $R=C_6H_5$
5: $R=CH_3$
6: $R=C_6H_5$
7: $R=CH_3$

In the absence of Fe-poly PC, 1, α-bromodeoxybenzoin (2), and α-bromopropiophenone (3) underwent no reaction with benzenethiol in dry benzene at 80°C under a nitrogen atmosphere in a sealed tube. Employing 80 vol% aqueous methanol as the solvent, however, 1, 2, and 3 were converted to the corresponding α-phenylthio ketones (6 and 7) in high yields, as Table 1 shows (n=0). The reduction of the α-halo ketones with benzenethiol did not occur at all.

Fe-poly PC (Fe, 5.8%), which was prepared by the method described in our previous paper,[2] was suspended in a solution containing α-halo ketones and benzenethiol in dry benzene or 80 vol% aqueous methanol and the solution was heated at

80°C under the conditions similar to those used in the absence of Fe-poly PC.

The α-halo ketone, **1**, was reduced selectively to **4** by the action of Fe-poly PC (Table 1), while benzenethiol was oxidized to diphenyl disulfide in this reaction. However, the amount of the diphenyl disulfide was ambiguous, since benzenethiol was easily oxidized to diphenyl disulfide with air in the presence of Fe-poly PC. The amount of **4** produced increased with the passage of time. When the Fe(II) ion/α-halo ketone molar ratio (n) was 1, the reaction time ($t_{50}$) required for 50% formation of **4** was 15 hr in dry benzene and 9 min in 80 vol% aqueous methanol. At n = 0.1, the value of $t_{50}$ was 1 hr in the case of 80 vol% aqueous methanol. Thus, Fe-poly PC acted as an effective catalyst for the reductive dehalogenation of **1** with benzenethiol.

Table 1. The reductions of α-halo ketones with benzenethiol in 80 vol% aqueous methanol (80°C)a)

| Ketones | nb) | Time, min | Yields,%c) | | Recovery,%c) |
|---|---|---|---|---|---|
| | | | **4** or **5** | **6** or **7** | Ketones |
| **1** | 0 | 30 | 0 | 59 | 37 |
| **1** | 1 | 30 | 92 | 0 | — |
| **1** | 0.1 | 120 | 67 | 0 | 23 |
| **2** | 0 | 5 | 0 | 96 | <1 |
| **2** | 1 | 5 | 87 d) | 0 | — |
| **3** | 0 | 5 | 0 | 80 | 20 |
| **3** | 1 | 30 | 58 | 24 | 0 |

a) The concentration of α-halo ketones; $2.8\text{x}10^{-2}$ mol/l and the molar ratio of benzenethiol to α-halo ketones; 4 : 1.

b) The value of n represents the Fe(II) ion/α-halo ketone molar ratio.

c) The amounts of the products and the recovered α-halo ketones were determined by means of glc, with biphenyl or 1,2-diphenylethane as an internal standard.

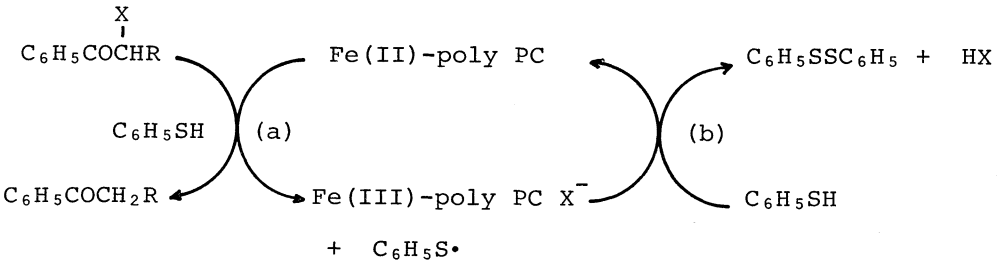
d) Isolation yield: 70%.

The catalytic activity of Fe-poly PC for the formation of **4** in the reductive dehalogenation of **1** was compared with that of various metal complexes. The reaction was carried out using dry benzene as the solvent with the metal complexes at n = 1 (80°C). The yields of **4** and **6** after a reaction of 48 hr are described below (%): Fe(II)-poly PC (75; 0), Fe(II)-PC(3) (83; 14), Co(II)-PC(3) (64; 0), Fe(III)(acac)$_3$ (72; 20), Fe(OAc)$_3$ (31; 3), $FeCl_3$ (11; 0), $FeCl_3/2C_5H_5N$ (36; 0), and $H_2$-PC (0; 0). The Fe(II), Fe(III), and Co(II) complexes, in which the bond between metal ion and ligand has the covalent character, exhibited high activity. This result agreed with that observed in the metal complex-catalyzed reduction of 1 with 1-benzyl-1,4-dihydronicotinamide.1) Moreover, Fe-poly PC brought about the selective formation of 4, although the reduction of 1 using Fe(II)-PC or Fe(III)(acac)$_3$ was accompanied by the formation of 6.

The reaction of 2 with benzenethiol in 80 vol% aqueous methanol in the presence of Fe-poly PC gave selectively 4 in a high yield, as Table 1 shows. However, the yield of the reduction product became lower in the case of 3 (Table 1). α-Bromoacetophenone reacted with benzenethiol in dry benzene in the presence of Fe-poly PC ($n = 1$) to give acetophenone and α-phenylthioacetophenone in 16 and 62% yields, respectively, with 22% recovery of α-bromoacetophenone after a reaction of 24 hr.

The reaction of phenacylpyridinium bromide with benzenethiol in 80 vol% aqueous methanol in the presence of Fe-poly PC ($n = 1$) at 80°C gave acetophenone in 42% yield with 50% recovery of phenacylpyridinium bromide after a reaction of 72 hr.

The reduction of α-phenylthio ketones with benzenethiol in the presence of Fe-poly PC did not occur at all, although it has been reported previously that α-alkylthio ketones are reduced by a thiolate anion to the parent ketones.4) It has been already reported that organic halogen compounds are reduced by iron-porphyrins5) and thiols are oxidized by the Fe(III) complexes, such as $Fe(CN)_6^{3-}$ and ferric octanoate, in the absence of oxygen to disulfides.6) In view of these facts, the Fe-poly PC-catalyzed dehalogenation of α-halo ketones with benzenethiol would be explained to proceed by an electron-transfer mechanism which may be made up by the combination of the reduction of α-halo ketones with Fe(II)-poly PC (a) and the oxidation of benzenethiol with Fe(III)-poly PC $X^-$ (b), as shown in the following scheme.



## References and Notes

1) H. Inoue, R. Aoki, and E. Imoto, Chem. Lett., 1974, 1157.

2) H. Inoue, Y. Kida, and E. Imoto, Bull. Chem. Soc. Japan, 40, 184 (1967); ibid., 41, 684 (1968).

3) Fe(II)-PC and Co(II)-PC were prepared according to the methods described in the following literature; P. A. Barrett, C. E. Dent, and R. P. Linstead, J. Chem. Soc., 1936, 1719.

4) M. Ōki, W. Funakoshi, and A. Nakamura, Bull. Chem. Soc. Japan, 44, 828 (1971).

5) C. E. Castro, J. Amer. Chem. Soc., 86, 2310 (1964).

6) G. Capozzi and G. Modena, "The Chemistry of the Thiol Group," S. Patai, Ed., Part 2, Wiley, New York, N. Y., 1975, Chapter 17 and references therein.

(Received September 6, 1975)