

### SELECTIVE REMOVAL OF ORTHO HALOGENS BY A DIORGANOLANTHANOID

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**Abstract:** Reaction of halogenobenzoic acids with bis(pentafluorophenyl)ytterbium(II) in tetrahydrofuran results in selective removal of ortho halogen substituents.

Reaction of pentafluorobenzoic acid with bis(pentafluorophenyl)ytterbium(II) followed by acidification yields 2,3,4,5-tetrafluorobenzoic acid.<sup>1</sup> This contrasts with electrochemical reduction which gives 2,3,5,6-tetrafluorobenzoic acid<sup>2</sup> and reduction by ytterbium diiodide giving a mixture of 2,3,4,5- and 2,3,5,6-tetrafluorobenzoic acids. We have now reacted bis(pentafluorophenyl)ytterbium(II) with a range of halogenobenzoic acids and find that the organolanthanoid is a selective reducing agent for ortho halogens.

Solutions of bis(pentafluorophenyl)ytterbium(II) in tetrahydrofuran prepared by the reported method,<sup>3,4</sup> were reacted with a series of halogenobenzoic acids (Table 1) at -78°C for 1 h under dry oxygen-free nitrogen. The reaction mixtures were then hydrolysed, the acid products were methylated with diazomethane, and the methyl esters were identified and their yields determined by g.l.c. (Table 1).

With a mole ratio of  $(C_6F_5)_2Yb : RCO_2H$  of ca. 1:1, there was no reduction of o-fluorobenzoic acid, some reduction of o-chlorobenzoic acid, and more reduction of o-iodobenzoic acid. This is consistent with increasing polarizability as the size of the halogen increases. By contrast with o-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m- and p-ClC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H were essentially unaffected. A similar reaction of 2,4-dichlorobenzoic acid led to partial dehalogenation specifically of the ortho-chlorine, and substantial conversion to p-chlorobenzoic acid was achieved by increasing the  $(C_6F_5)_2Yb : RCO_2H$  mole ratio to ca. 5:1. Similarly 2,5-dichlorobenzoic acid underwent selective reduction to m-chlorobenzoic acid in high yield, whilst 2,6-dichlorobenzoic acid yielded a mixture of benzoic and o-chlorobenzoic acids (Table 1). Thus, selective reduction of ortho halogens occurs and indeed two such substituents can be removed.

Dehalogenation can be explained by protolysis giving a carboxylatopentafluorophenyl-ytterbium(II) complex, electron transfer to the ortho halogen via a six-membered transition state, and hydrogen capture from tetrahydrofuran (see Ref.<sup>1</sup>) or on hydrolysis.

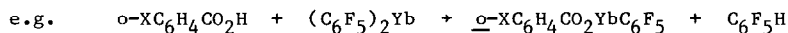
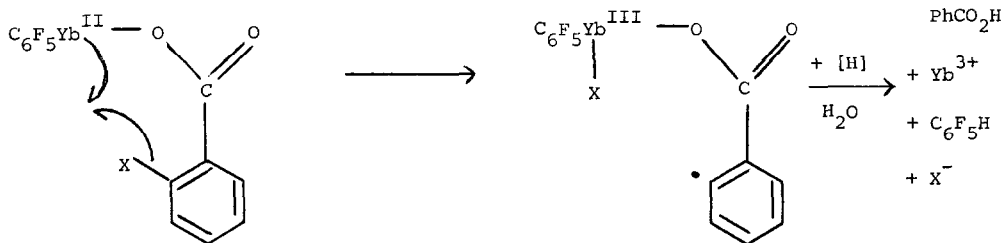


Table 1: Reactions of bis(pentafluorophenyl)ytterbium(II)<sup>a</sup> with halogenobenzoic acids<sup>b</sup>

| $(C_6F_5)_2Yb$<br>(mmol) | Yb<br>(mg.at.) | Reactant: $RCO_2H$    |        | Product: $R'CO_2H$                 |       | Unchanged<br>Reactant (%) |
|--------------------------|----------------|-----------------------|--------|------------------------------------|-------|---------------------------|
|                          |                | R                     | (mmol) | R'                                 | (%)   |                           |
| 3.23                     | 11.04          | <u>o</u> - $FC_6H_4$  | 3.23   | Ph                                 | 0     | 74                        |
| 2.95                     | 9.29           | <u>o</u> - $ClC_6H_4$ | 2.95   | Ph                                 | 12    | 65                        |
| 3.48                     | 7.87           | <u>o</u> - $IC_6H_4$  | 3.48   | Ph                                 | 33    | 49                        |
| 2.34                     | 4.88           | <u>m</u> - $ClC_6H_4$ | 2.35   | Ph                                 | 0     | 68                        |
| 2.39                     | 11.64          | <u>p</u> - $ClC_6H_4$ | 2.40   | Ph                                 | trace | 99                        |
| 2.40                     | 3.90           | 2,4- $Cl_2C_6H_3$     | 2.40   | <u>p</u> - $ClC_6H_4$              | 11    | 67                        |
| 5.10                     | 10.58          | 2,4- $Cl_2C_6H_3$     | 1.02   | <u>p</u> - $ClC_6H_4$ <sup>c</sup> | 76    | 0                         |
| 9.10                     | 21.13          | 2,5- $Cl_2C_6H_3$     | 1.84   | <u>m</u> - $ClC_6H_4$ <sup>c</sup> | 84    | 10                        |
| 2.83                     | 7.32           | 2,6- $Cl_2C_6H_3$     | 2.84   | <u>o</u> - $ClC_6H_4$              | 9     | 91                        |
| 10.13                    | 10.50          | 2,6- $Cl_2C_6H_3$     | 2.07   | <u>o</u> - $ClC_6H_4$              | 24    | 27                        |
|                          |                |                       |        | Ph                                 | 41    |                           |

<sup>a</sup> Prepared 'in situ' from the reagents in the first two columns in dry tetrahydrofuran (20 ml) under oxygen-free dry nitrogen. Near quantitative yields are obtained.<sup>4</sup> <sup>b</sup> The solid acid was added to the solution of  $(C_6F_5)_2Yb$ . <sup>c</sup> A trace of  $PhCO_2H$  was also obtained.



Similar dehalogenations may be possible in cases where a halogen is ortho to a donor group other than carboxyl.

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#### References

- G.B. Deacon, P.I. MacKinnon and T.D. Tuong, Aust. J. Chem., 1983, **36**, 43.
- F.G. Drakesmith, J. Chem. Soc., Perkin Trans. I, 1972, 184.
- G.B. Deacon, W.D. Raverty and D.G. Vince, J. Organomet. Chem., 1977, **135**, 103.
- G.B. Deacon, A.J. Koplick, W.D. Raverty and D.G. Vince, J. Organomet. Chem., 1979, **182**, 121.

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