

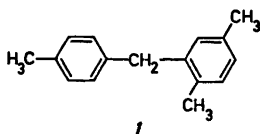
Metal Ion Oxidation. V.¹ The Mechanism of the Dehydrodimerization of *p*-Xylene by Perchloric Acid and Iron(II) Chloride in Acetic Acid

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One of us has earlier reported on the reaction between iron(III) chloride and methylbenzenes and its mechanism.²⁻⁴ The reaction shows similarities with the anodic oxidation of methylbenzenes yielding biaryls and/or diphenylmethanes.² In a recent report it was shown that selective formation of diphenylmethanes can be achieved by the oxidation of methylbenzenes using various iron(III) salts (chloride, sulfate, nitrate, acetate and perchlorate) in the presence of perchloric acid using acetic acid as a solvent at elevated temperatures.⁵ In the absence of perchloric acid the yields were low. In many cases the reaction was catalytic in iron(III) and the authors proposed that reoxidation of iron(II) was caused by atmospheric oxygen. We have been studying a similar reaction for some time and now report results showing that the proposed mechanism⁵ is not correct and that the reoxidation of iron(II) is caused by perchloric acid.

When iron(II) chloride is heated with *p*-xylene in acetic acid and in the presence of perchloric acid **1** is formed (Table 1, run No. 1).



The yield of **1** is better than 100 % if one assumes that iron(III) is the oxidant responsible for converting *p*-xylene into **1**. The reaction would then require 2 mol of iron(III) for each mole of **1** formed. A prolonged reaction time (run No. 2) increased the yield of **1** slightly. Runs Nos. 3 and 4 show that no reaction takes place in the absence of either iron(II) or perchloric acid. Reactions 1-4 were carried out in an air atmosphere. Run No. 5 was carried out under pure nitrogen (with careful exclusion of oxygen) which resulted in a slightly lower yield of **1** but the reaction was still catalytic. Thus, the results of these experiments (runs Nos. 1-5) do not indicate that oxygen plays a major role in the oxidation of iron(II) to iron(III). Finally, we carried out a reaction where perchloric acid was replaced by trifluoromethanesulfonic acid, a strong non-oxidizing acid (run No. 6); a low yield of **1** was obtained.

We believe that an explanation of our results is consistent with the assumption that the major reaction path involves perchloric acid oxidation of iron(II) to iron(III). The latter species acts as the oxidant towards *p*-xylene. Oxygen plays only a minor role in the reoxidation of iron(II) as indicated by the result of run No. 6. It is well known that perchloric acid is a weak oxidant at room temperature but a strong one at temperatures above 100 °C.⁶ The results from run No. 4 shows that perchloric acid is not the oxidant responsible for the formation of **1**.

We have also studied the reaction between iron(III) chloride and *p*-xylene in acetic acid and verified the low yield of **1** previously reported.⁵ This is, however, not surprising. When iron(III) chloride is heated in acetic acid a red iron(III) compound is formed. At room temperature it precipitates from acetic acid.^{6,7} We found that the red iron(III) compound is inactive as an oxidant. Since some oxidation took place between iron(III) chloride and *p*-xylene in acetic acid, there are probably other iron(III) compounds formed acting as oxidants. A recent report on the analysis of

Table 1. Yields of **1** in the oxidation of *p*-xylene (80 mmol) in acetic acid (50 ml) at 114 °C for 5 h.

| Run No. | FeCl ₃ /mmol | HClO ₄ ^a /mmol | 1 ^b /mmol | mol of 1 /mol of FeCl ₃ |
|---------|-------------------------|--------------------------------------|-----------------------------|---|
| 1 | 5 | 40 | 2.91 | 0.58 |
| 2 | 5 | 40 | 3.17 ^c | 0.63 ^c |
| 3 | 5 | 0 | 0 | 0 |
| 4 | 0 | 40 | 0 | 0 |
| 5 | 5 | 40 | 2.72 ^d | 0.54 ^d |
| 6 | 5 | 0 | 0.31 ^e | 0.06 ^e |

^a 70 % HClO₄. ^b Determined by GLC. ^c 17 h. ^d In a pure nitrogen atmosphere. ^e In the presence of CF₃SO₃H (40 mmol).

the products in the reaction between iron(III) chloride and acetic acid shows that four iron(III) compounds are formed depending on the reaction conditions.⁷ One of these is the red precipitate mentioned above. We have found that treating solid iron(III) chloride with a solution of dichloromethane containing slightly more than one equivalent of acetic acid produces a soluble iron(III) species. This compound reacts with methylbenzenes producing diphenylmethanes selectively. A full report of this reaction will be published later.

Experimental. Commercial anhydrous iron(III) chloride and acetic acid was used without further purification. The reaction conditions are given in Table 1. The reaction mixtures were worked up adding dichloromethane (100 ml), washing the solution 3 times with water. The organic phase was dried over anhydrous sodium sulfate, filtered and concentrated by evaporation *in vacuo*. The resulting solution was analyzed by GLC using an HP 6830 A instrument equipped with an electronic integrator on a 2 m x 0.3 cm 3 % OV-17 on Chromosorb W column. *1* was identified by comparison with an authentic sample (GLC, MC). The yields were determined by calculation of the GLC peak areas after calibration of *1* against a standard.

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1. Nyberg, K. and Wistrand, L.-G. *Acta Chem. Scand. B* 29 (1975) 629.
2. Nyberg, K. *Chem. Scr.* 5 (1974) 105.
3. Nyberg, K. *Chem. Scr.* 5 (1974) 120.
4. Review: Kovacic, P. In Olah, G. A., Ed., *Friedel-Crafts and Related Reactions*, Interscience, New York 1965, Vol. IV, p. 114.
5. Uemura, S., Tanaka, S. and Okano, M. *J. Chem. Soc. Perkin Trans. 1* (1976) 1966.
6. Downs, A. J. and Adams, C. J. In Trotman-Dickenson, A. F., Ed., *Comprehensive Inorganic Chemistry*, Pergamon, Oxford 1973, Vol. 2, p. 1444.
7. Rosenheim, A. and Müller, P. *Z. Anorg. Allg. Chem.* 39 (1904) 175.
8. Paul, R. G., Narula, R. C., Kaur, S. and Vasiskti, S. K. *Transition Met. Chem.* 1 (1976) 284.

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Protonation and Deprotonation of Enamines. III. On the Use of Ion Exchange Resin for Selective Protonation of Enamines

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In a previous paper¹ we reported that the isomeric enamines obtained from isopropyl methyl ketone and morpholine, *1a* and *2a* (Fig. 1), could be easily separated by treating the tautomeric mixture with gaseous HCl or trifluoroacetic acid (which can afford a selective protonation of *1a*). We have studied whether this technique could be improved to achieve the separation either by column chromatography or by batch procedure using acid ion exchange resin. Different types of resins were examined for enamine protonating abilities. "Amberlyst 15", a macroreticular resin with aromatic sulfonic acid groups and only ca. 2 % of moisture content, was found to be suitable. Other strongly acidic resins of the polystyrene-divinylbenzene type have a moisture content of ca. 50 % causing hydrolysis of the enamines. Drying of these resins evidently altered their properties since the dried resins were almost devoid of enamine protonating ability when used in pentane. The enamines studied were the tautomeric equilibrium mixtures obtained from morpholine and isopropyl methyl ketone, (*1a*, *2a*), cyclopentyl methyl ketone, (*1b*, *2b*) and cyclohexyl methyl ketone, (*1c*, *2c*). The isomer distribution (pentane solution, room temperature) was *1a*:*2a* = 29:71, *1b*:*2b* = 9:91 and *1c*:*2c* = 65:35.

Results. Preliminary experiments have shown that adding Amberlyst 15 to a pentane solution of *1a* and *2a* (equilibrium mixture) changed the isomeric distribution with a relative increase of *2a*, i.e. a selective protonation of *1a*. A study of the effects of amount of resin (1–3 equivalents/*1a*), concentration of enamine solution (0.5–2.0 M) and temperature (–78 to 25 °C) showed that neither the amount of resin nor the enamine concentration affected selectivity. The temperature is the only important factor, and that low temperature does not give selectivity, is probably due to a rapid non-

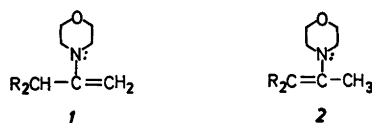


Fig. 1. The enamines studied. *a*, R = CH₃; *b*, R₂ = –(CH₂)₄–; *c*, R₂ = –(CH₂)₆–.