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 × 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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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 paper[1] 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-

1 *2*

Fig. 1. The enamines studied. *a*, R = CH_3; *b*, $R_2 = -(CH_2)_4-$; *c*, $R_2 = -(CH_2)_5-$.

selective *N*-protonation and a too slow selective rearrangement to the alternative *C*-protonated immonium salt. At 0 °C and even at room temperature the reaction is selective and gives an isomer ratio in solution *2a*:*1a* = 95:5 (^{1}H NMR), with yields 90 – 95 % (internal standard, ^{1}H NMR) after 30 min. No change was found by increasing this time to 2 h. A preparative scale experiment (40 mmol) gave 86 % as isolated yield with the isomer ratio *2a*:*1a* = 92:8. Evaporation of the solvent inevitably gave some isomerisation since ^{1}H NMR analysis prior to removal of solvent showed 95 % *2a*. Selectivity was also found in benzene solution; after 30 min at room temperature an isomer distribution *2a*:*1a* = 92:8 was obtained. In chloroform no selectivity was found.

Unfortunately, the scope of the method is limited since no selectivity in protonation by ion exchange resin was observed to occur with the enamines obtained from cyclopentyl methyl and cyclohexyl methyl ketone. However, using trifluoroactic acid as described in Ref. 1, *2b* was obtained in 98 % isolated yield with a purity better than 99 %, and *2c* was obtained in quantitative yield with a purity of 96 %.

Attempts at liberating the enamine from the resin bound immonium salt by treatment with base have not been successful. The immonium salt seems to be rather inert and tightly bound to the resin, such that not even a concentrated solution of amine base at reflux temperature was effective in liberating the enamine.

Experimental. The enamines were prepared by the titanium tetrachloride method.[2] Ion exchange resin Amberlyst 15 was purchased from FLUKA and washed with diethyl ether, finally with pentane boiling from a piece of sodium in a Soxhlet apparatus and dried *in vacuo* over solid paraffin. The capacity was determined to 4.5 mmol H^+/g of resin.

Selective protonation of 1a *using Amberlyst 15.* To 6.21 g of a mixture of *1a*:*2a* = 30:70 (40 mmol) in 40 ml of pentane was added 3.00 g of Amberlyst 15. After stirring at room temperature for 30 min the resin was removed by filtration and washed three times with 5 ml of pentane. A few crystals of 1,8-bis(dimethylamino)naphthalene were added to the filtrate to suppress acid catalyzed isomerisation and the solvent was removed by evaporation under reduced pressure giving 3.72 g of enamine *2a*:*1a* 92:8, (86 % calculated from the amount of *2a* present in the starting material). When this isomeric mixture was dissolved in 25 ml of pentane and treated with 0.60 g of Amberlyst 15 the amount of *1a* dropped to less than 5 % within 30 min.

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Organic Electrosyntheses. X.[1] Preparation of *N*-Benzylidene-*tert*-butylamine-*N*-oxide

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The title compound *3* has been used as a radical scavenger[2] and is normally obtained by isomerization of the corresponding oxaziridine[3] or by direct condensation of the components.[4] We here describe a simple procedure for its preparation using as a key step the cathodic reduction of 2-methyl-2-nitropropane *1*:

$$(CH_3)_3CNO_2 \xrightarrow[HCl/EtOH]{4e^- + 4H^+} (CH_3)_3CNHOH,HCl$$

1 85 – 90 % *2*

$$\xrightarrow[NaOAc/EtOH]{C_6H_5CHO} (CH_3)_3C-N(\downarrow O)=CHC_6H_5$$

80 – 85 % *3*

The electrochemical reduction of *tert*-nitroalkanes to the corresponding *N*-alkylhydroxylamines is a general reaction proceeding with high yields[5] and in the present case has the advantage that the crude, wet *2* from the permanganate oxidation of *tert*-butylamine[2] can be used directly in the electrolytic step.[6] Furthermore, the product *N*-*tert*-butylhydroxylamine *2* from simple evaporation of the catholyte (giving the hydrochloride) is also used without purification for the condensation with benzaldehyde in the presence of sodium acetate to form the desired nitrone *3* in about 50 % overall yield from *tert*-butylamine on a 0.5 mol scale. Thus the handling of the free base of *2* (which is easily oxidized)[2] is avoided and manual work kept at a minimum by using essentially the same approach as for 2-methyl-2-nitrosopropane.[6] Also unsophisticated electrolytic