70. *The Reactions of Grignard Reagents with Some Zinc Chloride Double Salts of Diazonium Compounds.*

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The complex decompositions which occur when Grignard reagents from bromo- and iodo-compounds are treated in dry ether with zinc chloride double salts of diazotised amines, $(ArN_2^{++})_2\{ZnCl_4^{--}\}$, include (*a*) the formation of aryl halides but not aryl chlorides; (*b*) the production of mixed azo-compounds, *e.g.*, methyl-, ethyl-, or phenyl-azo-benzenes and -naphthalenes, (*c*) the formation of $\alpha\alpha'$- and $\beta\beta'$-azonaphthalenes from the double salts with diazotised α- and β-naphthylamines. In no cases were alkyl-benzenes or -naphthalenes or phenylnaphthalenes observed.

No study is on record of the reactions of Grignard reagents with aromatic diazo-compounds, and since such reactions must of necessity be carried out in anhydrous media, the double salts of zinc chloride with diazonium compounds were selected for the purpose; these salts can be adequately dried and are stable for considerable periods of time. It was first established that neither metallic magnesium nor methyl iodide, ethyl bromide or iodide, or phenyl bromide reacted with the diazo-double salts, so the vigorous reactions occurring when these salts were added to the solutions of the Grignard compounds in dry ether could only be due to the latter compounds as such. After the reactions were completed, the mixtures were steam-distilled; they were not previously acidified owing to the danger of decomposing any azo-compound that might have been formed and also in order to avoid any conversion of an alkyl azo-compound into the isomeric hydrazine (cf. Wieland, " Die Hydrazine," Stuttgart, 1913, pp. 130 *et seq.*).

From a consideration of both the steam-volatile and the non-volatile products, it was obvious that several simultaneous reactions had taken place.

(*a*) The production of volatile bromo- and iodo-compounds (a chloro-compound was never detected) indicates that the Grignard reagent must have reacted in similar fashion to the anionoid halogen in the Sandmeyer reaction (cf. Hodgson and Birtwell, J., 1941, 770). Iodination by the Grignard reagent, which, in the dry ether employed, could only have occurred *via* anionoid iodine, since ionisation of the Grignard reagent is excluded, supports the earlier observation by Hodgson and Birtwell (*loc. cit.*) that potassium iodide will not react with a diazo-compound in acid solution in presence of a reducing agent, and consequently indicates that iodination occurs *via* the anionoid iodine in the anion I_3'.

(*b*) From the formation of mixed azo-compounds, the anionoid alkyl or aryl group of the Grignard reagent must have become attached at the nitrogen atom more remote from the carbon atom to which the diazo-group is attached. When the double salts of zinc chloride with diazotised aniline and *p*-toluidine reacted with methyl- and ethyl-magnesium halides, no azobenzene or azotoluene was detected, so the azobenzene and *p*-benzeneazotoluene obtained with phenylmagnesium bromide must have resulted from the reaction of its phenyl group.

(*c*) After reaction, however, of the Grignard reagents with the double salts of zinc chloride and diazotised α- and β-naphthylamine, the radicals left after the liberation of nitrogen either combine with each other to form dinaphthyls, as with the double salts from diazotised aniline and *p*-toluidine, which afford some diaryl, or they react with undecomposed diazo-salt to form αα′- and ββ′-azonaphthalene, a reaction not given by the aniline and *p*-toluidine double salts. The yield of azo-compounds, however, is almost negligible when the decompositions are carried out with methyl- and ethyl-magnesium halides, but reaches 20% when phenylmagnesium bromide is used. It would appear, therefore, that the naphthyl radicals are more prone than the aryl radicals to unite with themselves; in no case, however, could phenylnaphthalene be detected, the phenyl radical thus resembling the methyl and the ethyl radical in not forming methyl- and ethyl-benzenes or -naphthalenes in the Grignard decompositions.

Experimental.

Preparation of the Zinc Chloride Double Compounds of Aryl- or Naphthyl-diazonium Chlorides.—The amine (0·1 g.-mol.) is dissolved in hydrochloric acid (24 c.c., *d* 1·18) and water (24 c.c.) (with heating if necessary), diazotised at 0° with sodium nitrite (7 g.) dissolved in water (24 c.c.), and filtered. (If ice is added, the total volume should not exceed 150 c.c.) Solid zinc chloride (7 g.) is now added, and the resulting double chloride is filtered off, washed with a few drops of water, and dried first on filter-paper by suction and then in a desiccator for several days.

Reaction of Grignard Reagents with Zinc Chloride Double Salts: General Procedure.—The Grignard reagent was prepared in one equivalent excess by reaction of the alkyl or aryl halide in excess with magnesium (0·5 g.) in dry ether (50 c.c.), a crystal of iodine being added as catalyst. Reagents designated A, B, C, and D respectively were thus obtained from methyl iodide, ethyl bromide and iodide, and phenyl bromide, and these were treated with the dry finely powdered benzene- or naphthalene-diazonium chloride double salt with zinc chloride (0·01 g.-mol.). After the violent evolution of nitrogen had abated, the mixtures were refluxed for a further 15 minutes and then steam-distilled. The steam-distillate contained aryl or naphthyl bromide or iodide, but no chloro-compound, and also, when bromobenzene was used, diphenyl, the corresponding dialkyl from the aliphatic halides having been evolved as a gas. In addition, some azo-products were also steam-volatile, but otherwise they were identified in the steam-flask residues.

Data from Individual Reactions.—In all cases the name of the parent amine stands for the double salt $(ArN_2^{++})_2\{ZnCl_4^{--}\}$.

Aniline. With A, the whole of the reaction product was volatile in steam and contained iodobenzene, diphenyl, and methylazobenzene (*ca.* 15%), which was detected by reduction and diazotisation of the steam distillate (see under B); neither toluene nor azobenzene was detected.

With B, the products were diphenyl, bromobenzene, and ethylazobenzene; the last was estimated by reduction of the steam-volatile liquid with zinc dust and hydrochloric acid, whereupon, after filtration, 3 c.c. of N-sodium nitrite were absorbed, corresponding to the formation of 15% of ethylazobenzene from the double salt; no azobenzene was observed.

With C, the products were as with B, but iodobenzene was formed in greater amount than bromobenzene in B.

With D, the steam-distillate contained diphenyl and azobenzene; on reduction as for B, the latter required 4·2 c.c. of N-sodium nitrite, corresponding to 21% conversion of the double salt.

p-*Toluidine.* Reagent A afforded a large yield of *p*-iodotoluene, together with *pp*′-ditolyl and a little methylazotoluene, detected by reduction and diazotisation as above. B and C gave a little ethylazotoluene, but the yield of *p*-iodotoluene from C exceeded that of bromobenzene from B. With D, *p*-bromotoluene and *p*-benzeneazotoluene came over with the steam, the latter compound (identified by m. p. and mixed m. p. with an authentic specimen) in 21% yield.

α-*Naphthylamine.* With A, the steam-volatile compounds were naphthalene, α-iodonaphthalene, and α-methylazonaphthalene; the azo-compound was found in 7% yield but could not be isolated owing to its admixture with much greater amounts of the other substances and to its great solubility in all solvents tried. The non-volatile matter was αα′-dinaphthyl (*ca.* 1 g.), identified by m. p. and mixed m. p. with an authentic specimen. Azonaphthalene could not be detected in the non-volatile product, which gave no colour with concentrated sulphuric acid, and when treated with hydrochloric acid and zinc dust afforded no α-naphthylamine. With B, the steam-volatile product contained α-bromonaphthalene and *α-ethylazonaphthalene* (5% yield); the latter crystallised from the steam-distillate in yellow prisms, m. p. 25—27° (Found: N, 15·3. $C_{12}H_{12}N_2$ requires N, 15·2%), which were very soluble in light petroleum and dissolved in concentrated sulphuric acid to give a yellow solution. The amount of azonaphthalene in the non-volatile product was negligible, and the yield of αα′-dinaphthyl 0·7 g. With D, the steam-distillate contained only diphenyl and α-bromonaphthalene; the non-volatile matter (*ca.* 2·0 g.) was reduced in the steam flask with zinc and hydrochloric acid, and the mixture made alkaline with sodium hydroxide and steam-distilled; aniline passed over, and titration with N-sodium nitrite (0·6 c.c.) indicated the formation of 6% of α-phenylazonaphthalene. The flask liquor, when acidified and titrated, required 5·15 c.c. of N-sodium nitrite, corresponding to the formation of 22·75% of αα′-azonaphthalene from the double salt. A separate experiment, in which the non-volatile residue was reduced, afforded 0·6 g. of αα′-dinaphthyl (m. p. and mixed m. p.) by extraction from the insoluble matter with boiling ethyl alcohol.

β-Naphthylamine. With A, the steam-volatile products included naphthalene, β-iodonaphthalene, and β-methylazonaphthalene. The last solidified in yellow crystals (in about 5% yield) but could not be separated from its companions. The non-volatile product (*ca.* 1 g.) was ββ′-dinaphthyl, only a trace of ββ′-azonaphthalene being formed. With B, the steam-volatile product included naphthalene, β-bromonaphthalene, and *β-ethylazonaphthalene* (10% yield). The last crystallised from the distillate in yellow prisms, m. p. 65—68° (depressed by naphthalene) (Found: N, 15·4. $C_{12}H_{12}N_2$ requires N, 15·2%). The non-volatile matter was treated as for that from α-naphthylamine and afforded 2·5% of ββ′-azonaphthalene, with ββ′-dinaphthyl (0·8 g.) as the main constituent. With D, the steam-volatile products were diphenyl, naphthalene, and β-bromonaphthalene; the non-volatile residue (2·2 g.), treated as for that from α-naphthylamine, was a mixture of ββ′-dinaphthyl, ββ′-azonaphthalene (20%), and β-phenylazonaphthalene (7%).

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