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AMALGAMATED ALUMINIUM IN METHYLENE CHLORIDE AS REDUCING AGENT.A NEW CONVENIENT METHOD FOR PINACOLIC REDUCTION OF ALIPHATIC AND CYCLOALIPHATIC KETONES.

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The known methods for the reduction of aliphatic and cycloaliphatic ketones to the corresponding pinacols leave much to be desired.The most employed is the reduction with amalgamated magnesium or aluminium in boiling benzene for 3 - 12 hrs,yields of 30% (related to ketone) being typical (1).The resulting metal pinacolate forms a thick voluminous gel,difficult to stir.The reduction with sodium and water (2),implying a basic medium gave a maximum yield of 50% for the reduction of acetone,but higher ketones gave lower yields.Electrolytic methods (3) use also acidic or basic solutions not suitable for sensitive ketones and the establishment of the optimum set of parameters for each new case is tedious.Some other methods occasionally employed are neither better nor general (4).

We found that aliphatic and cycloaliphatic ketones are reduced in milder conditions and higher yields using amalgamated aluminium either in methylene chloride or tetrahydrofuran as solvents.The formed aluminium pinacolates are very soluble in both solvents.Aliphatic ditertiary pinacols are obtained at once in a very satisfactory purity,usually not needing recrystallization.Darkening or tar formation are usually absent or very slight.The procedure consists esentially in the amalgamation of aluminium foil with a solution of $HgCl_2$ in THF in the reaction flask,washing the metal with solvent,then adding solvent and ketone and bringing to reflux.An exothermic reaction soon starts and the mixture is maintained at gentle reflux for 1-4 hrs.A <u>solution</u> of pinacolate results,which is then separated from excess metal(moisture avoided),then hydrolyzed by dropping in cold dilute acid.Hydrolysis may be carried out in situ with saturated brine (ca 100% excess) under rapid stirring,followed by filtration,repeated extraction of the aluminium oxide cake with CH_2Cl_2 or boiling $CHCl_3$,concentration of the combined extracts and precipitation of the pure pinacol with petroleum ether.

Acetone, cyclohexanone and cyclopentanone were reduced in CH_2Cl_2 with 45%, 55% and 40% isolated yields; in THF the first two produced 51% and 31% pinacol. These yields are superior to the best reported. Benzophenone (I), acetophenone (II) and benzaldehyde (III) reacted with Al/CH_2Cl_2 (III very energetic) giving complex mixtures, from which we isolated the corresponding pinacols in moderate yields (I:23-57% ; II:21-38% ; III:poor isolation). The 2,3-diphenyl-2,3-butanediol isolated from the reduction of II was the DL-stereomer, containing before recrystallization less than 1% meso-isomer (NMR spectra(5)), the mother liquors contained also little or no meso-isomer (IR spectra(6)). Thus, Al/CH_2Cl_2 seems to act with a stereoselectivity not common in pinacolic reductions.

Another point of interest is isolation from the reaction mixtures of the corresponding stilbenes: tetraphenylethylene from I, trans-α,α'-dimethylstilbene from II, and trans-stilbene from III. Secondary alcohols and pinacolones were also present, III produced also benzyl alcohol, benzoin and benzil. I was reduced in THF to 50% benzpinacol.

The Al/CH_2Cl_2 system seems suitable for other reducing reactions, too. Thus, trans-1,2-dibromocyclohexane was dehalogenated smoothly and efficiently. Amalgamated magnesium in CH_2Cl_2 reacted also with ketones, but very irregularly.

Notes and references

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