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Hydroalkylation of imines by cyclohepta-1,3,5-triene

Lidiya P. Yunnikova

D. N. Pryanishnikov State Agricultural Academy, 614000 Perm, Russian Federation. Fax: +7 3422 32 4779

Reactions of *N*-arylmethyleneanilines with cyclohepta-1,3,5-triene in the presence of anhydrous zinc(II) chloride in tetrahydrofuran result in the formation of *N*-aryl-*N*-arylmethyl-1-(2,4,6-cycloheptatrienyl)amines, which are readily hydrolysed to the corresponding *N*-arylmethylanilines.

The ability of cyclohepta-1,3,5-triene to form a tropylium cation due to the transfer of a hydride ion to an acceptor has been confirmed in many examples.[1] This allows one to suggest that in reactions with imines cycloheptatriene can manifest itself as a donor of the hydride ion, similar to silicon organohydrides. The solution of this problem is of basic significance, because it provides a quite new approach to the synthesis of amines by hydroalkylation of imines and illustrates several points relevant to a study of the mechanism of hydride transfer from compounds with reactive carbon–hydrogen, silicon–hydrogen, and metal–hydrogen groups.

Imines react with silanes to form silylamines, which can be readily hydrolysed to secondary amines in the presence of acids.[2,3]

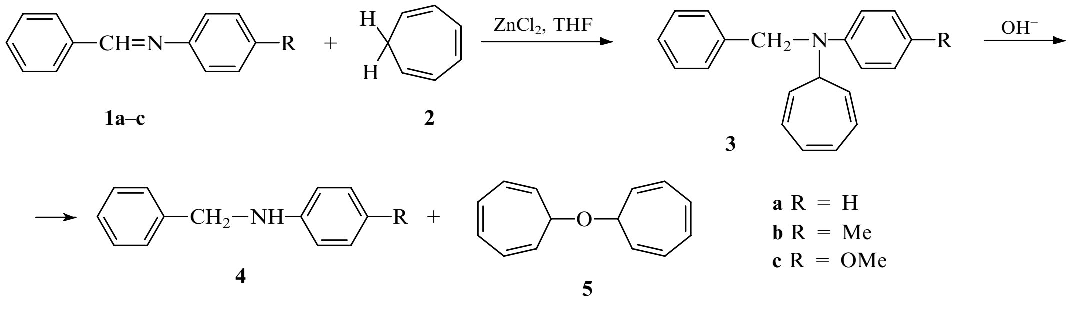
Previously[4] we attempted to perform hydroalkylation and hydrogenation of imines involving cycloheptatriene under hydrosilylation conditions and established the possibility of preparing high-boiling products, whose hydrolysis allowed us to isolate *N*-arylmethylanilines corresponding to the initial imines.

We assumed that unidentified, high-boiling substances are the products of hydroalkylation of imines by cycloheptatriene, *N*-aryl-*N*-arylmethyl-1-(2,4,6-cycloheptatrienyl)amines **3** formed according to Scheme 1.

The reactions of azomethines **1** with cycloheptatriene **2** occur in the presence of anhydrous zinc(II) chloride in tetrahydrofuran at 100 to 105 °C in an air or argon atmosphere at an imine : cycloheptatriene : $ZnCl_2$: THF ratio of 1 : 4 : 0.25 : 3. It should be mentioned that the imine polymerizes at a ratio of the initial components **1** and **2** of 1 : 1, and only traces of secondary amine can be isolated by hydrolysis of the reaction mass.

Amines **3a**,**b** formed due to distillation *in vacuo* are colourless liquids, which are easily hydrolysed in the presence of acid and moisture.

Their formation is confirmed by the following facts. A



Scheme 1

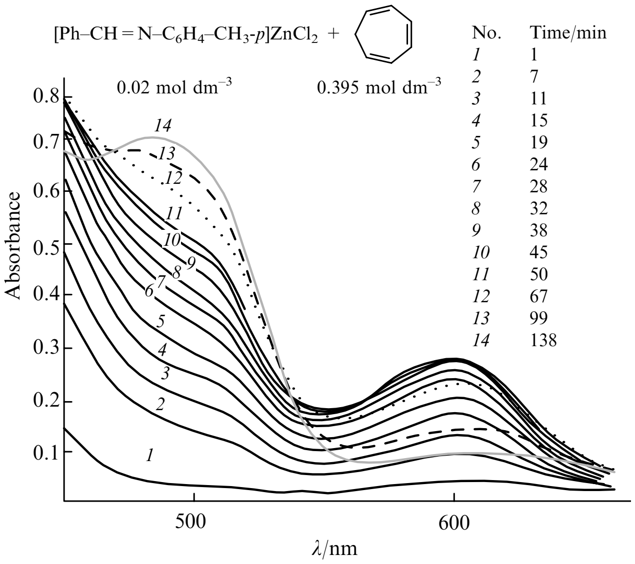


Figure 1 Time change in the electronic spectrum of the reaction mixture in THF at 18 °C.

molecular ion with m/z 273 is observed in the mass-spectrum of the reaction mass (before distillation) and in the mass-spectrum of the fraction in which the presence of *N*-aryl-*N*-arylmethyl-1-(2,4,6-cycloheptatrienyl)amine **3a** is proposed. Elemental analysis of this fraction to C, H and N atoms corresponds to the theoretically calculated composition. The alkaline hydrolysis of the reaction mass (before distillation) results in the isolation of *N*-benzylaniline **4a**[10] in a yield of 86% and the ditropyl ether **5**, bp 105 °C/0.5 mmHg and n_D^{20} 1.5702, which corresponds to the literature data.[5] Hydrolysis of the high-boiling fraction makes it possible to isolate *N*-benzylaniline in 35% yield. A decrease in the yield of compound **4a** can be explained by secondary processes occurring upon distillation. Two fractions [secondary amine (pentane as an eluent) and yellow oil (benzene as an eluent), whose structure is under study] can be isolated by chromatography of the reaction product on a column with Al_2O_3.[†]

The formation of amines **3** is preceded by the appearance of an intense black colour and a broad absorption band with λ_{max} 600 nm (Figure 1) is observed in the electronic spectrum of a solution of compounds $[Ph–CH = N–C_6H_4–CH_3]\cdot ZnCl_2$ (0.02 mol dm^{-3}) and cycloheptatriene (0.395 mol dm^{-3}) in THF obtained by differential spectroscopy,[6] which allows one to assume that a charge-transfer complex between the initial reagents is initially formed. The intensity of this band decreases in time after reaching a maximum and is accompanied by a growth of the absorption band with λ_{max} 490 nm, which is likely to correspond to the radical anion of imine. It is noteworthy that the intensities and forms of the absorption bands with λ_{max} 600 nm and λ_{max} 490 nm in two parallel experiments, in one of which oxygen is excluded, do not differ, which indicates that oxygen is not an oxidant in this case.

It is known that some methylene-active compounds (heteroanalogues of cycloheptatriene, for example, *N*-methylacridan[7] and 1,3-dimethyl-2-phenylbenzimidazoline[8]) under certain conditions are dehydrogenated according to the −e, −H scheme and, hence, are monoelectron donors. In turn, azomethines, according to the data of ref. 9, can be monoelectron acceptors.

Therefore, it can be assumed that the electron transfer from cycloheptatriene to imines is one of the stages of hydroalkylation.

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[†] *General procedure for the synthesis of* N-*aryl*-N-*arylmethyl*-1-(2,4,6-*cycloheptatrienyl)amines* **3a**,**b** *and* N-*arylmethylanilines* **4a**–**c**. Anhydrous zinc(II) chloride (1.75 g) was dissolved on heating in 3 cm^3 of THF (THF was distilled over benzophenoneketyl prior to use), the mixture was cooled, and imine **1a**–**c** (0.05 mol) and cycloheptatriene (0.20 mol) were added. The mixture was heated at 100 to 105 °C for 1.5 to 2 h.

Amines **3a**,**b** can be isolated by distillation *in vacuo*. **3a**: reaction time 2 h, yield 35%, bp 150–165 °C/0.5 mmHg, MS (CI) m/z 273 (M$^+$, 100%), 196(15), 183(30), 182(41), 91(15), 77(4). **3b**: reaction time 1.5 h, yield 32%, bp 180–190 °C/0.5 mmHg. Treatment of the reaction mass before distillation with a 10% solution of NH_4OH results in the crystallization of secondary amines **4a**,**c**, whose melting points correspond to the literature data for **4a**[10] (yield 86%) and **4c**[11] (yield 90%).