Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

Formation of anions and carbanions in the reaction of ethylmagnesium bromide with aromatic hydrocarbons

F.J. REINDERS and R. PRINS
Koninklijke/Shell-Laboratorium, Amsterdam, (Shell Research N. V.) (The Netherlands)

(Received September 16th, 1970)

Extensive investigations in recent years have shown that transition-metal sandwich compounds with substituted benzenes as ligands can be easily prepared by reduction of trivalent metal complexes with Grignard reagents or trialkylaluminium compounds in the presence of the aromatic hydrocarbon[1]. We have used this type of reaction to try and prepare CrA_2 compounds, where A is a polynuclear aromatic hydrocarbon, but so far have had no success. However, in the course of the investigation we found that ethylmagnesium bromide is able to reduce several of the aromatic hydrocarbons to the corresponding anions and carbanions, and we now describe these findings.

When a dry oxygen-free solution of C_2H_5MgBr in ether is mixed with a similar solution of tetracene in dimethoxyethane (DME), a dark green colour develops. If an excess of C_2H_5MgBr is present and the solution is allowed to stand for a few hours the colour gradually changes to yellow. This indication that different types of hydrocarbon ions are being formed is confirmed by ESR and electronic absorption spectra. The green solution gives a nicely resolved ESR spectrum, and from hyperfine coupling constants it follows that the paramagnetic species must be the tetracene negative ion A^-. On the other hand, the electronic absorption spectrum (Fig.1) shows a large number of bands between 10 and 30 kK (1 kK = 1000 cm^{-1}) which cannot be attributed to a single molecular species. Comparison with published spectra of the tetracene anion A^- [3] and carbanion AH^- [4] shows that the bands between 11 and 15 kK and those between 25 and 30 kK are due to A^-, while those at 16.3 and 21.0 kK belong to AH^-. Pure solutions of AH^- are yellow in colour and show no magnetic resonance signal.

Reduction of perylene in DME with an ethereal solution of C_2H_5MgBr gives a dark blue solution. ESR spectra show the presence of perylene mononegative ions, while according to electronic absorption measurements both A^- and the dinegative ion A^{2-} [3] are present in minor quantities. Strong absorption bands found at 15 and 22 kK are probably due to the dinegative ion of dihydroperylene[4].

A solution of anthracene in DME takes on a faintly blue colour when C_2H_5MgBr in ether is added, but after some time the colour changes to yellow. ESR spectra indicate that the anthracene mononegative ion has been formed. However, electronic absorption

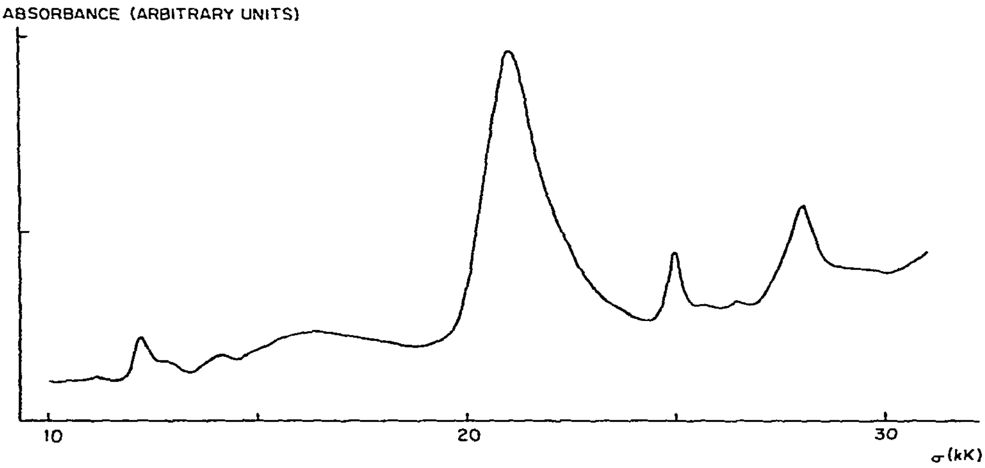

Fig.1. Absorption spectrum of C_2H_5MgBr and tetracene in a mixture of DME and ether.

spectra reveal that most of the anthracene has been left unchanged and only a small proportion has been reduced to the anion $A^{\cdot-}$ and carbanion AH^-.

On addition of C_2H_5MgBr to naphthalene no reaction seems to take place. There is no colour change, no ESR spectrum and no new bands in the electronic absorption spectrum.

Concerning the mechanism of the reduction of the aromatic hydrocarbons by C_2H_5MgBr we can only speculate. The principal step is probably electron transfer from the Grignard reagent to the aromatic hydrocarbon:

$$C_2H_5MgBr + A \rightarrow C_2H_5^{\cdot} + MgBr^+ + A^{\cdot-}$$

(Such a reaction has been proposed to explain the ketyl-type radicals formed when Grignard reagents interact with benzophenone[5,6].)

The resulting ethyl radicals may combine to form butane, or disproportionate to ethane and ethylene or ethylene and hydrogen. Evolution of gas was observed in all the reactions, except in the case of naphthalene.) In a subsequent reaction the anion $A^{\cdot-}$ may be protonated to the carbanion AH^- by ethyl radicals or hydrogen molecules. No $AH^{\cdot}$ radicals will be formed since this has a much higher electron affinity than the corresponding molecule A.

Such a scheme would explain why the anions $A^{\cdot-}$ and carbanions AH^- were found in the case of anthracene and tetracene. As for perylene, where no AH^- was observed but the $AH_2^{2\cdot-}$ anion was found instead, this is in accord with results obtained by Velthorst and Hoytink[4], who found that the perylene carbanion disproportionates to $AH_2^{2\cdot-}$ and A.

How the magnesium cations are surrounded in solution is uncertain. It may be that $MgBr^+$ disproportionates to Mg^{2+} and $MgBr_2$, which would account for the cloudy white precipitate that is formed in all the reactions except in the case of naphthalene.

The ESR and absorption spectra indicate that the aromatic hydrocarbon anions and carbanions of anthracene and tetracene are "free" ions. The location of the absorption bands, for instance, agrees very well with those assigned to free ions in a study of association between alkali metals and aromatic anions and carbanions in THF and DME[4,8].

The fact that naphthalene does not react with C_2H_5MgBr and anthracene gives only minor quantities of the anion and carbanion, while the tetracene and perylene molecules are completely converted into the anions and carbanions, is in agreement with what is known about the reduction potentials of aromatic hydrocarbons in THF and DME[9]. In DME, for instance, the reduction potential of naphthalene and the electrode potential of sodium are about equal. Since magnesium has a higher electrode potential than sodium, it is therefore to be expected that a magnesium derivative should be unable to reduce naphthalene to its mononegative ion, although it might be able to reduce anthracene, tetracene and perylene.

The results thus show that a Grignard reagent can reduce large polynuclear aromatic hydrocarbons which have a sufficiently high electron affinity.

REFERENCES

1 E.O. Fischer and J..Müller, *Z. Naturforsch., B,* 17 (1962) 776; 18 (1963) 413; G. Henrici-Olivé and S. Olivé, *Z. Physik. Chem. N.F.,* 56 (1967) 223.
2 J.P. Colpa and J.R. Bolton, *Mol. Phys.,* 6 (1963) 273.
3 G.J. Hoytink, N.H. Velthorst and P.J. Zandstra, *Mol. Phys.,* 3 (1960) 533.
4 N.H. Velthorst and G.J. Hoytink, *J. Amer. Chem. Soc.,* 87 (1965) 4529; 89 (1967) 209.
5 K. Maruyama, *Bull. Chem. Soc. Japan,* 37 (1964) 897.
6 G.A. Russell, E.G. Janzen and E.T. Strom, *J. Amer. Chem. Soc.,* 86 (1964) 1807.
7 G.J. Hoytink, J. van Schooten, E. de Boer and W.Y. Aalbersberg, *Rec. Trav. Chim., Pays Bas,* 73 (1954) 355.
8 K.H.J. Buschow, J. Dieleman and G.J. Hoytink, *J. Chem. Phys.,* 42 (1965) 1993.
9 J. Jagur-Grodzinski, M. Feld, S.L. Yang and M. Szwarc, *J. Phys. Chem.,* 69 (1965) 628.