Studies of the reactions of magnesium anthracene with sulphur, selenium and some sulfides, disulfides and diselenides

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The reaction of Mg-anthracene with sulphur, selenium and some sulfides, disulfides and diselenides in THF or toluene furnish different reaction products which depend on structure of starting compound and of reaction conditions. The reactions are performed at different temperatures under argon. The most useful application of this reaction is in the synthesis of diaril-disulfo- and diselenomagnesium compounds.

The addition of anthracene to a THF suspension of commercial magnesium powder activated with ethyl bromide at room temperature, leads to the formation of a bright orange complex having the composition Mg(anthracene)₂·3THF. Mg-anthracene shows bivalent reactivity. It can dissociate homolytically to give zerovalent magnesium or react with transfer of 1 or 2 electrons from the metal to the anthracene to give the blue radical anion or dianion (Scheme I). Both the reactions have many synthetic uses.

Electron transfer pathway is of interest as a method of preparing substituted 9,10-anthracene derivatives. In some reactions Mg-anthracene does indeed behave as a source of atomic magnesium (some organic halides react to give Grignard reagents or coupling products). In other cases, a mixture of products resulting from both reaction types is obtained.

The most useful application of Mg-anthracene as a source of magnesium is in the synthesis of organotransition metal complexes. The use of commercial magnesium powder for this reaction results in only a 10% yield of the product. Mg-anthracene is also involved in the conversion of Mg into magnesium hydride. Commercial Mg powder reacts only reluctantly with hydrogen.

A highly active, pyrophoric form of magnesium can be prepared by heating Mg-anthracene in vacuo at c.a. 150-70°C. It can be used to prepare Grignard reagents from less reactive organic halides. Of considerable interest is the fact that this active magnesium reacts readily with hydrogen at normal pressure and 150-220°C. This reaction forms the basis of the use of magnesium hydride as a hydrogen storage system.

We were, therefore, interested in exploring how Mg-anthracene (1) behave in the reaction with some sulphur and selenium compounds and have therefore undertook a study of the reaction of 1 with S, Se and some compounds containing S and Se (sulfides, disulfides and diselenides).

It is well known that aliphatic and aromatic sulfides can be reduced to thiols or desulphurised with different reagents (lithium aluminium hydride, lithium triethyl borohydride and sodium borohydride). Benzyl sulfides are not desulfurised but reduced to mercaptans.

Partial desulfurisation of disulfides to sulfides was accomplished by treatment with triis-diethylamino phosphine in good yields. Complete desulfurisation to hydrocarbons resulted when disulfides were refluxed in ethanol with Raney nickel or nickel boride.

But in our cases desulfurisation did not take place. Magnesium incorporated in the molecule in the reaction of MgA with disulphides and diselenides (Scheme II).

On the other hand sulfides caused decomposition of MgA. S and Se gave MgS and MgSe. Some sulfides and selenides did not react with MgA.

Results and Discussion

Mg-anthracene for this purpose was prepared using well-known procedure in an inert atmosphere. The reactions were carried out under argon in tetrahydrofuran or toluene as the solvent. The ratio of the substrate and reagent usually was 1:1. The reactions were performed at different temperatures, depending on the nature of the substrate used. In agreement with this, the reaction times were also different in all cases (Table I).

In order to complete the reactions, the reaction conditions were varied. After the completion of the
The reaction mixture was filtered and the product obtained was washed with solvent and then dried in vacuo. The isolated products were analysed and characterised. Sometimes there was a problem with purification of isolated product (especially with traces of anthracene).

The results show that in some cases reaction products formed are very fast and in some other cases long time is required. Sometimes, after many days reaction did not complete.

The type and the structure of the reaction products depended on the structure of starting compounds. It was also observed that if the reaction did not occur in one solvent, the change of the solvent made reaction possible. In some cases problems in identification of reaction products were experienced.

Sulphur and selenium reacted with MgA to produce MgS and MgSe in quantitative yield which is not possible with Mg under the same reaction conditions. The most interesting reaction was reaction of MgA with diethylsulfides. The reaction mixture burns when an air come inside and it was impossible to identify the products. Other sulfides after a few hours influenced a reaction of decomposition of starting materials and produced corresponding thiols.

All investigated disulfides and diselenides gave dialkyl- or dialkyl- disulpho- and diseleno- magnesium compounds (Scheme II)

**Experimental Section**

Gas chromatography was done on Siemens instruments, Models 1, 119, HP, 121, BP 427, CE and 4100/2 for analytical purposes; the columns consist of 40 m PS 240/H 1728 a, 40 m PS quo/H 1728 a, 50 m PS 343,5 FS (K) 158, 45 m FS 106, 37 m SE-54/H 1774 B, 31 m PS 240/H 1826 B, 49 m PS 240/H 1830 A, 75m PS 240 and (K) 204. IR spectra were recorded on Perkin-Elmer model 137B and Nicolet 7000 FT spectrophotometers. NMR spectra on Varian FT 80A (80 MHz), Bruker AM 200 (200 MHz) and mass spectra on Varian spectrometer CH 5 and CH 7. Elemental analysis was performed by Dornis and Colbe, Microanalytical Laboratory, Mullheim a.d. Ruhr. All solvents were purified by distillation and dried. All spectra are available in the Max-Planck-Institut fur Kohlenforschung, Mullheim a.d. Ruhr.

**General procedure.** A solution of 5.07g MgA (12 mmole) in 60 mL THF (or toluene) was cooled to 0°C under argon. Small portion of reactant (12 mmole S, Se, sulfides, selenides or disulfides) was slowly added. The resulting reaction mixture was stirred until completion of the reaction. The colour of reaction mixture changed from orange through green to yellow (or to some other colour which depended on reaction products). After completion of the reaction insoluble
Table I—Reaction of MgA with S, Se and some sulfides, disulfides and diselenides

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Reaction products</th>
<th>Solvent</th>
<th>Reaction Temp</th>
<th>Reaction time</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>A+ MgS</td>
<td>THF</td>
<td>0°</td>
<td>Immediately</td>
</tr>
<tr>
<td>Se</td>
<td>A+MgSe</td>
<td>THF</td>
<td>60°</td>
<td>7hr</td>
</tr>
<tr>
<td>PhSSPh</td>
<td>No reaction</td>
<td>THF</td>
<td>Reflex</td>
<td>52hr</td>
</tr>
<tr>
<td>PhSSPh</td>
<td>A+PhSMgSPh</td>
<td>Toluene</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>PhSeSePh</td>
<td>A+PhSeMgSePh</td>
<td>THF</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(CH₃C₆H₄)₂S</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PhSPh</td>
<td>A+Mg</td>
<td>MgA</td>
<td>THF</td>
<td>3hr</td>
</tr>
<tr>
<td>(CH₃)₂C-S-C-(CH₃)₂</td>
<td>Decomposed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₅-S-C₂H₅</td>
<td>A+Unindentified</td>
<td>Toluene</td>
<td>110°</td>
<td>48hr</td>
</tr>
<tr>
<td>C₂H₅-S-C₂H₅</td>
<td>A+Unindentified</td>
<td>MgA</td>
<td>Reflux</td>
<td>11 days</td>
</tr>
<tr>
<td>C₂H₅-S-C₂H₅</td>
<td>No reaction</td>
<td></td>
<td>Room temp.</td>
<td>24hr</td>
</tr>
</tbody>
</table>

A = Anthracene

*Sulphur did not react with magnesium under the same reaction conditions at room temperature and with reflux for 3 hr.
*Selenium did not react with magnesium even after refluxing for 24 hr.
*Diphenyldisulfide did not react with magnesium at 0°, room temperature and under reflux for 5 hr.
*Diphenyldiselenide react with magnesium but not under the same reaction conditions. Reaction occurred after 48hr refluxing.

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References

2. Freeman P K & Hutchinson L L, J Org Chem, 48, 879