can be decreased by complexation which does not alter energy levels. Xenon is reported to lengthen the triplet lifetime of naphthalene by forming a xenon–naphthalene complex which induces no energy change (D. A. Head, A. Singh, M. G. Cook, and M. J. Quinn, *Can. J. Chem.*, **51**, 1624 (1973)).

(14) In ref 3a the authors attribute an ionic strength dependent decrease in ϕ_f (τ_p decreased and ϕ_p increased) for aromatic amino acids in water–sucrose glasses at 77 K to a salt-induced solvent structure change which perturbs the chromophore.

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The Preparation of HMgX Compounds

Sir:

Hydridomagnesium halides (HMgX, where X = halogen) represent a novel new class of compounds which have been highly sought after and which presumably can function as selective reducing agents toward organic substrates[1] and as intermediates in the preparation of novel complex magnesium hydrides. Wiberg and Strebel[2] in 1957 reported the preparation of THF soluble HMgCl and HMgBr by the reaction of ethyl Grignard reagents with diborane. However, we showed later[3] that such compounds are not formed under the conditions described. Sometime later, Dymova and Eliseeva[4] reported that HMgX compounds could be prepared in diethyl ether as insoluble solids by the hydrogenolysis of ethylmagnesium halides. They also reported that these compounds disproportionated to MgH_2 and MgX_2 when THF was added. We have also repeated this work in detail and have shown that the solid products obtained in these reactions involving diethyl ether as a solvent are actually physical mixtures of MgH_2 and MgX_2 as determined by x-ray powder diffraction analysis.[5] A third route reported by Rice and co-workers[6] for the preparation of nonsolvated HMgBr, involved the pyrolysis of ethylmagnesium bromide. This report was supported by x-ray powder pattern data. However, when we desolvated $MgBr_2 \cdot Et_2O$ to correspond to the exact amount of ether present in $HMgBr \cdot 0.27Et_2O$, then the powder diffraction patterns were the same showing that the $HMgBr \cdot 0.27Et_2O$ was actually a physical mixture of MgH_2 and $MgBr_2 \cdot 0.54OEt_2$.[7]

We would now like to report that hydridomagnesium halides (HMgX, where X = Cl and Br) have been prepared by the reaction of magnesium halides with an active form of magnesium hydride slurried in THF (eq 1). The active form of magnesium hydride was prepared by the reaction of Ph_2Mg or Et_2Mg with equimolar amounts of $LiAlH_4$ in diethyl ether (eq 2). The MgH_2 is insoluble in ether

$$MgH_2 + MgX_2 \xrightarrow[\text{room temp}]{\text{THF}} 2HMgX \qquad (1)$$

$$R_2Mg + LiAlH_4 \xrightarrow{Et_2O} MgH_2 + LiAlH_2R_2 \qquad (2)$$

and was isolated from the soluble $LiAlH_2R_2$ by filtration. A slurry of this MgH_2 in freshly distilled THF was then allowed to react at room temperature with a THF solution of MgX_2 (where X = Cl or Br). The reaction is exothermic and results in the formation of a clear solution within a few minutes. Analysis of the resulting solution of HMgBr in THF showed a Mg:H:Br ratio of 1.00:0.97:1.02 and for HMgCl a Mg:H:Cl ratio of 1.00:0.98:1.04.

No reaction was observed when the THF solvent was replaced by diethyl ether, probably because of the insoluble nature of HMgX compounds in diethyl ether. Interestingly, HMgCl and HMgBr are both soluble and quite stable in THF contrary to earlier reports. A 1.5 M solution of HMgCl and a 0.5 M solution of HMgBr in THF could be prepared. Ebullioscopic molecular weight studies on HMgCl and HMgBr in THF showed both compounds to be dimeric in dilute solution and gave some indication of associating further in more concentrated solution to form trimers (Figure 1). Infrared spectra have been recorded in THF solution (HMgCl: 1380 m, 1345 m, 1320 m, 1290 mb, 1120 s, 990 vs, 800 sh, 710 vs, 600 m, 580 m, 550 m, 396 m; HMgBr: 1410 m, 1380 m, 1345 m, 1260 mb, 1118 s, 1010 vs, 800 vs, 700 s, 670 vs, 570 mb, 390 m). NMR spectra of HMgCl and HMgBr in THF did not give any fruitful information regarding the Mg–H proton.

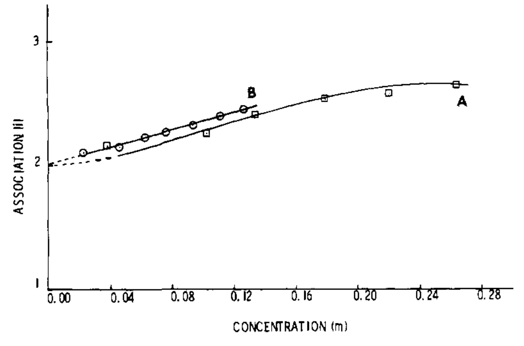
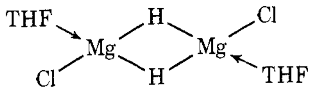


Figure 1. Molecular association studies of HMgCl (A) and HMgBr (B) in tetrahydrofuran.

The Mg–H stretching band in HMgBr and HMgCl was determined by preparing DMgBr and DMgCl by the method above (eq 1–2) using $LiAlD_4$ and comparing the infrared spectra of the HMgX and DMgX compounds. The bands at 1260 and 1290 cm^{-1} observed for HMgBr and HMgCl in THF were shifted to ~940 cm^{-1} in the case of DMgBr and DMgCl indicating 1260 and 1290 cm^{-1} as the Mg–H stretching bands for HMgBr and HMgCl, respectively.[8]

When the THF solvent was removed from HMgCl, a solid of empirical formula HMgCl·THF was formed. The x-ray powder diffraction pattern of this solid was identical with that of $MgCl_2 \cdot 2THF$. However, the solid redissolved immediately when THF was added. DTA–TGA studies of this solid showed decomposition at 300 °C with hydrogen evolution. The x-ray powder pattern for HMgBr·1.5THF formed on removal of THF from the solution prepared above, gave lines identical with $MgBr_2 \cdot 3THF$ indicating disproportionation of HMgBr to MgH_2 and $MgBr_2$ in the solid state.

On the basis of molecular weight and spectroscopic studies, the molecular structure of HMgCl in THF is suggested to be that represented below:



Because of the insoluble nature of MgI_2 in THF, an attempt was made to prepare HMgI by addition of a solution of MgI_2 in diethyl ether to MgH_2 slurry in diethyl ether and in THF. An x-ray powder pattern of the solid isolated after the removal of the solvent under vacuum showed strong lines due to $MgI_2 \cdot 6THF$ rather than the expected product HMgI·3THF. The nonreactivity of MgH_2 toward MgI_2 in THF is probably due to the insoluble nature of MgI_2 in THF. Interestingly, the DTA–TGA of this so-called mixture gave no hydrogen evolution at 310 °C as expected for MgH_2 decomposition, but instead showed extensive THF cleavage.

Both HMgBr and HMgCl in THF have been shown to reduce ketones such as benzophenone and 4-*tert*-butycyclohexanone to the corresponding alcohols. More importantly, these new soluble Mg–H compounds have been shown to add to both alkenes and alkynes thereby providing an alternate to those reactions involving hydroboration. We are actively engaged in a study to arrive at optimum conditions for effecting such addition reactions.

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*Book Reviews**

Catalysis in Organic Synthesis, 1976. Edited by P. N. RYLANDER and H. GREENFIELD. Academic Press, New York, N.Y. 1976. x + 363 pp. $16.50.

This is a volume of 17 papers given at the Fifth Conference on Catalysis in Organic Syntheses", held in Boston in 1975. The papers are reproduced directly from typescript, and are largely reports of original research, including some experimental detail. They are sorted into the groups "Engineering Aspects and Surface Catalysis", "Special Topics", "Polymer-attached Homogeneous Catalysis", "Catalytic Processes", and "Hydrogenation".

The first such conference was held in 1960, and previous proceedings have been published in *Annals of the New York Academy of Sciences*. The original sponsorship by the Academy has been superseded by the newly formed "Organic Reactions Catalysis Society". The topics cover a broad field, with papers ranging from Auger spectroscopy through enzymatic epoxidation to asymmetric hydrogenation with chiral catalysts. There is a slim subject index.

Spectroscopic Data. Volume 2. Homonuclear Diatomic Molecules. Edited by S. N. SUCHARD and J. E. MELZER. IFI/Plenum Press, New York, N.Y. 1976. vii + 585 pp. $57.50.

The first of this two-volume work was devoted to heteronuclear diatomic molecules and appeared in 1975. This volume is in effect one enormous table, in which the molecules are listed in alphabetic order. The overly broad title is misleading, for the spectroscopic data given are primarily electronic. The tables give in briefest form "Methods of Production and Experimental Technique", followed by description of the band systems and references to sources, spectroscopic constants, etc. The Introduction describes the basis of the search to compile the information presented, but unfortunately does not state the date up to which the compilation was made. The volume is nicely produced and the data are presented in an uncrowded manner.

The Heavy Transition Elements. By S. A. COTTON (University of East Anglia) and F. A. HART (University of London). Wiley/Halsted, New York, N.Y. 1975. xii + 272 pp. $23.50.

This text describes the inorganic chemistry of the second- and third-row transition elements. The level and quantity of material presented is well suited for a one-semester course for advanced undergraduate or beginning graduate students. The first eight chapters each start with a table showing some of the compounds formed by a 3d transition element and then describe the chemistry of the two heavy transition elements of the same group. The main topics covered are the metals, aqueous chemistry, oxides, halides, and coordination complexes (including organometallics). The ninth chapter deals exclusively with complexes of π-bonding ligands, and the concluding two chapters devote 73 pages to the lanthanides and actinides.

This book differs from some of the other popular inorganic texts in that the authors have concentrated on the descriptive chemistry and periodic trends of the elements with minimal discussion of the nuances of bonding, spectroscopic and magnetic properties, and applications. Literature references are given for only a few of the many reactions and compounds described. Lucid prose, ample use of structural drawings, and a good format keep the text readable despite a high density of information. As intended, the authors have written an accurate and detailed description of the heavy transition elements which is of manageable length but cannot be readily extended to provide an introduction to research.

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Annual Review of Biophysics and Bioengineering. Volumes 3 and 4. Edited by L. J. MULLINS, W. A. HAGINS, L. STRYER, and C. NEWTON. Annual Reviews, Inc., Palo Alto, Calif. Volume 3: 1974. 403 pp. Volume 4: 1975. $15.00. 604 pp.

The articles found in Volumes 3 and 4 of "Annual Review of Biophysics and Bioengineering" cover a tremendously broad range of scientific interests. Volume 3 includes articles on topics ranging from enzyme kinetics, DNA conformations, and x-ray data to articles on the analysis of convection and diffusion in capillary beds as well as scintillation scanning of the brain. Volume 4 includes topics ranging from tRNA structure, fluorescent probes and concentration correlation spectroscopy to computer methods in electrocardiography, artificial kidneys, and computer monitoring in patient care.

Clearly such a broad range of subject matter cannot be critically commented on by one reviewer. Therefore, articles selected for specific comment generally reflect the personal interests of the reviewer. However, without requiring great expertise in all the fields discussed, it should be mentioned that both volumes are extremely well written and well organized.

Articles selected for particular comment from Volume 3 include: Kinetics of Allosteric Enzymes; Applications of Calorimetry in Biochemistry and Biology; Properties of Water in Biological Systems; Conformational Changes in DNA Molecules. These four articles are written in such a way that very little specialized expertise is required to fully benefit from the material. In particular, the article by Cooke and Kuntz on the properties of water in biological systems represents a clear and important presentation of a significant yet poorly understood area.

In Volume 4 three articles warrant specific comment. These include Thermal Properties of Biomaterials; Quaternary Structure by Small Angle Neutron Scattering; and Concentration Correlation Spectroscopy. The latter article by Elson and Webb represents a particularly well-written and fascinating presentation of a new and potentially powerful biophysical probe.

Once again it should be mentioned that many of the articles in Volumes 3 and 4 that have not been specifically mentioned provide interesting and exciting reading. However, due to the breadth of the material covered, it is not possible for one reviewer to critically appraise all of the articles. It is therefore suggested that the contents of the two volumes be carefully examined by all those interested in topics related to biophysics and bioengineering.

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* Unsigned book reviews are by the Book Review Editor.