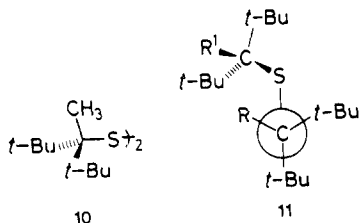


($\theta(\text{HOOH}) = 110\text{--}120^\circ$;⁵³ $\theta(\text{HSSH}) = 90.5^\circ$).⁵⁴ Nevertheless, we anticipate that structures 6-9, if capable of preparation, will show large and "abnormal" $\theta(\text{CSSC})$'s at least approaching the trans values.

Attempts to synthesize highly congested disulfides may encounter unexpected problems. We should like to point out, however, that synthetically more attractive but sterically less crowded goals may ultimately prove disappointing. For example, $\alpha,\alpha,\alpha',\alpha'$ -tetra-*tert*-butyldiethyl disulfide (10) is a reasonably crowded system. However



it is likely to adopt 11 ($R = R' = \text{CH}_3$) as its minimum energy conformation. As we have pointed out previously, the value of $\theta(\text{CSSC})$ is determined by the substituents R and R' . Three sets of S-S dihedral angles were identified as follows: $83\text{--}84^\circ$ ($R = R' = \text{H}$), $94\text{--}96^\circ$ ($R = \text{H}$, $R' = \text{CH}_3$), $112\text{--}114^\circ$ ($R = R' = \text{CH}_3$).¹ On this basis it is predicted that 10 would resemble *t*-Bu-SS-*t*-Bu and DAD in its value of $\theta(\text{CSSC})$. Finally, the recent observation of a trans planar conformation in bis(2-pyrimidyl) disulfide acting as a ligand to Cu(I) should be mentioned.⁵⁵ Geometric distortion arises via the agency of nitrogen-copper complexation, however, as confirmed by X-ray⁵⁵ and force field calculations⁵⁶ for the free ligand.

Experimental Section

The PE spectra were recorded on a PS-18 spectrometer (Perkin-Elmer) and calibrated with a mixture of argon and xenon

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gases introduced into the target chamber simultaneously with the sample. The recording temperatures for DAD and for 1-adamantanethiol were 97° and room temperature, respectively; the experimental resolution was 25-30 meV. The reported ionization potentials are averages of three determinations.

Bis(1-adamantyl) Disulfide. 1-Adamantanethiol⁵⁷ (4.4 g, 26 mmol) was slurried in a solution of sodium hydroxide (85% NaOH, 4.2 g, 85 mmol) in water (22 mL). A solution of potassium hexacyanoferrate(III) (8.7 g, 26 mmol) in water (42 mL) was added to the above-mentioned slurry during 3 h at room temperature. The reaction mixture was allowed to stand overnight. The reaction mixture was then extracted twice with ether. After the solution was dried with magnesium sulfate the ether was removed under reduced pressure, leaving the disulfide 5 as a white solid (3.7 g, 11 mmol, 84%). Recrystallization (pentane) gave 5 as colorless crystals, mp 223°C . Sublimation gave an analytical sample: ^1H NMR (CDCl_3 , Me_4Si) δ 1.68 (6 H, m), 1.85 (6 H, m), 1.93-2.04 (3 H, m); IR ν_{max} (KBr) 2900 (s), 2845 (s), 1450 (m), 1340 (m), 1310 (w), 1295 (m), 1255 (m), 1180 (w), 1100 (m), 1035 (m), 975 (m) cm^{-1} ; UV λ_{max} (CH_3CN) tailing to 280 nm; Raman ν_{max} (CCl_4) 532 cm^{-1} , ν_{max} (solid): 532, 542 cm^{-1} ; mass spectrum, m/e (relative intensity) 334 (M^+ , 8), 168 (2), 135 (100), 93 (7); ^{13}C NMR (CDCl_3 , Me_4Si) δ 30.1 (relative intensity 5.4), 36.2 (7.4), 43.2 (4.6), 47.3 (1.0). Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{S}_2$: C, 71.80; H, 9.04; S, 19.17. Found: C, 71.80; H, 9.29; S, 18.85.

Note Added in Proof. The X-ray structure determination of DAD has been completed and yields a value of $\theta(\text{CSSC}) = 110.5 (9)^\circ$,⁵⁹ in excellent agreement with the force field prediction of 113.8° . The PES estimate of the S-S torsion in DAD is obviously low, implying that the *t*-Bu-SS-*t*-Bu dihedral angle must be evaluated upward.⁵⁹

Acknowledgment. We are grateful to the Danish Natural Science Research Council for purchase of a photoelectron spectrometer and to Drs. E. Larsen (Risø National Laboratory) and O. F. Nielsen, (H. C. Ørsted Institute) for the mass spectroscopic and Raman determinations, respectively. We are also appreciative to Professor M. Charton (Pratt Institute) for providing unpublished results.

Registry No. 5, 34895-45-9; 6, 72610-42-5; 7, 72638-41-6; 8, 72610-43-6; 9, 72610-44-7; 1-adamantanethiol, 34301-54-7.

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Mechanism of Formation of Grignard Reagents. Corrosion of Metallic Magnesium by Alkyl Halides in Ethers¹

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Received August 23, 1979

Scanning electron microscopy and optical microscopy have been used to examine the surface of magnesium that has been allowed to react with ether solutions of organic halides. Initiation of the reaction is characterized by the formation of isolated corrosion pits. These pits grow and eventually overlap, and a major part of the reaction takes place at a smooth, polished surface. The rate of reaction of polished magnesium with alkyl halides is relatively insensitive to the magnesium lattice plane exposed, to dislocation densities, and to grain boundaries. Initiation occurs rapidly at dislocations, relative to initiation at unstrained, intragranular magnesium surfaces.

This work examines the changes that accompany the reaction of metallographically prepared magnesium with

organic halides in diethyl ether.³ Its objective was to develop answers to two general questions that are funda-

mental to the formation of organomagnesium reagents.

(1) Is there any practical way to increase the reactivity of magnesium toward organic halides? Can the reactivity of magnesium be increased by alloying⁴ or by increasing the density of dislocations in the metal? Are particular planes of crystalline magnesium unusually reactive? Is the exceptional reactivity of magnesium produced by the reaction of ethereal solutions of magnesium salts with metallic potassium simply a function of high surface area, or are other factors involved?^{3,5}

(2) The reaction between organic halides and magnesium often shows an induction period, which can be shortened by the use of "activators" and by deforming the metal in situ.³ Can initiation of the Grignard reaction be correlated with features visible on the magnesium surfaces, such as grain boundaries, defects, twins, or inclusions?

The work reported here is also pertinent to the assumptions underlying the "constant surface kinetics technique" described previously.⁶ This technique required that the magnesium surface remained relatively homogeneous in character during reactions, that is, that no large changes in surface area took place during reaction and that preferential reaction of impurity sites and grain boundaries at the surface did not occur.

In addition to these problems in synthetic and mechanistic organomagnesium chemistry, this work is pertinent to the general problem of corrosion of magnesium by organic liquids, a matter of practical technological concern.⁷

Technology and Techniques

The current focus of this research was an effort to correlate the surface morphology of magnesium—examined using optical microscopy and scanning electron microscopy (SEM)—with its reactivity toward organic halides.

The magnesium ordinarily used in the preparation of Grignard reagents consists of turnings from metallic stock that is approximately 99.5+ % pure. This material is not sufficiently well-defined for the studies described here for three reasons. First, it contains inclusions having different composition and reactivity from the bulk of the material. Second, it is polycrystalline. The grain boundaries have different surface free energies than the intragranular regions and may also have different chemical reactivity.⁸⁻¹⁰ Third, magnesium turnings are severely stressed and fractured as a result of the turning procedure. The re-

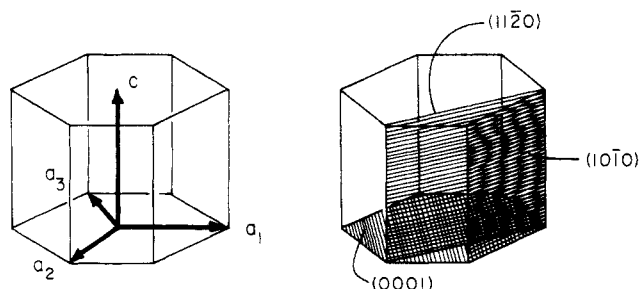


Figure 1. Unit cell and the indices of three planes drawn on a unit cell of hexagonal magnesium. The Miller-Bravais indices of a plane in the hexagonal system refer to the four axes a_1 , a_2 , a_3 , and c and are written $(hkil)$ where the index i is the reciprocal of the fractional intercept on the a_3 axis. Left side, the hexagonal unit cell with axes. Right side, three representative planes: the basal plane, (0001), one type of prismatic plane, (1010), and a second type of prismatic plane, (1120).

sulting high density of lattice defects can have a major influence on reactivity. To simplify experiments, we carried out much of our work with single-crystal magnesium of 99.999+ % purity. To minimize disorder at the surface when studying the reactivity of selected lattice planes,¹⁰⁻¹⁴ we spark cut the properly oriented¹⁵ crystals.¹⁶ Figure 1 summarizes the nomenclature used in describing lattice planes in the hexagonal closest packed system.

The surface of a pure metal is a mosaic of atomic and macro ledges and grain boundaries. Initially, magnesium metal is also covered by a film composed of magnesium oxide and magnesium hydroxide. To remove the oxide film and to decrease the density of defects generated in producing the surface, we polished the surface by using 6% aqueous nitric acid at 0 °C.⁷⁻²⁰ This treatment produced a surface having a low "pitting factor" (the ratio of deepest metal penetration to the average metal penetration). Magnesium samples that had been etched by contact with solutions of alkyl halides were rinsed, dried, and transferred to the stage of an optical microscope or scanning electron microscope.^{19,21} SEM yields photomicrographs which have better depth of field than those obtained with optical techniques; optical microscopy has a shallow depth of field but is normally better than SEM in emphasizing grain and twin structure.

Results and Discussion

Reaction of single-crystal magnesium spheres with alkyl halides shows no selectivity for specific lattice planes. We initially examined the partial dissolution of a small mag-

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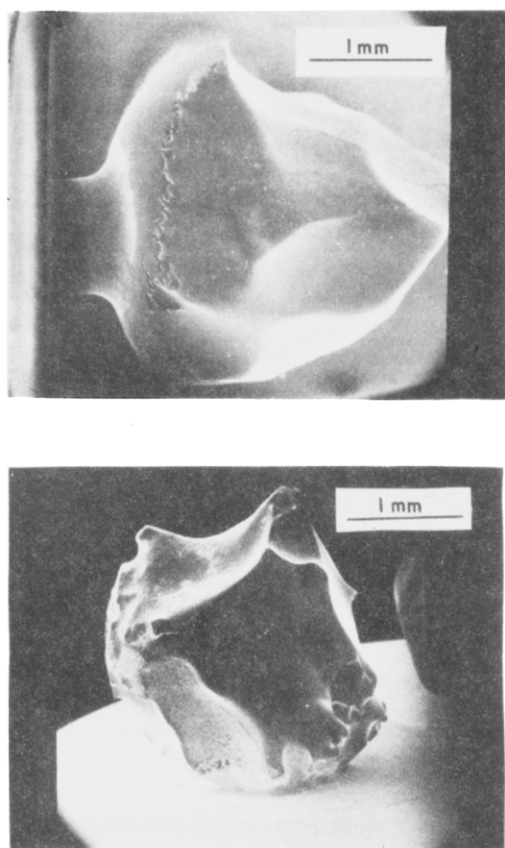


Figure 2. Single-crystal magnesium spheres after Grignard reaction pitting. The top photomicrograph shows the final shape of a crystal sphere with stem after pitting in ca. 0.05 M ethyl bromide in diethyl ether at 0 °C. At the left is a portion of the original surface. The bottom photomicrograph shows the final shape of a sphere after pitting in ca. 0.05 M ethyl bromide in tetrahydrofuran at 0 °C.

nesium single-crystal sphere in an alkyl halide solution. Since every possible plane in a crystal is parallel to the surface of a sphere at some point, selective reaction involving one or several planes will be reflected by a transformation of the starting sphere to a regular polyhedron during the reaction. Spheres of single-crystal magnesium 0.125 in. in diameter were prepared by spark cutting, followed by careful chemical polishing under an argon atmosphere to minimize dislocations and surface films. These spheres were allowed to react with a dilute solution of an alkyl halide in an ethereal solvent at ca. 0 °C. Under these conditions, reaction was slow: ca. 60% of the mass of the spheres had disappeared after 1 h. These reactions followed a course that, with qualitative variations, was common to all the pittings examined. Reaction initiated spontaneously at a number of discrete points on the surface (this initiation is discussed in greater detail below). These pits grew and eventually overlapped. After ca. 35% of the mass of the spheres had corroded, the original surface was nearly or completely gone. As the reaction proceeded, the pitting factor became smaller: that is, the surface became smoother and more polished. No single geometrical form was produced at any time during these reactions. Figure 2 reproduces SEM photographs of two representative spheres after reaction.

The fact that no apparent preference was observed at any lattice plane, even after a major part of the spheres' surface had become involved in reaction, argues convincingly that there is no strong preference for reaction at one plane. These experiments are not, however, sufficiently sensitive to detect small differences in reactivity between

planes, since these might be masked by nonuniform initiation, by convection, by the irregular shape of the fully etched sample, or by other experimental artifacts.

Pits formed by reaction of crystals oriented and cut to expose the (0001), (10 $\bar{1}$ 0), and (11 $\bar{2}$ 0) planes provide evidence for small differences in reactivity between planes. Alkyl bromides and chlorides produce different types of pits. Samples of single-crystal magnesium (99.999+ % purity) were oriented, spark cut, polished chemically, and allowed to react for a short time with an alkyl halide in diethyl ether. The resulting small pits, characteristic of the early stages of the reaction, were examined by SEM and optical microscopy. Under most reaction conditions, all pits had irregular, noncrystallographically defined boundaries and rounded bottoms. When the pitting reactions were required to proceed very slowly, using low concentrations of alkyl halides and keeping the temperature at 0 °C, some fraction of the small pits had well-defined hexagonal shapes. This shape-selective pitting occurred to an extent determined by the crystallographic plane exposed, the reaction conditions, the pit size, and the procedure used to prepare the sample.

In control experiments, ethyl bromide, pentyl bromide, 1,4-dibromobutane, and phenyl bromide were each allowed to react with reagent grade, polycrystalline magnesium and high-purity (99.99 %) magnesium-4.75 wt % lithium alloy. Under constant experimental conditions, the corrosion of a particular type of magnesium by each of the four bromides was indistinguishable. When the (0001), (10 $\bar{1}$ 0), and (11 $\bar{2}$ 0) planes were allowed to react with ethereal 1,4-dibromobutane or ethyl bromide at 0 °C, only the basal plane, (0001), displayed shape-selective pitting (Figure 3). Hexagonal pits were produced, having diameters up to a maximum size of ca. 25 μ m; larger pits were irregular. Approximately 80% of the pits that were 8 μ m in diameter or smaller were hexagonal. The pitting selectivity was generally observable only at the surface of the crystal: the interiors of the hexagonal pits were conical or rounded, with no visible, defined planes.

When the three different crystal planes were pitted with ethereal 1,4-dichlorobutane at 0 °C, the reaction proceeded much more slowly and with greater geometrical selectivity. Under these conditions the prismatic planes, (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0), produced pits up to 25 μ m in diameter that displayed planar sides, a small percentage of which were nearly perfectly hexagonal. The basal plane produced hexagonal pits up to ca. 200 μ m in diameter. In addition, most of the hexagonal pits in the basal plane developed planar sides (Figure 4).

To determine whether the greater geometrical selectivity in the pitting with alkyl chlorides relative to alkyl bromides was influenced by the slower rates of reaction with alkyl chlorides, we allowed samples of high purity (99.99 %) magnesium-1.5 wt % lithium alloy and a 99.99+ % pure magnesium single crystal displaying the (11 $\bar{2}$ 0) plane to react in ethereal benzyl chloride as well as in ethereal benzyl bromide at 0 °C. Both of these halides react with magnesium at mass transport limited rates.⁶ The benzyl chloride containing solution nonetheless displayed greater geometrical selectivity in pitting than the solution containing benzyl bromide: the former generated angular or oblong pits and the latter pits that were close to circular (Figure 5). The selectivity observed in pitting by benzyl chloride was lost when an excess of bromide ion (1 mol each of benzyl chloride and magnesium bromide) was added to the reaction mixture. Benzyl chloride with bromide ion was found to pit magnesium with the same selectivity as benzyl bromide with an excess of chloride ion.

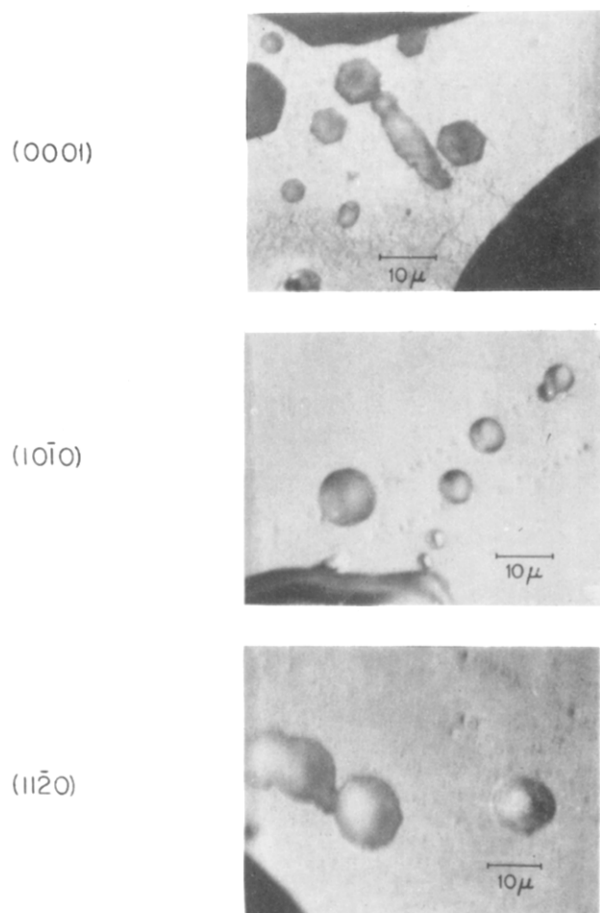


Figure 3. Corrosion of the (0001), (10 $\bar{1}$ 0), and (11 $\bar{2}$ 0) planes of magnesium with ethereal 1,4-dibromobutane. The top photomicrograph shows the hexagonal pits developed on the basal plane, and the lower photomicrographs show the spherical pits developed on the two prismatic planes (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0).

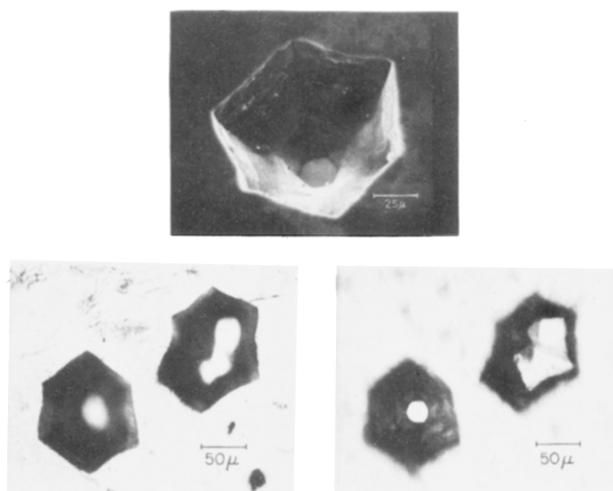


Figure 4. Hexagonal pit produced by reaction of the basal plane with ethereal 1,4-dichlorobutane. The top photograph is a scanning electron photomicrograph showing the hexagonal symmetry of the pit at all depths. The bottom photographs were taken with an optical microscope. The photomicrograph at the bottom left was taken with the focus on the pit surface while the photomicrograph at the bottom right was taken with the focus on the pit bottom.

It is not evident whether the shapes of the pits in these experiments are determined by initiation or pit propagation, but it is clear that the halide ion present in the solution influences the course of the reaction.

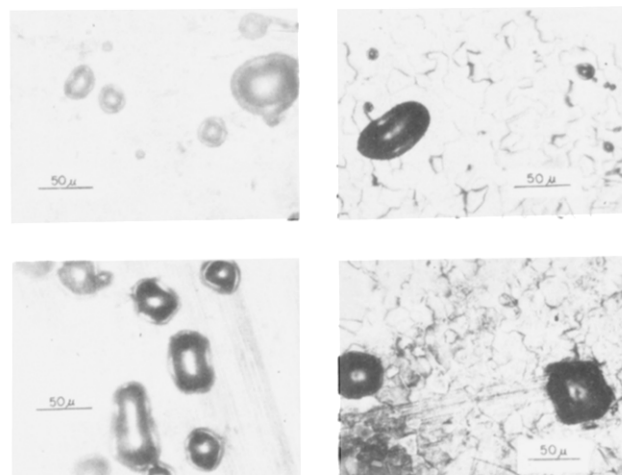


Figure 5. Alkyl chlorides pit magnesium more selectively than alkyl bromides. The photograph at the top left shows pitting on the (11 $\bar{2}$ 0) plane of single-crystal magnesium by 1.0 M benzyl bromide in ethyl ether at 0 °C. The photograph at the top right shows pitting on magnesium-1.5 wt % lithium by this medium. The photograph at the bottom left shows pitting on the (11 $\bar{2}$ 0) crystal face by 1.0 M benzyl chloride in diethyl ether at 0 °C, and the photograph at the bottom right shows pitting on the magnesium-1.5 wt % lithium alloy by this medium.

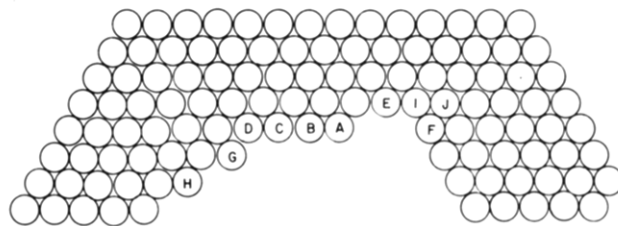


Figure 6. Illustration of crystal dissolution at an atomic level. For simplicity, the pit is assumed to be confined to a single plane.

The development of crystallographically defined pits is adequately rationalized by the kinematic theory of crystal growth and dissolution.^{22,23} For simplicity, we will assume that the pit is confined to the single plane shown (Figure 6); the extension of these arguments to three-dimensional arrays is clear. The least energy is required to remove the atom having the smallest number of nearest neighbors. Thus, in loss to the solution as an organomagnesium species or magnesium ion during formation of Grignard reagent, atoms of type A should be lost, then those of type B, and then those of type C. The observation of hexagonal pits on treating single-crystal magnesium with an alkyl chloride suggests that magnesium atoms are lost sequentially along ledges (A, B, C, ...) more rapidly than from unbroken steps (E or F) or from even less accessible sites (I or J). The facts that crystallographically defined pits are formed only in slow reactions and that this definition is lost with large pits indicate that any preference for loss of magnesium from particular lattice planes is relatively small.

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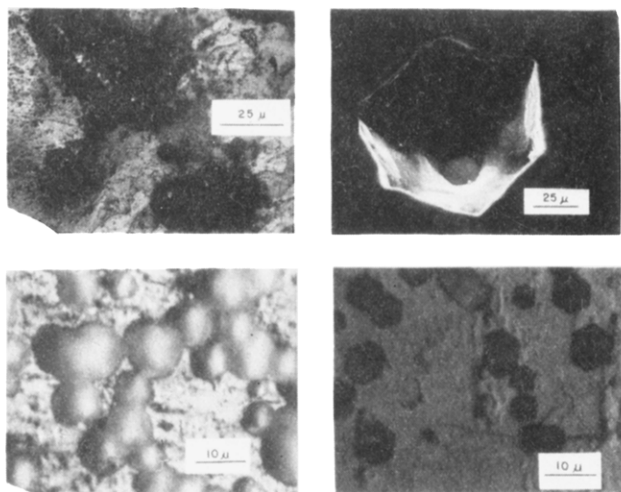


Figure 7. Geometrical selectivity in Grignard pit formation is greater at surfaces with low densities of dislocations than at those with high densities. The top photomicrographs are of the basal plane of a 99.999% pure magnesium single crystal; the bottom photomicrographs are of magnesium–4.75 wt % lithium alloy. At top left are the nondescript pits produced when the basal plane was prepared by mechanical polishing alone; at top right is a well-developed hexagonal pit produced when the basal plane was prepared by mechanical polishing followed by thorough chemical polishing. At bottom left are the nondescript pits produced when the Mg–Li alloy was prepared by mechanical polishing alone; at bottom right are the hexagonal pits produced when the Mg–Li alloy was prepared by mechanical polishing followed by chemical polishing. Etheral 1,4-dichlorobutane at 0 °C was the corrosion medium in all cases.

As expected from this type of argument, the history of the surface has a significant influence on the type of pit produced. Hexagonal pits were only observed with surfaces that had been carefully polished chemically to remove surface defects. Figure 7 contrasts the behavior of chemically polished and mechanically polished surfaces of samples of pure magnesium and magnesium–lithium alloy. The mechanically polished surfaces have high densities of defects. Since defects afford opportunities for initiation and possibly for propagation of pit growth (also see below), conical or rounded pit walls in the mechanically worked samples reflect the disorder of the defects rather than the crystalline order.²⁴

These studies of the pitting of single-crystal magnesium contribute two useful results to an understanding of the mechanism of formation of Grignard reagents. First, the reaction is normally not selective with respect to crystallographic plane. This conclusion simplifies the interpretation of the kinetics reported earlier⁶ and indicates that an effort to increase the reactivity of magnesium toward alkyl halides by exposing selected crystal faces would not be useful. Second, with carefully selected conditions, it is possible to observe crystallographically defined pitting. Further, alkyl chlorides pit magnesium differently than do alkyl bromides. Although we do not yet understand how the carbon–magnesium bond of the product Grignard reagent is formed,²⁵ the latter observation indicates that the halide ion must be involved in the release of some of the magnesium atoms from the surface.

Pitting in polycrystalline magnesium establishes unexceptional reactivity for grain boundaries and confirms similar reactivity for different lattice planes.

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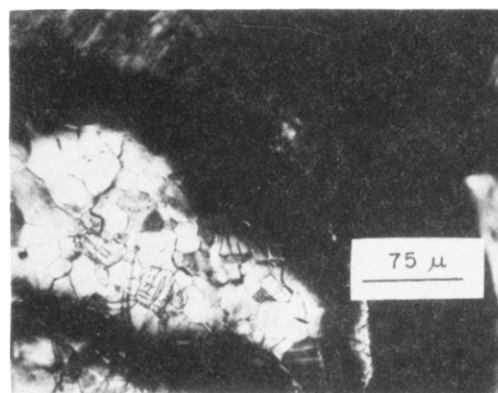


Figure 8. Optical photomicrograph of the flat bottom of a large Grignard reaction pit in polycrystalline magnesium showing grain structure and twin structure.

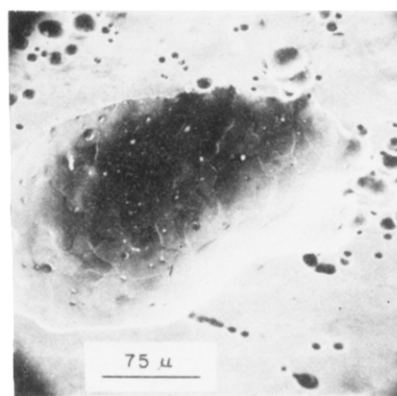


Figure 9. SEM photomicrograph of a large pit in polycrystalline magnesium displaying smooth walls and bottom.

Polycrystalline magnesium offers, in effect, the opportunity to examine the reactivity of grains, grain boundaries, and inclusions by direct competition. The size of the larger pits in all the magnesium samples studied exceeded the grain size. If different grains (different crystal lattice orientations) corroded in etheral alkyl halides at different rates, one would observe pits displaying irregular sides and bottoms. In fact, the pit walls were very smooth. There was no evidence that some grains were reacting more rapidly than others or that grain boundaries or other interfacial regions were exceptionally reactive toward alkyl halides. Figure 8 shows an optical photomicrograph of a large pit covering many different grains and twinned regions; Figure 9 shows an SEM picture of a similar pit.

These observations confirm those reported in single-crystal studies—that magnesium crystals normally react isotropically—and extend this conclusion to grain boundaries and to other regions included in polycrystalline magnesium that have low purity or are regions of high surface energy. They are important in justifying the assumption made in the “constant surface kinetics” procedures⁶ that the magnesium surface is not physically altered in any substantial manner during reaction and that, in consequence, its active surface area does not change for small extents of reaction.

Magnesium–lithium alloys are slightly more reactive toward alkyl halides than is pure magnesium; magnesium–calcium, –copper, and –silver and magnesium–zinc–iron alloys are less reactive. Experiments already described indicate that the reactivity of pure magnesium toward alkyl halides can only be increased by increasing its exposed surface. Alloying might, however, offer a method of increasing reactivity.⁴ It is difficult to compare

Table I. Relative Reactivities of Magnesium Alloy Samples toward 1-Bromopentane, as Measured by the Loss in Weight of Standard Samples in Competitive Experiments^a

alloy (composn, %) ^b	% wt loss ^c	alloy (composn, %) ^b	% wt loss ^c
Mg (95.25), Li (4.75)	32	Mg (94.7), Ca (5.3)	9
Mg (98.5), Li (1.5)	21	Mg (95), Cu (5)	4
Mg (99.9 ⁺)	11	Mg (93), Zn (3), Fe (4)	4
Mg (ASTM)	10	Mg (95), Ag (5)	1

^a [1-Bromopentane]₀ = 1.0 M, diethyl ether, 0 °C. Magnesium samples (10 × 12 × 2 mm) were mechanically ground and polished to 0.600 ± 0.005 g. ^b Weight %.
^c Average of two experiments.

in any quantitative way the reactivity of two magnesium alloys toward a common alkyl halide: the initiation step plays an important part in determining the overall rate of conversion of magnesium to alkylmagnesium halide, and initiation is not a reproducible process. Standard techniques for studying corrosion are not applicable.²⁶

Without a quantitative method for activating a magnesium surface uniformly, a qualitative procedure for testing the relative reactivity of magnesium alloys toward alkyl halides was employed. A number of samples of alloys having uniform size, weight, and surface area were mechanically ground and polished and then allowed to compete for 1-bromopentane in ether at 0 °C. After partial reaction (ca. 55% of the most reactive alloy had corroded), the reaction was quenched, and the weight lost by each sample was taken as proportional to its reactivity. These results are summarized in Table I.

This procedure does not separate initiation from reaction. Although the rate of reaction of 1-bromopentane with magnesium is itself only ca. 20% less than the mass transport limited rate,⁶ the apparent reactivity of magnesium-4.75 wt % lithium alloy appears in this test to be approximately 3 times greater than that of magnesium.²⁷ It is possible that some part of this difference is due to development of a higher surface roughness for the alloy than for the metal during the corrosion reaction or that the alloy may simply initiate more rapidly. This apparent difference may reflect enhanced reactivity of the alloy toward the intermediate alkyl radicals present during reaction. At the other extreme of reactivity, the least reactive alloy samples seemed to leave a dark film (presumably of the alloying metal) on the surface during reaction and to retain substantial amounts (ca. 50%) of the original surface.

The density of initiation sites on a magnesium surface is not changed by chemical "activation". The first phase of the reaction between an alkyl halide and magnesium is a clearly defined period of activation: the solution close to the magnesium may become turbid, and localized pits form on the magnesium surface. As the reaction proceeds, the turbidity disappears, and the pits grow in size until they overlap and lose their individual identity. This initiation phase is practically very important in preparing Grignard reagents: it may be annoyingly prolonged, and

until initiation has occurred, no significant quantity of Grignard reagent is formed. There seems to be no convenient, absolute method of following the initiation reaction. We have settled on a semiquantitative procedure in which a number of magnesium samples are carefully prepared metallographically in a uniform way and then allowed to corrode in the same ethereal alkyl halide solution at 0 °C in the absence of stirring. If two or more pieces of magnesium are allowed to react in such a corrosion medium until the solution gives evidence that initiation has taken place, examination of the surfaces could show two limiting types of pitting (and, of course, in practice, any type between the two). The surface could show many small pits, densely covering the surface, or a small number of large pits. The observation of many small pits indicates that the rates of formation of pits and of their subsequent growth are comparable; a small number of large pits indicates that their rate of formation is less than their rate of growth. Since the rate of growth appears to be roughly the same for a given type and concentration of organic halide, temperature, and solvent, the rates of initiation can thus be compared, at least qualitatively: the observation of many small pits suggests a high rate of initiation of pits; few large pits suggest a low rate of initiation. This argument presupposes that pits are initiated continuously, rather than simultaneously. Although we have no way of checking this supposition directly, the observation of a distribution of pit sizes on any sample is entirely compatible with it.

Using the number and size of pits formed on the magnesium sample surface just after the first evidence of reaction as the basis for a semiquantitative estimate of the relative rates of initiation of reaction, we observed that an interesting fact emerged on studying the behavior of magnesium samples that had been activated by using iodine, bromine, or tetraethyl orthosilicate.^{3,28,29} A number of samples were prepared by the usual procedure: the surface was polished mechanically and then chemically. Some samples were allowed to stand in contact with the air to build up a thick coat of oxide, some were used immediately after polishing, and some were activated and then used. After these samples gave observable evidence of reaction in the alkyl halide medium, they were removed and examined by optical microscopy. The density of pits on the surface of each sample was similar: that is, the activators apparently did *not* generate new initiation sites. Initiation thus appears to occur at sites that are determined by the surface structure of the metal rather than by the initiating reagent. This reagent does, however, influence the *rate* of formation of nuclei for corrosion.

In related experiments, the surface density of pits was used to estimate the initiation tendency of surfaces that had been subjected to mechanical polishing, to mechanical polishing followed by chemical polishing, and to mechanical and chemical polishing followed by annealing³⁰ (500 °C, 26 h). The mechanically polished sample showed the highest surface pit density, the chemically polished surface an intermediate density, and the annealed surface a low density. Figure 10 illustrates the difference in pit densities for chemically polished and chemically polished and annealed surfaces.

All of these observations suggest that initiation occurs at defects on the magnesium surface. The mechanically

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(27) These experiments could not be extended to alloys of magnesium with sodium or potassium, since these elements are insoluble in magnesium in all proportions. C. Sheldon Roberts, "Magnesium and its Alloys", Wiley, New York, 1960, Chapter 3. M. Hansen, "Constitution of Binary Alloys", McGraw-Hill, New York, 1958, p 909.

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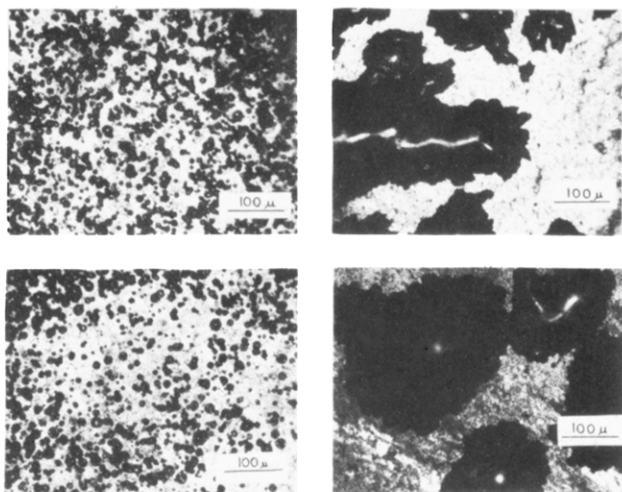


Figure 10. Four optical photomicrographs of four different samples of polycrystalline, 99.9% pure magnesium that demonstrate that annealing decreases the density of initiation sites in the Grignard reaction. The two samples at the left were first polished mechanically and then polished chemically. The two samples at the right were mechanically and chemically polished by analogous procedures and then annealed at 500 °C for 26 h. All four specimens were allowed to react in the same vessel [Et_2O , $\text{Cl}-(\text{CH}_2)_4-\text{Cl}$, 0 °C] to provide a uniform corrosion medium.

polished surface is expected to have a very high density of dislocations in the vicinity of the surface. Many of these are removed by the chemical polishing process. Annealing should reduce the number that remain after chemical polishing. The indication that the number of sites available for initiation is independent of the action of activators is compatible with the idea that a surface defect serves as the nucleus for pit formation.

In passing, it is worthwhile mentioning that under similar conditions, reaction with alkyl chlorides gives higher pit densities than with alkyl bromides, reactions in diethyl ether produce higher pit densities than in THF, and reactions at low temperatures give higher pit densities than reactions at high temperatures³¹ (Figure 11). Reactions involving surfaces activated by amalgamation with zinc chloride, zinc bromide, or mercuric bromide gave areas that had low pit densities and others that never lost their surface amalgam coating.

Initiation occurs rapidly at dislocations. Qualitative conclusions based on the density of pits initiating in a surface suggested that defects in the surface, particularly dislocations,³¹ provide nuclei for corrosion. The high reactivity often associated with dislocations can be due either to strain or to impurities concentrated at the dislocations. Our studies of the relation between dislocations and reactivity in initiation employed 99.999+% pure single-crystal magnesium. This magnesium should contain negligible amounts of impurities at dislocations.

It is difficult simultaneously to detect dislocations present in magnesium³³ and to observe etch pits.³⁴ We

(31) The number of etch pits formed by the thermal etching of crystalline copper has been shown to be a function of the temperature of etching. Cf. F. W. Young and A. T. Gwathmey, *J. Appl. Phys.*, **31**, 225 (1960).

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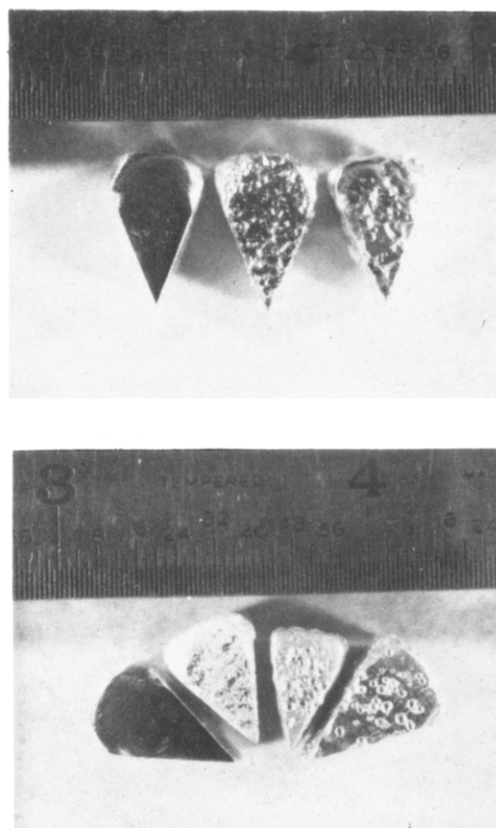


Figure 11. Etch-pit size as a function of solvent (top) and reaction temperature (bottom): Mg control chip, polycrystalline, 99.9% pure, chemically polished (left, top); chip pitted by $\text{C}_6\text{H}_5\text{Br}$, 0 °C, in Et_2O (middle, top); chip pitted by $\text{C}_6\text{H}_5\text{Br}$, 0 °C, in THF (right top); Mg control chip, polycrystalline, 99.9%, chemically polished (left, bottom); chip pitted by $\text{C}_6\text{H}_5\text{Br}$ in Et_2O at -20 °C (second from left, bottom); chip pitted by $\text{C}_6\text{H}_5\text{Br}$ in Et_2O at 0 °C (third from left, bottom); chip pitted by $\text{C}_6\text{H}_5\text{Br}$ in Et_2O at 66 °C (right, bottom). Fine graduations on the displayed scale are $1/64$ -in. intervals.

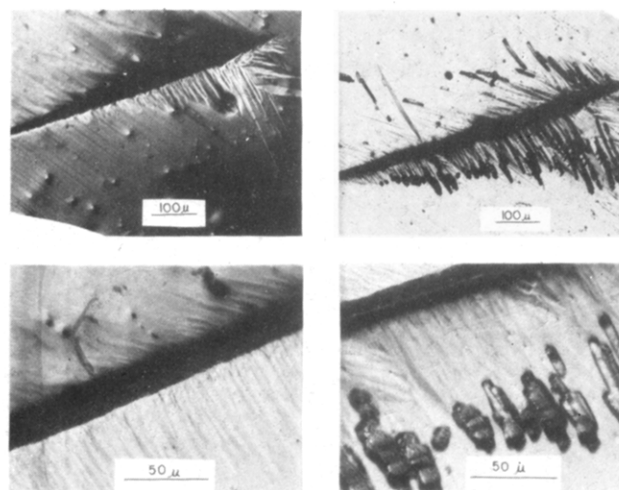


Figure 12. Grignard reagent pits nucleate selectively at dislocations in crystalline magnesium. All samples are the chemically polished (1010) faces containing a Knoop hardness test indentation. Photomicrographs at left are taken before Grignard reaction; those at right are taken after Grignard reaction and show pit nucleation only along slip lines adjacent to the hardness indentation. Photomicrographs above are at 80 \times ; those below are at 320 \times . Ethereal 1,4-dichlorobutane at 0 °C was the corrosion medium in all cases.

introduced dislocations into a small, identifiable region of a prepared magnesium surface by plastic deformation.

Disks of single-crystal magnesium were spark cut and chemically polished to minimize dislocations. An indentation made in the surface with a Knoop hardness testing device^{35,36} produced a high density of slip lines perpendicular to the indentation. The disk was treated with ethereal 1,4-dichlorobutane for 1–2 min, removed (before any detectable signs of reaction), washed with water, and dried. Microscopic examination of the surface revealed a large number of etch pits localized on the slip lines adjacent to the indentation (Figure 12).

Summary and Conclusions

Under reactions typical of those used in preparing Grignard reagents, there are only small differences between the rates of loss of magnesium atoms from different types of sites on the metal surface. As expected, the small differences observed can be rationalized by using an often invoked model in which the magnesium atoms having the fewest nearest neighbors are lost most rapidly from the surface. The reactivity of magnesium toward alkyl bromides is increased by alloying with lithium and decreased by alloying with more electronegative metals: since the reaction of magnesium itself with alkyl bromides occurs close to or at a transport-limited rate, the increase in reactivity probably reflects an increase in the rate of initiation, at least in part. Once reaction has started, the reactivity of the metal is not greatly influenced by defect structure or grain orientation. The initiation step takes place preferentially at dislocations.

If the reaction of alkyl halides with single-crystal magnesium is carried out slowly, pits are formed whose boundaries appear to reflect the crystal orientation. This observation leads to two useful conclusions. First, since other evidence implicates free alkyl radicals as intermediates in the reaction, this selectivity suggests that the carbon–magnesium bond of the product Grignard reagent is not formed irreversibly on collision of the radical with the surface. Second, the observation that slightly different pitting behavior is observed for alkyl bromides and alkyl chlorides suggests that halide ion is involved in the step in which some significant fraction of the magnesium atoms are lost from the lattice.

The picture of the magnesium surface reaction that emerges from these studies is compatible with practical synthetic experience with the Grignard reaction. Initiation is assisted by any process that generates dislocations at the magnesium surface. Magnesium turnings have high dislocation densities, and new dislocations are produced by crushing or scratching the magnesium. Once the reaction is initiated, the major factor in determining the reaction rate is the magnesium surface area. High surface area magnesium prepared *in situ* by reduction⁵ or by evaporation³⁷ should represent a practical extreme of this method of increasing magnesium reactivity.

Experimental Section

General Methods. All Grignard reagents were prepared under an argon atmosphere. Diethyl ether was distilled from lithium aluminum hydride under an argon atmosphere. Tetrahydrofuran (THF) and dimethoxyethane (DME) were purified by distillation from dark purple solutions of sodium benzophenone ketyl under nitrogen. Dibromoethane was treated three times with concen-

trated sulfuric acid, distilled through a column of glass helices, and stored over anhydrous magnesium sulfate. All other halides used in the experiments were reagent grade and were used without purification. Photomicrography was carried out by using either a Cambridge Mark I scanning electron microscope equipped with a 4 in. × 5 in. Polaroid Model 500 camera or a Leitz Wetzlar MM5 metallograph with a high-intensity 450-W xenon lamp equipped with a 4 in. × 5 in. Polaroid Model 545 camera. Photomicrographs were taken with a Polaroid MP-3 Land camera. Knoop hardness test indentations were made by using a Model LL tester with a 900-g load. Laue X-ray diffraction and spark cutting were carried out in the MIT Department of Materials Science and Engineering.

Materials. A cylinder of single-crystal magnesium 0.5 in. in diameter and 2 in. long of 99.999+ % purity was purchased from Research Organic/Inorganic Chemical Corp. A second cylinder of single-crystal magnesium 0.125 in. in diameter and 0.5 in. long of a minimum starting purity of ca. 99.95 % was grown by J.V.S. Magnesium rods of 99.9 % purity were obtained from Research Organic/Inorganic Chemical Corp. Magnesium rods of 99.95 % purity were obtained from United Mineral and Chemical Corp. Magnesium rods of ca. 99 % minimum purity were obtained from Fisher Scientific Co. Reagent-grade magnesium turnings of 99.9 % purity were obtained from Mallinckrodt. Ultrapure magnesium that contained 1 ppm of manganese and less than 1 ppm of calcium, chromium, copper, iron, and silicon by spectrographic determination was obtained from Johnson Matthey Co. The sample of magnesium–5.3 wt % calcium alloy was a gift from Dr. Mary Woodville of Dow Chemical Co. The samples of magnesium–1.5 wt % lithium and magnesium–4.75 wt % lithium alloys were gifts from Professor Morris E. Fine, Northwestern University. Spectrographic analysis of these magnesium–lithium alloy samples indicated that the only detectable impurity was 0.001 % iron. Five samples of magnesium–3 wt % zinc–4 wt % iron of ca. 99 % purity were a gift from Professors Merton C. Flemings and Edwin Backman, MIT Department of Materials Science and Engineering.

Magnesium–5 wt % copper and magnesium–5 wt % silver alloys were prepared on a 20-g scale. Requisite amounts of ultrapure magnesium and either 99.99 % pure copper or 99.5 % pure silver were carefully weighed, mechanically polished to remove surface oxides, and placed in a graphite crucible. The graphite crucible was immediately placed in a vertical-tube vacuum furnace that was subsequently flushed with argon and evacuated twice. Argon at atmospheric pressure was then maintained in the system. Argon flow was monitored by a bubbler attached to the check valve at the top of the tube furnace. A glass-jacketed coil of 0.5-in. copper tubing was placed outside the tube furnace. Heat for melting was supplied to the coil by a Lepel 20-kV high-frequency (ca. 250 kHz) power supply. Water was passed through the copper-tubing induction-heating coil for cooling. The temperature was taken to 800 °C or higher and maintained for a few minutes. After a cooling time of 1 h under an argon flow of 60 mL/min the tube furnace was disassembled and the magnesium alloy ingot removed, mechanically polished with medium-grade sandpaper, and cut into small disks. The disks were then reintroduced into the graphite crucible in reverse order such that the bottom disk became the top disk for the second melting. The entire melting procedure was repeated three times. The resulting alloys were characterized by optical microscopy. The magnesium–5 wt % copper alloy had an average grain size of ca. 60 μm and a 3 % volume fraction of foreign inclusions. The magnesium–5 wt % silver alloy had an average grain size of ca. 110 μm and a 5 % volume fraction of foreign inclusions.

Preparation of Magnesium Samples for Corrosion. Three different metallographic methods were used to prepare the various magnesium and magnesium-alloy samples used for this study. Polycrystalline, 99+ % pure magnesium rods were cut into disks weighing ca. 1 g each. The flat surfaces of these disks were then smoothed with medium and very fine sandpaper and with "0" emery paper. The chips were chemically polished in a gently stirred 6 % aqueous solution of nitric acid at 0 °C. Chemical polishing was carried out for a minimum of 15 min, during which time the disks had lost ca. one-third of their weight. The samples were washed quickly with water and anhydrous ether.

All samples of single-crystal magnesium were spark cut. The two spheres of single-crystal magnesium were spark cut from the 0.125 in. × 0.5 in., ca. 99.95 % pure crystal; the samples displaying

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the (0001), (10 $\bar{1}$ 0), and (11 $\bar{2}$ 0) planes were spark cut from the 0.5 in. \times 2.0 in., 99.999+ % pure crystal. All spark-cut crystal samples were chemically polished by lowering them with tweezers into a vigorously stirred 5% aqueous solution of nitric acid at 0 °C under argon. The samples were not allowed to contact the magnetic stirring bar. The samples were washed as described above.

Magnesium alloys were cut into rectangular solids of ca. 10 \times 12 \times 2 mm weighing 0.7–0.9 g. Chemical polishing of alloy samples in aqueous, methanolic, or ethanolic nitric acid at 0 or –20 °C or at ambient temperature was unsuccessful. Under all these conditions, the more electropositive metal in the alloy sample (usually magnesium) was preferentially leached from the sample, thereby changing the surface composition. Consequently all alloy samples were metallographically prepared by mechanical polishing. The alloy samples were ground with medium and very fine sandpaper and polished with “0”, “00”, and “0000” emery paper.

Annealing of magnesium (alloy) samples was carried out by placing the samples in Carius combustion tubes, flushing the tubes with argon, sealing them, and heating the sealed tubes to 500 °C for 26 h.

General Procedure for Grignard Reaction of Metallographically Prepared Magnesium Samples and Microscopic Analysis of the Resulting Corrosion. The magnesium (alloy) sample (0.5–0.7 g, depending on the experiment) was placed in either a 40-mL centrifuge tube or a three-necked, 50-mL, round-bottomed flask immediately after metallographic preparation, and the flask was flame dried again under argon. Reaction vessels were not equipped with magnetic stirring bars—stirring of the reactant solutions was done by swirling gently by hand to minimize abrasion of the metallic sample. Anhydrous solvent (10 mL) was added to the reaction vessel by syringe followed by 0.01 mol (ca. 1 mL) of alkyl halide. The reaction vessel was swirled until a faint cloudiness indicated the start of reaction. The vessel was immediately placed in the appropriate temperature bath (usually ice–water, 0 °C). Gentle manual stirring was continued for several minutes or until reaction was proceeding vigorously. A large percentage of the reactions failed to proceed due to in-

sufficient initiation. Reaction was terminated by removing the magnesium (alloy) sample from solution with tweezers and immediately and thoroughly washing the sample with water and with acetone.

Corrosion of Single-Crystal Spheres. The corrosion of magnesium spheres with alkyl halides was carried out by using the metallographical preparation procedure, the Grignard reaction procedure, and the workup procedure for SEM observation described above. Two spheres 0.125 in. in diameter were spark cut from a magnesium single crystal of 99.95% maximum purity and metallographically prepared for reaction. One sphere was allowed to corrode in 0.05 M ethyl bromide in diethyl ether at 0 °C for 1 h. The reaction vessel was swirled occasionally. The second sphere was corroded under the same conditions by using THF in place of diethyl ether. Both corroded spheres were examined on nearly all surfaces at several magnifications by SEM.

Corrosion Initiation at Dislocations. Disks of single-crystal 99.999+ % pure magnesium displaying (0001) and (10 $\bar{1}$ 0) planes were prepared metallographically. Four to six indentations were made in the chemically polished surfaces with a Knoop hardness testing device equipped with 900-g load. The indented disks were allowed to react in 1 N ethereal 1,4-dichlorobutane for 1–2 min, worked up, and prepared for observation under an optical microscope as described above.

Acknowledgment. We are indebted to Dr. Mary Woodville (Dow Chemical Co.), Professor Morris Fine (Northwestern University), and Professors Merton Flemings and Edwin Backman (MIT) for samples of magnesium alloys.

Registry No. Mg, 7439-95-4; Mg(98.5),Li(1.5), 72428-31-0; Mg(95.25),Li(4.75), 72428-30-9; Mg(94.7),Cu(5.3), 72428-29-6; Mg(95),Cu(5), 72428-32-1; Mg(93),Zn(3),Fe(4), 72428-33-2; Mg(95),Ag(5), 72428-34-3; 1-bromopentane, 110-53-2; ethyl bromide, 74-96-4; 1,4-dibromobutane, 110-52-1; 1,4-dichlorobutane, 110-56-5; benzyl bromide, 100-39-0; benzyl chloride, 100-44-7; C₆H₅Br, 108-86-1.

Reactions of Magnesium Hydride. 4. Stereoselective Reduction of Cyclic and Bicyclic Ketones by Lithium Alkoxy-magnesium Hydrides

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Received May 24, 1979

A series of lithium alkoxy-magnesium hydrides [LiMgH₂(OR)] were prepared and allowed to reduce 4-*tert*-butylcyclohexanone (I), 3,3,5-trimethylcyclohexanone (II), 2-methylcyclohexanone (III), and camphor (IV). It was found that very bulky secondary cyclic alkoxy groups such as 2,2,6,6-tetramethyl- and 2,2,6,6-tetra-benzylcyclohexoxy were very stereoselective in the reduction of these ketones. For example, LiMgH₂(2,2,6,6-Me₄-c-HxO) reduced ketone I to provide 89% of the axial alcohol compared to 83% for HMg(2,6-*i*-Pr₂PhO) which previously had provided the greatest degree of selectivity among the new hydrides of magnesium. The dialkoxyhydrides, LiMgH(OR)₂ [where RO = 2,2,6,6-Me₄-c-HxO or 2,6-*t*-Bu₂PhO], were also found to reduce ketones I, II, III, and IV stereoselectively but to a lesser extent than the monoalkoxyhydrides, LiMgH₂(OR). These reactions were also accompanied by more enolization than observed for the monoalkoxy reagents.

The use of metal hydrides as stereoselective reducing agents in organic chemistry has received considerable attention.^{1–3} Although numerous reports have appeared in the literature concerning the reduction of cyclohexanones by hydrides of boron and aluminum, little is known about reductions with MgH₂ or its derivatives. The reason for

this is presumably due to the reported lack of reactivity of MgH₂ and its insolubility in all solvents studied and also because derivatives of magnesium hydride have been unknown until recently.⁴ We have prepared some THF-soluble magnesium–hydrogen compounds of the types HMgOR⁵ and HMgNR₂⁶ which have been shown to exhibit considerable stereoselectivity toward cyclic and bicyclic ketones.⁷ Since HMgOR compounds are such good ste-

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