Related work in progress is directed to (a) the characterization of the reactivities of the various species **1**, **2**, and **3** with other functional groups (alcohols, amines, conjugated and nonconjugated polyolefins, thiols, ascorbic acid, α-tocopherol, and model substrates for lignin) and polyfunctional substrates, (b) the development of other ML_x/solvent systems for the selective formation of reactive intermediates **1**, **2**, and **3** (metals: Co, Cu, Mn, Cr, V, Mo, and Ru), and (c) the complete characterization of the various species **1**, **2**, and **3** by electrochemical, spectroscopic, magnetic, and kinetic measurements. Preliminary results indicate that (a) the $Fe^{II}(bpy)_2^{2+}$/HOOH/py system is an effective reaction mimic (via production of species **1**) for ligninase (selectively dehydrogenates 3,4-$(MeO)_2$PhOH)[32,33] and (b) several $Cu^{II}L_x$ complexes activate HOOH in a manner similar to that of $Co^{II}(bpy)_2^{2+}$.[3]

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-9106742, the Welch Foundation under Grant No. 1042A, and the State of Texas under the Texas Advanced Research Program. We are grateful to Professor D. H. R. Barton (of this department) for making available preprints of related investigations and for his assistance, encouragement, and stimulating discussions.

Registry No. $Fe^{II}(PA)_2$, 46940-39-0; $Fe^{II}(DPA)_2^{2-}$, 71605-20-4; $Fe^{III}Cl_3$, 7705-08-0; $[Fe^{II}(O_2bpy)_2](ClO_4)_2$, 139657-03-7; $[Fe^{II}(OPPh_3)_4](ClO_4)_2$, 28959-14-0; $[Fe^{II}(MeCN)_4](ClO_4)_2$, 97690-72-7; $[Fe^{II}(bpy)_2](ClO_4)_2$, 16581-25-2; $[Co^{II}(bpy)_2](ClO_4)_2$, 78624-86-9; $[Fe^{II}(H_2O)_6](ClO_4)_2$, 15305-57-4; $[Co^{II}(MeCN)_4](ClO_4)_2$, 139657-04-8; HOOH, 7722-84-1; *t*-BuOOH, 75-91-2; c-C_6H_{12}, 110-82-7; $PhCH_2CH_3$, 108-88-3; c-C_6H_{10}, 110-83-8; *cis*-PhCH=CHPh, 645-49-8; D_2, 7782-39-0; (Me_4N)PA, 139657-01-5; $(Me_4N)_2$DPA, 124443-96-5; PAH, 98-98-6; $DPAH_2$, 499-83-2; $bpyO_2$, 7275-43-6; bpy, 366-18-7; $C_{10}H_{16}$, 281-23-2; $C_6H_{10}(O)$, 108-94-1; C_6H_{11}py, 15787-49-2; $PhC(O)CH_3$, 98-86-2; $PhCH(OH)CH_3$, 98-85-1; $HOPhCH_2CH_3$, 25429-37-2; PhCH(O), 100-52-7; $HOPhCH_3$, 1319-77-3; $C_6H_8(O)$, 25512-62-3; $C36H_9OH$, 25512-63-4; c-C_6H_{10} epoxide, 286-20-4; c-C_6H_{11}OOBu-*t*, 15619-54-2; c-$C_6H_{11}OH$, 108-93-0; $PhCH(OOBu\text{-}t)CH_3$, 28047-94-1; $PhCH_2OOBu\text{-}t$, 18774-10-2; PhSeSePh, 1666-13-3; *m*-ClPhC(O)OOH, 937-14-4; PhC(O)C(O)Ph, 134-81-6; $(c\text{-}C_6H_{11})_2$, 92-51-3; PhSe(c-C_6H_{11}), 22233-91-6; PhSe(py), 87803-47-2; $C_{10}H_{14}(O)$, 700-58-3; 1-$C_{10}H_{15}O$, 768-95-6; 1-$C_{10}H_{15}$-2-py, 29768-05-6; 1-$C_{10}H_{15}$-4-py, 60159-38-8; *cis*-PhCH=CHPh epoxide, 1689-71-0; $PhCH_2CH_2OH$, 60-12-8; $PhCH_2OH$, 100-51-6.

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The Surface Nature of Grignard Reagent Formation[1]

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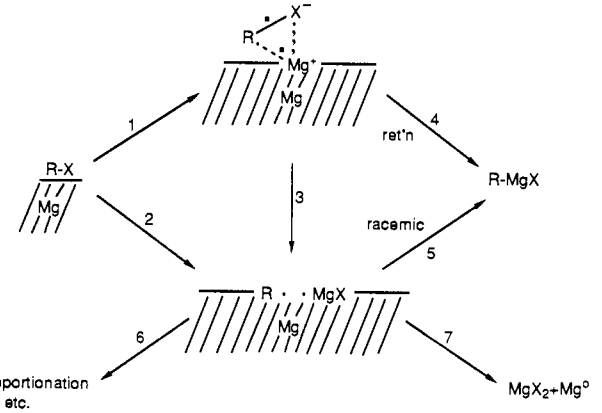
Contribution from the Dittmer Laboratories of Chemistry, Florida State University, Tallahassee, Florida 32306. *Received November 20, 1991*

Abstract: The reaction of *exo*-2-norbornyl bromide with Rieke magnesium in ether at −70 °C in the presence of *tert*-butyl alcohol-*O-d* gave exclusively *exo*-2-deuterionorbornane whereas the epimer *endo*-2-norbornyl bromide yielded a 1:1 mixture of *endo*- and *exo*-2-deuterionorbornane. Reaction of the epimeric bromides with Rieke magnesium in the presence of *tert*-butyl alcohol and a 10-fold equivalent excess of the radical trap deuterated dicyclohexylphosphine resulted in only 8% deuterium incorporation in the products. Treatment of *exo*-5-bromo-2-norbornene under identical conditions (*tert*-butyl alcohol-*O-d*, −70 °C) yielded a 65:35 mixture of *exo*-5-deuterio-2-norbornene and 3-deuterionortricyclene. In the presence of *tert*-butyl alcohol and a 10-fold excess of deuterated dicyclohexylphosphine the reaction of *exo*-5-norbornenyl bromide gave the same mixture of products but with only 8% deuterium incorporated. These results strongly support the surface nature of the Grignard formation reaction.

Introduction

In 1964, on the basis of experimental evidence involving stereochemical studies as well as analyses of products, we proposed our initial mechanism for Grignard reagent formation.[2c] This mechanism was elaborated[2e] upon in 1973 and is depicted in Scheme I. There is general agreement that the reaction is initiated by an electron transfer from the magnesium surface to the σ^* antibonding orbital of the carbon–halogen bond (outer sphere, pathway 1) to produce a tight radical anion–radical cation pair and that this is the rate-determining step of the reaction.[2-8] There is also agreement that free radicals are involved in this reaction, formed either directly by inner-sphere electron transfer from the

Scheme I. Proposed Mechanism for Grignard Reagent Formation



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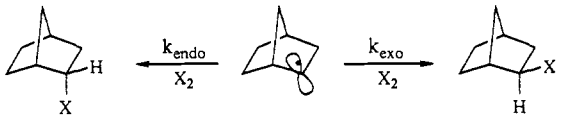
magnesium surface (pathway 2) or by collapse of the tight radical anion–radical cation (pathway 3) to yield a loose radical pair. It is at this juncture that there is disagreement. We have provided evidence that most of the radicals remain adsorbed on the magnesium surface to form Grignard reagent either by collapse of the tight radical anion–radical cation pair (pathway 4) or by combination of the radical with magnesium halide (pathway 5). The surface radicals can also undergo dimerization and disproportionation (pathway 6), and some can escape the surface and react in solution. The experimental evidence in support of this mechanism has recently been reviewed.[2lm] Recently a model, the "D-model", based on diffusion theory has been proposed[9] for Grignard reagent formation whose basic tenet is "that all radicals leave the surface and diffuse freely in solution at all times". Our mechanism and the D-model have recently been reviewed.[10] We now present our findings on the reaction of *exo*- and *endo*-2-norbornyl bromide as well as 5-*exo*-norbornenyl bromide with magnesium which provide further evidence in support of the *surface nature* of Grignard reagent formation.

The 2-norbornyl system was selected for investigation because the 2-norbornyl radical has been thoroughly investigated. The radical is a planar π-radical[11] which is attacked largely from the less hindered exo side. Therefore, whether one starts with the exo or endo precursor of the 2-norbornyl radical, a mixture of exo and endo products is obtained, with the exo product always predominating, $k_{exo} \gg k_{endo}$. Thus, conversion of substituted



2-norbornanecarboxylic acids to the corresponding 2-norbornyl bromides by the Hunsdiecker or related reactions gives the same product ratio (69% exo, 31% endo) independent of the stereochemistry of the starting material.[12] Oxidation of epimeric tri-2-norbornylboranes with oxygen leads to a mixture containing 76% *exo*- and 24% *endo*-2-norbornanol,[13] and the same product ratio is obtained in the autooxidation of 2-norbornylmagnesium halides.[14] Also, free radical chlorination or bromination of norbornane yields 70% exo product, and halogen abstraction by the 2-norbornyl radical from carbon tetrachloride affords 95% *exo*-2-chlorononorbornane.[15] In solution, reductions of epimeric 2-norbornylmercuric bromides with metal deuterides were found to give predominantly exo products (84–92%), again independent of the stereochemistry of the starting material.[16] However, it is significant and of interest to note that the reductions of epimeric 2-norbornylmercuric acetates[16b] and *exo*- and *endo*-(3-methoxy-2-norbornyl)mercuric chlorides[17] proceed with complete retention of configuration when the reductions are performed using sodium amalgam, *a surface reaction.*

The literature provides a clear picture of the behavior of the norbornyl free radical in solution. If this radical is produced in the reaction forming the Grignard reagent and if "all the radicals leave the surface and diffuse freely in solution at all times", then one should observe the same ratio of *endo*- to *exo*-norbornylmagnesium halide *regardless of which epimer* of 2-norbornyl bromide is used since this radical is a planar π-radical. However, as we shall see this is clearly not the case.

Results and Discussion

It has been demonstrated that the carbon–magnesium bonds in vinyl and cyclopropyl systems are configurationally stable at room temperature in aprotic solvents.[2] It has been shown that sp^3 hybridized secondary carbon–magnesium bonds undergo slow inversion on the NMR time scale[18] and, as expected, the 2-norbornylmagnesium bond behaves in a similar manner. The endo–exo equilibrium composition is obtained only after allowing a sample to remain at ambient temperature for 1 day.[19] There is agreement that the epimerization is slow but the reported endo:exo ratios at equilibrium vary from 54:46 for 2-norbornylmagnesium chloride[20] to 59:41 for 2-norbornylmagnesium bromide.[14,19] On the other hand, Hill[21] found the equilibrium mixture for 2-norbornylmagnesium chloride to be 50:50. In our hands we find a 47:53 endo:exo ratio at equilibrium starting from the exo bromide and a 48:52 endo:exo ratio starting from the endo bromide.

The reactions of the epimeric 2-norbornyl bromides were carried out in ether with Rieke magnesium[22] which is known to react with organic halides even at −70 °C. The presence of 4 equiv of *tert*-butyl alcohol-*O-d* in the reaction mixture assures rapid quenching of the organomagnesium species and also provides a marker in the products for analytical purposes.[2j] At the same time it reduces the possibility of epimerization of the Grignard reagents. The reference samples of *exo*- and *endo*-2-deuterionorbornane were prepared starting with the corresponding bromides which were treated with *tert*-butyl lithium at −70 °C followed by quenching with methanol-*O-d*. The ^2H NMR chemical shifts found were at δ = 1.1 ppm for exo and δ = 0.8 ppm for the endo isomer.

The reaction of *exo*-2-norbornyl bromide with Rieke magnesium at −70 °C in the presence of *tert*-butyl alcohol-*O-d* gave exclusively *exo*-2-deuterionorbornane, as evident from the ^2H NMR spectrum of the product (δ = 1.1 ppm). On the other hand, when *endo*-2-norbornyl bromide, the sterically hindered epimer, was reacted under the same conditions a mixture of products containing 50% exo and 50% endo derivative was formed. Thus, the less hindered exo epimer reacts almost exclusively via pathways 1 and 4 whereas the more hindered endo epimer can also proceed by pathways 1–3–5 or −6 and/or 2–5 or −6 in Scheme I. Even when both reactions were run at room temperature, the difference between them, although much smaller, was still detectable. Starting from the exo bromide, the product ratio was 88% exo and 12% endo, whereas from the endo bromide the composition was 79% exo and 21% endo. We have observed the same temperature effect pre-

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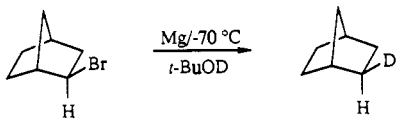
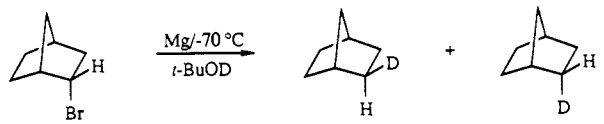
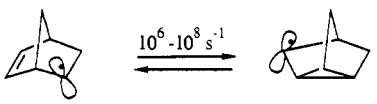




viously in the reaction of (*S*)-(+)-1-bromo-1-methyl-2,2-diphenylcyclopropane under the same conditions.[2j] At −65 °C, the hydrocarbon (*R*)-(−)-1-deuterio-1-methyl-2,2-diphenylcyclopropane was obtained with an optical purity of 43% whereas at +20 °C the same hydrocarbon was formed but with an optical purity of 18%.

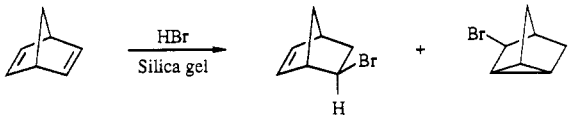
In order to determine experimentally whether the 2-norbornyl radicals did indeed leave the surface of the magnesium and "...diffuse freely in solution at all times", as proposed by the diffusion theory based D-model, we selected the radical trap dicyclohexylphosphine. This reagent has been shown to be a very effective radical trap[23] and has been used by Ashby[24] in the Grignard reaction for this purpose rather than using a nitroxyl radical as a trapping agent.[5e] The latter, a frequently used radical trapping agent, should not be used for Grignard reactions since they have been found to oxidize the Grignard reagents[25] and induce further radical reactions. Thus, the Grignard reactions of epimeric norbornyl bromides were conducted, at room temperature, in ether with Rieke magnesium in the presence of 10 equiv of deuterated dicyclohexylphosphine, which should trap the free radicals allegedly floating in solution, to give CD products. Also present in solution was 4 equiv of *tert*-butyl alcohol in order to quench the organomagnesium species to yield CH products. The reaction mixtures were analyzed by the GC–MS technique. Essentially no deuterium incorporation was found in the case of *exo*-2-norbornyl bromide and only 8% deuterium incorporation was found when the endo bromide was used. These results clearly indicate that even at room temperature the relatively high percentage of epimerization should be attributed to pathway 3 in Scheme I, where rotation of the radicals on the surface can occur. Diffusion of the radicals into the solution seems to be a minor process. At low temperatures, −70 °C, the results obtained for exo and endo bromides show a great deal of retention of configuration, indicating that pathway 4 is competing effectively with pathway 3. These observations unambigously indicate the surface nature of the Grignard reaction.

The Norbornenyl–Nortricyclenyl System. The rearrangement of the 5-norbornenyl radical to the 3-nortricyclenyl radical has been thoroughly studied and found to be a very useful radical clock.[26] The rate constant for this rearrangement has been



established using kinetic electron paramagnetic resonance (EPR) spectroscopy and found to be 6×10^2 s^{-1} at −130 °C and greater than 10^6–10^8 s^{-1} at 25 °C.[27,23a] At equilibrium, in solution, the mixture was found to consist mainly of the nortricyclenyl derivative. Davies et al.[28] showed that the cobaltous chloride catalyzed reaction of 5-bromo-2-norbornene and 3-bromonortricyclene with methylmagnesium bromide leads to an identical mixture of products consisting of 30% 2-norbornene and 70% nortricyclene. Free radical (SET) reactions of trimethyltin sodium with 5-norbornenyl and 3-nortricyclenyl halides gave almost the same equilibrium mixture of products[23a] as did the tri-*n*-butyltin hydride reduction of these same halogens.[29] On the other hand, sodium amalgam reductions of acetoxy-substituted 5-norbornenyl- and 3-nortricyclylmercuric halides proceed with complete retention of configuration at carbon,[16b] obviously excluding a free radical pathway and speaking for the *surface nature* of this reaction.

The Grignard reaction of *exo*-5-bromo-2-norbornene was carried out in ether with Rieke magnesium at −70 °C exactly following the conditions described above for norbornyl bromides. In order to establish ^{2}H NMR chemical shifts for the possible products *exo*-5-deuterionorbornene and 3-deuterionortricyclene, it was necessary to prepare reference samples of these compounds as well as their bromide precursors. A sample of 3-bromonortricyclene was prepared by phase-transfer-catalyzed addition of hydrobromic acid to norbornadiene, which gave mainly the rearranged nortricyclyl product isolated by preparative gas chromatography. Since it was impossible to separate the desired *exo*-5-bromo-2-norbornene from a small amount of its endo epimer, we had to devise another method for its synthesis. We found that low-temperature addition of hydrogen bromide to norbornadiene gives, in the presence of silica gel,[30] mainly the *exo*-5-norbornenyl bromide, some of a nortricyclyl product, and no endo isomer. The *exo*-5-norbornenyl bromide could now be isolated by using preparative gas chromatography.



The hydrolysis of the Grignard reagents prepared from either 3-bromonortricyclene or *endo*-5-bromo-2-norbornene produces nortricyclene and 5–10% of unsaturated hydrocarbon.[31] Freeman[32] has reported that heating the Grignard reagents formed from a 54:46 endo/exo mixture of 5-chloro-2-norbornene in di-*n*-butyl ether to 130 °C followed by hydrolysis yielded 92% nortricyclene and 7% 2-norbornene. The 3-chloronortricyclene, under the same conditions, gave 87% nortricyclene and 13% 2-norbornene. This represents the thermodynamic equilibrium mixture of the Grignard reagents.

Finally the Grignard reaction of *exo*-5-norbornenyl bromide was conducted under previously described conditions (−70 °C, *tert*-butyl alcohol-*O*-*d*). The product was analyzed by ^{2}H NMR and GC and found to be a 65:35 mixture of two compounds. The minor product showed a chemical shift δ = 1.0 ppm, identical with that of 3-deuterionortricyclene.[33] The major product (δ = 1.4 ppm) was identified as *exo*-5-deuterionorbornene by GC analysis (comparison with authentic samples).

The same reaction was repeated in the presence of a 10-fold excess of deuterated dicyclohexylphosphine and *tert*-butyl alcohol. The product mixture was then analyzed by the GC–MS technique. Again two products were found, norbornene (65%) and nortricyclene (35%). The deuterium incorporation in norbornene was barely detectable (~2%) whereas the nortricyclene contained 22%

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deuterium. This amounts to about 8% total deuterium incorporation. These results are understandable in light of the mechanism proposed in Scheme I. The norbornene is formed by pathways 1 and 4 and corresponds to the retention of configuration we observed in the chiral systems;[2] very little, if any, deuterium would be expected to be incorporated since we are dealing with a surface-bound radical anion–radical cation intermediate. The collapse of this intermediate to the loose radical pair (pathway 3) would permit the 5-norbornenyl radical to form 5-norbornenylmagnesium bromide and also to rearrange to 3-nortricyclenyl radical which can then form the corresponding Grignard reagent (pathway 5) at the surface. Some of the 3-nortricyclenyl and 5-norbornenyl radicals, whose ratio is not known, leave the surface and go into solution (pathway 6) where the 5-norbornenyl radical is largely converted to the 3-nortricyclenyl radical (10^6–10^8 s^{-1} at 25 °C), and the radicals can react with the deuterated dicyclohexylphosphine.

Conclusion

Our experimental results provide further confirmation of the view that Grignard reagent formation is largely a surface reaction and that the basic premise of the D-model "that all radicals leave the surface and diffuse freely in solution" is untenable.

Experimental Section

The solvents tetrahydrofuran and ether were dried by refluxing and distilling from sodium–potassium alloy. *tert*-Butyllithium was titrated before use. All experiments were conducted in a dry argon atmosphere.

IR spectra were taken on a Perkin-Elmer 257 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Varian 300-MHz instrument (75 MHz for ^{13}C nuclei). ^2H NMR and ^{31}P NMR spectra were taken with a Bruker 270-MHz instrument operating at 41 MHz for deuterium nuclei and at 109 MHz for phosphorus nuclei. ^2H NMR chemical shifts are reported relative to deuteriochloroform, whose chemical shift was assumed to be 7.24 ppm. Mass spectra and GC–MS analyses were performed using a Finnigan 4500 automated gas chromatograph/EI mass spectrometer equipped with a DB-5 fused silica capillary column (J&W Scientific). Deuterium incorporation was calculated from the data for the parent ions using standard procedures. Vapor pressure chromatography (VPC) analyses were performed with a Hewlett-Packard 5710 gas chromatograph with 20% SE-30 as a stationary phase. Preparative GC separations were performed with a Varian Aerograph Model 700 gas chromatograph with 15% SF-96 on chromosorb W as a stationary phase.

General Procedure for the Preparation of Rieke Magnesium. Rieke magnesium was prepared according to the original procedure of Rieke[22] using 10 mmol of magnesium bromide (prepared in situ from magnesium turnings and ethylene dibromide) and 19 mmol of potassium in 25 mL of THF. The black slurry of Rieke magnesium was allowed to cool, and the solvent was removed by filtration using a positive pressure of argon. It was then washed with ether and filtered, and 20 mL of fresh ether was added.

Preparation of *exo*-2-Deuterionorbornane. A solution of *exo*-2-norbornyl bromide[34] (0.9 g, 5 mmol) in ether (20 mL) was treated with a 1.5 M solution of *tert*-butyllithium in pentane (8 mL, 12 mmol) at −70 °C, and the reaction mixture was stirred at −70 °C for an additional 1 h, quenched with methanol-*O*-*d*, and washed with water. The organic layer was separated and dried over magnesium sulfate, and 5 mL of chloroform was added. The solvents were then removed by distillation using a spinning band. The residue was then analyzed by GC, and the product *exo*-2-deuterionorbornane was identified by GC–MS and ^2H NMR: MS (EI) *m*/*e* 97 (M^+); ^2H NMR δ = 1.1 ppm.

Preparation of *endo*-2-Deuterionorbornane. The procedure described above was followed but starting with *endo*-2-norbornyl bromide:[35] ^2H NMR δ = 0.8 ppm.

Grignard Reactions of *exo*- and *endo*-2-Norbornyl Halides with Rieke Magnesium at −70 °C. The slurry of Rieke magnesium (10 mmol) in ether (20 mL) was cooled to −70 °C, and the solution of 2-norbornyl bromide (5 mmol) and *tert*-butyl alcohol-*O*-*d* (20 mmol) in ether (2 mL) was added. The reaction mixture was stirred for 4 h at −70 °C, allowed to reach −40 °C within 0.5 h, and quenched with saturated ammonium chloride solution. The organic layer was separated and dried over magnesium sulfate. Chloroform (5 mL) was then added, and solvents were removed by distillation using a spinning band column. The distillation was stopped when the boiling point of chloroform was reached. The residual solution was then analyzed by GC, GC–MS, and ^2H NMR techniques. The product 2-deuterionorbornane was identified by GC comparison with authentic samples and the GC–MS technique.

When *exo*-2-norbornyl bromide was used as a starting material, only *exo*-2-deuterionorbornane could be detected by ^2H NMR (δ = 1.1 ppm). *endo*-2-Norbornyl bromide, on the other hand, gave 50% exo product (^2H NMR δ = 1.1) and 50% endo derivative (^2H NMR δ = 0.8 ppm): MS (EI) *m*/*e* 97 (M^+).

Grignard Reactions of *exo*- and *endo*-Norbornyl Halides with Rieke Magnesium at Room Temperature. A solution of norbornyl bromide (5 mmol) and *tert*-butyl alcohol-*O*-*d* (20 mmol) in ether (2 mL) was injected into the slurry of Rieke magnesium in ether at room temperature. The reaction mixture was stirred for 4 h at room temperature and worked up as described above. The product ratio was analyzed by the ^2H NMR technique.

When *exo*-norbornyl bromide was used as a starting material, the product consisted of 88% *exo*-2-deuterionorbornane (^2H NMR δ = 1.1 ppm) and 12% endo derivative (^2H NMR δ = 0.8 ppm).

When *endo*-norbornyl bromide was used as a starting material, the product composition was 79% *exo*- (^2H NMR δ = 1.1 ppm) and 21% *endo*- (^2H NMR δ = 0.8 ppm) 2-deuterionorbornane.

Equilibration Experiments. A solution of norbornyl bromide (5 mmol) in ether (2 mL) was added to the slurry of Rieke magnesium in ether, and the reaction mixture was stirred under reflux, quenched with *tert*-butyl alcohol-*O*-*d* (20 mmol), and worked up as usual. The product ratio was determined using the ^2H NMR technique.

Starting from *exo*-2-norbornyl bromide, the ratio was 65% exo, 35% endo after 0.5 h of reflux, 60% exo, 40% endo after 3 h of reflux, and 53% exo, 47% endo after 10 h of reflux. Starting from *endo*-2-norbornyl bromide, the ratio was 52% exo, 48% endo after 1 h of reflux as determined by ^2H NMR.

Dicyclohexylphosphine. The literature procedure[36] was followed to give the product: ^{31}P NMR δ = −21.21 ppm; ^1H NMR δ = 0.80–1.22 (m, 12 H), 1.56–1.74 (m, 10 H); ^{13}C NMR δ = 26.09 (s), 26.87 (d, *J* = 9.1 Hz), 29.49 (d, *J* = 7.9 Hz), 32.46 (d, *J* = 11.4 Hz); IR (film) 2260 cm^{-1} (P–H).

Preparation of Deuterated Dicyclohexylphosphine. A solution of dicyclohexylphosphine (9.9 g, 50 mmol) in ether (100 mL) was treated with a 2.5 M solution of *n*-butyllithium in hexane (40 mL, 100 mmol) at −70 °C. The reaction mixture was allowed to warm to 10 °C, and within 1 h a yellow precipitate was formed. The mixture was cooled to −70 °C, quenched with methanol-*O*-*d*, and filtered through a short pad of Celite under an argon atmosphere and the solvent stripped in vacuo. The residue was distilled in Kugelrohr (80 °C at 0.3 Torr) to give 8.0 g (80% yield) of deuterated dicyclohexylphosphine: ^{31}P NMR δ = −27.28 ppm; ^1H NMR δ = 0.82–1.22 (m, 12 H), 1.56–1.74 (m, 10 H); ^{13}C NMR δ = 25.99 (s), 26.76 (d, *J* = 9.1 Hz), 29.37 (d, *J* = 7.9 Hz), 32.45 (m); IR (film) 1657 cm^{-1} (P–D).

Grignard Reaction in the Presence of Deuterated Dicyclohexylphosphine. A mixture of 2-norbornyl bromide (5 mmol), deuterated dicyclohexylphosphine (50 mmol, 10-fold excess), and *tert*-butyl alcohol (20 mmol) was added to the slurry of Rieke magnesium in ether at room temperature. The reaction mixture was stirred for 4 h at room temperature and worked up as usual. The deuterium incorporation into the product was determined using the GC–MS technique.

In the case of *exo*-2-norbornyl bromide the deuterium incorporation was not detectable, whereas in the case of *endo*-2-norbornyl bromide the deuterium incorporation was 8%.

Preparation of 3-Nortricyclyl Bromide.[31,37] Concentrated hydrobromic acid (50 mL) was added to a solution of norbornadiene (21.6 mL, 200 mmol) in methylene chloride (100 mL) containing tetrabutylammonium bromide (50 mg). The resulting two-phase mixture was vigorously stirred at room temperature for 3 h and then diluted with water. The organic layer was separated, washed with saturated sodium bicarbonate solution and water, and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was distilled to give 19.3 g (53%) of the product, bp 68–70 °C (20 Torr). The product was analyzed by GC and ^1H NMR and found to consist of 69% 3-nortricyclyl bromide, 27% *exo*-5-norbornenyl bromide, and 4% *endo*-5-norbornenyl bromide. A sample of the nortricyclyl bromide was isolated by using preparative gas chromatography (75 °C) to give the following data: ^1H NMR δ = 1.18–1.22 (m, 1 H), 1.24–1.45 (m, 5 H), 1.98 (d, *J* = 11.3 Hz, 1 H), 2.08 (s, 1 H), 3.90 (s, 1 H). The two epimeric norbornenyl bromides were not separable by using this technique.

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Preparation of *exo*-5-Norbornenyl Bromide.[38] Dry hydrogen bromide was passed at −70 °C through a solution of norbornadiene (21.6 mL, 200 mmol) in methylene chloride containing 5 g of silica gel. The saturated solution was washed with water, saturated sodium bicarbonate solution, and water. The organic layer was dried over magnesium sulfate and the solvent evaporated under reduced pressure. The residue was distilled in vacuo to give the product, 16.9 g, (49% yield), bp 68–70 °C (20 Torr). The product composition was determined by GC and ^{1}H NMR and was found to be 75% *exo*-5-norbornenyl bromide and 25% 3-nortricyclyl bromide. *endo*-5-Norbornenyl bromide was not detectable. The desired *exo*-5-norbornenyl bromide was isolated by using preparative gas chromatography (75 °C): ^{1}H NMR δ = 1.59–1.64 (m, 1 H), 1.81–2.01 (m, 3 H), 2.88 (s, 1 H), 3.08 (s, 1 H), 3.73–3.78 (m, 1 H), 5.96 (dd, J = 3.3 Hz, J = 5.1 Hz, 1 H), 6.17 (dd, J = 3.3 Hz, J = 5.1 Hz, 1 H).

Preparation of Deuterated Nortricyclene. 5-Nortricyclyl bromide (173 mg, 1 mmol) was dissolved in ether, cooled to −70 °C and treated with a 1.5 M solution of *tert*-butyllithium in pentane (2.5 mmol, 1.7 mL). The reaction mixture was stirred for 1 h at −70 °C and quenched with methanol-*O*-*d*, washed with water, and dried over anhydrous magnesium sulfate and chloroform (5 mL) added. The solvents were removed by distillation through a spinning band column until the boiling point of chloroform was reached. The residual solution was analyzed by GC–MS and ^{2}H NMR: MS (EI) m/e 95 (M^+); ^{2}H NMR δ = 1.0 ppm.

Grignard Reaction of *exo*-5-Norbornenyl Bromide with Rieke Magnesium. A mixture of *exo*-5-norbornenyl bromide (350 mg, 2 mmol) and *tert*-butyl alcohol-*O*-*d* (8 mmol) was added to the slurry of Rieke magnesium in ether at −70 °C, and the reaction mixture was stirred at this temperature for 4 h. The mixture was allowed to warm to −40 °C within 0.5 h, and the excess Rieke magnesium was destroyed with saturated ammonium chloride solution. The reaction mixture was then washed with water and dried and chloroform (5 mL) added. The solvents were removed by distillation through a spinning band column until the boiling point of chloroform was reached. The products were identified by GC comparison with authentic samples, and the product ratio was determined by GC and ^{2}H NMR: ^{2}H NMR δ = 1.4 ppm (*exo*-5-deuterionorbornene, 65%), δ = 1.0 ppm (deuterionortricyclene, 35%).

Grignard Reaction of *exo*-5-Norbornenyl Bromide with Rieke Magnesium in the Presence of Deuterated Dicyclohexylphosphine. The Grignard reaction was carried out under the conditions described above using 2 mmol of *exo*-5-norbornenyl bromide, 8 mmol of *tert*-butyl alcohol, and 20 mmol of deuterated dicyclohexylphosphine. After the usual workup the sample was analyzed by GC–MS. Two products were found: 65% norbornene (2% deuterium incorporation) and 35% nortricyclene (22% deuterium incorporation).

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Photoisomerization of Polyenes. 30.† Quantum Chain Processes in Photoisomerization of the All-Trans, 7-Cis, and 11-Cis Isomers of Retinal

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Abstract: Quantum chain processes in the photoisomerization of retinal isomers (all-trans, 7-cis, and 11-cis) are reflected in the dependence of quantum yield of isomerization on concentration of retinal (to values exceeding unity), the presence of one-photon multiple-bond isomerization, and changes of product distribution on retinal concentration. The processes are believed to take place exclusively from the triplet states. Reaction schemes involving participation of 12-(*S*)-cis conformers in the quantum chain processes have been advanced to account for all of the results.

Introduction

The concept of propagation of light quanta (quantum chain process) in an isomerization process, first postulated in 1969,[1] was firmly established in dienes by Saltiel and co-workers,[2] followed by cases of trienes.[3] The involvement of the quantum chain process was characterized by increasing quantum yield of isomerization at higher substrate concentrations (to greater than unity) and by the presence of one-photon two-bond isomerization. Since then, similar phenomena have been demonstrated in hindered styryl derivatives[4] and in diphenylbutadiene.[5]

Photoisomerization of retinal has been investigated in great detail by many workers. Those studies preceding 1988 are covered in an extensive review by Becker.[6] More recently, Jensen et al.[7] reexamined the triplet-state reaction in detail, emphasizing the relation between rates of triplet sensitization (energy transfer) with quantum yields of isomerization and photostationary-state compositions. They further clarified some of the ambiguities from conflicting reported data. No attempts were made to examine the effects of retinal concentration although some of their quantum yield data, particularly those from the hindered 11-cis isomer, nearly exceeded unity. The latter situation would have suggested possible involvement of quantum chain processes in retinal isomerization, a possibility that was then demonstrated in the hindered

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