a pinch of $NaHSO_3$. The contents were shaken, and the oil layer was removed. The oil was dissolved in ether, clarified over Norit, and filtered, and the ether was removed at reduced pressure to give 15.4 g (0.0586 mol, 92% yield) of a clear oil. The oil was used without further purification to prepare *erythro*-1-chloro-2-iodo-1-phenylpropane: NMR δ 1.72 (d, J = 7 Hz, 3 H), 4.45 (dq, J = 4.0, 7.0 Hz, 1 H), 4.86 (d, J = 4.40 Hz, 1 H), 7.29 (s, 5 H); irradiation of the δ 1.72 doublet collapsed the δ 4.45 (dq) into a doublet (J = 4.0 Hz).

***threo*-1-Chloro-2-iodo-1-phenylpropane** was prepared in 78% yield by the same method as the erythro isomer but by using *threo*-2-iodo-1-phenyl-1-propanol: bp 92 °C (0.3 mmHg); NMR δ 1.87 (d, J = 7.0 Hz, 3 H), 4.56 (dq, J = 6.0, 7.0 Hz, 1 H), 4.96 (d, J = 6.0 Hz, 1 H), 7.33 (s, 5 H); irradiation of the δ 1.87 doublet collapsed the δ 4.56 multiplet into a doublet (J = 6.0 Hz). Anal. Calcd for $C_9H_{10}ICl$: C, 38.53; H, 3.59. Found: C, 38.46; H, 3.75.

***threo*-2-Iodo-1-phenyl-1-propanol** was prepared in 78% yield by the same method as the erythro isomer but by using (Z)-1-phenylpropene as the starting alkene. Recrystallization from pentane gave a white solid: mp 37–38 °C; NMR δ 1.78 (d, J = 6.5 Hz, 3 H), 4.37 (m, 2 H), 7.31 (s, 5 H); irradiation of the δ 1.78 doublet formed a singlet at δ 4.37 indicating that the two methine protons have equivalent chemical shifts. Anal. Calcd for $C_9H_{11}IO$: C, 41.26; H, 4.20. Found: C, 41.01; H, 4.32.

***erythro*-2-Chloro-3-iodobutane** was prepared by adding a solution of 2.54 g (15.6 mmol) of ICl in 10 mL of CH_2Cl_2 dropwise to a vigorously stirred solution of 1.14 g (16.5 mmol) of (E)-2-butene in 25 mL of CH_2Cl_2. The reaction was carried out at room temperature, and the reaction vessel was shielded from light by covering it with aluminum foil. After several minutes of stirring, the reaction mixture was transferred to a separatory funnel and washed with 5% aqueous $NaHSO_3$ solution, water, and saturated NaCl solution. The CH_2Cl_2 layer was dried over anhydrous Na_2CO_3 and filtered, and CH_2Cl_2 was removed at reduced pressure. Distillation gave the product: 2.20 g (10.1 mmol, 65% yield); bp 35–37 °C (5 mmHg) [lit.[15] bp 34.8–35.3 °C (5 mmHg)]; NMR δ 1.66 (d, J = 6.5 Hz, 3 H), 1.98 (d, J = 6.5 Hz, 3 H), 4.03 (qu, J = 6.54 Hz, 1 H), 4.23 (qu, J = 6.5 Hz, 1 H).

***threo*-2-Chloro-3-iodobutane** was prepared in 73% yield by the same method as the erythro isomer but by using (Z)-2-butene as the starting alkene: bp 35–37 °C (5 mmHg) [lit.[15] bp 33.2–33.5 °C (4 mmHg)]; NMR δ 1.59 (d, J = 6.5 Hz, 3 H), 1.89 (d, J = 6.5 Hz, 3 H), 4.04 (dq, J = 3.0, 6.5 Hz, 1 H), 4.43 (dq, J = 3.0, 6.5 Hz, 1 H).

2-Chloro-3-iodo-2,3-dimethylbutane was prepared by the same method as *erythro*-2-chloro-3-iodobutane but by using 2,3-dimethyl-2-butene as the starting alkene: bp 66–65 °C dec; NMR δ 2.13 (s, 6 H), 1.89 (s, 6 H). Anal. Calcd for $C_6H_{12}ICl$: C, 29.24; H, 4.86. Found: C, 29.35; H, 4.95.

Product Analysis of Exchange Reaction. The following general procedure was used in all cases. A solution of ICl in CCl_4 (0.070–021 M) was added to a solution of the organic vicinyl iodochloride also in CCl_4 (0.042–0.059 M). The reaction mixture was protected from light and placed in a thermostated bath at 25 °C for 20 h. The reaction mixture was then washed with a 5% aqueous $NaHSO_3$ solution, water, and a saturated NaCl solution. The CCl_4 layer was dried over anhydrous Na_2CO_3 and filtered, and CCl_4 was removed at reduced pressure. The products of the reaction of ICl and the 2-chloro-3-iodobutanes were analyzed by GLC on a 2 m × 6 mm 30% Carbowax 20M on Chromosorb P (60/80 mesh) column. The retention times at a flow rate of 96 mL/min and 56 °C are as follows: *meso*-2,3-dichlorobutane, 4.5 min; *dl*-2,3-dichlorobutane, 5.0 min. The products of the reaction of ICl and the 1-chloro-2-iodo-1-phenylpropanes were analyzed by NMR. The methyl protons of the threo isomer of 1,2-dichloro-1-phenylpropane are upfield relative to those of the erythro isomer.[6]

Kinetics of the Exchange Reaction of ICl and 2-Chloro-3-iodo-2,3-dimethylbutane. Separate solutions of ICl in CCl_4 and 2-chloro-3-iodo-2,3-dimethylbutane in CCl_4 were equilibrated at 25 °C in a thermostated bath. Equal volumes of the two preequilibrated solutions were rapidly mixed, and a sample was transferred immediately to a 1.0-cm quartz UV cell placed in the thermostated cell compartment of the spectrometer. The reactions were followed to about 25% completion. The above procedure was then repeated in order to obtain absorbance–time curves at the two wavelengths, 462 and 518 nm, for each set of solutions. Values of absorbances of the solution at zero reaction time were obtained by extrapolation of the absorbance–time curves to zero time. The values of $(\mathrm{ICl})_t$ were calculated according to eq 4. Published values[16] were used for $\epsilon_{\mathrm{I}_2}{}^{518}$ and $\epsilon_{\mathrm{I}_2}{}^{462}$.

$$(\mathrm{ICl})_t = (\mathrm{ICl})_0[\mathrm{Abs}_t{}^{518}\cdot\epsilon_{\mathrm{I}_2}{}^{462} - \mathrm{Abs}_t{}^{462}\cdot\epsilon_{\mathrm{I}_2}{}^{518}]/[\mathrm{Abs}_0{}^{518}\cdot\epsilon_{\mathrm{I}_2}{}^{462} - \mathrm{Abs}_0{}^{462}\cdot\epsilon_{\mathrm{I}_2}{}^{518}] \tag{4}$$

Acknowledgment. Continued financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. ICl, 7790-99-0; *erythro*-$CH_3CHICHClCH_3$, 39160-00-4; *threo*-$CH_3CHICHClCH_3$, 39159-99-4; *erythro*-$C_6H_5CHClCHICH_3$, 87261-44-7; *threo*-$C_6H_5CHClCHICH_3$, 87261-45-8; 2-chloro-3-iodo-2,3-dimethylbutane, 87261-43-6; *erythro*-2-iodo-1-phenyl-1-propanol, 87261-46-9; *threo*-2-iodo-1-phenyl-1-propanol, 87261-47-0.

---

[15] Lucas, H. J.; Garner, H. K. *J. Am. Chem. Soc.* **1950**, *72*, 2145.

[16] de Main, P. A. D. *J. Chem. Phys.* **1957**, *26*, 1192.

Configurational Stability of a Cyclopropyl Grignard Reagent Containing a Metalated 2-Hydroxymethyl Group[1]

Herman G. Richey, Jr.,* and L. Meredith Moses

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

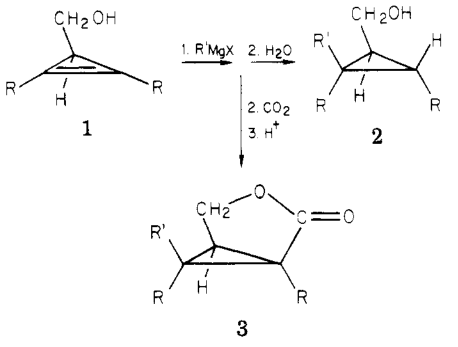
Received July 7, 1982

Mixtures of *cis*- and *trans*-2-bromo-3-(hydroxymethyl)-1,1-dimethylcyclopropane were treated with methylmagnesium bromide to metalate the hydroxyl groups and then with magnesium to form metalated Grignard reagents. The compositions of products obtained upon hydrolysis with D_2O indicated that the metalated Grignard reagents in refluxing diethyl ether did not undergo signficant cis–trans isomerization. This work provides an example of the configurational stability of a cyclopropyl Grignard reagent with a secondary rather than a tertiary α-carbon. Because of these results with cyclopropyl Grignard reagents containing a metalated hydroxyl group, prior observations on additions of allylic Grignard reagents to 3-(hydroxymethyl)cyclopropenes only of products resulting from a cis relationship of magnesium and hydroxymethyl must be due to the stereochemistry of the addition process rather than to a subsequent isomerization.

In an earlier study, we investigated reactions of allylic Grignard reagents (in excess) with 3-(hydroxymethyl)cyclopropenes (1).[2] That study was part of a program to determine the stereochemical relationships between the

0022-3263/83/1948-4013$01.50/0

involved groups in reactions of alkenes in which an internal (metalated) hydroxyl group assists addition by polar, main-group organometallic compounds.[3] Products obtained by hydrolysis (**2**) or carbonation (**3**) had a cis relationship of the organic group (R′) from the organomagnesium compound and the hydroxymethyl group (eq 1). These results suggest a mechanistic preference for

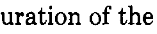


(1)

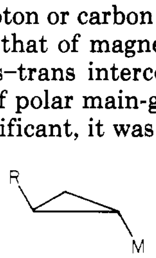
R = Me or Et; R′ = allyl or substituted allyl

attachment of R′ to the face of the double bond that is nearer to the hydroxyl group, a conclusion also reached from a study of additions to hydroxybicyclo[2.2.1]hept-2-enes.[4]

The configuration of the proton or carbon dioxide that replaces magnesium must be that of magnesium at the time of quenching. Since cis–trans interconversion of cyclopropyl organometallics of polar main-group metals (**4** ⇌ **5**)[5] is not ordinarily significant, it was tempting to



4



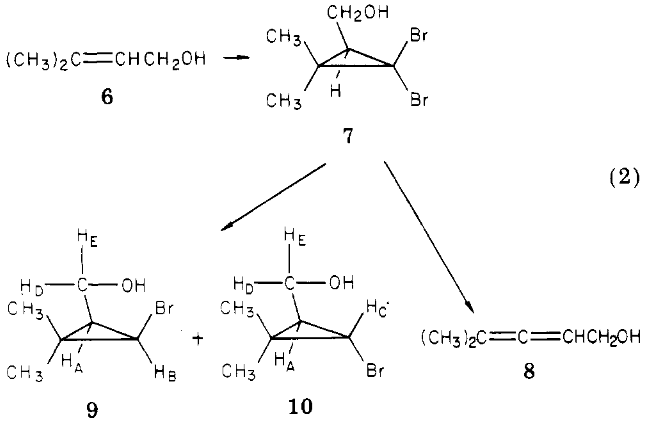
5

assume that the hydroxymethyl group and magnesium also were cis immediately following addition. Indeed, it was because of the unusual configurational stability of cyclopropyl organometallics that (hydroxymethyl)cyclopropenes were chosen as substrates. However, configurational stability of cyclopropyl Grignard reagents has been demonstrated only for the 1-methyl-2,2-diphenylcyclopropyl system.[6,7] The Grignard reagents that are formed by addition to **1** differ from this system in having a metalated hydroxymethyl group, and it seemed conceivable that this function might facilitate isomerization. Therefore, we decided to prepare a cyclopropyl Grignard reagent containing a metalated, *trans*-2-hydroxymethyl group and to determine if it would isomerize readily to the corresponding cis isomer.

Results and Discussion

We wanted to prepare a halide whose Grignard reagent would closely resemble those resulting from addition to the compounds having structure **1**. We chose to prepare **10** or an even closer analogue, the homologue of **10**, that has a methyl group in place of H_C.

Addition of dibromocarbene to **6** by using a procedure that has worked successfully with other allylic alcohols produced **7**.[8] We hoped then to use an excess of an organolithium compound to replace one bromine of **7** by lithium. The resulting organolithium compound could either be hydrolyzed to a mixture or **9** and **10** or treated with methyl iodide to produce the corresponding methyl homologues. Such metalations followed by hydrolysis[9,10] or by methylation[11] have been successful with a variety of *gem*-dibromocyclopropanes. However, there is a report that reactions of *gem*-dibromocyclopropylmethanols and methyllithium give allenic alcohols.[12] Even though we used conditions sufficiently mild that significant amounts of **7** were recovered, large amounts of allene **8** were found after treating **7** with methyllithium or butyllithium followed by protonation. No significant NMR absorptions corresponding to those subsequently assigned to **9** and **10** were observed.



(2)

Lithium aluminum hydride[13] and sodium bis(2-methoxyethoxy)aluminum hydride[14] have been used to reduce *gem*-dibromocyclopropanes to monobromocyclopropanes. However, when we used lithium aluminum hydride to reduce **7**, employing conditions under which some **7** was recovered, significant amounts of **8** formed. The product mixture exhibited NMR absorptions corresponding to those subsequently assigned to **9** and **10**; these compounds were present in approximately equal amounts, but in low yield.

Tributyltin hydride has been used to reduce *gem*-dibromocyclopropanes to monobromocyclopropanes.[10,15,16] The ^{1}H NMR spectrum of the product mixture obtained in 75% yield from a reaction of **7** and tributyltin hydride indicated it to be a mixture of 74% **9** and 26% **10** (these figures are probably accurate to ±2%). The amounts of **9** and **10** were assigned on the basis of the relative areas of the absorptions due to H_B of **9** and H_C of **10**. The

---

(1) This work is taken from: Moses, L. M. M.S. Dissertation, The Pennsylvania State University, University Park, PA, 1981.

(2) Richey, H. G., Jr.; Bension, R. M. *J. Org. Chem.* **1980**, *45*, 5036.

(3) For pertinent references, see ref 4 and: Richey, H. G., Jr.; Wilkins, C. W., Jr.; Bension, R. M. *J. Org. Chem.* **1980**, *45*, 5042.

(4) Richey, H. G., Jr.; Wilkins, C. W. Jr. *J. Org. Chem.* **1980**, *45*, 5027.

(5) Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965; Chapter 3.

(6) Walborsky, H. M.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3288. Walborsky, H. M.; Aronoff, M. S. *J. Organomet. Chem.* **1973**, *51*, 31.

(7) Reference 5 describes some unpublished experiments of J. D. Roberts and co-workers that show that cyclopropyl Grignard reagents in diethyl ether are configurationally stable on the NMR time scale at 175 °C.

(8) Kleveland, K.; Skattebøl, L.; Sydnes, L. K. *Acta Chem. Scand., Ser. B* **1977**, *B31*, 463.

(9) See the following and references cited therein: Barlet, R. *Tetrahedron Lett.* **1976**, 4171.

(10) Maskill, H. *J. Chem. Soc., Perkin Trans. 2* **1975**, 197.

(11) Kitatani, K.; Hiyama, T.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3288.

(12) Bertrand, M.; Maurin, R. *Bull. Soc. Chim. Fr.* **1967**, 2779.

(13) Jefford, C. W.; Kirkpatrick, D.; Delay, F. *J. Am. Chem. Soc.* **1972**, *94*, 8905. Hatem, J.; Waegell, B. *Tetrahedron Lett.* **1973**, 2023. Chapleo, C. B.; Dreiding, A. S.; Dyllick-Brenzinger, R. A.; Oth, J. F. M. *Helv. Chim. Acta* **1976**, *59*, 1311.

(14) Sydnes, L.; Skattebøl, L. *Tetrahedron Lett.* **1974**, 3703.

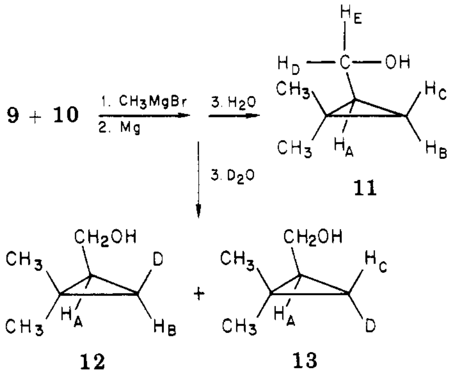
(15) Seyferth, D.; Yamazaki, H.; Alleston, D. L. *J. Org. Chem.* **1963**, *28*, 703.

(16) Sydnes, L. K. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 47.

doublet at δ 2.97, J = 7.6 Hz, was assumed to be due to H_B and the doublet at δ 2.69, J = 4.0 Hz, to H_C. These coupling constants and chemical shifts are in good agreement with those expected for H_B and H_C.[17] The predominant formation of the product with bromine and hydroxymethyl cis is in contrast to the predominant formation of trans isomers observed upon reduction of three other hydroxymethyl-substituted *gem*-dibromocyclopropanes.[16,18] However, because of the pattern of methyl substitution, each of these other dibromocyclopropanes has less steric hindrance at the face syn to the hydroxymethyl group relative to that anti than is present in **7**.

Zinc in acetic acid has also used to reduce *gem*-dibromocyclopropanes to monobromocyclopropanes.[10,18,19] Such a reduction of **7** gave a 45% yield of a mixture containing approximately 85–90% **9** and 10–15% **10**. A preponderance of the isomer with bromine and the hydroxymethyl groups cis has also been observed in reduction of a closely related substrate.[19]

A diethyl ether solution of a 74:26 mixture of **9** and **10** was treated first with methylmagnesium bromide to metalate the hydroxyl group and then with 1 equiv of magnesium to convert the mixture to the corresponding metalated Grignard reagents (eq 3). There are prior examples of converting halides containing hydroxyl groups to metalated Grignard reagents.[20] After about 3 h at ambient temperature, most of the magnesium had disappeared, an indication of substantial Grignard reagent formation. A portion of the solution was hydrolyzed with D_2O to produce a mixture of **12** and **13**. The remainder was heated at reflux for 16 h; then one-half was hydrolyzed with D_2O to produce a mixture of **12** and **13** and one-half with H_2O to produce **11**.



(3)

Analysis of the products was greatly facilitated by use of 360-MHz ^1H NMR spectroscopy. The absorptions due to H_B and H_C of **11** could be assigned unambiguously since their chemical shifts and coupling with H_A were in excellent agreement with those expected.[17] The absorption of H_B was a doublet of doublets at δ 0.48 with J_{AB} = 8.5 Hz, and that of H_C a doublet of doublets at δ 0.13 with $J_{AC} \simeq 4.9$ Hz (J_{AC} and J_{BC} are similar in magnitude and only an average value was obtained).

The two samples resulting from hydrolysis with D_2O exhibited virtually identical ^1H NMR spectra. In these spectra, the absorption of H_B was a doublet, J_{AB} = 8.3 Hz, and that of H_C a doublet, J_{AC} = 5.2 Hz. Small amounts of the more complex absorptions due to H_B and H_C of **11** could also be detected, but (see Experimental Section) **11** was only about 6% of the **11**–**13** mixtures. From the relative areas of absorptions due to H_B and H_C (corrected for the small contributions of the absorptions of these hydrogens of **11**), the relative amounts of **12** and **13** are 77:23 in the sample obtained immediately after Grignard reagent formation and 73:27 in the sample obtained after the Grignard reagent solution had been heated at reflux. Within the experimental error (about ±2 area units), there was no significant change in composition. We assume that deuterium replaces Mg with retention of configuration,[5,21] so these compositions correspond to those of the Grignard reagents.

Another experiment used a mixture of 85–90% **9** and 10–15% **10**. After about 4 h, most of the magnesium had disappeared and one-half of the reaction mixture was hydrolyzed by addition of D_2O. The remainder of the solution was stirred for 16 h and then hydrolyzed with D_2O. The two resulting **11**–**13** mixtures exhibited virtually identical ^1H NMR spectra. Determination of the relative amounts of the components was less accurate than for the experiment described above because more **11** was present and because 200- rather than 360-MHz spectroscopy was used for the analysis. However, it was evident that the relative amounts of **12** and **13**, about 85:15, did not change significantly with time and that the amount of **12** was relatively somewhat higher than in the experiment described above.

It would have been more elegant to have used pure **10** rather than mixtures of **9** and **10** for Grignard reagent formation. We expected, however, that a cis–trans mixture of Grignard reagents also would result from **10**, since it is known that during Grignard reagent formation some epimerization can occur at the α-carbon, presumably due to the intermediacy of radical intermediates.[6] In there careful studies of Grignard reagent formation from chiral 1-halo-1-methyl-2,2-diphenylcyclopropanes, the only examples involving cyclopropyl systems, Walborsky and his co-workers observed extensive racemization—more than 80% in the case of the bromide.[6] The portion of nondeuterated product **11** that we observed when the Grignard reagent was hydrolyzed with D_2O may have arisen, at least in part, from attack on the solvent by intermediates in the formation of the Grignard reagent. Such products were observed in Walborsky's studies.[6] The ratios of cis and trans Grignard reagents that we infer from the relative amounts of **12** and **13** obtained on hydrolysis are similar to the compositions of the halide mixtures (**9** and **10**) used for their preparation. This suggests that the tendency for isomerization during Grignard reagent preparation is less in this system than in Walborsky's system. Limitations in the accuracy of our NMR analyses of cis–trans isomer composition, however, may mask a significant tendency for isomerization if quenching of the radical intermediates happens, coincidentally, to favor formation of cis–trans compositions of Grignard reagents similar to the compositions of the halide mixtures (mainly cis) that we started with.

We conclude that after Grignard reagent formation, cis–trans isomerization does not occur significantly under the conditions—heating at reflux temperature in diethyl ether—used in this study. For two reasons, it is unlikely that the particular compositions that we observed resulted from rapid isomerization of the Grignard reagents to form

---

(17) Wiberg, K. B.; Barth, D. E.; Schertler, P. H. *J. Org. Chem.* **1973**, *38*, 378.

(18) Hofmann, K.; Orochena, S. F.; Sax, S. M.; Jeffrey, G. A. *J. Am. Chem. Soc.* **1959**, *81*, 992.

(19) Santelli, C. *Tetrahedron Lett.* **1979**, 1165.

(20) Umio, S.; Ueda, I.; Kanaya, T. Japanese Patent 76 39 214, 1976; *Chem. Abstr.* **1976**, *86*, 189475. Gahiez, G.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1978**, 3013. Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 5229.

(21) Nesmeyanova, O. A.; Rudashevskaya, T. Y.; Kazanskii, B. A. *Dokl. Chem.* (*Engl. Transl.*) **1972**, *207*, 999; *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1972**, *207*, 1362.

equilibrium mixtures. First, somewhat different product ratios were observed in the experiments starting with **9**–**10** mixtures having somewhat different compositions. Second, the observation of cis–trans mixtures in this study constrasts to the isolation from Grignard reagent additions to compounds of structure **1** only of products (**2** and **3**) derived from one of the two possible isomeric Grignard reagents.

This work provides a second example, and one with a secondary rather than a tertiary α-carbon, of configurational stability of a cyclopropyl Grignard reagent. It demonstrates, moreover, that a metalated hydroxymethyl group does not lead to rapid cis–trans isomerization of cyclopropyl Grignard reagents. Except that they have an alkyl group rather than a hydrogen at the α-carbon, the isomeric Grignard reagents that could be intermediates in additions to **1** should closely resemble those formed from **9** and **10**. Since the ease of epimerization at an α-carbon of a Grignard reagent decreases with increasing alkyl substitution,[22] isomerization should be, if anything, more difficult in the Grignard reagents formed by addition to **1** than in those prepared from **9** and **10**. Moreover, the additions to **1** were at ambient temperature while, in this work, no isomerization was noted even at reflux temperature. Therefore, we conclude that in additions to **1**, isomerization of the Grignard reagent subsequent to its formation was unlikely; the configurations of the products obtained on quenching represent the stereochemistry resulting from addition rather than from a subsequent isomerization. In additions to alkenols, not only the organic group of an allylic Grignard reagent but also the magnesium becomes attached preferentially to the side of the double bond nearer the hydroxyl group.

Experimental Section

Some ^{1}H NMR spectra were taken at 60 MHz, and Me_4Si was used as an internal standard. The 200-MHz spectra were taken with a Bruker WP200 spectrometer and the 360-MHz spectra with a Bruker WM360 spectrometer; $CHCl_3$ was used as an internal standard and $CDCl_3$ as an internal lock. Absorptions are reported with the following notations: s, singlet; d, doublet; t, triplet; m, a more complex multiplet; c, complex overlapping absorptions. Mass spectra were obtained with a Kratos MS 9-15 mass spectrometer. Analytical and preparative GC separations were performed with a thermal conductivity instrument using helium as the carrier gas and the following column: 5% SE-30 on Gas Chrom Q (80–100 mesh), 0.25 in × 5 ft (aluminum tubing). Small samples were collected for spectral analysis by using glass U-shaped tubes cooled in liquid nitrogen and inserted into the exit port of the chromatograph.

Preparation of 3-Methyl-2-buten-1-ol (6).[23] A solution of 3-methyl-2-butenoic acid (20.0 g, 200 mmol) in diethyl ether (100 mL) was added over 1.5 h to a stirred and cooled (ice bath) suspension of lithium aluminum hydride (9.48 g, 250 mmol) in diethyl ether (150 mL). The still-cooled reaction mixture was hydrolyzed by successive additions of water (10 mL), an aqueous sodium hydroxide solution (15%, 10 mL), and water (30 mL). The resulting mixture was filtered, the precipitate washed with diethyl ether, and the filtrate dried (Na_2SO_4). Most of the solvent was removed from the filtrate at reduced pressure and the residue was distilled to give **6** (10.42 g, 121 mmol, 60%): bp 67 °C (40 torr) [lit.[24] bp 54–55 °C (25 torr)].

Preparation of 1,1-Dibromo-2,2-dimethyl-3-(hydroxymethyl)cyclopropane (7). Triethylbenzylammonium chloride (0.233 g, 1.02 mmol) that had been dried under vacuum and stored over calcium chloride was added to a stirred solution of **6** (10.0 g, 116 mmol) in bromoform (58.8 g, 233 mmol). Then a solution of sodium hydroxide (14.0 g, 350 mmol) in water (14 mL) was added rapidly. Since heat was evolved, the flask was immersed in a water bath for a few minutes to return the contents to ambient temperature. Then the mixture was stirred vigorously for 24 h. Water (50 mL) was added, the layers were separated, the aqueous layer was extracted with three 50-mL portions of dichloromethane, and the combined organic layers were dried ($MgSO_4$). Most of the solvent was removed at reduced pressure, and the residue was distilled to give **7** (10.69 g 41.4 mmol, 36%): bp 65–75 °C (0.1 torr) [lit.[12] bp 82 °C (0.5 torr)] (the sample mostly solidified on standing); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.24 (s, 3, $CH_3CC\mathit{H}_3$), 1.45 (s, 3, $C\mathit{H}_3CCH_3$), 1.60 (t, 1, J = Hz, CH), 2.20 (s, 1, OH), 3.73 (d, 2, J = 7 Hz, CH_2).

Reactions of 7 with Methyllithium and with Butyllithium. A diethyl ether solution of methyllithium (Ventron Corp., 1.3 M, 41.7 mL, 54 mmol) was added over 30 min to a stirred and cooled (dry ice bath) solution of **7** (4.0 g, 15.5 mmol) in diethyl ether (30 mL, dried over sodium wire) maintained under argon. The resulting mixture was kept in the dry ice bath for 4.5 h and stirred. Then the mixture was allowed to warm to 0 °C and water (25 mL) was added. The layers were separated, the aqueous layer was extracted with three 25-mL portions of diethyl ether, and the combined organic layers were washed with water and dried (Na_2SO_4). Most of the solvent was removed at reduced pressure, and the residue was distilled to give a fraction (0.45 g) that was shown to be **8**: bp 46 °C (4 torr) [lit.[12] bp 53–54 °C (7 torr)]; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.60 (s, 3, $CH_3CC\mathit{H}_3$), 1.65 (s, 3, $C\mathit{H}_3CCH_3$), 3.07 (s, 1, OH), 3.99 (d, 2, J = 6 Hz, CH_2), 5.07 (m, 1, CH). The ^{1}H spectrum closely resembles one that has been reported.[12] The ^{1}H NMR spectrum of the pot residue (0.95 g) showed it to consist mainly of **7** (~55%) and **8** (~45%). The total amount of **8** (approximately 0.88 g, 9.0 mmol) in the distillate and pot residue corresponded to a yield of 58%.

A hexane solution of butyllithium (Ventron Corp., 2.3 M, 4.4 mL, 10 mmol) was added over 5 min to a stirred and cooled (−95 °C bath) solution of **7** (1.29 g, 5.0 mmol) in tetrahydrofuran (10 mL, dried over sodium and distilled from the sodium ketyl of benzophenone) maintained under argon. The stirred solution was left in the −95 °C bath for 10 min more and then methanol (1.0 mL) was added. The resulting mixture, still in the −95 °C bath, was stirred for 30 min and then allowed to warm to ambient temperature. Water (30 mL) was added and the layers were separated. The aqueous layer was saturated with sodium chloride and then extracted with three 50-mL portions of diethyl ether. The combined organic layers were dried (Na_2SO_4), and then most of the solvents were removed at reduced pressure. A ^{1}H NMR spectrum ($CDCl_3$) of the residue (0.58 g) showed it to consist mainly of **7** (~60%) and **8** (~40%).

Reaction of 7 and Lithium Aluminum Hydride. A solution of **7** (3.00 g, 11.6 mmol) in diethyl ether (45 mL, dried over sodium wire) was added over 30 min to a stirred and cooled (ice bath) suspension of lithium aluminum hydride (1.88 g, 50 mmol) in diethyl ether (50 mL) that was under argon. The mixture was allowed to warm to ambient temperature and was stirred overnight. It was then cooled in an ice bath and hydrolyzed by successive additions of water (2.0 mL), an aqueous sodium hydroxide solution (15%, 2.0 mL), and water (6.0 mL). The mixture was filtered, the solid washed with diethyl ether, and the filtrate dried (Na_2SO_4). Most of the solvent was removed under reduced pressure and the residue was distilled to give two fractions. The ^{1}H NMR spectrum ($CDCl_3$) of fraction 1 (0.14 g), bp 33–35 °C (1.2 torr), showed it to be principally **8**. Some additional absorptions were present, but they did not belong to **9** or **10**. The ^{1}H NMR spectrum of fraction 2 (0.77 g), bp 60–82 °C (1.2–1.8 torr), showed it to contain significant amounts of **7** and **8** as well as a mixture of **9** and **10** and some unidentified materials. The **9**:**10** ratio was approximately 0.45.

Reaction of 7 and Tributyltin Hydride: Preparation of 9 and 10. A solution of tributyltin hydride (Ventron Corp., 14.7 g, 50.5 mmol) in diethyl ether (25 mL) was added dropwise over 15 min to a stirred and cooled (ice bath) solution of **7** (12.4 g, 48.1 mmol) in diethyl ether (50 mL) that was under an argon atmosphere. After addition was complete, the ice bath was removed and the solution was stirred at ambient temperature for 3.5 h.

---

[22] Whitesides, G. M.; Roberts, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4878. Pechold, E.; Adams, D. G.; Fraenkel, G. *J. Org. Chem.* **1971**, *36*, 1368.

[23] This compound has been prepared before by lithium aluminum hydride reduction of 3-methyl-2-butenoic acid, but no procedure was described.[24]

[24] Green, M. B.; Hickinbottom, W. J. *J. Chem. Soc.* **1957**, 3262.

After removal of most of the solvent at reduced pressure, the residue was distilled to give a mixture of **9** and **10**: 6.48 g (36.2 mmol, 75%); bp 55–70 °C (1 torr). Since the ^{1}H NMR spectrum showed that this material still contained a few percent of **7**, a portion (3.50 g) was redistilled to give a purer sample of **9** and **10** (1.74 g): bp 50–55 °C (0.5–0.7 torr); ^{1}H NMR (360 MHz, $CDCl_3$) δ $\sim$1.11 (c, H_A of **9** and **10**), 1.130 and 1.136 (s and s, CH_3s of **9**), 1.141 (s, CH_3s of **10**), 2.28 (s, OH of **9** and **10**), 2.69 (d, J_{AC} = 4.0 Hz, H_C of **10**), 2.97 (d, J_{AB} = 7.6 Hz, H_B of **9**), 3.67 and 3.75 (each a d of d, J_{AD} = 6.2 Hz, J_{AE} = 8.2 Hz, J_{DE} = 11.6 Hz, H_D and H_E of **9**), 3.55 and $\sim$3.72 (each a d of d, J_{AD} = 8.0 Hz, J_{AE} = 13.8 Hz (?), J_{DE} = 11.4 Hz, H_D and H_E of **10**); mass spectrum, *m/z* (M^+ too weak for high-resolution mass determination) 146.9787 and 148.9803 ($M^+ - CH_2OH$), calcd for C_5H_8Br 146.9799 and 148.9779. The composition of this mixture was determined from the relative areas of the ^{1}H NMR absorptions of H_B of **9** and H_C of **10** to be 74% **9** and 26% **10** (these figures are probably accurate to ±2%).

Reaction of 8 and Zinc: Preparation of 9 and 10. Zinc powder (J.T. Baker, 40 g, 612 mmol) was added in small portions over a 2-h period to a stirred and heated (47 °C bath) solution of **7** (8.0 g, 31.0 mmol) in glacial acetic acid (250 mL) that was under an argon atmosphere. The mixture was maintained in the 47 °C bath and stirred for 42 h. Then the mixture was cooled to ambient temperature and filtered, and the solids were washed with diethyl ether. Most of the diethyl ether and some of the acetic acid were removed from the filtrate at reduced pressure. Water was added to the remainder, and aqueous sodium hydroxide solution (6 M) was added until the solution was strongly alkaline. The solution was extracted with four 50-mL portions of diethyl ether, and the combined extracts were washed with water (25 mL) and dried (Na_2SO_4). The ether was removed at reduced pressure and the residue distilled to give a mixture of **9** and **10**: 2.59 g (14.5 mmol, 47%); bp 30–60 °C (1 torr). A ^{1}H NMR spectrum ($CDCl_3$) of this material and also of material collected from the gas chromatograph (85 °C) showed the composition to be 80–85% **9** and 10–15% **10** (the determination of composition was less accurate than in the experiment above since 60-MHz ^{1}H NMR spectra were used).

Formation and Hydrolysis of a Metalated Grignard Reagent from 9 and 10. A diethyl ether solution of methylmagnesium bromide (Ventron Corp., 4.76 M, 3.52 mL, 16.8 mmol) was added dropwise over a few minutes to a stirred solution of **9** and **10** (74% **9** and 26% **10**, 1.50 g, 8.4 mmol) in diethyl ether (60 mL, dried over sodium wire) under an argon atmosphere. The solution was allowed to stir for 1 h, and then magnesium (Johnson Matthey Chemicals Limited Puratronic, 0.204 g, 8.4 mmol) and ethylene bromide ($\sim$0.1 g) were added. After the resulting mixture had been stirred for 3 h, most of the magnesium had disappeared. A portion of the solution (20 mL) was transferred to another flask and D_2O (1 mL) was added. Then the ether solution was decanted from the solid and filtered through a plug of glass wool and the filtrate was dried (Na_2SO_4). The remainder of the reaction was refluxed for 16 h. Then one-half of the solution was hydrolyzed as above with D_2O and the other one-half in the same manner but with H_2O. Most of the ether was removed from each portion under reduced pressure. GC analysis (50 °C) of each residue showed only one significant peak past that due to the solvent.

The material resulting from H_2O hydrolysis was collected and found to be **11**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.13 (d of d, 1, $J_{AC} \simeq$ 4.9 Hz, $J_{BC} \simeq$ 4.9 Hz, H_C), 0.48 (d of d, 1, J_{AB} = 8.5 Hz, J_{BC} = 4.3 Hz, H_B), 0.91 (m, 1, H_A), 1.08 and 1.12 (s and s, 3 each, CH_3s), 1.40 (s, 1, OH), 3.52 and 3.69 (each a d of d, 1 each, J_{AD} = 6.7 Hz, J_{AE} = 11.3 Hz, H_D and H_E).

The two samples resulting from D_2O hydroysis were collected and found to exhibit virtually identical ^{1}H NMR spectra (360 MHz, $CDCl_3$) that showed them to be mixtures principally of **12** and **13**. Most of the absorption of H_B was a doublet (J_{AB} = 8.3 Hz) due to **12** and for H_C also principally a doublet (J_{AC} = 5.2 Hz) due to **13**. The relative areas of the H_B and H_C absorptions were 74:26 for the first sample and 70:30 for the sample taken after the reaction mixture had been refluxed (the relative areas are probably accurate to ±2 units). The H_B absorption of **12** and the H_C absorption of **13** were shifted upfield ($\sim$0.015 ppm) from those of **11**, so that the peak at lowest field both in the H_B multiplet and in the H_C multiplet of **11** was visible.[25] From the areas of these downfield peaks, it can be estimated that **11** was about 6% of both of the **11**–**13** mixtures obtained from D_2O hydrolysis and therefore contributed 6 units to both the H_B and H_C absorptions. If this contribution is substracted from the area ratios above, then the relative compositions of **12** and **13** are 77:23 for the first sample and 73:27 for the second sample.

In another experiment similar to that above, a sample of **9** and **10** was used that was approximately 85–90% **9** and 10–15% **10**. After the reaction mixture had been allowed to stir at ambient temperature for 4 h, most of the magnesium had disappeared. One portion of the solution was removed and hydrolyzed with D_2O; the remainder was stirred for an additional 16 h and then hydrolyzed with D_2O. GC analysis of each sample showed only one significant peak past that due to the solvent. ^{1}H NMR spectra (200 MHz, $CDCl_3$) of the collected samples were virtually identical. Determining the relative amounts of **12** and **13** was somewhat less accurate than for the reaction above since more **11** was present and the spectra were taken at 200 MHz rather than at 360 MHz. However, the relative amounts of **12** and **13** were about 85:15.

Acknowledgment. We are grateful to the National Science Foundation for the support of this research and for aiding in the purchase of the NMR spectrometers and the mass spectrometer. We thank Dr. Robert D. Minard for obtaining the mass spectra and Alan J. Freyer for obtaining the high-field NMR spectra.

Registry No. 6, 556-82-1; 7, 17219-12-4; 8, 2425-45-8; 9, 86597-75-3; 10, 87050-58-6; 11, 930-50-7; 12, 87050-59-7; 13, 87050-60-0; 3-methyl-2-butenoic acid, 541-47-9; bromoform, 75-25-2.

---

[25] Comparable shifts of ^{1}H NMR absorptions due to an α-deuterium have been observed: Allred, A. L.; Wilk, W. D. *J. Chem. Soc. D* **1969**, 273.

A Convenient Synthesis of *N*-Vinylpyridinium Perchlorate and a Study of *N*-Vinylpyridinium Cations as Michael Reaction Acceptors

Alan R. Katritzky* and Olga Rubio

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received June 6, 1983

The title compound is easily prepared from 1-(2-bromoethyl)pyridinium bromide and sodium hydroxide. 1-Vinylpyridinium and 1-vinyl-2,4,6-triphenylpyridinium cations add N, S, and C nucleophiles in Michael-type reactions.

Several *N*-vinyl heterocycles are of considerable commercial importance as monomers for polymerization, e.g., *N*-vinylimidazoles,[1] *N*-vinylcarbazoles, and *N*-vinylpyrrolidones[2] are in widespread use. Surprisingly, despite