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The Reactions of Grignard Reagents with Norbornene Oxides

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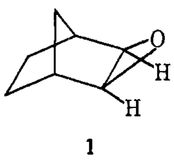
Reaction of phenylmagnesium bromide with *exo*-norbornene oxide (1) gave a 3.3:1.0 molar mixture of 7-*syn*-norbornenol to 2-*exo*-phenyl-7-*syn*-norbornanol. Other aryl Grignard reagents behaved similarly. Methylmagnesium iodide reacted with 1 to give a mixture of 7-*syn*-norbornenol, 2-*exo*-methyl-7-*syn*-norbornanol, and 2-*exo*-methyl-7-*anti*-norbornanol. Phenylmagnesium bromide reacted with 2-phenylnorbornene 2,3-*exo*-oxide to give the nonrearranged exo addition product, 3,3-diphenyl-2-*exo*-norbornanol.

Part A

The preparation of norbornene 2,3-*exo*-oxide, or simply norbornene oxide (**1**), was reported initially and simultaneously by Walborsky and Loncrini[1] and Kwart and Vosburgh.[2] Acidic reagents cause facile oxirane ring opening to give rearrangement products. Crandall[3] has shown that acid hydrolysis of **1** gives four isomeric norbornanediols, all products of rearrangement. Reaction with 48% hydrobromic acid gives the bromohydrin, 2-*exo*-bromo-7-*syn*-norbornanol (**2**).[4]



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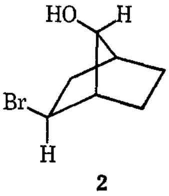

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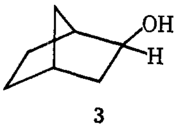
Reductions of **1** with metal hydrides, principally lithium aluminum hydride (LiAlH$_4$), have been successful. LiAlH$_4$ reduction in ether proceeds very slowly;[5] more polar and higher boiling solvents such as tetrahydrofuran (THF),[5,6] *N*-ethylmorphiline (NEM),[1,5] and THF–diglyme[6] have been employed. The major product from reduction in NEM and THF is *exo*-norbornanol (**3**), with minor amounts of the rearrangement product, 7-norbornanol (**4**), which amounts were dependent on solvent composition and reaction temperature. Recently, a new convenient procedure for the facile reduction of norbornene oxides without rearrangement was developed, utilizing lithium in ethylenediamine.[7] The slower hydride reduction of I may be ascribed to the difficulty accompanying endo nucleophilic attack from the approximate direction of the C$_6$ endo hydrogen.[8]



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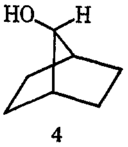

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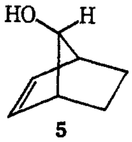
In view of the extensive synthetic utility of the Grignard reaction, it is surprising that no report of such a reaction with I has appeared to date. For the purpose of providing a useful synthetic route to various substituted norbornanols, we decided to investigate the addition of various Grignard reagents to **1**.

Results and Discussion

By using a 1.5:1.0 molar ratio of phenylmagnesium bromide to **1**, a 3.3:1.0 mixture (molar) of two products was obtained (glc analysis). The more volatile and more plentiful component was shown to be 7-*syn*-norbornenol (**5**), by nmr analysis and by conversion to the known derivative, 7-*syn*-norbornenyl tosylate.[4a] The less volatile component was identified as 2-*exo*-phenyl-7-*syn*-norbornanol (**6**). Its properties differed from those of 3-*endo*-phenyl-2-*exo*-norbornanol,[9] the product expected from endo attack (trans oxirane open-



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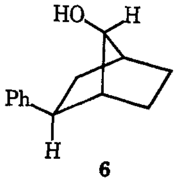

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(1) H. M. Walborsky and D. F. Loncrini, *J. Amer. Chem. Soc.*, **76**, 5396 (1954).

(2) H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954).

(3) J. K. Crandall, *J. Org. Chem.*, **29**, 2830 (1964).

(4) (a) S. Winstein and E. T. Stafford, *J. Amer. Chem. Soc.*, **79**, 505 (1957); (b) H. M. Walborsky and D. F. Loncrini, *J. Org. Chem.*, **22**, 1117 (1957).

(5) H. Kwart and T. Takeshita, *ibid.*, **28**, 670 (1963).

(6) N. . M. Yoon and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 2927 (1968).

(7) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **92**, 6914 (1970).

(8) T. G. Traylor, *Accounts Chem. Res.*, **2**, 157 (1969).

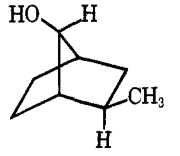
(9) D. C. Kleinfelter, T. E. Dye, J. E. Mallory, and E. S. Trent, *J. Org. Chem.*, **32**, 1734 (1967).

ing), and of 3-*exo*-phenyl-2-*exo*-norbornanol,[9] the product expected from unrearranged exo attack (cis oxirane opening).

The reactions of *p*- and *o*-tolylmagnesium bromides with **1** proceeded similarly, giving a product distribution of **5** to 2-*exo*-aryl-7-norbornanol of 3.2:1.0 and 5.7:1.0 (molar), respectively. While all three aryl Grignard reactions gave greater amounts of **5** than of aryl adduct, the availability of norbornene and **1** makes this route an attractive one for such 2-*exo*-aryl-7-*syn*-norbornanols and derivatives. In addition, the reaction provides a simpler route to **5** than previously reported.[4]

Somewhat different results were obtained from the reaction of methylmagnesium iodide with **1**. In eight of nine determinations of product distributions, **5** and two less volatile components, separable by preparative vapor phase chromatography (vpc), were formed. Their elemental analyses and mass spectra ($M\cdot^+ = 126$) indicated them to be isomeric methylnorbornanols. From analysis of their nmr spectra structures **7** and **8** were assigned to the more volatile component (mp 150–151°) and less volatile component (amorphous glassy solid), respectively.

In one of the nine reactions of methylmagnesium iodide with **1**, the iodohydrin, 2-*exo*-iodo-7-*syn*-norbornanol (**9**), was isolated in *ca.* 11% yield.[10]



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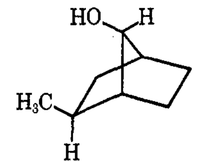

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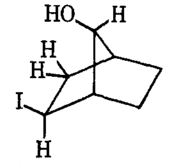

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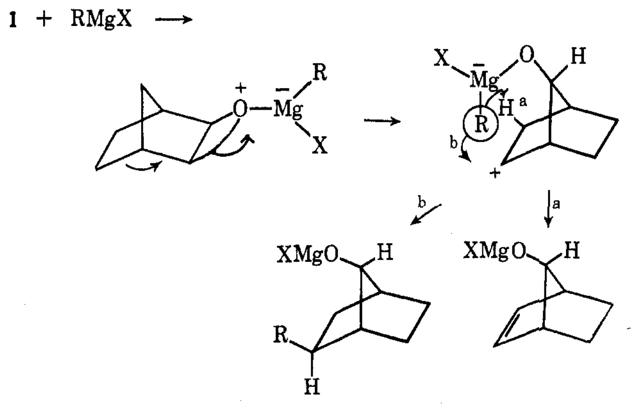
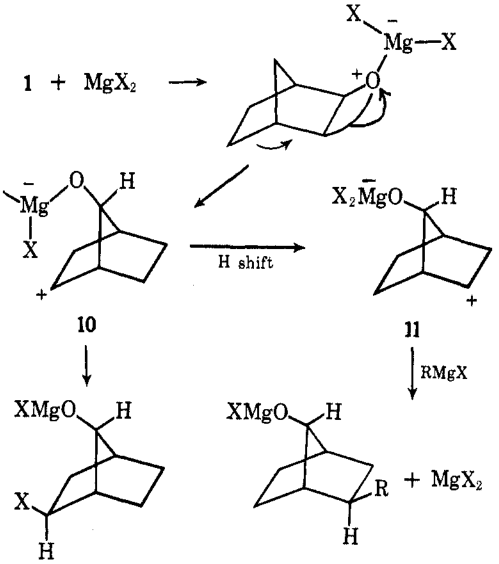
SCHEME I



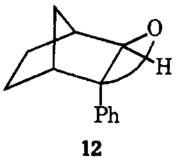
The products of the reactions of the aryl Grignard reagents with **1** may be rationalized *via* mechanistic Scheme I. This scheme satisfactorily explains the formation of products **5** and **6**. However, the additional formation of the anti isomer **7** and the iodo addition product **9** requires an extension of this scheme. Reactions of Grignard reagents with epoxides are known to be complicated by the inhomogeneity of solutions due to the equilibrium $2RMgX \rightleftharpoons R_2Mg + MgX_2$.[11]

SCHEME II



If one assumes that MgX_2 also complexes with **1**,[12] then the formation of the additional products **7** and **9** is understandable (Scheme II). Intermediate **10** may add X^- intramolecularly to give **9** or undergo hydride shift to give intermediate **11**, which may then add R to give anti product **2**. The nature of the Grignard reagent is known to be dependent upon the variables of solvent concentration, R group, and halide.[13] Evidently there is sufficient MgI_2 present to compete with RMgI for the oxirane ring complexation in the reaction with the methyl Grignard reagent, but there is insufficient $MgBr_2$ present with the phenyl Grignard reagent or it does not compete favorably with PhMgBr for the oxirane ring complexation. It was felt that use of a bulky Grignard reagent in which the initial complexation of RMgX may be sterically hindered, or in which the reaction of RMgX with the cationic center may be sterically encumbered, might lead to greater halohydrin formation through greater MgX_2 involvement. Reaction of "*tert*-butylmagnesium bromide" with **1** led to a 51% yield of the bromohydrin **2**. This represents a better yield of **2** and a simpler preparative procedure than that previously reported.[4]

One substituted norbornene oxide, 2-phenylnorbornene 2,3-*exo*-oxide (**12**), was treated with phenylmagnesium bromide. The product was 3,3-diphenyl-2-*exo*-norbornanol (**13**), formed *via* cis oxirane ring opening, rather than the rearrangement product, 1-phenyl-2-*exo*-phenyl-7-*syn*-norbornanol (**14**). Structure **13** was assigned from its nmr and ir spectra.



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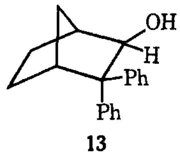

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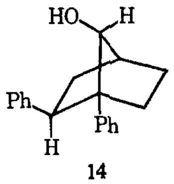

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[10] The only difference noted for this reaction was the use of a fresh bottle of methyl iodide; all reactions were carried out under practically identical conditions of time, temperature, work-up, etc.

[11] N. G. Gaylor and E. I. Becker, *Chem. Rev.*, **49**, 413 (1951).

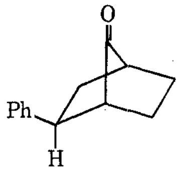
[12] J. K. Crandall (ref 3) reported that $MgBr_2$ reacts with **1** in ether to give minor amounts of **5**, norcamphor, and nortricyclanol; the two major components were probably the syn bromohydrin **2** and its anti isomer. From this latter mixture there was crystallized a compound with mp 72–74°, close to that reported for **2** (mp 75–76°).[4]

[13] R. M. Salinger and H. S. Mosher, *J. Amer. Chem. Soc.*, **86**, 1782 (1964), and references therein; E. C. Ashby, *Quart. Rev., Chem. Soc.*, **21**, 259 (1967).

Rearrangements accompanying reactions of Grignard reagents with epoxides are common,[14] but generally the rearrangement is an initial magnesium halide catalyzed isomerization of the epoxide to an aldehyde or ketone which then reacts with RMgX or R_2Mg. The reactions of phenylmagnesium bromide and methylmagnesium iodide with **1** represent, to our knowledge, the first instances of a Wagner-Meerwein rearrangement and a 1,3-hydride shift accompanying a Grignard addition. It is of interest to note that the reaction of MeMgI with **1** gives the same type rearrangement products as from acid hydrolysis, and that **12** reacts with PhMgBr to give nonrearranged addition product as it does with methanol and other reagents.[15] Evidently it is the Lewis acid nature of the Grignard reagent that is controlling the mode of reaction with **1**.

Part B

Chemical and Spectra Proofs of Structure.—The structure of 2-*exo*-phenyl-7-*syn*-norbornanol (**6**) was confirmed by analysis of its nmr spectrum and by Sarett oxidation[16] to 2-*exo*-phenyl-7-norbornanone (**15**). The three stretching vibrations of 1834 (m), 1771 (s), and 1740 cm^{-1} (w) are consistent with those reported for the carbonyl group of 7-norbornanones.[17] Lithium aluminum hydride reduction of **15** produced the original alcohol **6**. This latter result confirms the exo-syn relationship between the phenyl and hydroxyl groups. The analogous reduction of 7-*syn*-phenyl-2-norbornanone (**16**) gives 7-*syn*-phenyl-2-*exo*-norbornanol (**17**).[18] Hydride attack at the carbonyl group in both **15** and **16** occurs from the side away from the phenyl substituent.



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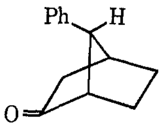

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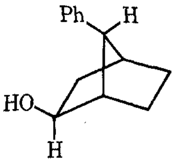

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The principal OH stretching vibration of **6** was observed at 3623 cm^{-1} with a barely discernible shoulder of 0.6 relative intensity at *ca.* 3604 cm^{-1}. This contrasts with the single absorption of 3591 cm^{-1} ($\Delta\nu$ = 29 cm^{-1}) reported[19] for its counterpart (**17**). Even if one uses the 3631-cm^{-1} OH band of 2-*exo*-methyl-7-*syn*-norbornanol as the reference-free OH band, **6** definitely experiences weaker and less intramolecular OH---π bonding than **17**.

Whereas **9** and all other secondary phenylnorbornanols previously reported[9,19] display singlets in the phenyl region of their nmr spectra, the spectrum of **6** displays a multiplet centered at δ 7.18. Apparently the phenyl ring is somewhat twisted on edge with respect to the syn hydroxyl, and the proximity of the hydroxy group to the ortho protons causes the resulting magnetic nonequivalence. The previously reported orientational preference of the exo phenyl ring, orthogonal to the eclipsed exo C-H bond,[9] is evidently largely maintained in **6** despite the fact that a different alignment would lead to an energetically favorable OH---π bond. Other distinguishing features of the nmr spectrum of **6** are the 7 anti proton absorption at δ 3.84 (δ 3.90, 7 H of 7-norbornanol) and the 2-endo benzylic proton at δ 2.84 (δ 2.71, 2n H of 2-*exo*-phenylnorbornane[9]).

The 7-proton absorptions do not differ appreciably in the nmr spectra of **7**, **8**, and **4**. The spectrum of **4** shows a broad absorption centered at δ 1.90 (4 H) assignable to the two bridgehead protons, H-1 and H-4, and to the two exo protons, H-2x and H-3x, syn to the hydroxyl group. Snyder and Franzus[20] reported that a syn hydroxyl group deshields exo protons. The spectrum of **7** shows a similar broad absorption centered at δ 1.90 (4 H) assigned to the same protons, but that of **8** shows a downfield absorption at δ 1.97 integrating for only one proton. This δ 1.97 absorption may be assigned to one of the bridgehead protons. The shielding ability of adjacent methyl groups has been observed and commented on by Musher[21] and Eliel.[22] Only the 3-exo proton of **8** can be deshielded by a syn hydroxy group, but the greater shielding ability of the eclipsed 2-methyl easily counteracts this effect. At most then only two protons, the bridgehead protons, should appear downfield; however, only one of the two is observed downfield.

These nmr structural assignments were confirmed by comparison of the nmr dilution curves of **7** and **8** with that of 2-*exo*-cyclohexyl-7-*syn*-norbornanol (**18**), prepared by catalytic hydrogenation of **6**. These curves are shown in Figure 1. The syn alcohols show smaller slopes, $(d\delta/dx)_{x=0}$, in that portion of the plot presumably involving dimer-monomer or oligomer-monomer equilibria.[23] The slopes for **8** and **18** of 28 and 27, respectively, contrast with the value of 57 for the less encumbered hydroxyl of **7**. Oulette[24] has obtained similar results with 2-*exo*-norbornanols with 7-methyl substituents.

The structure of 2-*exo*-iodo-7-*syn*-norbornanol (**9**) was assigned on the basis of the following spectral data. A broad singlet assigned to H-7a appeared at δ 4.17. An eight-line absorption at δ 3.89 was assigned to H-2n. The multiplet spacings, J'[25] of 7.8, 4.2, and 1.2 Hz, may be assigned to coupling of H-2n with H-3n, H-3x, and H-7a, respectively. In the infrared spectrum of **9** OH stretching vibrations

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[14] R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959); J. D. Morrison, R. L. Atkins, and J. E. Tomaszewski, *Tetrahedron Lett.*, 4635 (1970), and references therein.

[15] T. J. Gerteisen, D. C. Kleinfelter, G. C. Brophy, and S. Sternhell, *Tetrahedron*, in press.

[16] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, **75**, 422 (1953).

[17] C. F. H. Allen, T. Davis, D. W. Stewart, and J. A. Van Allen, *J. Org. Chem.*, **20**, 306 (1955); C. F. H. Allen and J. A. Van Allen, *ibid.*, **20**, 323 (1955); P. Wilder, Jr., and A. Winston, *J. Amer. Chem. Soc.*, **78**, 868 (1956); W. R. Hatchard and A. K. Schneider, *ibid.*, **79**, 6261 (1957); P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964); P. G. Gassman and J. L. Marshall, *J. Amer. Chem. Soc.*, **88**, 2822 (1966); E. J. Corey and R. S. Glass, *ibid.*, **89**, 2600 (1967).

[18] J. H. Long, Jr., Ph.D. Thesis, University of Tennessee, 1968.

[19] D. C. Kleinfelter, *J. Org. Chem.*, **32**, 3526 (1967).

[20] E. J. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964).

[21] J. I. Musher, *Mol. Phys.*, **6**, 94 (1963).

[22] E. L. Eliel, M. H. Gianni, Th. H. Williams, and J. B. Stothers, *Tetrahedron Lett.*, No. 17, 741 (1962).

[23] For a discussion of the various effects contributing to the chemical shifts of hydroxyl protons and pertinent references, see J. W. Emsley, J. Feeney, and L. H. Sutcliff, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1965, p 537-547, 816-818.

[24] R. J. Oulette, G. E. Booth, and K. Liptak, *J. Amer. Chem. Soc.*, **87**, 3436 (1965).

[25] Since the 3-proton signals were overlapped by peaks from the remaining methylene hydrogens, the actual coupling constants, J, could not be determined from the spectra. $J' \cong J$ if $\Delta\nu(3x - 3n)$ is large compared to $J_{3x,3n}$.

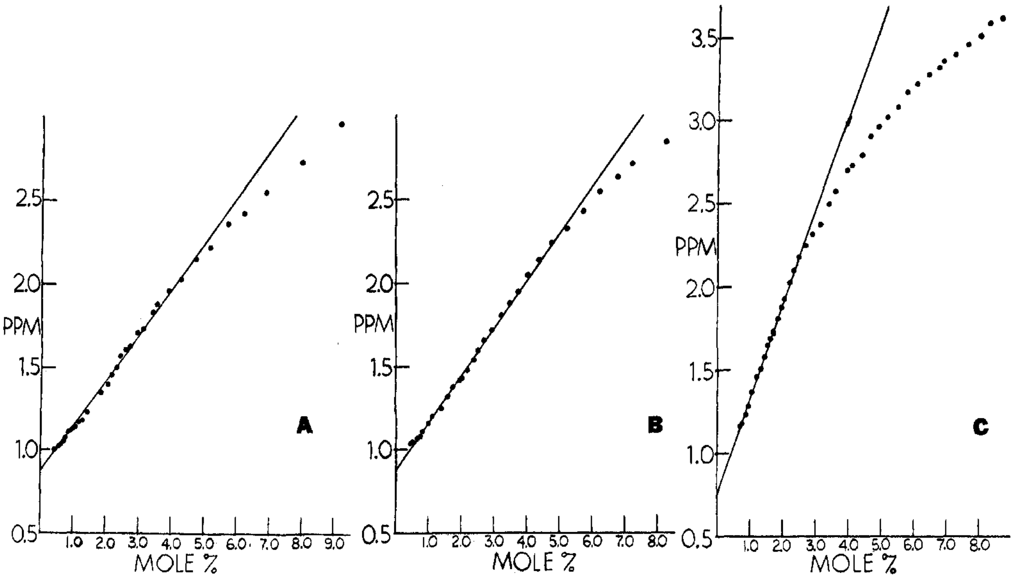

Figure 1.—Plots of chemical shifts *vs.* mole percentages for (a) 2-*exo*-cyclohexyl-7-*syn*-norbornanol (**18**), (b) 2-*exo*-methyl-7-*syn*-norbornanol (**8**), and (c) 2-*exo*-methyl-7-*anti*-norbornanol (**7**).

were observed at 3620 (free) and 3574 cm^{-1} (OH---I bond) with a $\Delta\nu$ of 46 cm^{-1}. Thus the exo-iodo, syn-OH assignments are confirmed.

The nmr spectrum of 3,3-diphenyl-2-*exo*-norbornanol (**13**) showed the following significant absorptions: a broad singlet at δ 4.43 (H-2n), broad singlets at δ 3.07 and 2.20 (H-4 and H-1, respectively), and a broadened doublet (separation *ca.* 10 Hz) at δ 2.10 (H-7s). The ir spectrum showed the OH stretching vibration at 3587 cm^{-1}, corresponding to a $\Delta\nu$ of 33 cm^{-1} with respect to the 3620-cm^{-1} absorption[19] for *exo*-norbornanol. The $\Delta\nu$ for 3-*exo*-phenyl-2-*exo*-norbornanol is 30 cm^{-1}. These spectral data are incompatible with the rearranged product 1-phenyl-2-*exo*-phenyl-7-*syn*-norbornanol (**14**).

Experimental Section

Melting points were determined in soft capillary tubes using a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.) and are uncorrected. Infrared spectra for the 3-μ region were recorded on a Perkin-Elmer Model 257 grating spectrometer calibrated against polystyrene standard. A Varian A-60 nmr spectrometer, calibrated with tetramethylsilane (δ = 0) and chloroform (δ = 436.5 cps), was used for the nmr determinations. Chemical shifts are presumed correct to ± 0.01 ppm. For the nmr spectra, s = singlet, m = multiplet, b = broad, and exch = exchanges on shaking with D_2O. Relative intensities are given in numbers of protons, *e.g.*, "3 H" denotes a relative intensity of three protons. The mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E recording mass spectrometer (the University of Tennessee, Mr. William Peed, operator), or with a Consolidated Electronics Corp. 21-104 recording mass spectrometer (Phillips Morris Research Laboratoris, Richmond, Va., Dr. Paul H. Chen, operator). Vpc analyses were run on a Varian A90-P3 gas chromatograph equipped with a 6 ft × 0.25 in. 20% SE-30 on a Chromosorb W column (typical flow rate 50–75 cc min^{-1} of helium, column temperature of 130–185°) or on a Varian A600-D flame ionization detector gas chromatograph equipped with a 5 ft × $^1/_8$ in. 3% SE-30 on a Chromosorb W column. Preparative scale vpc separations were performed with an Aerograph Autoprep A-700 gas chromatograph equipped with a 20 ft × $^3/_8$ in. 30% SE-30 on a Chromosorb P column (typical flow rate 100 cc min^{-1} of helium, column temperature of 120–160°). Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., and by F. B. Strauss Microanalytical Laboratory, Oxford, England.

Unless otherwise specified, all ether and ligroin solutions of products were dried over anhydrous sodium sulfate prior to removal of solvent. Ligroin was distilled over potassium permanganate and had bp 40–55°.

Reaction of Phenylmagnesium Bromide with Norbornene Oxide (**1**).—To an ether solution of phenylmagnesium bromide, prepared from magnesium turnings (2.0 g, 0.084 g-atom) and bromobenzene (10.7 g, 0.0700 mol), was added an ether solution of **1** (6.60 g, 0.0600 mol), mp 125–126° (lit.[1] mp 125–127°). Reflux was maintaned for 3 hr, water was added, and solvent was removed by flash evaporation with gentle heating from a warm water bath,[26] leaving 7.11 g of light yellow oil. Glc analysis indicated two products in the weight ratio of 2.13:1.00.

A combined distillation and sublimation of 7-*syn*-norbornenol (**5**) *in vacuo* was accomplished by gentle heating. Purification by preparative vpc gave crystalline **5**, mp 79–80°. The *p*-toluenesulfonate, prepared in the usual manner,[27] recrystallized from ether–ligroin gave mp 66–67° (lit.[4a] mp 67–68°). Reduction of **5** with hydrogen and platinum oxide in ethyl acetate gave 7-norbornanol (**4**), mp 148–150° (lit.[28] mp 150–151°). The high-resolution ir spectrum of **4** (CCl_4) showed absorption at 3632 cm^{-1} (OH); that of **5** showed absorption at 3575 cm^{-1} (lit.[29] 3572 cm^{-1}).

Addition of ligroin to the residue left from distillation of **5** affected crystallization of **6**, mp 75–77° from ligroin (*Anal.* Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 83.16; H, 8.39). The nmr and ir spectra are discussed in the body of the paper. The *p*-toluenesulfonate of **6**, prepared in the usual manner,[27] gave mp 78–79° from ether (*Anal.* Calcd for $C_{20}H_{22}SO_3$: C, 70.16; H, 6.48. Found: C, 69.96; H, 6.47). The weight of **5** and **6**, 7.19 g, represents a yield of 93% (vpc). The molar ratio of **5** to **6** formed was 3.5:1.0; the average for four reactions was 3.3:1.0.

Oxidation of 6 to 2-*exo*-Phenyl-7-norbornanone (**15**).—To a solution of chromium trioxide (2.0 g, 0.020 mol) in pyridine (20 ml) was added **6** (1.0 g, 0.0053 mol) dissolved in pyridine (20 ml). After stirring for 24 hr at room temperature, the mixture was poured into water and filtered over celite, and the filtrate was extracted with benzene. The benzene solution was washed with water and dried, and the solvent was flash evaporated. A light yellow oil, 0.70 g (69%), of pure (ir, nmr, vpc) **15** was obtained.

Pertinent ir data are listed in the text; nmr (CCl_4) δ 7.11 (5 H, Ar H's), 2.93 (1 H, m, H-2n), 2.3–1.5 (8 H, m, remaining H's).

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[26] Caution must be observed at this point to keep the 7-*syn*-norbornenol from escaping by sublimation.

[27] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1180.

[28] S. Winstein, M. Shatavwky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955).

[29] R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

Reduction of **15** (1.35 g, 0.0140 mol) with lithium aluminum hydride (0.27 g, 0.0070 mol) in ether in the standard manner[30] gave pure **6** (1.14 g, 84.0%) as shown by melting point, ir, and nmr.

Preparation of 2-*exo*-Cyclohexyl-7-*syn*-norbornanol (18).—A mixture of acetic acid (30 ml), 2-*exo*-phenyl-7-*syn*-norbornanol, **6** (1.00 g, 0.00532 mol), and platinum oxide (0.20 g) was hydrogenated in a Paar apparatus for 10 hr under 45-psi hydrogen pressure. After filtration through Celite, the acetic acid solution was stirred with sodium carbonate solution and extracted with ether, and the ether extracts were washed with sodium carbonate solution. To this dried ether solution was added lithium aluminum hydride (0.75 g) to reduce the acetate that formed during the hydrogenation. Work-up in the usual manner gave **18**, (0.82 g, 80%): mp 75–77°, from ligroin (*Anal.* Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.13; H, 11.28); ir (CCl_4) 3635, 3627 cm^{-1} doublet (OH); nmr (CCl_4, 9.2 mol %) δ 3.86 (1 H, b s, H-7a), 2.96 (1 H, s, exch, OH), 2.2–0.8 (20 remaining H's, m).

Reaction of *p*- and *o*-Tolymagnesium Bromide with 1.—The reactions were carried out in a manner similar to that used for the preparation of **6**. For the *p*-tolyl Grignard reagent a 3.0:1.0 molar ratio of **5** to *p*-tolyl adduct was formed. The *p*-tolyl analog of **6** had mp 70–71° from ligroin (*Anal.* Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.97; H, 8.86); ir (CCl_4) 3624, 3604 cm^{-1} sh (intensity ratio 1.22:1.00); nmr similar to **6**. For the *o*-tolyl Grignard reagent a 5.7:1.0 molar ratio of **5** to *o*-tolyl adduct was formed. The *o*-tolyl analog of **6**, a light yellow oil, was converted to its *p*-toluenesulfonate derivative in the usual manner,[27] which gave mp 110–112° from ether–ligroin (*Anal.* Calcd for $C_{21}H_{24}SO_3$: C, 70.78; H, 6.74. Found: C, 70.64; H, 6.72). For the alcohol, ir (CCl_4) showed 3621, 3604 cm^{-1} sh (intensity ratio 1.24:1.00); nmr similar to **6**.

Reaction of Methylmagnesium Iodide with 1.—The reaction was carried out in a manner similar to that used for the preparation of **6**. Using iodomethane (19.6 g, 0.140 mol), magnesium turnings (7.25 g, 0.300 g-atom), and **1** (10.0 g, 0.0909 mol), there was obtained 7.96 g of pale yellow oil. Vpc analysis gave 25.3% (molar) **5**, 33.6% **7**, and 41.5% **8**. The average for three preparations was 28.0% **5**, 31.9% **7**, and 40.1% **8**. The per cent yield based on the three products was 71.6%; the average for three preparations was 74.1%. Gentle distillation *in vacuo* with trapping in a Dry Ice–acetone bath separated most of **5** from the methylnorbornanols. Preparative vpc gave pure **8**, a white crystalline solid, mp 150–151° from ligroin, and **7**, a clear, glassy, amorphous solid of low melting point (*Anal.* Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found (for **8**): C, 75.90; H, 10.92. Found (for **7**): C, 75.90; H, 11.08). In their ir spectra (CCl_4) both absorbed at 3631 cm^{-1}; the significant nmr spectral data are discussed in the text.

Isolation of 2-*exo*-Iodo-7-*syn*-norbornanol (9).—In one of the nine reactions of methylmagnesium iodide in which there were reacted iodomethane (29.8 g, 0.210 mol), magnesium turnings (10.1 g, 0.414 g-atom), and **1** (15.0 g, 0.136 mol) in the usual manner, removal of the ether solvent in the work-up left some white solid and oily material. Addition of ligroin dissolved the oil after which the solid was filtered to give **9** (3.63 g, 11.3%): mp 72–73.5° from ligroin (*Anal.* Calcd for $C_7H_{11}IO$: C, 35.29; H, 4.62. Found: C, 35.04; H, 4.58); ir (CCl_4) 3620 (ν_f), 3574 cm^{-1} (ν_b), $\Delta\nu$ 46 cm^{-1} (intensity ratio = 1.0:1.0); pertinent nmr assignments in text. Vpc analysis of the filtrate gave 29.5% **5**, 10.0% **7**, and 49.2% **8**, relative to total moles of the four products.

Reaction of *tert*-Butylmagneium Bromide with 1.—The reaction was carried out in a manner similar to that used for the preparation of **6**. From *tert*-butyl bromide (19.0 g, 0.139 mol), magnesium turnings (4.0 g, 0.16 g-atom), and **1** (9.20 g, 0.0836 mol) there was obtained 13.44 g of colorless oil. Addition of ligroin with stirring caused precipitation of white solid. Filtration in the cold gave 8.06 g (50.5%) of 2-*exo*-bromo-7-*syn*-norbornanol, mp 75–76° (lit.[4a] mp 75–76°). The nmr spectrum of the ligroin-evaporated filtrate showed that a small amount of 7-*syn*-norbornenol was present. No attempt was made to determine further the composition of this filtrate (5.38 g). For the bromohydrin, ir (CCl_4) showed 3621 sh (ν_f), 3577 cm^{-1} (ν_b), $\Delta\nu$ 44 cm^{-1} (intensity ratio = 1.0:2.2); nmr (CCl_4) δ 4.01 (1 H, s broad, H-7a), 3.95 (1 H, m, H-2n), 2.50 (1 H, s, exch OH), 2.8–0.85 (8 H, remaining H's).

Reaction of Phenylmagnesium Bromide with 2-Phenylnorbornene 2,3-*exo*-Oxide (12).—The reaction was carried out in a manner similar to that used for the preparation of **6**. Using bromobenzene (9.42 g, 0.0600 mol), magnesium turnings (1.92 g, 0.0800 g-atom), and **12** (5.00 g, 0.0270 mol), there was obtained *ca.* 6.0 g of light yellow oil. Chromatography over alumina, using ligroin eluent, removed the biphenyl and other impurities. Elution with ether gave 5.00 g (70.4%) of alcohol **13**, mp 75.5–77.0° from ligroin (*Anal.* Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.08; H, 7.66). The ir and nmr spectra are discussed in the text.

Registry No.—**1**, 3146-39-2; **2**, 31337-62-9; **5**, 13118-70-2; **6**, 31337-64-1; **6** *p*-toluenesulfonate, 31337-65-2; **6** *p*-tolyl analog, 31337-66-3; **6** *o*-tolyl analog *p*-toluenesulfonate, 31337-67-4; **7**, 31337-68-5; **8**, 31337-69-6; **9**, 31337-70-9; **12**, 31337-71-0; **13**, 31337-72-1; **15**, 31337-73-2; **18**, 31337-74-3; phenylmagnesium bromide, 100-58-3; *p*-tolylmagnesium bromide, 4294-57-9; *o*-tolylmagnesium bromide, 932-31-0; methylmagnesium iodide, 917-64-6; *tert*-butylmagnesium bromide, 2259-30-5.

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