cooled slightly. Acetyl chloride (1.584 g) in benzene (5 ml) was added dropwise and the mixture was stirred at room temperature for 3 hr. The benzene layer was decanted from an oily solid residue which was rinsed with additional benzene. The combined benzene solutions were evaporated to give oily crystals of the amide. This material was recrystallized with difficulty from hexane to yield 300 mg of colorless needles, mp 44–48°.

Imino Ether 36. Amide **35** (201 mg) was treated as above with 400 mg of Meerwein's reagent in dry methylene chloride to give **36** as a colorless oil after preparative scale vpc purification, ν_{max}^{neat} 1680 cm^{-1}.

Anal. Calcd for $C_6H_{11}NO$: C, 63.68; H, 9.80; N, 12.39. Found: C, 63.33; H, 9.65; N, 12.44.

Protonations with Trifluoroacetic Acid. To a solution of the imino ether in chloroform was added a slight excess of trifluoroacetic acid. The excess acid and solvent were removed *in vacuo* during 1–2 days. The residue was then dissolved in the appropriate solvent.

Acknowledgment. The authors are indebted to the National Science Foundation for a grant (GP-8678) which provided financial support for this work. We wish also to thank Badische Anilin und Soda Fabrik for the generous gift of cyclooctatetraene which made possible the synthesis of **24**.

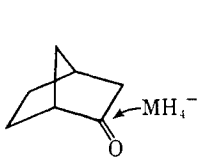
Additions to Bicyclic Olefins. I. Stereochemistry of the Hydroboration of Norbornene, 7,7-Dimethylnorbornene, and Related Bicyclic Olefins. Steric Effects in the 7,7-Dimethylnorbornyl System[1]

Herbert C. Brown and James H. Kawakami[2]

Contribution from the Richard B. Wetherill Laboratory, Purdue University, Lafayette, Indiana 47907. *Received September 15, 1969*

Abstract: A systematic study of addition reactions of norbornene, 7,7-dimethylnorbornene, and related bicyclic olefins has been undertaken in order to define more precisely the role of steric effects in controlling the stereochemistry of the additions and the nature of the intermediates in such addition reactions. The addition of borane to norbornene proceeds almost exclusively *exo* (99.5%), whereas the corresponding addition to 7,7-dimethylnorbornene proceeds preferentially *endo* (78%). Similarly, hydroboration of 2-methylenenorbornane gives preferentially *exo* (85%), whereas 2-methylene-7,7-dimethylnorbornane gives preferentially (85%) *endo* product. Similar results were realized with 1-methylnorbornene, 2-methylnorbornene, bornene, and 2,7,7-trimethylnorbornene. Consequently, hydroboration of norbornene, 1- and 2-methylnorbornene, and 2-methylenenorbornane goes predominantly *exo*, evidently reflecting the greater steric availability of the *exo* position in this bicyclic system. However, the presence of 7,7-dimethyl substituents causes the addition to proceed preferentially from the *endo* direction. Consequently, in hydroboration the 7,7-dimethyl substituents alter the normal direction of addition to olefins of the norbornane structure, irrespective of whether the double bond is endocyclic, directly under the 7,7-substituents, or exocyclic, located to the side of the substituents.

A major argument for the σ-bridged norbornyl cation is the almost exclusive *exo* substitution realized in the solvolysis of 7,7-dimethylnorbornyl derivatives.[3,4] The reduction of norcamphor by sodium borohydride[5] or lithium aluminum hydride[6] proceeds preferentially from the *exo* direction (**1**) to give the *endo* alcohol predominantly. On the other hand, the reduction of camphor or apocamphor takes place preferentially from the *endo* direction (**2**) to give the *exo* alcohol.



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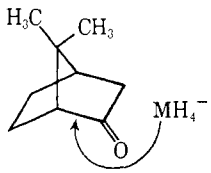

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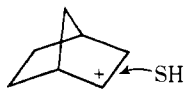
On the other hand, solvolyses of both norbornyl (**3**) and apobornyl (**4**) derivatives give the *exo* products almost exclusively. It was argued that the failure of the



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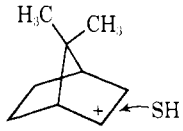

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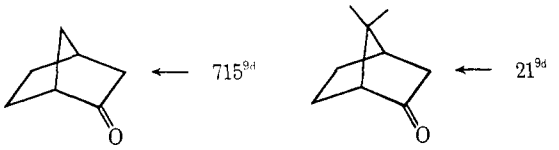
7,7-dimethyl substituents to control the stereochemistry of substitution in the cation, in the same manner that these substituents control the direction of attack by the complex hydrides, required something "special,"[3] σ bridging in the cation.

This is a reasonable argument. However, as was pointed out earlier,[7] it rests upon largely unexplored foundations. Implicit in the proposed argument is the assumption that because the 7,7-dimethyl substituents cause an inversion in the direction of attack by complex hydrides on the carbonyl group of apocamphor, these substituents should be expected to cause a similar

(1) Hydroboration. XXX.
(2) Graduate research assistant on grants (G 19878 and GP 6492X) supported by the National Science Foundation.
(3) J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Part I, Interscience Publishers, New York, N. Y., 1963, Chapter 3.
(4) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **87**, 376, 378, 379, 381 (1965).
(5) H. C. Brown and J. Muzzio, *ibid.*, **88**, 2811 (1966).
(6) S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956).
(7) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

inversion in all reactions of the 7,7-dimethylnorbornyl system. However, we really know very little about the relative steric requirements for the reaction of complex hydrides with ketones and the reaction of cations and ion pairs with solvents. Indeed, how uncertain[8] this implicit assumption may be is indicated by the recent observation that high *exo*:*endo* rate ratios are observed for base-catalyzed deuterium exchange, both in norcamphor (**5**) and in camphor[9] (**6**).



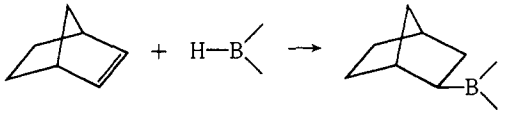
5 6

As a matter of fact, even in reduction of the ketone, camphor, use of diborane in place of the complex hydrides results in approximately 50:50 formation of the two epimeric alcohols.[10]

Consequently, we decided to undertake a systematic study of reactions of norbornyl and 7,7-dimethylnorbornyl systems in order to realize a better understanding of the factors influencing the direction of reaction in the norbornyl system and the magnitude of the influence of 7,7-dimethyl substituents on the reaction course. For a number of reasons the addition reactions of bicyclic olefins related to norbornene appeared particularly promising. Accordingly, we have examined the hydroboration (reported in the present paper), epoxidation,[11] oxymercuration,[12] hydrochlorination,[13] and other addition reactions of norbornene, 7,7-dimethylnorbornene, and related olefins.[14] These studies have led us to a new, promising interpretation of the steric influence of 7,7-dimethyl substituents in reactions of the norbornyl system[15] and has provided a considerable amount of interesting new information which will have to be accounted for in a complete theory of the behavior of the norbornyl cation. The present paper covers our study of the stereochemistry of hydroboration of norbornene, 7,7-dimethylnorbornene, and related olefins.

Results and Discussion

It was already known that the hydroboration–oxidation yields *exo*-norborneol predominantly.[16] However, the precise amount of the *endo* isomer formed had not been established previously. We established glpc conditions which permitted us to determine 0.3% *endo*-norbornanol in the *exo* isomer. Hydroboration–oxidation of norbornene indicated a yield of 100% of norbornanol, 0.5% *endo*, and 99.5% *exo* (1).

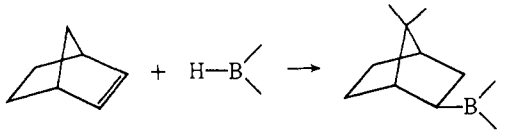


(1)

99.5%

This is a remarkable stereochemical preference of 200:1. The question arises as to what factor is responsible for this marked preference for reaction from the *exo* direction.[17] We have suggested that in many U-shaped molecules simple steric considerations are responsible for the greater reactivity of the more open *exo* face, as compared to the more hindered *endo* face.[18] It has been suggested that torsional effects may also play a role.[19] It was the original observation that high *exo*:*endo* rate ratios are frequently observed in *both* carbonium ion and noncarbonium ion reactions of the norbornyl system that led us to propose a reexamination[7] of the interpretation that σ participation is the factor which is responsible for the high *exo*:*endo* rate and product ratios in solvolytic reactions of norbornyl derivatives.[17]

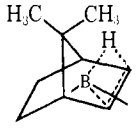
On the other hand, the hydroboration–oxidation of 7,7-dimethylnorbornene gave only 22% *exo* and 78% *endo* (2). Consequently, in this reaction the 7,7-dimethyl substituents do invert the stereochemistry of the addition process.



(2)

22%

The hydroboration reaction is believed to proceed through a concerted *cis* 4-center addition of the boron–hydrogen bond to the carbon–carbon double bond of the olefin.[16] Such a mechanism places the H–B< moiety directly under the bulky *syn*-7-methyl group (**7**).



7

Consequently, the large steric influence of the 7-methyl groups is not surprising. Perhaps the most unexpected feature is the observation that the two isomers are formed in an *exo*:*endo* ratio of only 1:3.5, indicating that the steric hindrance for addition in the *exo* direction is only moderately greater than the steric hindrance for addition in the *endo* direction.

Disiamylborane is a relatively hindered organoborane which is more sensitive than borane to the steric environment.[20] It readily adds to norbornene. How-

(8) Perhaps the word to be used is "treacherous." See (a) D. B. Braddon, G. A. Wiley, J. Dirlam,and S. Winstein, *J. Am. Chem. Soc.*, **90**, 1901 (1968); (b) S. Winstein, Abstracts, 21st National Organic Chemistry Symposium, Salt Lake City, Utah, 1969, p 152; (c) J. P. Dirlam and S. Winstein, *J. Am. Chem. Soc.*, **91**, 5906 (1969); (d) J. P. Dirlam and S. Winstein, *ibid.*, **91**, 5908 (1969).

(9) (a) A. F. Thomas and B. Willhalm, *Tetrahedron Lett.*, 1309 (1965); (b) J. M. Jerkunica, S. Borčić, and D. E. Sunko, *ibid.*, 4465 (1965); (c) A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Am. Chem. Soc.*, **89**, 68 (1967); (d) T. T. Tidwell, *ibid.*, in press.

(10) V. K. Varma, Ph.D. Thesis, 1967, Purdue University, Lafayette, Ind.

(11) H. C. Brown, J. H. Kawakami, and S. Ikegami, in preparation.

(12) H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Am. Chem. Soc.*, **89**, 1525 (1967).

(13) H. C. Brown and K.-T. Liu, *ibid.*, **89**, 466, 3898, 3900 (1967).

(14) For detailed reviews of electrophilic additions to olefins, with pertinent literature references, see R. C. Fahey in "Topics in Stereochemistry," N. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968; P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966; T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).

(15) H. C. Brown and J. H. Kawakami, *J. Am. Chem. Soc.*, **92**, 201 (1970).

(16) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).

(17) Many addition reactions of norbornene exhibit a similar marked preference for the *exo* face of the norbornyl structure. See G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

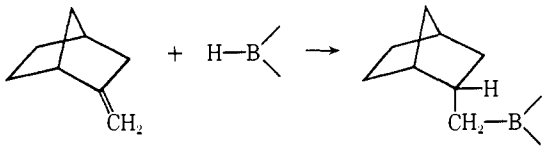
(18) H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *J. Am. Chem. Soc.*, **89**, 6381 (1967).

(19) P. von R. Schleyer, *ibid.*, **89**, 701 (1967).

(20) H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961).

ever, it failed to add to 7,7-dimethylnorbornene.[21] Consequently, toward hydroboration both the *exo* and *endo* directions of the double bond in 7,7-dimethylnorbornene are strongly hindered.[22]

The hydroboration of 2-methylenenorbornane also proceeds preferentially, 85%, from the *exo* direction[23]

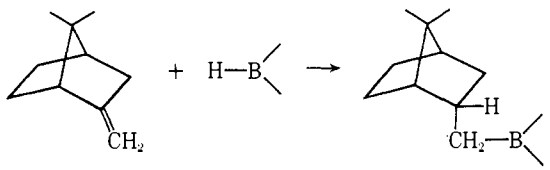


(3)

85%

(3). Hydroboration with disiamylborane is somewhat more selective, giving 91% *exo* addition. Hydrogenation over borohydride-reduced platinum[24] is somewhat less selective, giving 73% *endo*-2-methylnorbornane.[25]

On the other hand, hydroboration of 2-methylene-7,7-dimethylnorbornane (α-fenchene) takes place preferentially (85%) from the *endo* direction (4). Here, also, hydroboration with disiamylborane is somewhat



(4)

15%

more selective, giving 11% *exo* addition. Similarly, hydrogenation is less selective than hydroboration, giving 27% *exo* addition.[25]

Similar stereochemical results were realized with 1-methylnorbornene, 2-methylnorbornene, bornene, and ζ-fenchene (2,7,7-trimethylnorbornene). Consequently, these cases need not be discussed in detail.

The stereochemical results are summarized in Table I and pmr data for the olefins are summarized in Table II.

Table I. Hydroboration of Substituted Norbornenes

	exo Addition to substituted norbornenes, %		
	Borane[a]	Disiamylborane[b]	Hydrogenation[c]
Norbornene	99.5		
2-Methylenenorbornane	86.1,[d] 84.6[b]	91	73
7,7-Dimethylnorbornene	22		
α-Fenchene[e]	14.4,[b] 15.5[d]	11	27
1-Methylnorbornene	97		
Bornene	23.5		
2-Methylnorbornene	99.5[b]		97
ζ-Fenchene[f]	12,[b] 23		10

[a] Oxidation. [b] Protonolysis. [c] Reference 25. [d] Conversion of the alcohols to tosylates and reduction. [e] 2-Methylene-7,7-dimethylnorbornane. [f] 2,7,7-Trimethylnorbornene.

Table II. Pmr Data for Substituted Norbornenes[a]

	Vinyl, ppm[b]	Methyl, ppm[b]
Norbornene	5.95 t, J = 1.5 cps	
7,7-Dimethylnorbornene	5.90 t, J = 1.5 cps	0.90 s, 0.95 s
2-Methylenenorbornane	4.54 m, 4.80 m	
α-Fenchene	4.58 m, 4.80 m	0.98 s
1-Methylnorbornene	5.72 ud, 5.96 uq	1.33 s
Bornene	5.60 ud, 5.87 uq	0.73, 0.78 s, 1.0 s
2-Methylnorbornene	5.45 m	1.70 d, J = 2 cps
ζ-Fenchene	5.46 m	0.88 s, 0.96 s, 1.72 d, J = 2 cps

[a] The pmr spectra were on the Varian A60 in CCl_4 relative to tetramethylsilane. [b] The coupling patterns are triplet (t), doublet (d), multiplet (m), unsymmetrical doublet (ud), unsymmetrical quartet (uq), and singlet (s).

Conclusions

The very high stereochemical preference for *exo* hydroboration of norbornene, 200:1, is noteworthy, as is the very high *exo*:*endo* rate ratio, 715:1, observed for the base-catalyzed deuteration of norcamphor. It might be argued that, perhaps, these high stereoselectivities are exceptional, resulting from unusually high steric requirements for the reactants. However, we shall describe in later publications a number of other reactions of comparable stereoselectivities.[26] Consequently, the present results support the conclusion that the *exo* face of the U-shaped norbornyl structure is sterically far more open to attack by sterically demanding reagents than the hindered *endo* face.[18]

The fact that 7,7-dimethyl groups act to hinder tremendously concerted *exo* additions to the double bond is not unexpected. Reactions involving such additions place the adding moiety directly under the *syn*-7-methyl group. The unexpected feature is the evidence that such concerted additions are almost as badly hindered from the *endo* direction. Evidently, the rigid 5,6-ethylene bridge likewise provides a major steric handicap for *endo* additions to the double bond.

What should be the situation for reactions involving a single stage attack at the 2 position of the norbornane structure? Here, also, the *exo* position is clearly the position of preferred attack, as shown by the hydroboration results for 2-methylenenorbornane, the deuterium exchange results of Tidwell,[9d] and the halogenation results of Kooyman.[27]

What should be the effect of 7,7-dimethyl substituents on such reactions? In the past it has been assumed that such substituents will invariably cause the preferred course of the reaction to change from *exo* to *endo*. That is what is observed in the reaction of the ketones with complex hydrides, and it is also observed in the present hydroboration study. We believe that this will

(21) Over long periods of time a slow reaction occurs involving displacement of 2-methyl-2-butene from the reagent. For a related phenomenon, see H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Am. Chem. Soc.*, **86**, 397 (1964).

(22) In the reaction of phenyl azide with bicyclic olefins, a reaction which is believed to proceed through a similar concerted *cis* addition, norbornene reacts readily in a matter of hours to give the *exo* product, whereas 7,7-dimethylnorbornene failed to react over 14 days at 100°: K. Alder and G. Stein, *Ann.*, **515**, 185 (1935); P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libby, and G. P. Nowak, *J. Am. Chem. Soc.*, **87**, 306 (1965).

(23) Glpc analysis of the 2-methylol derivatives is difficult. In such cases we found it more convenient to analyze for the 2-methyl isomers. These were obtained either by protonolysis of the organoborane, or by oxidation to the methylol compound followed by reduction *via* the tosylate and lithium aluminum hydride, or both.

(24) C. A. Brown and H. C. Brown, *J. Org. Chem.*, **31**, 3989 (1966).

(25) H. M. Bell, Ph.D. Thesis, 1964, Purdue University, Lafayette, Ind.

(26) It should be pointed out that other reactions are known, especially involving free-radical additions, which exhibit lower stereoselectivities.[17]

(27) E. C. Kooyman, *Rec. Chem. Progr.*, **24**, 93 (1963).

be the effect of the 7,7-dimethyl substituents on reactions involving reagents of large steric requirements, requirements which bring them within the steric range of influence of the 7,7-dimethyl substituents.

However, suppose the reaction involves reagents of smaller steric requirements. We propose that in such reactions the attacking group may be far more influenced from the *endo* direction by the *endo*-6-hydrogen than it is by the *syn*-7-methyl. Such reactions should proceed preferentially *exo*. We have already called attention that reduction of camphor by borane gives a 50:50 distribution of *exo*:*endo* attack. Even more startling is the observation that the base-catalyzed deuteration of camphor shows an *exo*:*endo* rate ratio of 21. We now have many other reactions which reveal preferential *exo* attack in 7,7-dimethylnorbornyl derivatives in reactions not involving carbonium ion intermediates. Consequently, we believe that this new interpretation of the steric influence of 7,7-dimethyl substituents deserves an objective experimental test and we are proceeding to subject it to such testing.

Experimental Section

Analysis. All of the alcohols and hydrocarbons were analyzed on the Perkin-Elmer 226 or the 154 fitted with a flame ionization kit and a 150 ft × 0.01 in. stainless steel Golay column packed with the appropriate liquid phase.

Pmr Analysis. The spectra were run on the Varian A60, in carbon tetrachloride as solvent, using tetramethylsilane as an internal standard.

Procedure. The hydroborations were carried out at 0° using a slight excess of hydroborating agent. We observed small changes in the isomer distribution with larger excess of hydroborating agent, so we standardized on 10% excess. No significant change was observed in the isomer distribution with time (1–4 hr). Consequently, these must be the kinetically produced products.

Materials. The following were commercial products: norbornene, norcamphor, and *exo*-norbornanol (Aldrich Chemical Co.); isoborneol and octanoic acid (Matheson Coleman and Bell); *endo*-fenchol (K & K Laboratories); camphene (Hercules Powder Co.); tricyclene, mp 62.5°, from gas chromatographic separation of impurity in camphene (Columbia Chemicals Co.).

Preparation of Saturated Hydrocarbons. Brown□ hydrogenation[24] of the olefins and the Huang-Minlon modification of the Wolff–Kishner[28] reduction applied to the ketones were used to prepare the following hydrocarbons: 1-methylnorbornane, mp 21–22°, pmr methyl 1.1 ppm; 2-methylnorbornane (*exo* and *endo*), 97% *endo*, n^{20}D 1.4548 (lit.[29] n^{20}D 1.4549), pmr methyl 0.90 ppm (d, J = 6 cps); camphane (1,7,7-trimethylnorbornane), mp 150–151° (lit.[30] mp 156–156.5°); *endo*- and *exo*-2,3,3-trimethylnorbornane (73% *exo* and 27% *endo* from α-fenchene, n^{20}D 1.4625, and 90% *exo* and 10% *endo* from ζ-fenchene), n^{20}D 1.4630 (lit.[31] n^{20}D 1.4641); *exo*- and *endo*-β-fenchane from β-fenchene (5,5-dimethyl-2-methylenenorbornane), an impurity in α-fenchene; *endo*-β-fenchane from 15% γ-fenchene (2,5,5-trimethylnorbornene) in ζ-fenchene; fenchane, n^{20}D 1.4468 (lit.[32] n^{20}D 1.4471).

Preparation of Olefins and Tricyclic Hydrocarbons, 2-Methylenenorbornane, 2-Methylnorbornene, and 1-Methylnortricyclene. The potassium acid sulfate dehydration of 2-methyl-2-*endo*-norbornanol between 112 and 134° gave 69.3% 2-methylenenorbornane, 20.2% 2-methylnorbornene, and 10.5% 1-methylnortricyclene. Separation on a 24 in. Podbielniak column gave 1-methylnortricyclene, bp 108° (747 mm), n^{20}D 1.4548 (lit.[31] n^{20}D 1.4555); 2-methylnorbornene, bp 116° (747 mm), n^{20}D 1.4625 (lit.[33] bp 118° (760 mm), n^{20}D 1.4621), and 2-methylenenorbornane, bp 123° (747 mm), n^{20}D 1.4738 (lit.[34] n^{25}D 1.4719).

Bornene. Bornyl chloride from the hydrogen chloride addition to α-pinene[35] was eliminated with a 100% excess of potassium *t*-butoxide in dimethyl sulfoxide at 50° for 5 days to give a mixture of bornylene and bornyl chloride. Distillation through a 30-cm Vigreux column gave pure bornene, mp 111–112.5° (lit.[35] mp 112–112.5°).

α-, ζ-, and Cyclofenchene. The mixture of 82.5% α-, 7.8% cyclofenchene, 4.3% ζ-fenchene, and about 5.5% of a higher boiling unknown was prepared by the method of Hückel and Volkmann.[31] The distillate, n^{20}D 1.4732, was purified by preparative gas chromatography on 4 ft × 0.5 in. 20% tricresyl phosphate on 60–80 firebrick column to give in order of increasing retention time: cyclofenchene, n^{20}D 1.4511 (lit.[36] n^{20}D 1.4513); ζ-fenchene, n^{20}D 1.4595 (lit.[31] n^{20}D 1.4601); and α-fenchene, n^{20}D 1.4744 (lit.[31] n^{20}D 1.4742). Analysis with a squalane column at 80° indicated 98% pure α-fenchene and pmr analysis showed about 15% γ-fenchene in ζ-fenchene.

7,7-Dimethylnorbornene was prepared from camphenilone by a procedure described in another publication,[37] mp 45–46° (lit.[38] mp 38°).

Apocyclene was prepared from the hydrazone of camphenilone, mp 40–41° (lit.[39] mp 41–42°). It was 99% pure on UCON LB 550X at 70°.

5,5-Dimethylnorbornene was prepared by the method of Berson[40] by Professor D. E. McGreer.[41]

1-Methylnorbornene was from Professor P. von R. Schleyer, n^{20}D 1.4519.

Preparation of Bicyclic Alcohols. 2-Methyl-2-*endo*-norbornanol was prepared from the Grignard reaction, mp 29° (lit.[29] mp 34°).

2-Methyl-2-*exo*-norbornanol was prepared from the solvolysis of the tertiary *exo*-chloride from 2-methyl-2-*endo*-norbornanol, mp 81–82.5° (lit.[29] mp 80.5–82°).

5,5-Dimethyl-2-*exo*-norbornanol was prepared from the solvolysis of *endo*-camphenilol brosylate in 60% aqueous diglyme,[42] alumina chromatography, and preparative gas chromatography, mp 61.3–62.3° (lit.[43] mp 60–60.5°).

7,7-Dimethyl-2-*exo*-norbornanol was prepared as above, mp 142–143.5° (lit.[43] mp 141–142.5°).

Camphene hydrate was prepared by the basic hydrolysis of camphene hydrochloride, mp 151° (lit.[44] mp 151°).

Methylcamphenilol was prepared by the Grignard reaction on camphenilone, mp 112.5–114.5° (lit.[45] mp 118°).

Isoborneol and Borneol. Reduction of camphor with lithium aluminum hydride gave 10% borneol and 90% isoborneol.

Epiborneol and Epiisoborneol. Epiborneol, mp 191–192°, and epiisoborneol, mp 199.5–200°, were from Professor P. Hilsjarvi, University of Helsinki, Finland.

***exo*-Fenchol** was prepared from the reduction of fenchone with aluminum isopropoxide[46] and purified *via* its oxalate, mp 117.5° (lit.[46] mp 120–121°), alcohol 98% by glpc.

Typical Hydroboration–Oxidation Procedure.[47] To a 50-ml one-necked flask, fitted with a thermometer well, magnetic stirring bar, reflux condenser, and serum cap outlet, was added 20 mmoles of olefin and 20 ml of dry tetrahydrofuran. The mixture was cooled to 0° under nitrogen and 22 mmoles of hydride (33 mmoles for the more hindered olefins which form R_2BH) from a 1 *M* diborane–tetrahydrofuran solution was added over a 3-min period at 0–3°. After about 5 min the ice bath was removed and the reaction mixture stirred at 20–25° until the hydroboration was complete. The consumption of olefin was followed on a 3 ft × 0.25 in. di-*n*-decyl phthalate column on the Perkin-Elmer 154 by quenching the reaction with acetone and analyzing for unreacted olefin. When the reaction was complete, the excess hydride was destroyed by the careful addition of water or wet tetrahydrofuran. The organoboranes

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(43) S. Beckmann and R. Bamberger, *Ann.*, **574**, 76 (1951).
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(47) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

were oxidized to the alcohols with sodium hydroxide and hydrogen peroxide at 40° in 2 hr. After the reaction mixture was worked up, an internal standard was added and the mixture analyzed on the Perkin-Elmer 226 or 154D flame ionization model.

Typical Hydroboration–Protonolysis Procedure. To a 50-ml two-necked flask, fitted with a thermometer well, magnetic stirring bar, pressure-equalized addition funnel, reflux condenser, and serum cap outlet, was added 20 mmoles of olefin, 20 ml of dry diglyme or triglyme, and 5.5 (8.25) mmoles of sodium borohydride. With stirring, under nitrogen, at room temperature was added 7.33 g (11.0 mmoles) of boron trifluoride etherate in 3 ml of diglyme or triglyme in 15 min. (The larger quantities in parentheses were used for trisubstituted olefins which undergo hydroboration to the R_2BH stage.) The reaction was stirred at 20° until complete, the excess hydride destroyed with ethylene glycol, and 50 mmoles of octanoic acid was added and the flask fitted for a distillation. The mixture was heated at 160° (200°) (for 3–24 hr) until the distillation of the hydrocarbons stopped. Both the pot residue and distillate were analyzed for hydrocarbons after the addition of internal standards.

Hydroboration–Oxidation of Norbornene. The hydroboration mixture was oxidized after 95% hydride uptake in 3 hr at 0–5°. Analysis on UCON LB 550X (40–140° at 10°/min) indicated 99.5 ± 0.3% *exo*- and 0.5 ± 0.3% *endo*-norbornanol. Previous runs at room temperature gave the same results.

Hydroboration–Oxidation of 2-Methylenenorbornane. Conversion of the Alcohols to Tosylates and Reduction with Lithium Aluminum Hydride. The hydroboration–oxidation mixture was worked up, and the solvent evaporated. Then a stoichiometric amount (29 mmoles) of *n*-butyllithium in hexane was added to a 15-ml methylene chloride solution of the mixture of alcohols at such a rate as to maintain a fairly vigorous reflux. The lithium salt precipitates as it is formed. After a few minutes, 29 mmoles of toluenesulfonyl chloride in methylene chloride was added *via* a syringe, and the mixture stirred overnight at room temperature under nitrogen. (Actually only several hours are necessary for completion of the reaction.) Filtration of lithium chloride and evaporation of solvent gave the crude tosylate. To 1.46 g (5.35 mmoles) of tosylate in 2 ml of dry tetrahydrofuran at −78° was added 15 ml (10.5 mmoles) of a 0.7 *M* lithium aluminum hydride solution in THF. The 20-ml ampoule was sealed and heated at 50° for 6 hr. Decomposition of hydride and vpc analysis on UCON LB 550X (40–140° at 10°/min) indicated a 57% yield based on starting olefin of 86.1% of 2-*endo*- and 13.9% of 2-*exo*-methylnorbornane.

Hydroboration–Protonolysis of 2-Methylenenorbornane. In the protonolysis, the hydrocarbons started to distil after 3 hr at 160°. The distillation was continued until pure diglyme began to distil. Analysis as before indicated a 73% yield of 84.6% *endo*- and 15.4% *exo*-2-methylnorbornane.

Hydroboration–Oxidation of 7,7-Dimethylnorbornene. After 12 hr with 20% excess hydride for R_2BH at 0–25°, destruction of excess hydride at 0–3°, and oxidation, there was obtained an 84.5% yield of 20.8% *exo*- and 79.2% *endo*-7,7-dimethylnorbornanol from analysis on UCON LB 550X (100–140° at 10°/min). The vpc retention time on UCON LB 550X and Carbowax 20M of the minor hydroboration isomer corresponded to the major isomer in the aqueous solvolysis of *endo*-camphenilyl brosylate[42] and lithium aluminum hydride reduction of apocamphor.[48] The major isomer in hydroboration corresponded to the minor one in the hydride reduction of apocamphor. Repetition of the hydroboration with only a slight excess (10%) of hydride (R_2BH) gave 77.8% *endo* and 22.2% *exo* alcohol. However, when the hydroboration was carried out with a 46% excess of hydride at 0–5° for 1 hr and at 23° for 4 hr, a 76.3% yield of 73% *endo*- and 27% *exo*-7,7-dimethylnorborneol was obtained.

Hydroboration–Oxidation of α-Fenchene. Destruction of hydride after 12 hr and oxidation gave a 66% yield of 15.5% *endo*-7,7-dimethylnorbornanemethanol and 84.5% *exo*- on Carbowax 20M (100–140° at 10°/min). The reduction of the corresponding tosylates at 50° for 15 hr gave a 28% yield from starting olefin of 14.4% *endo*- and 85.6% *exo*-2,7,7-trimethylnorbornane. Comparison by glpc retention times indicated that the major isomer corresponded to the major isomer obtained in the hydrogenation of 2,7,7-trimethylnorbornene (ζ-fenchene) and α-fenchene. Also the minor isomer (14.4%) corresponded to the hydrocarbon obtained in the sodium borohydride trapping of the 2,7,7-trimethyl-2-norbornyl cation.[49] Analyses were performed on a 50-ft squalane–150-ft TCP at 80° with the following order of retention times: cyclofenchene, fenchane, ζ-fenchene (γ-fenchene), camphane (β-fenchene), β-fenchane, α-fenchene, *endo*- and *exo*-2,3,3-trimethylnorbornane.

Hydroboration–Protonolysis of α-Fenchene. After 3 hr at room temperature, 25 mmoles of octanoic acid was added to give 14 mmoles of hydrogen. This meant that only 4 mmoles of hydride was consumed by the olefin and 11 mmoles of octanoic acid was available for protonolysis. The reaction mixture was heated between 170 and 200° for 6 hr and analyzed to give a quantitative yield of 14.4% of *exo* and 85.6% of *endo* addition product based on reacted olefin.

Hydroboration–Oxidation of 1-Methylnorbornene. Analysis of the oxidation mixture on UCON LB 550X (120–140° at 10°/min) indicated 49.9% 2-*exo*-, 1.9% 2-*endo*-, 47.0% 3-*exo*-, and 1.2% 3-*endo*-1-methylnorbornanol or 97% *exo* and 3% *endo* addition.

Hydroboration–Oxidation of Bornene. With 23% excess hydride in 3 hr, there was obtained a 66% yield of 23% *exo* and 77% *endo* alcohol. This consisted of 12% isoborneol, 40% borneol, 11% epiisoborneol, and 37% epiborneol, analysis on UCON LB 550X, 10–140° at 10°/min. With 40% excess hydride in 7 hr, an 89% yield of 23.5% *exo* and 76.5% *endo* alcohols was obtained. When an 87% excess of hydride was used, an 85% yield of 26.8% *exo* and 73.2% *endo* alcohols was obtained in 5 hr. Authentic samples were obtained from Professor P. Hilsjarvi.

Hydroboration–Protonolysis of 2-Methylnorbornene. After 3 hr at 180° there was obtained 26.5% yield of 99.5% *endo*- and 0.5% *exo*-2-methylnorbornane. The hydroboration–oxidation reaction gave only one alcohol by glpc.

Hydroboration–Protonolysis of ζ-Fenchene. Heating at 200° for 3 hr and ~130° for 8.5 hr gave a 25% yield of 87.5% *exo*- and 12.5% *endo*-2,7,7-trimethylnorbornane. Protonolysis at 155–165° for 4 hr gave a 15% yield of 90% *exo*- and 10% *endo*-methyl hydrocarbons. The reaction mixture consisted of 64.8% products, 18.5% α-fenchene and β-fenchene, 8.1% ζ-fenchene, and 8.4% cyclofenchene. Isomerization of unreacted ζ-fenchene to α-fenchene occurred during protonolysis.

Hydroboration–Oxidation of ζ-Fenchene. A mixture of 85% ζ-fenchene and 15% γ-fenchene gave in 70% yield in 24 hr at 0–25°, 65.8% A, 19.7% B, and 14.5% C (UCON LB 550X, 60–140° at 10°/min). The pmr in CCl_4 indicated complex multiplets at 4.12 ppm for A and ~3.6 ppm for B and C for the proton adjacent to the hydroxyl group.

Oxidation of the Hydroboration Mixture with Chromic Acid. To a 10-ml pear-shaped flask fitted with a thermometer and a magnetic stirring bar was added 5 ml of ether and 0.290 g (1.88 mmoles) of the mixture of alcohols from the hydroboration of ζ-fenchene. A chromic acid solution was prepared from 5 g (17.5 mmoles) of sodium dichromate dihydrate (Technical grade) and 6.8 g (70 mmoles) of concentrated sulfuric acid, and diluted to 25 ml with water. Both the alcohol and the chromic acid solution were cooled to ~0° with a salt–ice bath. To the vigorously stirred solution was added 2.5 ml (100% excess) of the ice cold chromic acid solution at such a rate to keep the temperature ~0° (~5–10 min). After a total of 15 min at 0° sodium bisulfite was added to just destroy the excess chromic acid at ~0°. The addition of water and ether before the decomposition facilitated the stirring. (We have found that the separation of the ether and chromic acid layer after the addition of water and extraction of the acid layer several times with ether give good yields of ketone.) The ether layer was decanted from the chromium salts and washed with dilute sodium carbonate and water. Drying and evaporation of the solvent gave 0.33 g (100%) of a pale yellow liquid. Analysis indicates the presence of three ketones, 12.2% D and 87.8% E and F.

Reduction of Ketones D, E, and F. Lithium aluminum hydride reduction gave 3.7% A, 11.3% B, and 0.5% C. New alcohols of 13.0% G, 1.2% H, and 70.3% J were also obtained. The pmr of the mixture in CCl_4 indicated a sharp doublet at 3.75 ppm (J = 8 cps) for the major isomer J, indicating a *cis-exo* structure.[50] These results indicate 77% *endo* (A) and 23% *exo* (B) addition to ζ-fenchene.

Hydroboration–Protonolysis of 2-Methylenenorbornane with Disiamylborane. To a solution of 3.12 g (44 mmoles) of 2-methyl-2-butene ($n^{20}D$ 1.3876) and 0.624 g (16.5 mmoles) of sodium boro-

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hydride in dry diglyme was added 6.1 ml of 3.65 *M* boron trifluoride diglymate (22 mmoles) dropwise at 0°. After 2 hr, 2.08 g (21 mmoles) of methylcyclohexane, an internal standard, and 2.3 g (21.4 mmoles) of 2-methylenenorbornane were added. After 18 hr, 35 ml of dry propionic acid was added and the mixture refluxed for 4 hr. The acid was neutralized with sodium hydroxide pellets, and the mixture extracted with pentane. Analysis indicated an 88% yield of 91% 2-*endo*- and 9% 2-*exo*-methylnorbornane.

Hydroboration–Protolysis of α-Fenchene with Disiamylborane. After 18 hr at room temperature, 35 ml of dry propionic acid was added and the mixture refluxed for 12 hr. Analysis indicated a 95% yield of 89% *exo*- and 11% *endo*-2,7,7-trimethylnorbornane.

Evidence for Twisted Norbornanes. X-Ray Diffraction and Valence Force-Field Calculations[1]

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Abstract: A quantitative description of skeletal torsional angles of eleven norbornanes, camphanes, and norbornenes is presented. These geometrical details of the molecules from X-ray structure determinations are compared with those obtained by computer calculations (full relaxation molecular mechanics approach) of the same or of similar systems. It is shown that good quantitative agreement is achieved. Moreover, the experimental and calculated structures demonstrate unequivocally that substituted norbornanes and camphanes may adapt themselves to strain induced by certain substituents by two possible modes of twist in which the entire skeleton takes part. "*synchro*" twist occurs readily in the presence of substituents on C(2), C(3), C(5), or C(6). "*contra*" twist is mainly limited to molecules carrying a bulky group on C(1), and to camphanes. The *synchro* twisting of the norbornane skeleton may attain surprising magnitudes in suitable cases, depending on size, position, and orientation of substituent groups. For example, the difference between the torsional angles defined by carbon atoms 7,1,2,3 and 2,3,4,7, respectively, is zero in a structure possessing C_{2v} symmetry. In contrast, differences of 5–10° commonly occur in the molecules investigated. In 2-*endo*-3-*exo*-disubstituted norbornane, a difference as large as 14° was recorded. The twisting effect caused by substituents seems to be a more or less additive property. The important role of β atoms (not directly bound to the ring) is discussed.

Derivatives of norbornane have been used extensively as a testing ground for theories concerning chemical reactivity, nmr spin coupling phenomena, and numerous others. One of the main attractions of the norbornane system is its supposed rigidity. We wish to report our observations and calculations concerning the *torsional angles* of substituted norbornanes and camphanes that show conclusively that these bridged systems can subtly adapt themselves to strain induced by certain substituents, by demonstrating two different modes of twist.

An illustrative way to describe the results of the X-ray determinations and of the force-field calculations of structures is to consider the norbornane skeleton as being assembled from two cyclopentane rings, R and L, to give a boat-shaped six-membered ring, B (these basic rings are notoriously flexible). The designation of torsional angles is shown in Figure 1.

Methods

The requisite experimental torsional angles have been obtained by standard methods from available atomic coordinates of norbornanes,[4,5] camphanes[6] and norbornenes[7] as determined by X-ray crystallography or electron-diffraction methods. Thus far, no author has reported these interesting geometrical parameters. The published X-ray analyses[8] vary widely with respect to the accuracy attained and customary significance criteria were applied.[9] The torsional angles in a structure are said to differ significantly when their difference exceeds 2.6σ.

(1) Communicated in part at the Eighth International Congress of Crystallography, Stony Brook, N. Y., Aug 13–23, 1969, Abstract XIII-43; *Acta Crystallogr. Suppl.*, **A25**, 141 (1969).

(2) To whom correspondence should be addressed at the Chemical Laboratories of the University, Leiden, The Netherlands. Work carried out during a leave of absence from the University of Leiden.

(3) A Fulbright-Hays Travel Grant from the U. S. Educational Foundation in The Netherlands is gratefully acknowledged.

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(7) (a) *anti*-7-Norbornenyl *p*-bromobenzoate (**12**), A. C. MacDonald and J. Trotter, *ibid.*, **19**, 456 (1965); (b) *syn*-7-benzonorbornenyl *p*-bromobenzenesulfonate (**13**), T. Sato, M. Shiro, and H. Koyama, *J. Chem. Soc., B*, 935 (1968); (c) *anti*-8-tricyclooctyl *p*-bromobenzenesulfonate (**14**), A. C. MacDonald and J. Trotter, *Acta Crystallogr.*, **18**, 243 (1965); this compound does not possess a double bond but its geometrical properties, due to the presence of the three-membered ring, are related to those in the norbornenes rather than in the norbornanes; (d) norbormide, S. Abrahamsson and B. Nilsson, *J. Org. Chem.*, **31**, 3631 (1966); not used in the present work.

(8) A number of interesting structures reported in the literature unfortunately had to be ignored in the present work because the necessary atomic coordinates were withheld from publication.

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