measured (room temperature) at 272 mμ.[28] The absorbance generally decreased by about 60% during the acetolysis. For runs at higher temperatures, aliquots of tosylate solutions similarly prepared were heated individually in sealed ampoules. The rate constants were determined graphically.

B. Hydrolysis. The *p*-nitrobenzoates were hydrolyzed in 50% aqueous acetone (volume per cent before mixing) and the rates measured as previously described.[5b]

The kinetic data are summarized in Table III.

(28) M. L. Sinnott, *J. Org. Chem.*, **34**, 3638 (1969).

Preparative Solvolysis of 2-OPNB. The *p*-nitrobenzoate (83 mg) in 25 ml of 50% aqueous acetone containing 1.5 equiv of 2,6-lutidine was sealed in 2 test tubes under nitrogen and heated for 24 hr at 125°. The cooled solution was concentrated and the product (15 mg, 44%,) isolated by ether extraction was identified as **2**-OH by nmr comparison.

Acknowledgment. We are grateful for financial support from Eli Lilly and Company through an unrestricted research grant, the National Institutes of Health, and the A. P. Sloan Foundation.

Additions to Bicyclic Olefins. V. The Effect of 7,7-Dimethyl Substituents on the Stereochemistry and Rates of Cyclic Additions to Norbornenes

Herbert C. Brown,* James H. Kawakami,[1] and Kwang-Ting Liu[2]

Contribution from the Richard B. Wetherill Laboratory, Purdue University, Lafayette, Indiana 47907. *Received October 12, 1972*

Abstract: Various cyclic additions to norbornene (**1**) and 7,7-dimethylnorbornene (**2**) have been studied to determine the effects of 7,7-dimethyl substituents on the stereochemistry and rates of additions to norbornyl systems. The 7,7-dimethyls exerted very large steric hindrance to exo attack, equal to or even greater than the hindrance to endo attack arising from the endo-5,6-hydrogen atoms. Certain reactions, such as silver ion complexation, addition of nitrosyl chloride, and addition of dichlorocarbene, proceed quite satisfactorily with **1**, but fail with **2**, presumably because the attack of the adding moiety is severely hindered by both the 7,7-dimethyl groups and the endo-5,6-hydrogen atoms. Comparative rate studies of exo attack of **1** *vs.* **2** indicate substantial rate retardations for reactions involving exo addition *via* cyclic processes in such reactions as epoxidation (1000), hydroboration with 9-BBN (480), diimide reduction (950), and addition of benzenesulfenyl chloride (1820), whereas the retardation factor is smaller for additions not involving cyclic species, such as the free radical reaction of thiophenol (30). The importance of the steric influence of 7,7-dimethyl substituents is also revealed by the stereochemistry of addition. For all known additions to **1**, the adding moieties come in preferentially from the exo side. Even the introduction of 7,7-dimethyl substituents does not reverse this exo stereoselectivity for additions proceeding through noncyclic processes. Thus, the two-stage addition of thiophenol is 99.5% exo with **1**, and 95% exo with **2**. However, for additions involving three- and four-membered ring cyclic processes, the preference for exo reaction is not retained in **2**, presumably because of the large steric crowding by the 7,7-dimethyl groups. For instance, hydroboration of **1** with 9-BBN gives 99.5% *exo*-norbornanol (**11**) but only 3% of 7,7-dimethyl-*exo*-norbornanol (**15**) from **2**. Similarly, addition of benzenesulfenyl chloride to **1** gives nearly 100% *exo*-2-phenylthio-*endo*-3-chlorononorbornane *via exo*-episulfonium ion, but gives only 4% 7,7-dimethyl-*exo*-2-phenylthio-*endo*-3-chlorononorbornane *via* the *exo*-episulfonium ion from **2**. Diimide, however, adds exo to both **1** and **2**. This exception is attributed to the larger six-membered cyclic transition state which does not interact as strongly as the three- and four-membered rings with the *syn*-7-methyl group.

It is generally accepted that the exo side of the norbornyl system is less hindered than the endo side toward attack by a wide variety of reagents. Introduction of bulky substituents on the bridge carbon, such as the *gem*-7,7-dimethyl groups, has long been recognized as causing a reversal in the preferred direction of reaction, as in the preferred transfer of hydride from complex hydrides to the endo side of camphor.[3] On the other hand, solvolysis of 7,7-dimethylnorbornyl derivatives leads to predominant exo substitution, and it has been argued that this requires the intermediacy of a σ-bridged species,[4,5] which blocks reaction from the endo direction. However, recent data indicate that the large endo preference for nonsolvolytic reactions is not the rule, providing the steric requirements of the attacking reagent are not too large. For example, the reduction of camphor by lithium aluminum hydride proceeds with 92% endo attack,[6,7] whereas reduction with borane in tetrahydrofuran involves approximately equal attack from both directions.[8]

It therefore appeared desirable to investigate the

(1) Graduate research assistant on grants (G 19878 and GP 6492X) supported by the National Science Foundation.

(2) Postdoctoral research associate (1968–1970) on a grant (GP 6492-X) supported by the National Science Foundation.

(3) (a) M. Hanack, "Conformation Theory," Academic Press, New York, N. Y., 1965, pp 286–296; (b) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 302–306.

(4) J. A. Berson in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 123–133.

(5) (a) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Amer. Chem. Soc.*, 87, 378 (1965); (b) R. Howe, E. C. Friedrich, and S. Winstein, *ibid.*, 87, 379 (1965).

(6) S. Beckmann and R. Mezger, *Chem. Ber.*, **89**, 2738 (1956).

(7) H. C. Brown and H. R. Deck, *J. Amer. Chem. Soc.*, 87, 5620 (1965).

(8) H. C. Brown and V. Varma, *ibid.*, **88**, 2871 (1966).

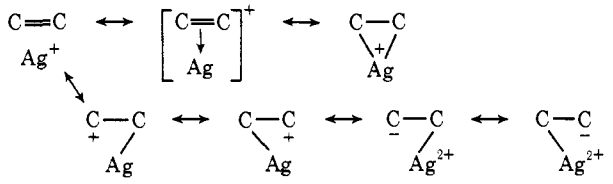
steric influence of the 7,7-dimethyl substituents more thoroughly. Accordingly, we undertook to study the comparative behavior of norbornene (**1**) and 7,7-dimethylnorbornene (**2**) in a number of representative

1 2

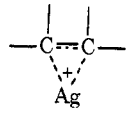
addition reactions. The details on additions involving cyclic processes will be presented in this paper.

Results

Silver Ion Complexation. It is well known that silver salts form π complexes with olefins. The structure of the π complex with an isolated carbon–carbon double bond has been considered as a resonance hybrid of the following contributing structures.[9] Therefore, it may

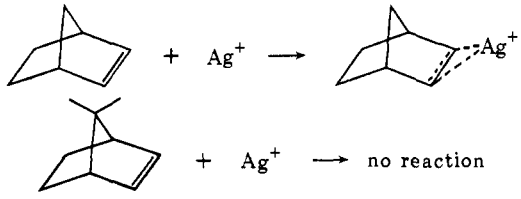


be represented as a cyclic formula, **3**, in which the bonds

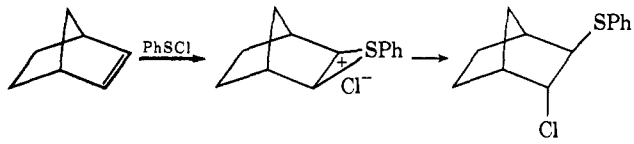


3

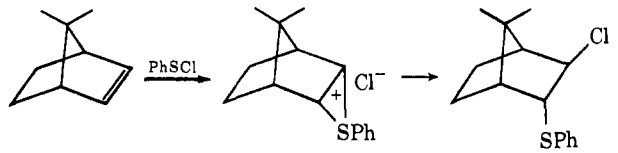
are looser than those in an onium species. Norbornene forms a very stable complex with silver nitrate,[10] presumably from the exo side. The complex formation can be demonstrated by a convenient glpc method. The retention time for **1** increased from 7.0 to 35.1 min in changing from an ethylene glycol column to silver nitrate–ethylene glycol column. On the other hand, the retention time for norbornane (**4**) remained unchanged with the two columns (5.9 min). However, both **2** and 7,7-dimethylnorbornane (**5**) exhibited identical retention time on the ethylene glycol column (10.3 min) and on the silver nitrate–ethylene glycol column (10.9 min) under the same conditions. Obviously, **2** fails to exhibit the slightest coordination with silver ion from either the exo or endo side.



Addition of Benzenesulfenyl Chloride. The addition of benzenesulfenyl chloride to olefins is considered to proceed *via* an episulfonium ion intermediate.[11] Norbornene was allowed to react with an equimolar amount of benzenesulfenyl chloride at −20 to −25° in methylene chloride solution containing a small amount of calcium carbonate.[12] The exclusive formation of the trans adduct, *exo*-2-phenylthio-*endo*-3-chlorononorbornane (**6**), through displacement by chloride ion on the *exo*-episulfonium ion, is established by the pmr spectrum,[13] and chemical transformations.[14,15] It was reported that the trans addition of the reagent to **2** afforded the *exo*-2-phenylthio-*endo*-3-chloro adduct with 85% selectivity.[12] However, hydrodechlorination of the purified adduct (mp 42.5–43°) with triphenyltin hydride gives 7,7-dimethyl-*endo*-norbornyl phenyl sulfide (**7**, *vide infra*).[14] Consequently, the major product obtained from the addition of benzenesulfenyl chloride to **2** must be 7,7-dimethyl-*endo*-2-phenylthio-*exo*-3-chloronorbornane (**8**) *via* the *endo*-



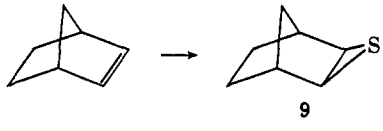
6



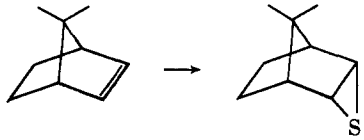
8

episulfonium ion intermediate. The yield of **8** was over 80%, as estimated by pmr using acenaphthene as internal standard. Hydrodechlorination of the crude adduct yields 7,7-dimethyl-2-norbornyl phenyl sulfides (**12** and **7**) with an exo/endo ratio of 4:96.

The addition of arenethiosulfenyl chloride to **1** and **2** followed by treatment with sodium amide or sulfide is reported to give 65% of *exo*-2,3-epithionorbornane (**9**). In contrast, **2** gave 50% of *endo*-2,3-epithio-7,7-dimethylnorbornane (**10**).[16] Apparently, the stereochemistry of the addition of arenethiosulfenyl chloride is controlled by the 7,7-dimethyl substituents in the same manner as the addition of benzenesulfenyl chloride.



9



10

The competitive addition of benzenesulfenyl chloride to **1** and **2** was also studied. The products were hydrodechlorinated with triphenyltin hydride and the composition of the mixed phenyl sulfides was determined

(9) (a) H. J. Lucas, R. S. Moore, and D. Pressman, *J. Amer. Chem. Soc.*, **65**, 227 (1943); see also G. W. Wheland, "Advanced Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1960, p 166 ff; (b) C. F. Wilcox, Jr., and W. Gaal, *J. Amer. Chem. Soc.*, **93**, 2453 (1971).

(10) M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962).

(11) W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, **8**, 482 (1969), and literature cited therein.

(12) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2075 (1968).

(13) W. H. Mueller and P. E. Butler, *ibid.*, **88**, 2866 (1966).

(14) H. C. Brown and K.-T. Liu, *ibid.*, **92**, 3502 (1970).

(15) For pioneer work on the addition of *p*-toluenesulfenyl chloride, see S. J. Cristol, *et al.*, *ibid.*, **79**, 6035 (1957).

(16) T. Fujisawa and T. Kobori, Abstracts, 23rd International Congress of Pure and Applied Chemistry, 1971, No. 125, p 51.

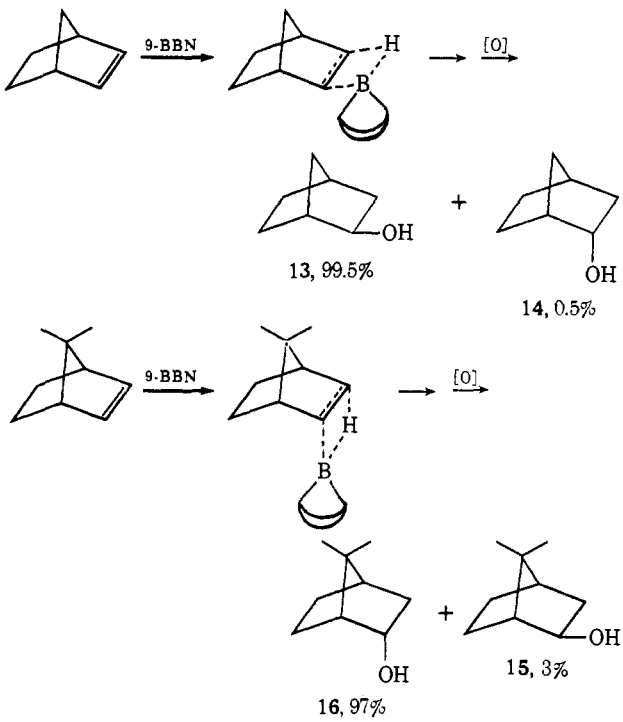
with glpc. The relative rate of exo addition to **1** and **2** could be estimated from the amount of *exo*-norbornyl phenyl sulfide (**11**) and of 7,7-dimethyl-2-norbornyl phenyl sulfide, **12** and **7**. The results are shown in Table I.

Table I. Competitive Addition of Benzenesulfenyl Chloride to Norbornene and to 7,7-Dimethylnorbornene

1, mmol	2, mmol	PhSCl, mmol	11/(12 + 7)	k_r[a]
0.50	2.00	0.50	9.84	1850
0.50	0.80	0.50	22.8	1800

[a] $k_r = k_{exo\text{-norbornyl}}/k_{7,7\text{-dimethyl-}exo\text{-norbornyl}}$.

Hydroboration with 9-BBN. The hydroboration reaction is believed to proceed through a concerted four-center addition of the boron–hydrogen bond to the carbon–carbon double bond of the olefin.[17] Hydroboration–oxidation of **1** gives 99.5% of *exo*-norbornanol (**13**) and 0.5% of *endo*-norbornanol (**14**) with either borane[18] or 9-BBN[19] as the hydroboration agent. With **2** borane yields 22% of 7,7-dimethyl-*exo*-norbornanol (**15**) and 78% of the 7,7-dimethyl-*endo*-norbornanol (**16**).[18] However, with an equivalent



amount of 9-BBN at room temperature for 1 day, **2** reacts to give only 3% of **15** and 97% of the endo **16**.

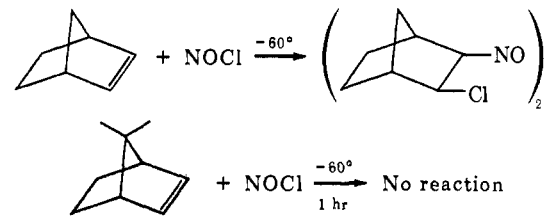
The relative rate of exo addition to **1** and **2** was determined by glpc using a competitive procedure. The pertinent data are shown in Table II.

Addition of Nitrosyl Chloride. The addition of nitrosyl chloride to **1** proceeds readily even at −60°. Introduction of nitrosyl chloride into a chloroform solution of **1** results in the instantaneous formation of nitrosochloride, as indicated by the appearance of a blue-green color.[20,21] The adduct was isolated as a white solid with a melting point and spectral data in good agreement with the properties ascribed to the 2-chloro-3-nitrosonorbornane dimer.[20,21] Under the same conditions **2** fails to react, even over considerably extended periods of time, which is consistent with the previously proposed four-center addition mechanism.[20]

Table II. Competitive Addition of 9-BBN to Norbornene and 7,7-Dimethylnorbornene

1, mmol	2, mmol	9-BBN, mmol	(13 + 14)/(15 + 16)	k_r[a]
0.744	0.836	0.54	7.9	440
0.447	0.621	0.42	6.0	520

[a] See footnote of Table I.



Diimide Reduction. The stereospecific cis reduction of olefins with diimide has been generally accepted as involving cyclic addition from the less hindered side.[22] Norbornene is very reactive toward diimide, the most reactive compound among nearly 40 cyclic, exocyclic, and acyclic olefins.[23] The stereochemistry of addition to **1** and substituted norbornenes is exo-cis.[24,25] Diimide may be generated *in situ* from potassium azodicarboxylate in methanol–acetic acid at room temperature.[24] With 50% excess of this reagent, **1** gave a quantitative yield of **4** in a matter of minutes. However, **2** reacted to give **5** only sluggishly.

The stereochemistry of addition was assigned by examination of the pmr spectra of the dideuteriodiimide reduction products. The pmr spectrum of dideuterionorbornane exhibited a broad singlet at δ 2.20 ($W_{1/2}$ = 6 Hz, 2 H) for the bridgehead protons, an apparent doublet with fine splittings at δ 1.5 (J = 9 Hz, 2 H) for the exo protons, and a complex pattern from δ 1.0 to 1.3 (6 H) for the remaining four endo protons and the two bridge protons, identical with the pmr spectrum of the *exo,exo*-2,3-dideuterionorbornane obtained from deuterioboration–deuteronolysis.[26] The pmr spectrum of **5** displayed a broad doublet at δ 1.78 (J = 8 Hz, 4 H) for the exo protons, an apparent triplet at δ 1.52 (J = 3.5 Hz, 2 H) for the bridgehead protons, a broad doublet at δ 1.17 (J = 8 Hz, 4 H) for the endo protons, and a sharp singlet at δ 0.98 (6 H)

(17) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 2544 (1961).
(18) H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 1990 (1970).
(19) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5281 (1968).
(20) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **85**, 2513 (1963); **87**, 4074 (1964).
(21) J. B. Miller, *J. Org. Chem.*, **26**, 4905 (1961).
(22) For reviews, see S. Hünig, H. R. Muller, and W. Thier, *Angew. Chem., Int. Ed. Engl.*, **4**, 271 (1965); C. F. Miller, *J. Chem. Educ.*, **42**, 254 (1965).
(23) E. W. Garbish, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Specher, *J. Amer. Chem. Soc.*, **87**, 2932 (1965).
(24) W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *ibid.*, **89**, 410 (1967).
(25) R. G. Weiss and E. I. Snyder, *J. Org. Chem.*, **35**, 1627 (1970).
(26) H. C. Brown and K. J. Murray, *ibid.*, **26**, 631 (1961). The correctness of the signal assignment was ensured by its agreement with a recent report; see A. P. Marchand and N. W. Marchand, *Tetrahedron Lett.*, 1365 (1971).

for the methyl protons. For the dideuterio derivative, **5**-d_2, the relative intensity of the exo protons at δ 1.78 decreased to about 2.1 H, whereas the other protons remained the same. Furthermore, the pattern of endo protons into a broad singlet overlapped on a broad doublet; obviously the geminal coupling with exo protons was partially eliminated. Mass spectral analysis indicated **5**-d_2 was 91% isotopically pure (83.2% d_2 and 17.7% d). Clearly, the addition is preponderantly exo-cis as in the case of **1**. However, in spite of the exo preference in **2**, competitive studies revealed that the relative rate of addition was large, approximately 950 (Table III).

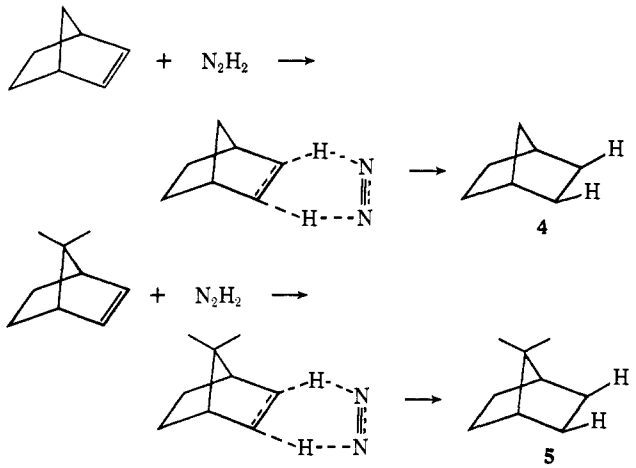
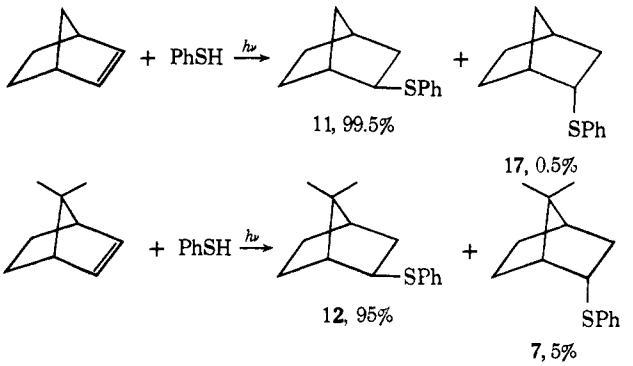


Table III. Competitive Addition of Diimide to Norbornene and to 7,7-Dimethylnorbornene

1, mmol	2, mmol	N_2H_2 mmol	4/1	2/5	k_r[a]
0.30	0.60	0.30	2.53	624	780
0.51	0.60	0.50	1.83	1174	1120

[a] See footnote of Table I.

Free-Radical Addition of Thiophenol. It has been demonstrated that the mechanism of free-radical addition of thiocresol to **1** involves only classical radical intermediates.[27] Thiophenol behaves like *p*-thiocresol,[28,29] and it adds exo-cis to **1**.[29] The addition of thiophenol to a mixture of **2** and apocyclene at 80° also produces the *exo*-phenyl sulfide.[30] However, the precise stereoselectivity, the exo/endo ratio, has not been elucidated in either case. In the present study, the photocatalyzed free-radical addition of thiophenol to **1** and **2** in hexane was carried out under kinetic controlled conditions. At 0°, the addition to **1** gave greater than 99.5% of **11** and less than 0.5% of *endo*-norbornyl phenyl sulfide (**17**). The product from **2** contained 95% of **12** and 5% of **7**. The constant exo/endo ratio with time and changing thiophenol concentration indicated that the addition step was irreversible at 0°.[31]



The ratio was determined by glpc by direct comparison with authentic samples. Authentic **17** was prepared by the SN2 reaction on *exo*-norbornyl brosylate with lithium thiophenoxide in dimethylformamide at room temperature, and authentic **12** was similarly prepared from 7,7-dimethyl-*endo*-norbornyl brosylate at 100°. SN2 reaction on 7,7-dimethyl-*exo*-norbornyl brosylate yielded a mixture of phenyl sulfides. Nevertheless, **7** could be obtained from hydrodechlorination of **8** followed by preparative glpc. Pmr spectra of all the four phenyl sulfides are consistent with the assigned structure (Table IV).

Table IV. Pertinent Pmr Data of Norbornyl Phenyl Sulfides and 7,7-Dimethylnorbornyl Phenyl Sulfides[a]

Sulfide	δ(α-H)	$\delta(CH_3)$
11	3.11 (ddd, J = 1.5, 4.9, 7.8 Hz)[b]	
17	3.45 (m)	
12	3.11 (dd, J = 6.5, 9 Hz)[b]	1.25, 0.95
7	3.78 (m)	1.04, 1.00

[a] Chemical shifts in ppm downfield from TMS in carbon tetrachloride solution; ddd, doublet of doublet of doublet; dd, doublet of doublet; m, multiplet. [b] First-order splitting assumed.

The relative rate of exo addition was also measured. Thiophenol was added to a mixture of **1** and **2** in hexane at 0°. After being irradiated with uv light for 10 min, the product was analyzed by glpc. The results are summarized in Table V.

Table V. Competitive Addition of Thiophenol to Norbornene and 7,7-Dimethylnorbornene

1, mmol	2, mmol	PhSH, mmol	(11 + 17)/(7 + 12)	k_r[a]
0.463	0.531	0.250	18.3	31.4
0.322	0.569	0.200	10.4	28.5

[a] See footnote of Table I.

Addition of Dichlorocarbene. Dichlorocarbene adds to **1** to form *exo*-3,3-dichlorotricyclo[3.2.1.$0^{2,4}$]octane.[32] A study of the addition of dichlorocarbene to **1** and **2** was also undertaken. The dichlorocarbene was generated from the potassium salt of triethylcarbinol and chloroform at 0°.[33] By the use of acenaphthene as

(27) G. D. Brindell and S. J. Cristol in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, Elmsford, N. Y., 1961, Chapter 13.
(28) J. A. Claisse, D. I. Davies, and D. K. Alden, *J. Chem. Soc. C*, 1498 (1966).
(29) D. I. Davies, L. T. Parifitt, C. K. Alden, and J. A. Claisse, *ibid.*, 1585 (1969).
(30) D. I. Davies and P. J. Rowley, *ibid.*, 1832 (1968).
(31) (a) C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, **81**, 1144 (1959); (b) N. P. Neureiter and F. G. Bordwell, *ibid.*, **82**, 5354 (1960); (c) R. H. Pallen and C. Sivertz, *Can. J. Chem.*, 35, 723 (1957).
(32) (a) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963); (b) R. C. DeSelms and C. M. Combs, *ibid.*, **28**, 2206 (1963).
(33) H. C. Brown and R. H. Prager, unpublished research.

internal standard, pmr revealed that **1** had reacted to about 30%, whereas **2** had remained unchanged.[34]

Discussion

Tables VI and VII assemble the results covered in the present study as well as previous work on epoxidation,[35] hydrogenation over borohydride-reduced platinum catalyst,[36] addition of phenyl azide,[37] chlorosulfonyl isocyanate,[38] and arenethiosulfenyl chloride.[16] The stereochemistry of additions are summarized in Table VI. The relative rates of exo addition are summarized in Table VII.

Table VI. Stereochemistry of Additions to Norbornene and 7,7-Dimethylnorbornene

	1		2	
Addend	Exo attack, %	Endo attack, %	Exo attack, %	Endo attack %
B_2H_6[a]	99.5	0.5	22	78
9-BBN[b]	99.5	0.5	3	97
Peracid[c]	99.5	0.5	12	88
H_2[d]	90	10	10	90
PhSCl[b]	~100		4	96
ArSSCl[e]	65			50[f]
N_2H_2[b]	~100		~100	
PhSH[b]	99.5	0.5	95	5
Ag^+ [b]	~100		N.R.	
NOCl[b]	~100		N.R.	
CCl_2[b]	~100		N.R.	
PhN_3[g]	~100		N.R.	
$ClSO_2NCO$[h]	~100		N.R.[i]	

[a] Reference 18. [b] Present study. [c] Reference 35. [d] Reference 36. [e] Reference 16. [f] These data refer to the isolated yield of product. No details on the formation of other isomers, presumably of either very low yield or not formed, are given. [g] Reference 37. [h] Reference 38. [i] Addition to 1,7,7-trimethylnorbornene.

Table VII. Relative Rates of Exo Additions to Norbornene and 7,7-Dimethylnorbornene

Addend	k_r[a]
Peracid[b]	1000
N_2H_2[c]	950
PhSCl[c]	1820
9-BBN[c]	480
PhSH[c]	30

[a] $k_{exo\text{-norbornyl}}/k_{7,7\text{-dimethyl-}exo\text{-norbornyl}}$. [b] Reference 35. [c] Present study.

Obviously, the introduction of 7,7-dimethyl substituents to norbornene exerts very large effects upon both the rates and stereochemistry of cyclic additions, *i.e.*, additions involving cyclic transition states or intermediates.[39] The relative rate of exo additions to **1** and **2**, $k_{exo\text{-norbornyl}}/k_{7,7\text{-dimethyl-}exo\text{-norbornyl}}$ (k_r), is very high, 480–1820, for cyclic additions such as epoxidation, hydroboration, diimide reduction, and addition of benzenesulfenyl chloride. On the other hand, for noncyclic additions, *i.e.*, additions involving "open" transition states or intermediates,[39] the relative rate ratio is comparatively low. For instance, k_r is 30 for addition of thiophenol and is only 2.2 for hydrochlorination.[39] Moreover, other cyclic additions like silver ion complexation, addition of nitrosyl chloride, addition of dichlorocarbene, addition of phenyl azide, and addition of chlorosulfonyl isocyanate occur readily with **1** but fail with **2**. This remarkable change from very high reactivity for **1** to inertness for **2** has not been observed for any known noncyclic addition.

In the case of cyclic additions involving three- and four-membered addenda, the presence of the 7,7-dimethyl substituents reverses the stereochemistry realized in norbornene itself, whereas the stereochemistry of noncyclic additions is not altered in any case now known. Thus, hydroboration, epoxidation, hydrogenation, and addition of benzenesulfenyl chloride proceed preferentially exo in **1**, but endo in **2**. Noncyclic additions, such as addition of thiophenol and hydrochlorination,[40] exhibit exo selectivity in both **1** and **2**. It must be concluded that the steric influence of the 7,7-dimethyl substituents must be much larger for cyclic processes involving three- and four-membered addenda than for two-state noncyclic addition processes.

There is general agreement that the consistent exo preference exhibited by various reactions of the norbornyl and norbornenyl systems largely results from the steric crowding of the endo side attributed predominantly to the endo-5,6-hydrogen atoms.[3,41] The exo side of norbornene is much less crowded, so that attack occurs primarily from this direction.

The presence of a bulky methyl substituent on the bridge carbon atom, syn to the double bond, modifies the steric environment. Obviously, the exo side becomes more crowded sterically and the substituent will exert steric hindrance toward reagents that attack the 2 and 3 positions. Consequently, two-stage additions to **2** will involve steric interactions of the attacking reagent with the *syn*-7-methyl group or with the endo-5,6-hydrogen atoms. In the past it has been assumed that the interactions with the *syn*-7-methyl group will always dominate the situation, forcing the reagent to add from the endo direction.[4,5] No differentiation was made between reagents of small or large steric requirements adding through cyclic or noncyclic processes. We believe that the results now available make it clear that the early interpretation represents an oversimplification.

Let us consider additions to **1** and **2** involving reactions which proceed through noncyclic processes. In such cases the reagents will attack at the corners, C-2 or C-3, of the norbornyl skeleton. Related to such additions will be substitution reactions of norbornane **4** and 7,7-dimethylnorbornane **5** and additions to norbornanone and 7,7-dimethylnorbornanone.

For the parent norbornyl system, the exo side is

(34) It was reported that halocarbenes also fail to react with 1,7,7-trimethylnorbornene: C. W. Jefford, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstract FLUO-4.

(35) H. C. Brown, S. Ikegami, and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 6914 (1970).

(36) H. M. Bell, Ph.D. Thesis, Purdue University, 1964.

(37) K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **501**, 1 (1933). The authors report that 7,7-dimethyl- and 1,7,7-trimethylnorbornene do not give a cycloadduct with phenyl azide in 0.5 year at 20°, nor in 14 days at 100°, nor in 4 days at 140°. This failure to add was attributed to steric hindrance by the *syn*-7-methyl: K. Alder and G. Stein, *ibid.*, **515**, 185 (1935). Pertinent data for addition of phenyl azide in carbon tetrachloride are described by R. Huisgen, G. Szeimies, and L. Möbins, *Chem. Ber.*, **100**, 2492 (1967): norbornene, 188; cyclopentene, 1.86; bicyclo[2.2.2]octene, 0.90; cyclohexene, 0.033.

(38) E. J. Moriconi and W. C. Crawford, *J. Org. Chem.*, **33**, 370 (1968).

(39) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **93**, 7335 (1971).

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

(41) T. G. Traylor, *Accounts Chem. Res.*, 2, 152 (1969).

clearly far less sterically crowded than the endo side. Irrespective of whether the reagent has large or small steric requirements, attack from the exo direction will be preferred. The presence of a *syn*-7-methyl group alters this situation. It is our thesis that for such two-stage additions involving attack at the corner, C-2 or C-3, of the norbornyl skeleton, the relative magnitude of the steric interactions causing the reaction to proceed preferentially from the exo or endo direction may well depend upon the steric requirements of the reagent. Thus, for a bulky reagent, steric interactions between the *syn*-7-methyl group and the reagent from the exo direction may be considerably larger than the interactions between the endo-5- or 6-hydrogen atom and the reagent on the endo side, directing the reaction to proceed from the endo direction.[42] On the other hand, for a reagent of small steric requirements, steric interactions with the *syn*-7-methyl group may well be smaller than the interaction with the endo-5- or -6-hydrogen atom. In such a case, the reaction can still exhibit a preference for exo.

Grignard reagents and complex hydrides exhibit the properties of reagents of large steric requirements. The exo direction of attack in norbornanone is inverted in 7,7-dimethylnorbornanone. Thus, the reaction of methylmagnesium iodide with 7,7-dimethylnorbornanone gives 97% of the endo adduct,[43] and lithium aluminum hydride reduction yields 90% exo alcohol (**15**) *via* endo attack.[5b,6] However, as the steric requirements of the reagent decrease, the amount of exo attack increases. For example, the exo reduction of camphor increases from 1% with lithium trimethoxyaluminohydride, to 8% with lithium aluminum hydride, to 14% with sodium borohydride,[44] and to about 50% with borane.[8] Moreover, the application of other reagents, presumably of smaller steric requirements, can cause the reaction to take place preferentially from the exo direction, even in the presence of 7,7-dimethyl substituents. Examples are deuterium exchange of camphor,[45,46] decomposition of 7,7-dimethylnorbornanone tosylhydrazone,[47] reaction of 7,7-dimethylnorbornyl radical,[48] elimination of 7,7-dimethylnorbornyl tosylate,[49] dehydration of 2-phenylisoborneol,[50] and noncyclic additions such as hydrochlorination,[51] hydrotrfluoroacetoxylation,[52] and the radical addition of thiophenol to **2**. The degree of exo selectivity obviously depends upon the nature of the specific reaction and of the attacking reagent.

Let us now consider reactions involving cyclic transition states or intermediates. It is convenient to discuss separately such reactions involving small (three- or four-membered) ring addenda, and those involving larger ring addenda, such as diimide reduction. For additions proceeding through cyclic processes involving such small rings, it is quite clear from models that the steric interactions of the syn methyl substituent with the cyclic addenda must be enormous. Consequently, it is not surprising that the presence of 7,7-dimethyl substituents has an enormous rate-retarding effect on such addition reactions; they either direct the addition to proceed predominantly endo, or cause the reaction to fail.

For example, hydroboration, epoxidation, hydrogenation, and the addition of benzenesulfenyl chloride proceed preferentially exo with **1**, attributed to the larger hindrance of the endo-5,6-hydrogen atoms, but endo with **2**, attributed to the greater steric retardation by the 7,7-dimethyl groups to the cyclic moiety. The endo preference in **2** increases with the increasing steric requirements of the addenda. Thus, hydroboration gives 78% endo alcohol **16** with borane and 97% with 9-BBN. In the case of other reagents proceeding through cyclic processes of this kind, such as phenyl azide, dichlorocarbene, nitrosyl chloride, silver ion, and chlorosulfonyl isocyanate, the reactions proceed readily with **1**, but fail with **2**. In these cases, the steric effects involving the adding moiety and the 7,7-dimethyl groups or the endo-5,6-hydrogen atoms must be sufficiently large so as to prevent the addition from taking place from either the exo or the endo direction.

As the ring size of the cyclic adduct becomes larger, the greater flexibility of the larger ring should diminish considerably the steric interactions with the *syn*-7-methyl substituent. Although steric interactions from the endo direction should also be decreased, an examination of models suggests that the latter should be less important than the former. Consequently, with larger rings we may anticipate a tendency to return to exo addition in **2** even for cyclic processes. This is observed for the diimide reaction, which proceeds with great difficulty with **2**, as compared to **1**, but exhibits exo preference in both cases. The diimide reaction involves a six-membered cyclic transition state,[22] whereas the other reactions previously discussed involve three- and four-membered cyclic transition states or intermediates.

Since completion of this study, we have learned from Professor Rolf Huisgen that in unpublished work,[53] the addition of diphenylnitrilimine to norbornene is >300 times faster for exo addition than for endo. For benzonitrile oxide, the exo preference is >100. The yields of cycloadducts are quantitative. 7,7-Dimethylnorbornene reacts much slower. However, exo adducts were still formed in yields of 26 and 34%, respectively.

Consequently, the present evidence would indicate

(42) The present discussion is restricted to alkyl substituents in the 7 position. It is apparent that the introduction of polar substituents, especially those with donor characteristics, such as the hydroxyl or alkoxyl groups, can exert effects which can influence and even alter the situation. Thus, coordination with an electrophilic reagent can occur, leading to selective reaction from the exo direction, in spite of the steric requirements of the substituent: B. Franzus, W. C. Baird, Jr., E. I. Snyder, and J. H. Surridge, *J. Org. Chem.*, **32**, 2845 (1967); W. C. Baird, Jr., and M. Buza, *ibid.*, **33**, 4105 (1968); **29**, 160 (1964). For a detailed discussion of the importance of the polar characteristics of 7,7-dichloro substituents on the stereochemistry of addition reactions of 1,2,3,4,7,7-hexachloronorborna-2,5-diene, see D. I. Davies, P. Mason, and M. J. Parrott, *J. Chem. Soc. C*, 3429 (1971). However, alkyl groups are essentially "nonpolar," incapable of coordinating with the usual electrophilic species. Consequently, the above phenomenon should not be a factor in the reactions examined in this study.

(43) H. C. Brown and S. Ikegami, *J. Amer. Chem. Soc.*, **90**, 7122 (1968).

(44) H. C. Brown and J. Muzzio, *ibid.*, **88**, 2811 (1966).

(45) A. F. Thomas, R. A. Schneider, and J. Meinwald, *ibid.*, **89**, 68 (1967).

(46) T. T. Tidwell, *ibid.*, **92**, 1448 (1970).

(47) K.-T. Liu and R. S. Shapiro, *J. Chin. Chem. Soc. (Taipei)*, **16**, 30 (1969).

(48) P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Helgeson, *Accounts Chem. Res.*, **3**, 177 (1970).

(49) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **92**, 200 (1970).

(50) J. C. Coxon, M. P. Hartshorn, and A. J. Lewis, *Chem. Ind. (London)*, 1145 (1970).

(51) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **89**, 3900 (1967).

(52) H. C. Brown, J. H. Kawakami, and K.-T. Liu, *ibid.*, **92**, 3816 (1970).

(53) W. Fliege, Ph.D. Thesis, University of Munich. We wish to express our appreciation to Professor Rolf Huisgen for calling this study to our attention.

that even for cyclic processes the 7,7-dimethyl substituents control the stereochemistry of addition rigorously only for reactions proceeding through three- and four-membered ring addenda. In the case of larger ring addenda, with five, six, and presumably more members, exo addition can occur even in the presence of 7,7-dimethyl substituents.

Clearly, the original belief that in the absence of σ bridging 7,7-dimethyl substituents must invariably divert the stereochemistry of reaction of norbornyl systems from exo to endo[4,5] is no longer tenable.

Conclusion

It would be desirable to have available objective criteria to help decide whether certain addition reactions involve cyclic processes or two-stage noncyclic processes.[41] It now appears that an examination of the addition reaction with norbornene (**1**) and 7,7-dimethylnorbornene (**2**) can contribute to a decision on the precise mechanism.

Thus, the data presently available indicate that the rates of all additions to norbornene involving cyclic processes are very strongly retarded by the presence of 7,7-dimethyl substituents, much more so than are addition reactions proceeding through noncyclic processes. Moreover, all known additions which proceed unambiguously through three- or four-membered ring moieties are altered in their stereochemistry from exo to endo by the presence of 7,7-dimethyl substituents, or the reactions fail to proceed.[54]

Consequently, one must question the importance of cyclic transition states which have been utilized to interpret the mechanism of oxymercuration,[55,56] hydrochlorination, and hydroacetoxylation[56] of norbornene and 7,7-dimethylnorbornene. The rates of these exo reactions[39] clearly argues against cyclic processes. Finally, it is important that the exo selectivity for diimide reduction of **2** cannot involve either σ bridging[5,6] or twist strain theory.[41,55] It is to be hoped that we are on our way to a more satisfactory understanding of the factors which control the reactions of rigid bicyclic systems.

Experimental Section[57]

Norbornene (1) and 7,7-Dimethylnorbornene (2). Norbornene, commercial product from Aldrich Chemical Co., was sublimed to ensure the purity. Pure 7,7-dimethylnorbornene may be obtained from synthetic sample[58] after being washed several times with aqueous silver nitrate.

Preparation of 7,7-Dimethylnorbornane (5). Hydrogenation[59] of **2** gave **5**, mp 88–89° (lit.[60] 89.5–90.5°) on distillation.

Detection of Complex Formation on Glpc. A Perkin-Elmer Model 154 vapor fractometer equipped with 6 ft × 0.25 in. glass column was employed. On the ethylene glycol (40% by weight on 60–80 Chromosorb P) column, the retention time was 5.9 min for **4**, 7.0 min for **1**, 10.3 min for **5**, and 10.3 min for **2**. On the ethylene glycol–silver nitrate (40% of the 0.32 *M* solution on 60–80 Chromosorb P) column, the retention time was 5.9 min for **4**, 35.1 min for **1**, 10.9 min for **5**, and 10.9 min for **2**.

Benzenesulfenyl Chloride. Freshly distilled sulfuryl chloride was slowly added to an equivalent amount of diphenyl disulfide in anhydrous methylene chloride containing some pyridine at ambient temperature.[12] A deep red liquid, bp 67° (4.4 mm), was obtained.

Addition of Benzenesulfenyl Chloride to 1 and 2. The addition was carried out at −10 to −30° in methylene chloride in the presence of a small amount of suspended calcium carbonate.[12] The norbornene adduct, bp 129° (0.9 mm) or 120° (0.55 mm) (lit.[12] 102–103° (5×10^{-5})), displayed a pmr spectrum identical with that of **6** as reported.[12–14] Recrystallization of the crude 7,7-dimethylnorbornene adduct yielded 60% of pure **8**, mp 42.5–43° (lit.[12] mp 35–38°). The pertinent pmr data also agreed with those reported.[12,14] *Anal.* Calcd for $C_{15}H_{19}SCl$: C, 67.52; H, 7.18; S, 12.02; Cl, 13.28. Found: C, 67.70; H, 7.10; S, 12.22; Cl, 13.48.

Preparation of Triphenyltin Hydride. Triphenyltin hydride was prepared from triphenyltin chloride and lithium aluminum hydride in ether.[61] Distillation yielded a colorless liquid, bp 146–148° (0.15 mm) (lit.[61] 162–168° (0.5 m)), which solidified on standing in a cold room, mp 24–25°.

Hydrodechlorination of 6 and 8 with Triphenyltin Hydride. The β-chloro sulfide **6** or **8** was heated for 1 hr at 80° with triphenyltin hydride in the presence of a catalytic amount of azobisisobutyronitrile.[62] From **6**, *exo*-norbornyl phenyl sulfide (**11**) was found the only hydrodechlorination product (>99%) by glpc on 150 ft × 0.01 in. open tubular Apiezon L column using Perkin-Elmer Model 226 gas chromatography. Similarly, crude **8** gave about 84% yield of 7,7-dimethyl-2-norbornyl phenyl thioethers, **12** and **7**, with exo/endo ratio of 4/96. From pure **8** (mp 42.5–43°), 7,7-dimethyl-*endo*-norbornyl phenyl sulfide (**7**) was isolated in 60% yield by preparative glpc. *Anal.* Calcd for $C_{15}H_{20}S$: C, 77.53; H, 8.67; S, 13.80. Found: C, 77.34; H, 8.60; S, 13.69.

Competitive Addition of Benzenesulfenyl Chloride to 1 and 2. Benzenesulfenyl chloride (0.0723 g, 0.50 mmol) was slowly added to a methylene chloride solution of 0.2444 g (2.00 mmol) of **2** and 0.0471 g (0.50 mmol) of **1** at −20°. The reaction mixture was then subjected to a rotary evaporator to remove the unreacted olefin and the solvent. Then it was treated with excess triphenyltin hydride to give a mixture of phenyl sulfides. Glpc analysis indicated the ratio of **11**/(**12** + **7**) was 9.84. A duplicate experiment with 0.0471 g (0.50 mmol) of **1**, 0.0976 g (0.80 mmol) of **2**, and 0.0722 g (0.50 mmol) of benzenesulfenyl chloride gave a ratio of 22.8. These data were then converted into $k_{exo\text{-norbornyl}}/k_{7,7\text{-dimethyl-exo-norbornyl}}$ as in Table I.

Addition of 9-BBN to 7,7-Dimethylnorbornene (2). To 2 ml of 1.0 *M* tetrahydrofuran solution of **2**, 3.4 ml of 0.60 *M* 9-BBN was added. The reaction mixture was maintained at room temperature (~25°) for 1 day. Then 2 ml of 6 *M* sodium hydroxide was added, followed by the addition of 2 ml of 30% hydrogen peroxide. The mixture was heated at 60° for 1 hr under good reflux condenser. To isolate the product, the reaction mixture was cooled to room temperature, and the organic layer was separated after being saturated with potassium carbonate. Glpc analysis on 150 ft × 0.01 in. UCON 50-HB-2000 open tubular column using a Perkin-Elmer Model 226 gas chromatography showed the ratio of **15**/**16** was 3:97. The ratio remained the same for a 2-day reaction.

Competitive Addition of 9-BBN to 1 and 2. 9-BBN was added to a mixture of **1** and **2**, and was allowed to react for 1 day. The product was isolated as usual (*vide supra*), and was analyzed using a Varian Aerograph Model 1200 instrument on a 6 ft × 1/8 in. 5% UCON 50 LB 550X column. The result was listed in Table II.

Addition of Nitrosyl Chloride. The literature process[20] was followed. As nitrosyl chloride (Matheson Co.) was bubbled slowly into the chloroform solution of **1**, the blue color appeared instantaneously. The adduct, mp 149–150°, was isolated after the blue color has been replaced by a yellowish brown color characteristic of excess nitrosyl chloride. The pmr spectrum (saturated perdeuteriobenzene solution) showed one α-methine proton at δ 4.93 (multiplet of doublet, J = 7 Hz), one at δ 4.09 (doublet of doublet J = 7, 2 Hz), one bridgehead proton at δ 2.84 (broad singlet), the syn-7 proton at δ 2.45 (multiplet of doublet, J = 11 Hz), one bridgehead proton at δ 2.11 (broad singlet), and the remaining five protons between δ 1.3 and 0.5. Infrared spectrum (Nujol) displayed strong absorption at 670 cm^{-1} (C–Cl) and 1230 cm^{-1} (NO for aliphatic nitroso dimer).

However, as nitrosyl chloride was bubbled into the solution of **2**

(54) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).
(55) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968).
(56) R. C. Fahey, *Top. Stereochem.*, **3**, 253 (1969).
(57) Melting points were taken in capillary tubes and were not corrected. Pmr spectra were recorded on a Varian A-60 or A-60A spectrometer.
(58) H. C. Brown, J. H. Kawakami, and S. Misumi, *J. Org. Chem.*, **35**, 1360 (1970).
(59) H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, **84**, 2829 (1962); C. A. Brown and H. C. Brown, *J. Org. Chem.*, **31**, 3989 (1966).
(60) W. von E. Doering, M. Farber, M. Sprecher, and K. B. Wiberg, *J. Amer. Chem. Soc.*, **74**, 3000 (1952).
(61) H. G. Kuivila and O. F. Benmel, *ibid.*, **83**, 1246 (1961).
(62) H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963).

at −60°, the yellowish brown color for nitrosyl chloride persisted for 1 hr and no blue color had formed.

Diimide Reduction of Norbornene (1). To a stirred suspension of 0.58 g (3.0 mmol) of potassium azodicarboxylate in 3 ml of methanol containing 0.190 g (2.0 mmol) of **1** was added a solution of 0.45 g (7.5 mmol) of acetic acid in 3 ml of methanol. After stirring had been continued for 20 min, water was added, and the product was extracted with pentane. The pentane extract was dried (K_2CO_3), and glpc analysis (SE-30 or UCON Polar) indicated no **1** remained. Pure norbornane (**4**) was isolated by sublimation.

Diimide Reduction of 7,7-Dimethylnorbornene (2). By the use of the same procedure, **2** was reduced to give, however, only less than 10% yield of **5**. About 40% reaction was realized if a tenfold excess of diimide was used. Preparative glpc on a 4 ft × 0.25 in. column of 10% SE-30 gave pure 5.

Dideuteriodiimide Reduction of 1 and 2. Under carefully dried conditions, dideuteriodiimide was generated *in situ* from potassium azodicarboxylate, methanol-*d* (Merck), and acetic acid-*d* (Merck), as described before. Dideuterionorbornane was obtained from **1**, and dideuterio-7,7-dimethylnorbornane was obtained from **2** after glpc separation. Mass spectral analysis of the latter, **5**-d_2, using direct probe with an ionizing energy of 20 eV (nominal) showed 82.3% of d_2 and 17.7% of d_1.

Competitive Addition of Diimide of 1 and 2. A solution of 0.05 g of acetic acid in 1 ml of methanol was added slowly with stirring to a suspension of 0.058 g of potassium azodicarboxylate (0.30 mmol) in 1 ml of methanol containing 0.0282 g of **1** (0.30 mmol) and 0.0732 g of **2** (0.60 mmol) at room temperature. The product was isolated after the mixture had been stirred for 15 min. Glpc analysis on a 6 ft × $^1/_8$ in. column of 5% SE-30 indicated the ratio of **4**/**1** was 2.53 and the ratio of **2**/**5** was 624. A duplicated run from 0.51 mmol of **1** and 0.60 mmol of **2** gave a ratio of 1.83 for **4**/**1** and 1174 for **2**/**5**.

Preparation of *endo*-Norbornyl Phenyl Sulfide (17). Anhydrous tetrahydrofuran (10 ml) and 1.10 g (10 mmol) of thiophenol were placed in a 50-ml flask fitted with a serum-capped side arm, a magnetic stirring bar, and a reflux condenser. To this stirred solution, under nitrogen, was added 6.25 ml (10 mmol) of 1.6 *M* *n*-butyllithium in hexane at such a rate to maintain a reflux temperature. After the exotherm subsided, the reaction mixture was cooled to room temperature. A 6-in. Vigreux column was attached, and the solvent was removed by distillation under a flow of nitrogen. The final trace of solvent was removed under vacuum at higher temperature. To the resulted white solid, 1.65 g (5 mmol) of *exo*-norbornyl brosylate in 10 ml of dry dimethylformamide was added. After 18 hr at room temperature, the reaction mixture was worked up by dissolving the thioether in 30 ml of pentane and washing the organic layer with 3 × 30 ml of water. The solution was dried ($MgSO_4$) and evaporated to dryness. The crude product, about 76% yield, was found to contain 98.4% of **17** and 1.6% of **11**. An analytical sample was obtained by preparative glpc, $n^{24}D$ 1.5814. *Anal.* Calcd for $C_{13}H_{16}S$: C, 76.40; H, 7.90. Found: C, 76.64; H, 7.77.

Preparation of 7,7-Dimethyl-*exo*-norbornyl Phenyl Sulfide (12). Using a similar procedure, 0.82 g (2.28 mmol) of 7,7-dimethyl-*endo*-norbornyl brosylate, prepared from the corresponding alcohol and *p*-bromobenzenesulfenyl chloride in pyridine, was heated at 100° for 48 hr with 5 mmol of lithium thiophenoxide in DMF. About 0.37 g (70%) of a pale yellow liquid was obtained after the reaction mixture had been worked up as before. Glpc analysis indicated a mixture of 82% of **12**, 3% of **7**, and 15% of unidentified material. Preparative glpc (4 ft × 0.25 in. SE-30) gave 98% pure **12**.

Addition of Thiophenol to 1. To a 50-ml Pyrex round-bottom flask fitted with a reflux condenser, magnetic stirring bar, and serum-capped side-arm, under nitrogen, was added a solution of 0.94 g (10 mmol) of **1** and 1.10 g (10 mmol) of thiophenol in 5 ml of hexane; the mixture was chilled in an ice bath and then irradiated with a 100-W General Electric H-4 lamp for 15 min. Glpc analysis after the usual work-up indicated the reaction was complete, and the product was greater than 99.5% of **11** and less than 0.5% of **17**. A 30-min reaction showed the same result. When the above reaction was run for 15 min with 100% excess of thiophenol, the result was again the same.

Addition of Thiophenol to 2. By using the above-mentioned procedure, 0.61 g (5 mmol) of **2** was allowed to react with 0.55 g (5 mmol of thiophenol at 0° under irradiation. The yield was 17% at 15 min, 52% at 1 hr, and 81% at 3 hr. Analysis by glpc showed the 95:5 exo/endo product ratio did not vary with time. The reaction run with a 100% excess of thiophenol also gave a constant exo/endo ratio (95:5) with time.

Competitive Addition of Thiophenol to 1 and 2. To a 10-ml round-bottom flask fitted with a magnetic stirring bar, a reflux condenser, and a serum-capped side arm, under nitrogen, was added a mixture of 0.0648 g (0.531 mmol) of **2** and 0.0435 g (0.463 mmol) of **1** in 0.5 ml of hexane at ice-bath temperature. Then 0.0268 g (0.25 mmol) of thiophenol was added, and the reaction mixture was irradiated with a sunlamp. The reaction was stopped after 10 min, and glpc analysis indicated the ratio of (**11** + **17**)/(**7** + **12**) was 18.3. A duplicate experiment with 0.569 mmol of **2**, 0.322 mmol of **1**, and 0.20 mmol of thiophenol gave the ratio of 10.4.

Addition of Dichlorocarbene to 1. Preparation of potassium salt of triethylcarbinol was achieved from heating potassium metal in excess triethylcarbinol at 140° under nitrogen. After all of the potassium was dissolved, the excess alcohol was distilled at about 5 mm. The residual triethylcarbinol was removed by codistillation with the then added heptane. A suspension of 2 mmol of the resulted potassium *tert*-heptoxide in 5 mmol of pentane containing 1 mmol of **1** and 0.5 mmol of acenaphthene (as internal standard) was treated at 0° slowly with 2 mmol of chloroform.[33] Water was added after 30 min, and the organic layer was separated and dried ($MgSO_4$). Pmr analysis by comparing the intensity of olefinic protons in **1** and methylene protons in acenaphthene indicated about 30% of **1** had reacted.

Reaction between Dichlorocarbene and 2. The above-mentioned procedure was employed to the attempted reaction of **2**. However, the relative intensity of olefinic protons in **2** and methylene protons in acenaphthene was the same before and after the reaction as was indicated by pmr analysis.