indicate that spin-rotation (SR) relaxation dominates for TMS near its boiling point (possibly vapor phase relaxation), and that spin-rotation relaxation contributes significantly even at fairly low temperatures. The experimental NOE values confirm that ^{29}Si-^{1}H dipole-dipole (DD) relaxation is not significant near room temperature. However, below −70°, dipole-dipole relaxation dominates for TMS. At −62.5°, the signal *null* temperature (see Figure 1b), the ^{29}Si-^{1}H dipole-dipole mechanism contributes 40% (calculated from $-1.0/-2.52$) to relaxation of the TMS silicon nucleus.

In larger molecules with nonprotonated silicon nuclei (silicons with no directly attached protons) Hunter and Reeves observed very long T_1 values.[2c] To determine the contribution of the dipole-dipole mechanism to nonprotonated silicon relaxation in larger molecules, we examined octamethylcyclotetrasiloxane. The ^{29}Si T_1 and NOE, 100 sec and −1.83, respectively (38°), indicate that dipole-dipole relaxation is more able to compete with spin-rotation relaxation in molecules significantly larger than TMS.

Protonated ^{29}Si nuclei are relaxed predominantly by ^{29}Si-^{1}H dipole-dipole interactions.[5] In diphenylsilane, T_1 for the silicon is 16.5 sec and the observed NOE is -2.51 ± 0.10 (sample: 25% acetone-d_6, at 38°). The ^{29}Si T_1 in diphenylsilane can be compared with the protonated carbon T_1 values observed in the same sample. The ^{13}C T_1 values, measured at 25.2 MHz, were C_o, 5.5 sec, C_m, 5.5 sec, and C_p, 3 sec.[6] ^{29}Si relaxation times (dipole-dipole) are expected to be *ca.* nine times longer than analogous ^{13}C T_1 values because of (a) longer bond lengths and (b) the smaller magnetic moment for ^{29}Si. The ring carbon T_1 values are for CH carbons; CH_2 carbons would relax approximately twice as fast. Taking the multiplicity of attached protons into account, the differential between the ^{29}Si and ^{13}C T_1 values is in close agreement with theoretical expectations.

Conclusions and Comments. (1) As a result of longer spin-lattice relaxation times and a smaller chemical-shift range, pulsed Fourier transform operation is not expected to give as much sensitivity advantage as for ^{13}C nmr. Refocusing pulse schemes such as DEFT[7] may help to overcome the longer T_1 values for ^{29}Si nuclei if the spin-spin relaxation times (T_2) are sufficiently long (and if ^{1}H coupling is restricted to a single frequency or a narrow bandwidth).

(2) Pulse-modulated ^{1}H decoupling methods such as the one proposed by Freeman[8] to suppress the NOE for decoupled ^{13}C spectra may be particularly suited for ^{29}Si{^{1}H} studies because of the long ^{29}Si relaxation times. Also, suppression of the NOE in ^{29}Si{^{1}H} spectra would eliminate the problem of *nulled* or *inverted* signals. In any case total signal strength will not be less than $1.0/1.52 = 67\%$ of the signal obtained with the NOE.

(3) TMS, with a relatively short T_1 and very low NOE at room temperature, should make a good ^{29}Si nmr standard for use above 0°.

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(5) *In very small molecules with protonated silicon nuclei, spin-rotation relaxation should be competitive.*

(6) T_1 for para carbons in substituted benzenes is $<T_1^{o,m}$: see G. C. Levy, *Chem. Commun.*, 47 (1972); G. C. Levy, D. M. White, and F. A. L. Anet, *J. Magn. Resonance*, **6**, 453 (1972).

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The Exo-Endo Steric Impediment in Norbornene. Electrocyclic Closure in Bicyclo[4.2.1]nona-2,4-dienes

Sir:

One of the most remarkable features of the chemistry of norbornene and its derivatives is the fact that electrophilic reagents nearly always attack from the exo side of the molecule.[1] The origin of this peculiarity has been vigorously debated for a number of years and the matter still remains unresolved.[2] A variety of reasons have been advanced: steric hindrance,[3] torsional interactions,[4] polar effects,[5] and stereoelectronic factors.[6] However, an adequate explanation is still lacking. One of the difficulties inherent in the problem is that all the examples cited concern additions in which the attacking reagent is forming a bond to the C-2 atom of the norbornene skeleton and that necessarily both electronic and steric effects are simultaneously and inextricably at play. Thus, an evaluation of just the steric factor by itself is hard, if not impossible, to get. We now report on an experiment in which steric factors alone are expected to determine the formation of exo and endo derivatives of norbornane.

The substrate we have selected is bicyclo[4.2.1]nona-2,4-diene (**1**). Photochemically the diene system may be expected to undergo two disrotatory closures either to give the exo cyclobutene derivative **2** or its endo isomer **3**.[7] Inspection of a suitable model of **1** indicates that the atoms of the diene moiety and the bridgehead atoms C-1 and C-6 all lie in the same plane. Consequently, electrocyclic closure between C-2 and C-5 will entail the formation of a σ bond in the plane defined by the C-1, C-2, C-5, and C-6 atoms and parallel to the axis which cuts through the C-1 and C-6 atoms. Accordingly, the creation of the norbornane skeleton by this internal bond should be electronically indifferent to the presence of the methylene or ethylene bridges. At the moment of junction, the configurational fate of the cyclobutene fragment should be de-

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(1) (a) G. D. Sargent, *Quart. Rev., Chem. Soc.*, **20**, 344 (1966); (b) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969); (c) R. C. Fahey, *Top. Stereochem.*, **3**, 253 (1969); (d) J. M. Brown and M. C. McIvor, *Chem. Commun.*, 238 (1969); (e) A. J. Fry and W. B. Farnham, *J. Org. Chem.*, **34**, 2314 (1969); (f) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201, 1990 (1970); (g) H. C. Brown, J. H. Kawakami, and K. T. Liu, *ibid.*, **92**, 6914 (1970).

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(3) H. C. Brown and K. T. Liu, *J. Amer. Chem. Soc.*, **89**, 3898, 3900 (1967); H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967); H. C. Brown and K. T. Liu, *ibid.*, **93**, 7335 (1971).

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(5) (a) C. W. Jefford and W. Wojnarowski, *Tetrahedron*, **25**, 2089 (1969); (b) W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *J. Amer. Chem. Soc.*, **89**, 410 (1967).

(6) (a) See Tidwell and Traylor, ref 2b; (b) R. Caple, F. M. Hsu, and C. S. Ilenda, *J. Org. Chem.*, **33**, 4111 (1968); (c) R. Caple, G. M. S. Chen, and J. D. Nelson, *ibid.*, **36**, 2870 (1971); (d) H. Kwart and J. L. Nyce, *J. Amer. Chem. Soc.*, **86**, 2601 (1964).

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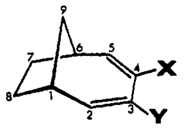
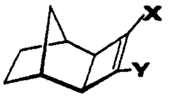
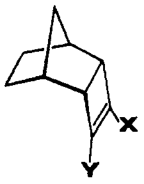
cided by those factors which are responsible for determining the preferred conformations of molecules in their ground states. Thus, the ratio of **2** to **3** should constitute a reliable index of the relative steric hindrances encountered on the exo and endo sides of norbornene. In order to confirm the generality of the reaction the photochemical experiment was carried out not only with the parent diene **1**, but also with its monochloro and dichloro derivatives **4** and **7**, respectively.[8]







1 X=Y=H	2 X=Y=H	3 X=Y=H
4 X=Cl,Y=H	5 X=Cl,Y=H	6 X=Cl,Y=H
7 X=Y=Cl	8 X=Y=Cl	9 X=Y=Cl

Solutions of **1**, **4**, and **7** (1.67, 1.3, and 0.53 mmol, respectively) in *n*-hexane (10 ml) under nitrogen were stirred and irradiated with an unfiltered 200-W Hanovia lamp at 25°. Periodically, samples were extracted and monitored by vapor-phase chromatography (5% SE-30 on Chromosorb G, column temperature of 100°, for the products from compound **1**, and 25% Apiezon L on Chromosorb W, column temperature of 120°, for the products from compounds **5** and **8**). Analysis revealed two major products which were the expected exo and endo cyclobutene derivatives.[9a] The parent compound **1** reacted smoothly, whereas the chloro derivatives **4** and **7** were more sluggish. After irradiation for 6 hr conversions to ring-closed products were 92, 42, and 17%, respectively.[9b] Compounds **1**, **4**, and **7** gave, respectively and reproducibly, the exo and endo cyclobutenes, **2** plus **3**, **5** plus **6**, and **8** plus **9** in percentage ratios of 30:70, 53:47, and 60:40 which were essentially invariant with time. The pair of isomers **8** and **9** had very similar retention times, but the other pairs (**2** and **3**, **5** and **6**) were easily separated and identified by nmr analysis.[10] The exo isomer in all cases had the shorter retention times. The essential feature which differentiated the exo from the endo isomers was the coupling of 4.5–5.0 Hz between the bridgehead protons (C-1 and C-2) which is characteristic of an exo disposition of the C-2 proton on the norbornane skeleton.[11,12]

These findings permit several observations and conclusions pertinent to the norbornene problem. The origin of these exo–endo preferences cannot reside in torsional interactions; indeed the direction of closure is the opposite of that predicted.[4a] A reasonable explanation is that in the transition state for cyclization a delicate balance of attractive and repulsive forces exists between the nascent double bond moiety at C-3–C-4 and the methylene or ethylene bridges. For the parent hydrocarbon **1** the endo side appears to be the least encumbered; however, the fact that peripheral substitution by chlorine brings about a displacement of the double bond moiety to the exo side could be ascribed to steering by attractive forces between the polarizable chlorine atom and the methylene bridge.[5a]

Lastly, it can be inferred for the hypothetical photochemical [2 + 2] cycloaddition of acetylene to norbornene that, in the absence of stereoelectronic control, the endo approach would be more navigable that the exo. Chloroacetylene would experience more or less equal steric difficulties on the two sides of the molecule, whereas dichloroacetylene would be directed to the exo side.

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[8] Compounds **1**, **4**, and **7** were prepared starting from the reaction of dichlorocarbene with bicyclo[3.2.1]octene-2 and its chloro derivatives. For the general method, see C. W. Jefford, J. Gunsher, D. T. Hill, P. Brun, J. Le Gras, and B. Waegell, *Org. Syn.*, **51**, 60 (1971), and C. W. Jefford, S. Mahajan, R. T. Medary, W. Wojnarowski, B. Waegell, and K. C. Ramey, *Chem. Commun.*, 310 (1967). Details of these syntheses will be published elsewhere (work of F. Delay).

[9] (a) For related cyclizations see H. M. Frey, J. Metcalfe, and J. M. Brown, *J. Chem. Soc. B*, 1586 (1970). (b) Minor products ($\sim$20%) resulted mainly from polymerization of starting material and to a lesser extent from further reaction of the primary photoproducts. Percentage conversions were corrected to account for loss of starting material by polymerization.

[10] Spectral analysis was carried out on a Varian Associates Model XL-100 spectrometer. The coupling constants were typically those found in cyclobutyl and norbornyl derivatives (ref 11 and 12).

[11] I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).

[12] P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

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*Book Reviews**

Microbiology. 1971. Edited by P. HEPPLE. Applied Science Publishers Ltd., Barking, Essex. 1971. v + 114 pp. £ 3.60.

This book contains the proceedings of a conference held in London and organized by the Institute of Petroleum. There are eight contributed chapters plus an opening address, panel discussion, and a summary. There is a considerable amount of chemistry included, as indicated by such representative titles as "Hydrocarbons as Carbon Substrates," "Microbial Degradation of Crude Oil," and "Enzymes as Industrial Catalysts."

Reagents for Organic Synthesis. Volume 3. By MARY FIESER and LOUIS F. FIESER (Harvard University). Wiley-Interscience, New York, N. Y. 1972. 401 pp. $16.95.

The latest volume to this useful series is divided between new information on previously listed reagents (about two-thirds) and reagents treated for the first time (about one-third). The term "reagent" is interpreted surprisingly broadly, for the book has entries for substances used only as solvents (*e.g.*, hexamethylphosphoramide). Many of the entries are for special applications of

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* Unsigned book reviews are by the Book Review Editor.