static considerations: log $K_{ML_2}(Ni(AMP5')_2)$ (a $-2,0$ interaction) $>$ log $K_{ML_2}(Ni(ADP)_2)$ (a $-1,-3$ interaction) $>$ log $K_{ML_2}(Ni(ATP)_2)_2$ (a $-4,-2$ interaction).

In conclusion, we have found several interesting features associated with the stability constants of magnesium and nickel with inorganic and nucleoside phosphates. They may be summarized as follows. First, for magnesium, potentiometric titration data show little or no difference between the presence or absence of a ring system for a given number of phosphates. Second, for nickel the interactions are more numerous, and several ligands show evidence for bis complexation. In addition, stability constants with nickel reflect considerable ring specificity. Third, all pK_a values and K values for magnesium agree well with previously published work, where comparisons can be made. Some differences, however, are obtained with nickel complexes, especially for systems which indicate substantial bis complexation.

Further work is under way in this laboratory on metal ion–nucleotide interactions, including thermodynamic studies as a function of temperature. The kinetics of complexation are also being studied. The kinetics show dramatic differences due to differences in binding strengths and sites. In addition these studies are being extended to other ring systems for which very little information is currently available (e.g., inosine and guanosine).[37]

(37) NOTE ADDED IN PROOF. M. S. Mohan and G. A. Rechnitz (*J. Amer. Chem. Soc.*, **94**, 1714 (1972) have recently demonstrated the existence of a Ca₂ ATP complex by means of a specific ion electrode, and have suggested the possibility of an analogous complex (*i.e.*, Mg₂ATP) with magnesium. Their value of K_{M_2L} for Ca₂ATP was about three orders of magnitude smaller than their value for the monoc omplex (CaATP). If the same type of M₂L complex is formed with magnesium, it is unlikely that we would have been able to detect it under our experimental conditions. In addition, if no proton is liberated, pH titration methods will be insensitive to such a species.

Communications to the Editor

Exo–Endo Steric Impediment in Norbornene. Specification of the Transition State for the Reaction of Singlet Oxygen with 2-Methylnorborn-2-ene and 2-Methylenenorbornane

Sir:

One of the enduring problems of mechanistic organic chemistry stems from the extraordinary fact that electrophilic additions to norbornene occur overwhelmingly on the exo side of the molecule.[1] Nevertheless, appropriately located substituents can play a key role in controlling the approach of a reagent attacking the double bond.[2] Steric effects have been shown to be particularly important in the case of one-step cyclic additions.[2c]

These properties intrinsic to the norbornene skeleton should be eminently suitable for examining the topical question concerning the course of the reaction of singlet oxygen with monoolefins.[3] It should be possible to specify the optimum geometry of the transition state and to make a decision between the one-stage cyclic process[6] and the two-stage perepoxide mechanism.[7] With this aim in mind we have investigated the reactivity of 2-methylnorborn-2-ene (1) and 2-methylenenorbornane (2).[8]

Compounds 1 and 2 were photooxidized in acetonitrile at 10–12° using two 500-W tungsten projector lamps (Silvana FFX) as the light source and Methylene Blue as sensitizer.[9] The primary oxidation products were reduced either with triphenylphosphine[10] or with sodium borohydride in methanol,[11] and the resulting mixture was analyzed by vapor phase chromatography (20% FFAP, Chromosorb W). Compound 1 gave exo-2-methylenenorbornan-3-ol (3) and endo-2-methylenenorbornan-3-ol (4) in proportions of 98.5 and 1.5% with a yield of 75–85%.

A similar reaction of 2 for 5 min gave 2-hydroxymethylnorborn-2-ene (5) and norbornanone (6) in

(1) For the previous paper in this series and relevant references cited therein, see: C. W. Jefford and F. Delay, *J. Amer. Chem. Soc.*, **94**, 4794 (1972).

(2) (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); (c) H. C. Brown and K. T. Liu, *ibid.*, **93**, 7335 (1971).

(3) Despite an abundant literature[4] dealing with structurally simple olefins, few bridged bicyclic structures have been examined so far.[5]

(4) (a) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968); (b) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968); (c) C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Lett.*, 4111 (1965); (d) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Amer. Chem. Soc.*, **90**, 975 (1968); (e) P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N. Y. Acad. Sci.*, **171**, 79 (1970); (f) G. O. Schenck, K. Gollnick, G. Buchwald, S. Schroeter, and G. Ohloff, *Justus Liebigs Ann. Chem.*, **674**, 93 (1964); (g) K. H. Schulte-Elte, B. L. Müller, and G. Ohloff, *Helv. Chim. Acta*, **54**, 1899 (1971); (h) K. H. Schulte-Elte, M. Gadola, and B. L. Müller, *ibid.*, **54**, 1870 (1971); (i) G. Ohloff, H. Strickler, B. Willhalm, C. Borer, and M. Hinder, *ibid.*, **53**, 623 (1970); (j) K. H. Schulte-Elte and G. Ohloff, *ibid.*, **51**, 494 (1968); (k) H. Takeshita, T. Sato, T. Muroi, and S. Itô, *Tetrahedron Lett.*, 3095 (1969); (l) S. Itô, H. Takeshita, T. Muroi, M. Ito, and K. Abe, *ibid.*, 3091 (1969).

(5) (a) G. O. Schenck, H. Eggert, and W. Denk, *Justus Liebigs Ann. Chem.*, **584**, 177 (1953); (b) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964); (c) M. F. Barnes, R. C. Durley, and J. MacMillan, *J. Chem. Soc. C*, 1341 (1970); (d) M. F. Barnes and J. MacMillan, *ibid.*, 361 (1967); (e) W. R Adams and D. J. Trecker, *Tetrahedron*, **28**, 2361 (1972).

(6) (a) A. Nickon and W. L. Mendelson, *J. Amer. Chem. Soc.*, **87**, 3921 (1965), and earlier papers cited therein; (b) C. S. Foote and R. W. Denny, *ibid.*, **93**, 5168 (1971); (c) C. S. Foote, T. T. Fujimoto, and Y. C. Chang, *Tetrahedron Lett.*, 45 (1972).
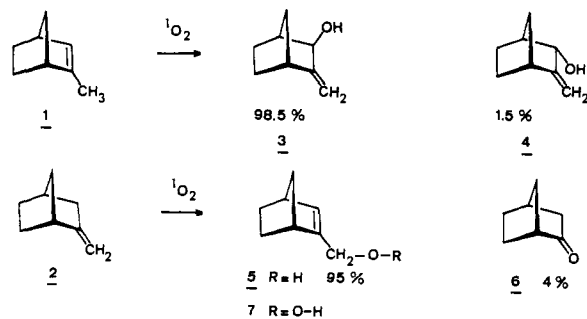
(7) (a) D. B. Sharp, Abstracts, 139th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, p 79P; (b) K. R. Kopecky and H. J. Reich, *Can. J. Chem.*, **43**, 2265 (1965); (c) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971); (d) W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 7771 (1969); (e) N. Hasty, P. B. Merkel, P. Radlick, and D. R. Kearns, *Tetrahedron Lett.*, 49 (1972).

(8) C. W. Jefford, S. Mahajan, J. Waslyn, and B. Waegell, *J. Amer. Chem. Soc.*, **87**, 2183 (1965).

(9) Hydroperoxidation did not occur in the absence of either light or sensitizer.

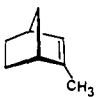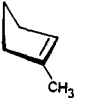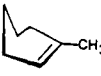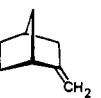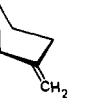(10) L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956).

(11) J. A. Sousa and A. L. Bluhm, *J. Org. Chem.*, **25**, 108 (1960).

proportions of 95 and 4%. Ketone **6** probably arose by cleavage of a dioxetane precursor rather than by decomposition of the allylic hydroperoxide.[12] However, the first-formed hydroperoxide **7** underwent further reaction with singlet oxygen, but at a rate about five times slower than the initial one.[13] After half the olefin had been consumed, 85–90% of the product consisted of **7**.

Although these reactions are smooth, their rates are governed by steric factors as comparison with the rates for 1-methylcyclopent-1-ene (**8**), 1-methylcyclohex-1-ene (**9**), and methylenecyclopentane (**10**) reveals. 2-Methylnorborn-2-ene reacts some 15 times more slowly than its flexible analog **8** and even more slowly than the cyclohexene **9**.[14,17] In contrast, both 2-methylene-norbornane (**2**) and its nonbridged analog **10** exhibit

similar rates which are half as fast as that of 2-methyl-norborn-2-ene (**1**) (see Table I).

The interpretation of these findings leads to the following conclusions about the transition state (TS). (1) Access of singlet oxygen to either side of 2-methyl-norborn-2-ene (**1**) is hampered relative to the reference olefin **8**, with hindrance being greater on the endo side as the composition of the kinetic product (exo:endo ratio of 66:1) clearly shows. (2) A corollary of point 1 is that the TS resembles the reactant (**1**) in that little double bond character develops between C-2 and the methyl carbon. (3) Although it is the relative steric environment about the double bond which steers the incoming singlet oxygen, nevertheless the steric exigencies are less severe than those experienced for typical one-step cyclic additions such as hydroboration or epoxidation[18] where the exo:endo ratio is 200:1. Accordingly, the singlet oxygen–ene reaction passes through a "loose" cyclic transition state in which steric factors present in the reactant are determinative.[19]

Similar considerations should apply to 2-methylene-norbornane, but await confirmation by labeling studies.

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Table I. Relative Reactivities of Acceptors

Acceptor	Rel Rate[a]
1	3.2
8	115.0[b]
9	9.5[b]
2	1.0
10	2.3

[a] Calculated from acceptor disappearance (error ±20%). [b] From ref 4a.

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(13) The photooxidation of Δ²-cholesten-3β-yl acetate follows the same course (W. Eisfeld, Ph.D. Thesis, University of Göttingen, 1965).
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Reductive Dehalogenation of Alkyl Halides with Lithium Aluminum Hydride. A Reappraisal of the Scope of the Reaction

Sir:

Complex metal hydrides possess considerable versatility as selective reagents for the reduction of a wide variety of organic molecules.[1] In the particular case of the reductive dehalogenation of alkyl halides, lithium aluminum hydride (LiAlH₄) is commonly used for reactive substrates,[2] whereas recourse is made to organotin hydrides to effect reduction of substrates conventionally regarded as inert.[3]

A wealth of literature attests to the fact that LiAlH₄ behaves as a nucleophile and displaces or replaces halide in either an S_N2 or an S_N1 process depending on the substrate.[4] We now present evidence to show that

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(4) (a) L. W. Trevoy and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 1675 (1949); (b) E. L. Eliel, *ibid.*, **71**, 3970 (1949); (c) E. R. Alexander, *ibid.*, **72**, 3796 (1950); (d) D. J. Malter, H. J. Wotiz, and C. A. Hollingsworth, *ibid.*, **78**, 1311 (1956); (e) E. J. Corey, M. G. Howell, A. Borton, R. L. Young, and R. A. Sneen, *ibid.*, **78**, 5036 (1956); (f) G. K. Helmkamp and B. Rickborn, *J. Org. Chem.*, **22**, 429 (1957); (g) P. R. Story and M. Saunders, *J. Amer. Chem. Soc.*, **84**, 4876 (1962); (h) M. S. Newman, J. R. Le Blanc, H. A. Karnes, and G. Axelrod, *ibid.*, **86**, 868 (1964); (i) R. A. Appleton, J. C. Fairlie, and R. McCrindle, *Chem. Commun.*, 690 (1967); (j) L. A. Paquette and P. C. Storm, *J. Org. Chem.*, **35**, 3390 (1970).