Table I. ^{13}C Nmr Chemical Shifts^{a,b}

	2a	2b	2c	2d	2e	3
C(2)	81.4	84.4	82.2	80.5	80.6	66.5
C(3)	58.0	58.0	58.2	57.4	55.0	49.0
C(5)	50.3	50.0	50.0	50.1	48.1	50.0
C(6)	36.3	36.0	36.8	35.0	37.3	36.4
C(7)	59.8	58.8	59.0	60.7	60.3	56.1
C(8)	139.8	135.8	138.6	135.7	140.1	139.5
C(9)	123.6	123.0	123.8	123.1	123.6	121.1
C(10)	121.0	117.8	120.8	118.9	121.1	119.0
C(11)	127.2	127.7	127.1^c	126.9	127.2	126.8
C(12)	112.0	105.6	110.8	109.0	112.7	110.9
C(13)	149.4	150.2	148.6	148.7	149.5	149.0
C(14)	128.5	127.7	127.6^c	128.2	20.7	126.5
C(15)	130.7	130.8	132.0	130.6	31.2	132.5
C(16)	39.2	37.0	36.8	39.4	40.2	43.4
C(17)	29.1	28.0	30.0	31.9	29.0	29.6
C(18)	7.4	9.0	7.4	7.8	7.5	31.6
C(19)	48.4	47.0	46.6	44.8	51.0	34.0
C(20)	46.2	45.6	48.0	47.8	44.5	35.0
C(21)	78.0	77.0	78.0	76.4	78.8	66.8
C=O	174.2	174.0	63.6^d	174.5	175.0	173.7
OMe	51.8	52.0		51.7	52.0	51.6
NMe		30.0				

^{a} See ref 5. ^{b} δ values with reference to internal TMS. ^{c} Signals may be reversed. ^{d} Oxymethylene signal.

The above arguments lead to the full chemical shift assignment for vindolinine and the allocation of structure **2a** to the alkaloid. Since an entire group of natural bases is founded on the old vindolinine structure **(1)**,^{12} a reinvestigation of the structures of its individual members may be now advisable.

(12) M. Hesse, "Indolalkaloide in Tabellen. Ergänzungswerk," Springer-Verlag, West Berlin and Heidelberg, 1968.

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Nickel(0) Catalyzed Cycloaddition of Bicyclo[2.1.0]pentane and Olefins. Contrasting Stereochemistry of the Thermal and Transition Metal Catalyzed Reactions^1

Sir:

Gassman and coworkers reported that bicyclo[2.1.0]-pentane reacts with electron-poor olefins *via* a stepwise, diradical mechanism to afford bicyclo[2.2.1]heptane

(1) Nickel Catalyzed Reactions Involving Strained Bonds. X. Part IX: H. Takaya, N. Hayashi, T. Ishigami, and R. Noyori, *Chemistry Lett.*, 813 (1973).

derivatives along with a variety of monocyclic adducts.^{2} 1,2-Disubstituted olefins enter into the cycloaddition in a nonstereospecific manner. They further established that olefins approach from the endo side of the bicyclo envelope, and consequently the hydrocarbon undergoes the reaction with double inversion of stereochemistry at the C-1 and C-4 positions. Recently we found that the $[_\sigma 2 + _\pi 2]$-type reaction takes place in the presence of
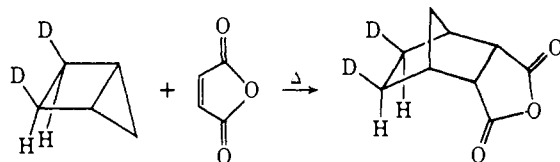
nickel(0) catalysts under milder reaction conditions and with higher selectivity.^{3} In the course of studying the reaction more in detail, we have discovered a new type of mutation by the transition metal complex, *i.e.*, an alternation in stereochemistry.

As shown in Scheme I, when a mixture of the deu-

Scheme I

$Z = COOCH_3$ + **2** (4%)   + **3** (30%)
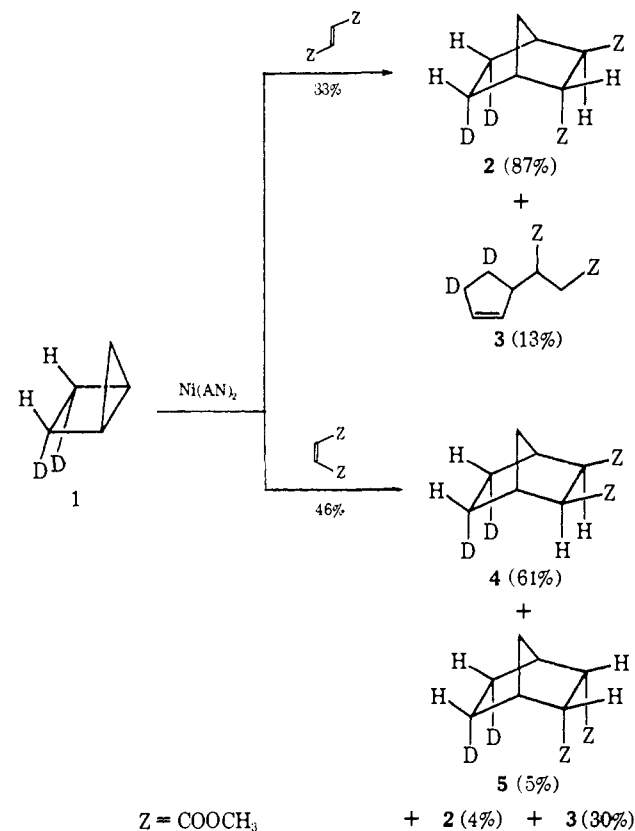
terated bicyclopentane **1**,^{2} dimethyl fumarate, and a catalytic amount of bis(acrylonitrile)nickel(0), [Ni-(AN)$_2$], in benzene was heated at 60° for 48 hr,^{3} the cycloadduct **2** and the monocyclic adduct **3** (a mixture of threo and erythro isomers) were obtained. In a similar fashion, reaction of **1** and dimethyl maleate afforded the 1:1 adducts **2–5**. The structures of the cycloadducts **2**, **4**, and **5** were unambiguously established by comparison of their nmr spectra with those of the undeuterated and exo,exo dideuterated derivatives

(2) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Amer. Chem. Soc.*, **91**, 1684 (1969).

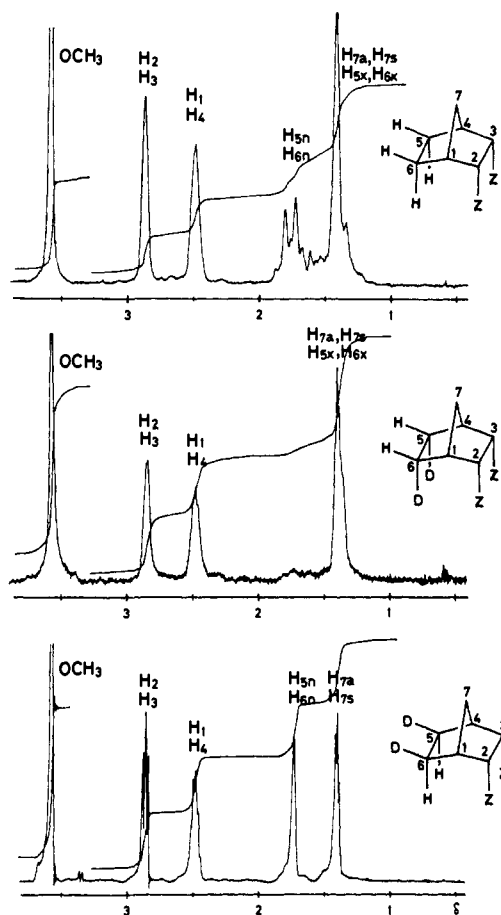(3) R. Noyori, T. Suzuki, and H. Takaya, *J. Amer. Chem. Soc.*, **93**, 5896 (1971).

Figure 1. Nmr spectra of 2,3-*endo,endo*-dicarbomethoxybicyclo-[2.2.1]heptane and its dideuterated derivatives (CCl₄, 100 MHz) (Z = COOCH₃).

(Figure 1).[4] Thus the stereochemistry of the catalyzed cycloaddition is virtually the reverse of that encountered in the purely thermal reaction; the hydrocarbon 1 under the influence of the Ni(0) complexes undergoes the reaction with retention of original configuration.

In order to investigate the course of the reaction forming the monocyclic adducts of type 3, the reaction was performed using 5,5-dideuterated substrate 6.[5] Reaction of 6 and methyl acrylate in the presence of Ni(AN)₂ (in benzene, 60°, 72 hr)[3] led to the formation of the 1:1 adducts 7-9. These adducts gave nmr spectra too complicated to allow direct analysis. The location of deuterium atoms, however, could be verified on the basis of the well-resolved spectra taken with the added shift reagent Eu(fod)₃ (Figure 2). Obviously the formation of the monocyclic adduct involves a specific deuterium shift.[6]

These findings are most reasonably explained by the mechanism outlined in Scheme II.[7] The approach of

(4) Prepared by catalytic reduction of the 5,6-dehydro derivatives using D₂ and 10% Pd–C (in heptane, 25°, 1 atm). *Cf.* D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Amer. Chem. Soc.*, **87**, 2596 (1965).

(5) Synthesized from cyclobutene, CD₂I₂, and diethylzinc using the procedure of S. Miyano and H. Hashimoto, *Chem. Commun.*, 1418 (1971).

(6) Rh(I)-catalyzed reaction of 1 is known to afford cyclopentene-*d*₂ in which deuteriums are randomly scrambled: P. G. Gassman, T. J. Atkins, and J. T. Lumb, *J. Amer. Chem. Soc.*, **94**, 7757 (1972).

(7) As a matter of simplicity, the oxidative addition concept is employed. At present, however, it is indistinguishable whether the edge-wise-coordinated complex 10 and the σ-complex 11 can exist as two distinct chemical entities or actually are canonical forms in a resonance hybrid.
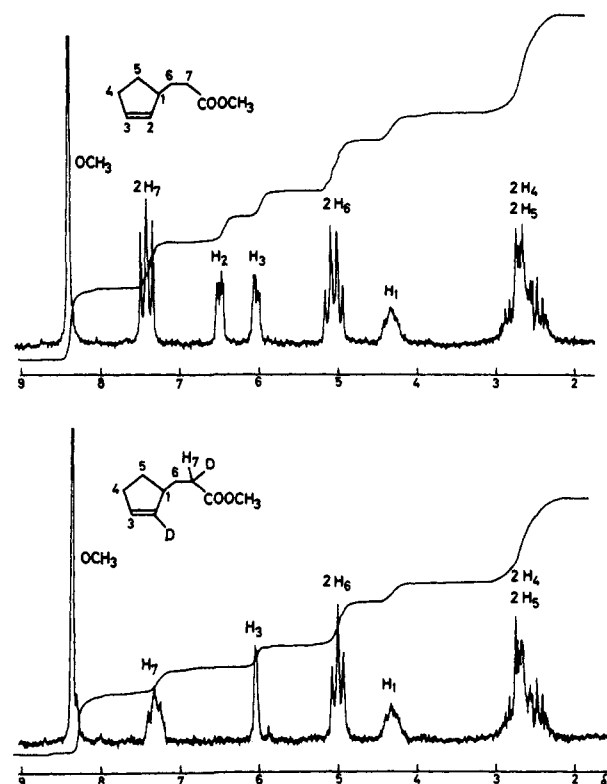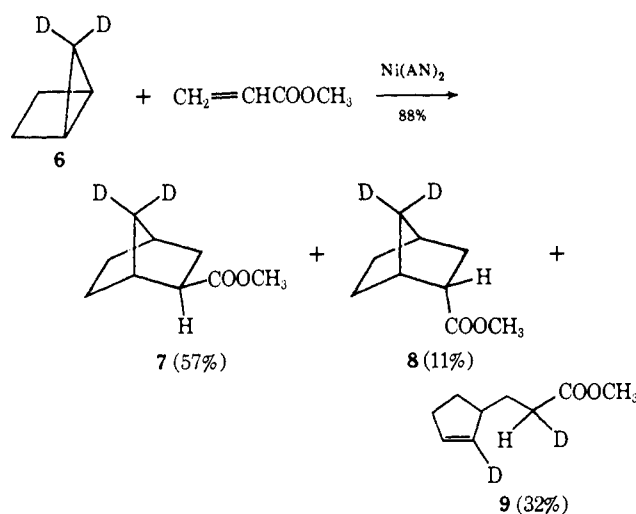

Figure 2. Nmr spectra of methyl 3-(cyclopent-2'-enyl)propionate and its dideuterated derivative (9) in the presence of Eu(fod)₃ (0.20 M solution of the substrate in CCl₄ containing 0.42 mol equiv of Eu(fod)₃, 100 MHz).


Ni(0) atom to the σ bond of bicyclopentane from the exo side of the flap could be ascribed to preferable [2 + 2] attraction between an antisymmetric d orbital of the transition metal atom and a symmetric region of the bicyclopentane envelope.[8,9]

In conclusion, the present reaction system is displaying the intriguing operations of transition metal complexes in organic reactions, *viz.*, (1) the activation of strained σ bonds under mild reaction conditions, (2) the promotion of cycloaddition involving σ bonds, (3) the catalysis of symmetry-restricted process (in a formal

(8) *Cf.* F. S. Collins, J. K. George, and C. Trindle, *J. Amer. Chem. Soc.*, **94**, 3732 (1972).

(9) Very recently an exo approach of metal ion was suggested for the Rh(I)-catalyzed isomerization of bicyclopentane derivatives. See K. B. Wiberg and K. C. Bishop, III, *Tetrahedron Lett.*, 2727 (1973).

Scheme II
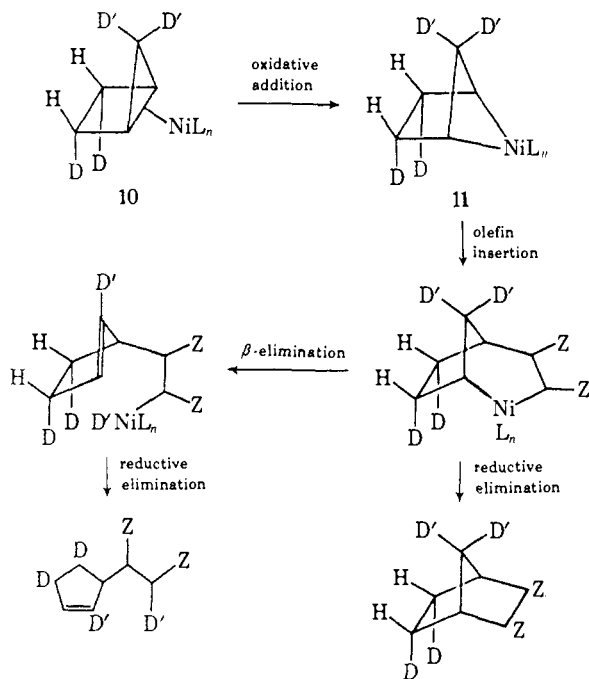
sense),[10] and (4) the reversal of stereochemical consequence observed for the purely thermal reaction.

(10) A number of examples are given in F. D. Mango and J. H. Schachtschneider, "Transition Metals in Homogeneous Catalysis," G. N. Schrauzer, Ed., Marcel Dekker, New York, N. Y., 1971, p 223, though the mechanistic implication described therein is losing its importance.

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The Cycloreversions of Diazabicyclo[4.2.0]octenes. A Test of the Bent Bond Requirement for Concert[1]

Sir:

The thermal decompositions of the diazabicyclo-[4.1.0]heptenes 1a–c to hepta-2,5-dienes are concerted cycloreversions. The facts[2] which support a concerted mechanism are (1) a rate of nitrogen evolution much greater than that of simple models, (2) the absence of ring-closure products (bicyclo[2.1.0]pentanes), and (3) high stereospecificity and exclusive adherence to that one of the "allowed"[3] pathways which has the best overlap of the orbitals of the breaking bonds (the C_1–C_6 bridge bond and the C–N bonds). Similarly, azo compounds 2 and 3a satisfy criteria 1 and 2 above and have been assigned a concerted mechanism of decomposition.[4]

Expansion of the cyclopropane unit of 1a–c to a cyclobutane, as in a diazabicyclo[4.2.0]octene, should decrease the bent character[5] of the bridge bond, weaken
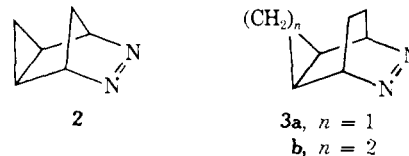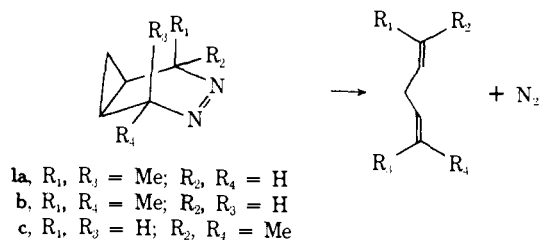
(1) This work was supported in part by a grant (GM-16962) from the National Institute of General Medical Sciences.

(2) J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **91**, 777 (1969); **92**, 1086 (1970).

(3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(4) E. L. Allred, J. C. Hinshaw, and A. L. Johnson, *J. Amer. Chem. Soc.*, **91**, 3382 (1969).

(5) (a) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949); (b) C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 2851 (1962); 3161 (1963); (c) *Cf.* also A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

1a, R_1, R_3 = Me; R_2, R_4 = H
b, R_1, R_4 = Me; R_2, R_3 = H
c, R_1, R_3 = H; R_2, R_4 = Me

2

3a, $n = 1$
b, $n = 2$

the overlap with the two breaking C–N bond orbitals in the concerted transition state, and thereby narrow not only the energy gap between the concerted paths but also that between the concerted and non-concerted ones. That the borderline with a non-concerted process may have been reached in a cyclobutane derivative is suggested by the behavior of 3b, which decomposes much more slowly than does its cyclopropane analog 3a and is reported to form ring-closure products.[6]

Two compounds appropriate for the application of all three criteria to a test of the bent bond requirement are *syn,cis*- and *trans*-2,5-dimethyl-3,4-diazabicyclo-[4.2.0]oct-3-ene (4 and 5). Syntheses of 4 and 5 are accomplished by the highly stereospecific routes shown in Scheme I[7]. The syn, cis configuration of 4 is con-

Scheme I
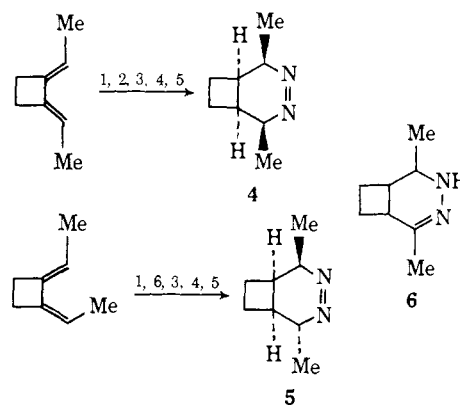
firmed by conversion of its precursor 7 to the urazole 8,[8] which in turn is obtained from the known[9] cyclo-octatriene–N-phenyltriazolinedione adduct 9 by ozonolysis of the unsaturated bridge and reduction in several steps.

Although heating cis azo compound 4 in diphenyl

(6) (a) E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1971); *Tetrahedron Lett.*, 387 (1972).

(7) Notes to Scheme I: (1) bisethylidenecyclobutane isomers prepared by the method of P. Heimbach and R. Schimpf, *Angew. Chem., Int. Ed. Engl.*, **8**, 206 (1969); (2) dimethyl azodicarboxylate; (3) H_2/Pt; (4) KOH–H_2O, then H+, all with rigorous exclusion of air; (5) vacuum line isolation of the volatile crystalline hydrazine followed by treatment of a benzene solution with oxygen; (6) N-methyltriazoline-3,5-dione. Compounds 4 and 5 show λ_{max} 395 nm, ϵ 150, and λ_{max} 392 nm, respectively, in ether. The nmr spectra are appropriate for the assigned structures. Both tautomerize irreversibly with extreme ease to the hydrazone 6.

(8) E. W. Petrillo, Jr., Ph.D. Dissertation, Yale University, 1973.

(9) (a) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967); (b) D. G. Farnum and J. P. Snyder, *Tetrahedron Lett.*, 3861 (1965).