tion of cyclopropenes.[9] Instead, these strained systems isomerize to α,β-unsaturated carbonyl compounds (**2** and **3**) at 0°.

The observed yields of cyclopropanone derived products (carbon monoxide and olefin) are also consistent with the proposed scheme. The amount of these products decreases as the migrating group is changed from chlorine to hydrogen to methyl. It has been demonstrated in other 1,3-biradical and 1,1,3-triradical systems that chlorine migrates faster than hydrogen,[10] while hydrogen rearranges more readily than methyl.[11]

A comparison of the reactions of cyclopropenes and allenes with atomic oxygen is of interest. For example, the products from 3-methyl-1,2-butadiene are carbon monoxide (67% yield), 2-methylpropene (45%), and 3-methyl-3-buten-2-one (8.6%); no 3-methylcrotonaldehyde (**2a**) is observed.[1] Carbon monoxide and 2-methylpropene are formed by decomposition of excited 2,2-dimethylcyclopropanone, the same cyclopropanone formed by reaction of **1a** with $O(^3P)$. However, no 3-methyl-3-buten-2-one was detected from the reaction of cyclopropene, **1a**. This observation would be consistent with the hypothesis that carbonyl compounds from allene reactions are produced by rearrangement of initially formed biradicals and not by rearrangement of excited cyclopropanones.

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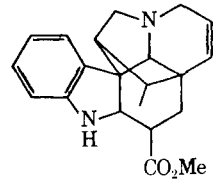
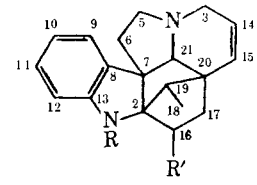
On the Structure of Vindolinine[1]

Sir:

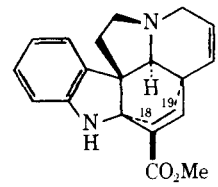
Vindolinine is a $C_{21}H_{24}N_2O_2$ alkaloidal constituent of a variety of *Catharanthus* species[2] to which structure **1** had been assigned some time ago mostly on the basis of mass spectral analyses.[3] Since the structure analysis of a new dimeric indole alkaloidal constituent of *Catharanthus longifolius*[4] required a ^{13}C nmr analysis of vindolinine, the natural abundance, proton decoupled and single frequency, off-resonance decoupled cmr spectra of the alkaloid were recorded.[5] They revealed one more nonaromatic, nonprotonated carbon and one less nonaromatic methine signal than demanded by formula **1**. Since the missing signal was that of an aminomethine and the new nonprotonated carbon signal (81.4 ppm) that of an oxy or amino carbon site, formula **2a** was considered a reasonable alternative to the previous structure. The following cmr analyses of vindolinine derivatives **2b–e** and comparison of their shifts with those of the structurally related alkaloid venalstonine (**3**)[6] confirm the new structure.



1



2a, R = H; R′ = CO_2Me
b, R = Me; R′ = CO_2Me
c, R = H; R′ = CH_2OH
d, 16-epi-**2a**
e, 14,15-dihydro-**2a**



3

The chemical shift assignments for compounds **2** were based on standard shift theory[7] and arguments made for alkaloids of the *Aspidosperma* type[8] and are listed in Table I. The aminomethylenes, C(3) and C(5), were differentiated by the expected change in their shifts on reduction of the olefinic bond,[8] while the C(6) and C(17) methylenes and C(16) and C(19) methines were recognized from the difference of their shifts in vindolinine (**2a**), alcohol **2c**, and 16-epivindolinine (**2d**). The shift contrast between **2a** and its N_a-methyl derivative (**2b**) supports strongly the C(2) attachment of the normal *Aspidosperma* 20-ethyl side chain. The C(2) and C(20) signals of vindolinine (**2a**) are 12–15 ppm downfield those of venalstonine (**3**) in analogy with the 13 ppm shift difference of the bridgehead carbons of norbornane[9] and bicyclo[2.2.2]octane.[10] The anomalous C(3) and C(21) shifts of vindolinine (**2a**) must reflect the extraordinary strain imposed on the piperideine ring by the norbornane unit.[11]

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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.

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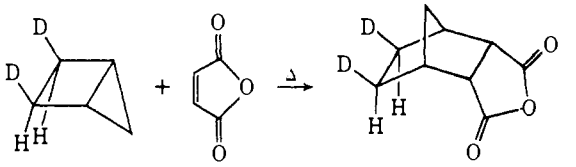
Nickel(0) Catalyzed Cycloaddition of Bicyclo[2.1.0]pentane and Olefins. Contrasting Stereochemistry of the Thermal and Transition Metal Catalyzed Reactions[1]

Sir:

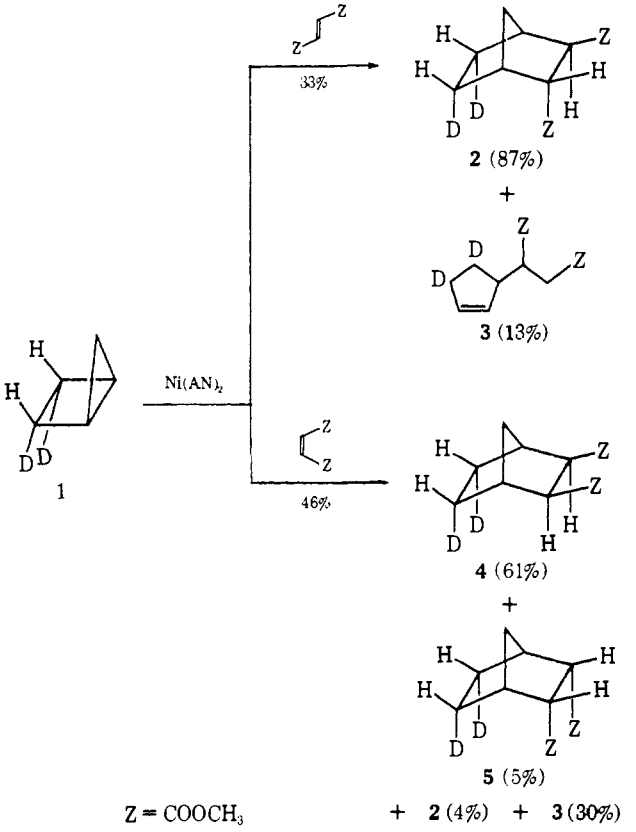
Gassman and coworkers reported that bicyclo[2.1.0]-pentane reacts with electron-poor olefins *via* a stepwise, diradical mechanism to afford bicyclo[2.2.1]heptane derivatives along with a variety of monocyclic adducts.[2] 1,2-Disubstituted olefins enter into the cycloaddition in a nonstereospecific manner. 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 deuterated 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

Scheme I



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