are produced in the decomposition of **2**. The allene and propyne result from addition of these carbon atoms to ethylene. Skell and coworkers[7] have observed allene and propyne as the principal products in the reaction of arc-generated carbon atoms with ethylene at −196°. Reaction of ethylene with higher energy carbon-11 atoms produced by nuclear transformation yields allene, propyne, acetylene, propylene, cyclopropane, and vinylacetylene.[8]

The hydrogen cyanide formed in the decomposition of **2** is most probably the result of insertion of a carbon atom into the N–H bond of another molecule of **2** followed by decomposition to HCN. While the mechanism of methane formation is uncertain, it appears that the most likely pathway is a series of hydrogen abstractions either by ^3P carbon or by CH produced during the decomposition of **2**.

The pyrolysis of **2** in the presence of ethylene oxide has also been examined. It has been shown,[9] in a similar system, that arc-generated carbon atoms react with propylene oxide to give carbon monoxide and propylene. Decomposition of **2** (0.75 mmol) in a reactor containing 145 mm (4.6 mmol) of ethylene oxide gave: nitrogen (1.4 mmol), carbon monoxide (0.4 mmol), ethylene (0.06 mmol), methane (0.16 mmol), and acetylene (0.05 mmol).

$$2 + \underset{H_2C\text{——}CH_2}{\overset{O}{\triangle}} \xrightarrow{\Delta}$$

$$N_2 + CO + H_2C{=}CH_2 + CH_4 + HC{\equiv}CH$$
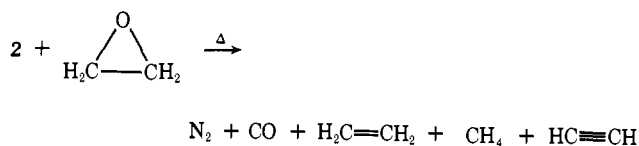
In this system ethylene and carbon monoxide are postulated to be the result of abstraction of oxygen from ethylene oxide by atomic carbon. Since the carbon monoxide yield exceeds that of ethylene in this reaction, it is proposed that a portion of the carbon monoxide is the result of hydrogen abstraction from ethylene oxide followed by decomposition of the resulting radical to carbon monoxide and a methyl radical. Abstraction of hydrogen from ethylene oxide in the gas phase is known to yield carbon monoxide and methyl radicals.[10,11] In the present case the abstracting species is probably either ^3P carbon or CH.

The formation of acetylene parallels the chemistry of energetic carbon atoms produced by nuclear transformation.[1] However, the mechanism of acetylene formation may not be similar since neat pyrolysis of **2** also produces acetylene in smaller yield. When **2** (0.75 mmol) was allowed to decompose in a degassed system the products were: nitrogen (0.43 mmol), hydrogen cyanide (0.09 mmol), and acetylene (0.03 mmol). In this reaction the most likely origin of the acetylene is either dimerization of atomic carbon to C_2 followed by hydrogen abstraction, or dimerization of CH. Hydrogen abstraction by C_2 has been observed in the reactions of arc-generated carbon species.[12] The re-

(7) P. S. Skell, J. E. Villaume, J. H. Plonka, and F. A. Fogone, *J. Amer. Chem. Soc.*, **93**, 2699 (1971).

(8) C. Makay, P. Polak, H. E. Rosenberg, and R. Wolfgang, *ibid.*, **84**, 308 (1962).

(9) P. S. Skell, J. H. Plonka, and R. R. Engel, *ibid.*, **89**, 1748 (1967).

(10) W. R. Trost, B. deB. Darwent, and E. W. R. Steacie, *J. Chem. Phys.*, **16**, 353 (1948).

(11) R. Gomer and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **72**, 101 (1950).

(12) P. S. Skell and J. H. Plonka, *ibid.*, **92**, 5620 (1970).

sults of the neat pyrolysis render the mechanism of acetylene production in the ethylene oxide system uncertain.

Thermal decomposition of **3** represents a convenient method for generating and studying the reactions of atomic carbon. While the spin state of the reacting carbon atom is unknown, the most probable species would appear to be ^1S.[6,13] Efforts toward the preparation of pure **1** are continuing in order to study its gas-phase photolysis.

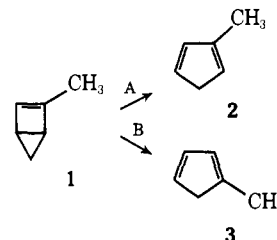(13) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *ibid.*, **92**, 3505 (1970).

Philip B. Shevlin
Department of Chemistry, Auburn University
Auburn, Alabama 36830

The Thermal Rearrangement of 2-Methylbicyclo[2.1.0]pent-2-ene

Sir:

Bicyclo[2.1.0]pent-2-ene undergoes a facile thermal valence isomerization to cyclopentadiene.[1] The 2-methyl homolog **1** undergoes an analogous reaction at a similar rate.[2,3] Whether this thermal isomerization of **1** follows path A to 2-methylcyclopentadiene (**2**) or path B to 1-methylcyclopentadiene (**3**) is of consid-

erable mechanistic importance, but the ready thermal equilibration of the isomeric dienes,[4] leading to a mixture containing **2** and **3** in the ratio 55:45 approximately, complicates a study of the thermal ring opening of **1**. It has recently been reported[3] that the thermal isomerization of **1** leads to **3** only, following path B and so providing evidence that the reaction is concerted and follows a symmetry-allowed path[5] described as $[_\sigma 2_s + _\sigma 2_a]$. The isomerization was carried out at 43°, and the diene **3** produced was trapped *in situ* as its adduct with N-phenylmaleimide, no trace of the isomeric adduct being found; it was stated that the N-phenylmaleimide was unreactive toward the starting bicyclopentene **1**, but reacted with the methylcyclopentadiene produced faster than **3** rearranged to **2**.

In our original study[2] of the thermal reaction of **1** we observed only the mixture of isomers **2** and **3** that re-

(1) J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968); J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *ibid.*, **88**, 846 (1966).

(2) S. McLean and D. M. Findlay, *Can. J. Chem.*, **48**, 3107 (1970).

(3) J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

(4) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2313, 2329 (1965).

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

sulted from thermal equilibration, but we now find that our attempts to trap the isomer formed first lead us to the conclusion opposite to that in the earlier report.[3] In our hands the reaction follows path A and **2** is at least the predominant product of this reaction.

A sample of the methylbicyclopentene **1** was divided in two parts and one part was dissolved in tetrahydrofuran and the other in chloroform-*d*, each solvent containing an excess of *N*-phenylmaleimide. The samples were placed in a bath at 43°, and the progress of the reaction was monitored by periodic observation of the nmr spectrum of the chloroform-*d* solution. The signals for the *N*-phenylmaleimide adduct of 2-methyl-cyclopentadiene were observed to grow with time, the methyl doublet at τ 8.18 and the vinyl multiplet at τ 4.24 providing a particularly useful basis for identification.[4] After 24 hr, when the reaction appeared to be complete, the product was predominantly the adduct of the 2-methyl isomer, and contained no more than 5% of the adduct of the 1-methyl isomer as judged by the strength of signals in the regions characteristic of this isomer.[4] The tetrahydrofuran solution was evaporated to dryness and the nmr spectrum of the residue showed that it was essentially the same product as that formed in the chloroform-*d* solution. Recrystallization of the residue provided a sample, mp 122–125°, which on admixture with an authentic sample of the adduct of 2-methylcyclopentadiene had mp 124–128°[6] and which was spectroscopically indistinguishable from the 2-methylcyclopentadiene adduct.

It is obviously difficult to reconcile our results with those reported previously[3] but, especially in the light of current interest in the limiting conditions for the Woodward–Hoffmann rules, it is important to find the explanation for the differences. In reactions of this type, particularly if the activation energies of the concerted and nonconcerted processes are of similar magnitude, the history of every reactant may be crucial. In the present study we have used all-glass apparatus throughout, and prior washing of the apparatus with base did not appear to influence the result. None of the reactants was in the presence of any metal, and the bicyclopentene **1** was not purified by vapor phase chromatography as formerly;[2] instead **1**, prepared photochemically from methylcyclopentadienes, was freed from unchanged dienes by treating the mixture with excess *N*-phenylmaleimide in anisole and distilling the unreacted material at low pressure. This process was repeated until the nmr spectrum of the distillate showed no trace of methylcyclopentadienes. The tetrahydrofuran used was carefully purified and redistilled from lithium aluminum hydride immediately before use. In some runs the thermal rearrangement was carried out in the presence of a base, pyridine, or 1,-8-bis(dimethylamino)naphthalene (Aldrich's "Proton Sponge"), but no significant difference in the distribution of isomers was observed in the product.

It should be noted that our result does not provide a decisive answer to the question of whether the rear-

rangement of the bicyclopentene is concerted or not. Although evidence has been presented[2,3] that the starting methylbicyclopentene is the 2-methyl isomer **1**, a small amount of the 1-methyl isomer could nevertheless be present in equilibrium with **1**, and the possibility that the reaction proceeds through the 1-methyl isomer cannot be completely ruled out. Furthermore, although the formation of **2** can most readily be explained by a nonconcerted opening of **1**, a concerted [$_\sigma 2_s$ + $_\sigma 2_a$] process, corresponding to that invoked previously[3] but with the migrating methylene group moving exclusively in the opposite direction (*i.e.*, to C-3 of **1**) to that required to form **3**, could also lead to **2**. It appears that a bicyclopentene with suitable double labeling will be required to resolve this ambiguity.

Stewart McLean,* D. M. Findlay,[7] G. I. Dmitrienko
*Department of Chemistry, University of Toronto
Toronto 5, Ontario, Canada*

Pakistanine and Pakistanamine, Two Novel Dimeric Isoquinoline Alkaloids[1]
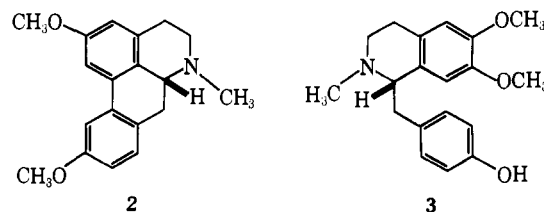
Sir:

We wish to report the isolation and structural elucidation of the phenolic aporphine benzylisoquinoline alkaloid pakistanine (**1a**) found in *Berberis baluch-*
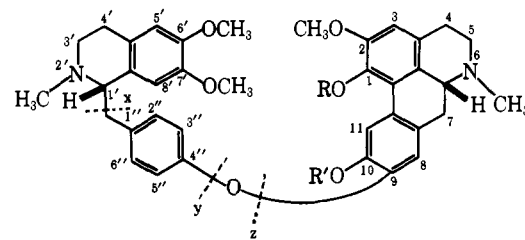
1a, R = R' = H
1b, R = R' = CH$_3$
1c, R = CH$_3$; R' = H

2

3

istanica Ahrendt (Berberidaceae): C$_{37}$H$_{40}$O$_6$N$_2$; mp 156°; $[\alpha]^{28}$D +106° (MeOH).[2]

O-Methylation of pakistanine **1a** with diazomethane yielded *O,O*-dimethylpakistanine (**1b**): C$_{39}$H$_{44}$O$_6$N$_2$;

(6) Fractional crystallization of the mixture of adducts obtained from the equilibrium mixture of **2** and **3** affords first the adduct of **3**, less soluble in common solvents, and this can be recrystallized to a high degree of purity (mp 179–180°). Later fractions yield material, mp ~114°, which is a constant melting mixture of the adducts of **2** (major component) and **3**. Recrystallization of this does not raise the melting point, but the diene **2**, purified by vpc, forms an adduct, mp 128–129.5°.[4]

(1) This research was supported by Grant No. 1RO1 CA11450 from the National Institutes of Health to M. S., and by a free grant from the Hoffmann-La Roche Foundation. The authors are grateful to Professor M. Tomita for a sample of authentic 2,10-dimethoxyaporphine.

(2) The plant was collected in the northern regions of West Pakistan, and was identified by Dr. A. R. Beg, Plant Taxonomist, Forest Research Institute, Peshawar, Pakistan. Elemental formulas were determined by high-resolution mass spectral analyses.