Me_2NCH_2Ph is rapidly metalated in the ortho position by the chloropalladate(II) ion whereas H_2NCH_2Ph is not metalated,[18] a "*gem*-dimethyl" effect. In these metalation reactions the formation of four-, five-, or six-membered rings is presumably promoted by enthalpy, entropy, and conformational effects which are analogous to those of the "Thorpe–Ingold" or "*gem*-dimethyl" effect. Masters[19] has shown that 3,3-dimethyl-pent-1-ene undergoes platinum catalyzed hydrogen/deuterium exchange at position 5. This presumably involves metalation of carbon atom 5 which could have been promoted by the *gem*-dimethyl group.

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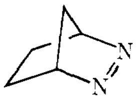
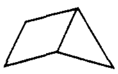
An Electron Spin Resonance Study of Matrix Isolated 1,3-Cyclopentadiyl, a Localized 1,3-Carbon Biradical[1]

Sir:

Short-chain localized carbon biradicals, particularly 1,3- and 1,4-biradicals, have been postulated as reaction intermediates with increasing frequency during the last decade.[2] In spite of their importance in mechanistic chemistry no direct detection of these molecules by physical methods has been reported.[3] In this communication we wish to present the results of an electron spin resonance study of a biradical of this type, 1,3-cyclopentadiyl (II).


I


II


III

When a dilute solution (~1% w/v) of 2,3-diazabicyclo[2.2.1]heptene-2 (I) in cyclohexane is rapidly frozen to a glassy matrix and irradiated at 5.5°K with ultraviolet light, a well defined ESR spectrum can be observed (Figure 1, upper trace).[4] At that temperature the spectrum persists after irradiation has been ceased although the intensity diminishes with a half-life of ~30 min. The ESR transitions can be described by the usual spin Hamiltonian for triplet states with fine structure parameters of $D/hc = -0.084$ cm^{-1} and $E/hc = \pm 0.0020$ cm^{-1}.[5] In addition to fine structure, hyperfine structure is also evident, particularly in the half-field transition. The assignment of the carrier of the spectrum to II is based on the zero-field splitting parameters and the change of the hyperfine structure with deuteration of I. The zero-field splitting parameters were calculated for an idealized planar structure of II with a bond angle of 110° at the carbon separating the two trivalent carbon atoms, and a C–C bond length of 1.52 Å. Including only the two-center interaction and using the semiempirical method suggested by van der Waals and Ter Maten for the evaluation of the integral, one obtains $D/hc = -0.106$ and $E/hc = 0.0055$ cm^{-1}.[6,7]

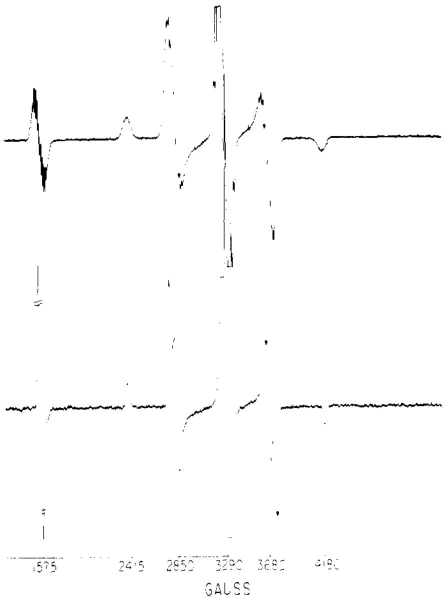


Figure 1. ESR spectra of II (upper trace) and II-d_8 (lower trace). Klystron frequency 9.204 GHz. In each case, the strong monoradical absorption at 3290 G was produced from the biradical by a secondary photoprocess.

The reasonable agreement between experiment and calculation for *D* is strong support for II being the carrier of the spectrum. As is usually the case the agreement for *E* is much poorer.[6] This discrepancy is at least partly due to the approximations inherent in the calculation but might also be caused by a slight deviation from planarity.

Although a large number of hyperfine lines are resolved, there are too many protons to obtain an unambiguous assignment of the coupling constants. To eliminate the possibility of a biradical derived from I in which only one C–N bond has been cleaved the spectrum of II-d_8 was examined (Figure 1, lower trace). The observed narrowing of the fine structure transitions is completely accounted for by replacing proton hyperfine with deuterium hyperfine coupling, thus eliminating any possibility of sizable nitrogen coupling.

The spectrum of II persists down to 1.3°K making it highly probable that II has a triplet ground state. In this connection it is of interest that preliminary CIDNP results obtained on benzophenone sensitized photolysis of I in solution at 300°K also support a triplet ground state for II. This conclusion is based on the observation of enhanced absorption for all NMR transitions of bicyclo[2.1.0]pentane (III), indicating predominant mixing of the upper Zeeman level of the triplet state with the singlet state of II.[8]

The decay kinetics of II and II-d_8 are highly unusual.[9] In several matrices, including microcrystalline I, the decay of the ESR signal is nonexponential over the whole tempera-

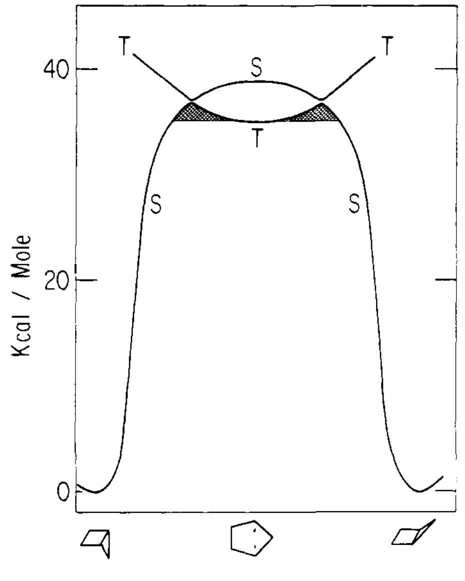


Figure 2. Schematic energy surface relating II and III. Height of singlet maximum (39 kcal/mol) is taken from J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 3250 (1962). The cross hatched area is the barrier through which the system tunnels via a normal mode consisting mainly of a ring bending vibration.

ture range studied with a difference between the fast and slow component of approximately a factor of two. This behavior has precedent[10] and is presumably due to an ensemble of slightly different host sites, differing in their restraining power for the out-of-plane motion accompanying the formation of III. In addition both components of the rate are essentially temperature independent between 1.3 and 20°K! Only above 20°K does the disappearance of II begin to show a significant temperature dependence. The rate of II-d_8 at 5.5°K is too slow to study. This behavior is characteristic for quantum mechanical tunneling through a low barrier.[11] Estimates of the shape of the barrier are made difficult by the fact that the extremely small transmission coefficient (10^{-15} to 10^{-16} sec^{-1}) has a contribution from the spin forbiddenness of the reaction. Nevertheless, considering the large reduced mass of the tunneling groups, it is hard to see how the barrier height could exceed 2 kcal/mol.[12] A more detailed study of the kinetic behavior above 20°K on II and II-d_8 should yield a better estimate.

The results reported here are of interest in connection with the problem of whether the singlet surface has a minimum associated with structure II. While thermochemical calculations indicate such a well to be 13 kcal/mol deep[13] our results appear to be more consistent with a surface as indicated in Figure 2 where there is no minimum with singlet character. This conclusion is in line with quantum mechanical calculations on trimethylene.[14]

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The Nonparticipation of α,β-Dehydrovalinyl Intermediates in the Formation of δ-(L-α-Aminoadipyl)-L-cysteinyl-D-valine

Sir:

The tripeptide δ-(α-aminoadipyl)cysteinylvaline was first isolated from *Penicillium chrysogenum* in 1960,[1] but the absolute configurations of its constituent amino acids were not determined. Subsequently, a similar noncyclic peptide was isolated from *Cephalosporium acremonium*, characterized as δ-(L-α-aminoadipyl)-L-cysteinyl-D-valine (ACV)[2] and shown to be formed from δ-(L-α-aminoadipyl)-L-cysteine and L-valine, but not D-valine, in cell extracts.[3,4] More recently, ACV was shown to be a precursor of penicillin N as manifested by its incorporation into the latter β-lactam antibiotic by a cell-free system obtained from protoplasts of *C. acremonium.*[5]

Several recent publications[6,7] report the asymmetric incorporations of chirally labeled methylvaline-*methyl*-^{13}C and methylvalines-*methyl*-d_3 into β-lactam antibiotics. We present here the results of biosynthetic studies with (2*S*,3*S*)-methylvaline-^{15}N,*3-methyl*-d_3 and experimental evidence for the nonparticipation of α,β-dehydrovalinyl intermediates in the biosynthesis of ACV.

Exposure of mesaconic-*methyl*-d_3 acid[7] to β-methylaspartase[8] in the presence of $^{15}NH_3$[9] afforded L-*threo*-β-methylaspartic-^{15}N,*methyl*-d_3 acid in 53% yield, which was transformed into (2*S*,3*S*)-methylvaline-^{15}N,*3-methyl*-d_3[10] via the sequence of reactions previously described[6] in an overall yield of 23%.

After incubation of (2*S*,3*S*)-methylvaline-^{15}N,*3-methyl*-d_3 with washed cells of *C. acremonium* mutant C91[11] for 10 hr, the resulting penicillin N and cephalosporin C were isolated[6] and subjected to mass spectrometric analyses[12] as their *N*-benzoylpenicillin N methyl ester and *N*-acetylcephalosporin C methyl ester derivatives,[7] respectively. The most intense mass fragments at *m/e* 174[13] and 230, possessing the valinyl moieties of penicillin N and cephalosporin C, respectively, were selected for the calculation of isotopic ratios. The data in Table I clearly demonstrate that the entire skeleton[14] of (2*S*,3*S*)-methylvaline-^{15}N,*3-methyl*-d_3 is incorporated intact into penicillin N and cephalosporin C. This conclusion is vindicated by the very prominent (P + 4) peak at m/e 178 and the (P + 3) peak at m/e 233, respectively. It is evident that the valine molecule underwent