In summary, π-facial stereoselectivities in the Diels–Alder reactions of the 5-heteroatom-substituted 1,3-cyclopentadienes can be predicted by the orbital mixing rule. In the HOMO and the NHOMO of the whole molecules, the orbitals at the reaction sites are distorted to favor the syn and anti attack, respectively. As the n-orbital energy of the heteroatoms rises, the π HOMO of the diene part contributes more to the NHOMO and less to the HOMO. The selectivities change from syn (X = OR) to syn/anti (X = SR) to anti (X = SeR, TeR). The effect of the V, VII heteroatom substituents will be described in the forthcoming full paper.

Acknowledgment. We are grateful to Prof. Shinichi Yamabe of Nara University of Education for helpful advice. The ab initio molecular orbital calculations with GAUSSIAN 80 and 82 programs were carried out on FACOM M-782 computer at Nagoya University computer center and HITAC M-680H computer at the Institute for Molecular Science, respectively. This work was supported by a Grant-in-Aid from the Ministry of Education, Science and Culture.

Chemical Model for the Pyridoxal 5′-Phosphate Dependent Lysine Aminomutases

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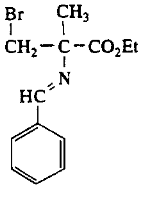
The reaction of *N*-benzylidene-(2-bromomethyl)-DL-alanine ethyl ester **1** with tributyltin hydride under free radical initiation conditions leads to *N*-benzylidene-2-methyl-β-alanine ethyl ester **2** and *N*-benzylidene-2-methyl-DL-alanine ethyl ester **3**. 1,2-Migration of the benzaldimino group through radical intermediates may be a chemical model for the pyridoxal 5′-phosphate (PLP) dependent lysine 2,3-aminomutase and β-lysine 5,6-aminomutase reactions.

Two enzymes of lysine metabolism catalyze 1,2 amino group migrations in the first and second steps of lysine catabolism in *Clostridia*.[1-3] Lysine 2,3-aminomutase catalyzes the interconversion of L-α-lysine and L-β-lysine, and β-lysine 5,6-aminomutase catalyzes the interconversion of L-β-lysine and L-3,5-diaminohexanoic acid. Both enzymes are PLP-dependent, and both have been postulated to involve radicals as intermediates.[4-7] β-lysine 5,6-aminomutase is also adenosylcobalamin-dependent, and the latter coenzyme is thought to initiate rearrangements by generating a substrate radical.[8,9] Lysine 2,3-aminomutase, on the other hand, is an iron- and *S*-adenosylmethionine-dependent enzyme;[2,3] and the putative radical rearrangement is thought to be initiated by a cofactor generated by the interaction of *S*-adenosylmethionine with a metal.[7]

No precedent for PLP catalysis of 1,2 amino migrations has been described in the literature, and no attractive mechanism can be written based on the known propensity of PLP to stabilize carbanions at the α- and β-carbons of amino acids. The hypothesis that PLP could facilitate 1,2 imino rearrangements in amino acid–PLP aldimine radicals has been advanced as a chemically attractive mechanism.[4-7] However, there appears to be no specific literature precedent for these rearrangements. We have, therefore, undertaken to determine whether a rearrangement of this type can be observed in a nonenzymatic reaction.

A model for the first radical intermediate for the lysine 2,3-aminomutase reaction is the radical produced by abstraction of Br$^\bullet$ from the β-carbon of compound **1**, which has been synthesized as the precursor for this radical.[10] Reaction of **1** (1.22 mmol) and a catalytic amount (0.05 mmol) of 2,2′-azobis(2-methylpropionitrile) in refluxing benzene with tributyltin hydride (0.9 mmol), added gradually over 2 h, led to **2** (62%) and **3** (4.7%), which were identified by referencing their proton NMR spectra to those of authentic samples.[11] Rapid addition of tributyltin hydride led exclusively to **3**, the product of radical quenching, rather than to **2**, the rearrangement product. Compound **2** was the favored product under rearrangement conditions, presumably owing to the stability of the α radical.



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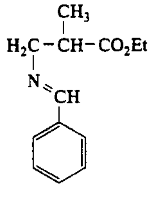

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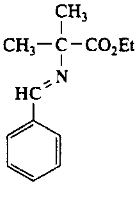
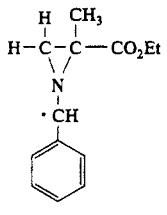


3

The rearrangement of **1** to **2** under radical-generating reaction conditions may be a chemical model for the PLP-dependent reactions catalyzed by lysine 2,3-aminomutase and β-lysine 5,6-aminomutase. This rearrangement joins other radical rearrangements recently reported by Halpern and Dowd and their co-workers, who have modeled carbon skeletal rearrangements catalyzed by adenosylcobalamin-dependent enzymes.[12-14] To the best of our knowledge, this is the first explicit example of a 1,2 imino rearrangement through a radical mechanism, although the mechanism has been discussed as a reasonable hypothesis.[4-7,15]

The rearrangement here described may be a precedent for PLP-dependent imino rearrangements to the extent that the benzyl radical **4** is valid as a model for the corresponding pyridoxyl radical



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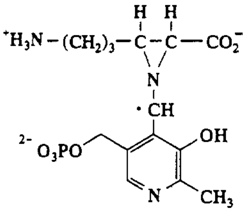

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(10) **1** was synthesized by reaction of benzaldehyde with DL-alanine ethyl ester hydrochloride in CH_2Cl_2 in the presence of crushed, activated 4-Å molecular sieves to form *N*-benzylidene-DL-alanine ethyl ester in 85% yield: ^{1}H NMR ($CDCl_3$) δ 1.28 (t, 7.3 Hz, 3 H), 1.53 (d, 7.0 Hz, 3 H), 4.14 (q, 7.0 Hz, 1 H), 4.21 (m, 2 H), 7.4–7.7 (m, aromatic, 5 H), 8.32 (s, 1 H). *N*-benzylidene-DL-alanine ethyl ester was converted to **1** by initial reaction with potassium *tert*-butoxide in the presence of 18-crown-6 in dry benzene to generate the α anion, followed by alkylation to **1** by reaction with CH_2Br_2. After removal of solvent, purified **1** was obtained in 80% yield by chromatography through Et_3N-washed silica gel, with ethyl acetate–hexane–Hunig's base (4:1:0.25) as the mobile phase. ^{1}H NMR ($CDCl_3$) δ 1.30 (t, 7.5 Hz, 3 H), 1.63 (s, 3 H), 3.75 and 3.87 (AB q, 9.9 Hz, 2 H), 4.26 (m, 2 H), 7.4–7.7 (m, 5 H), 8.28 (s, 1 H). Mass spectrum, FAB showed two parent ions ($[^{79}Br]:[^{81}Br]$ = 1:1) *m/e* 298 and 300 (1:1) for protonated **1**.

(11) **2** and **3** were synthesized by reaction of the corresponding amino acid ethyl esters with benzaldehyde as described for *N*-benzylidene-DL-alanine ethyl ester. For **2**: ^{1}H NMR ($CDCl_3$) δ 1.23 (t, 7.3 Hz, 3 H), 1.27 (d, 7.0 Hz, 3 H), 2.89 (sextet, 7.0 Hz, 1 H), 3.87 and 3.68 (ABXY, 11.7, 7.0, 1.3 Hz, 2 H), 4.14 (q, 7.3 Hz, 2 H), 7.4–7.9 (m, aromatic, 5 H), 8.28 (s, 1 H). For **3**: ^{1}H NMR ($CDCl_3$) δ 1.27 (t, 7.3 Hz, 3 H), 1.55 (s, 6 H), 4.18 (q, 7.3 Hz, 2 H), 7.4–7.8 (m, aromatic, 5 H), 8.28 (s, 1 H).

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5. Radical **4** is presumed to be the rearrangement intermediate for the production of **2** from **1** under radical-generating conditions, and **5** is the proposed lysine–pyridoxyl radical intermediate in the lysine 2,3-aminomutase reaction. Rearrangements via **4** are azo analogues of the well-known cyclopropyl carbinyl rearrangements.[16]

Acknowledgment. This research was supported by Grant DK 28607 from the National Institute of Digestive and Kidney Diseases.

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C_{60} Has Icosahedral Symmetry

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The class of molecules with icosahedral symmetry, the highest finite point group symmetry, is a very exclusive one. To date it has only two confirmed members—the borohydride anion[1,2] ($B_{12}H_{12}^{2-}$) and dodecahedrane[3] ($C_{20}H_{20}$), both with symmetry I_h. A new candidate molecule, dubbed Buckminsterfullerene, was proposed in 1985 by Kroto, Heath, O'Brien, Curl, and Smalley:[4] a 60-atom, pure carbon, truncated icosahedron with the geometry of a soccerball. They hit upon this remarkable structure in their struggle to understand the origin of the extraordinary abundance and inertness of C_{60}, observed in pioneering carbon cluster beam experiments carried out at Exxon[5] and Rice.[4] The idea that such a spectacular structure might be possible was considered as early as 1966 by Jones,[6] who mused about the problem of constructing closed two-dimensional nets of atoms. Other authors discussed this structure for a hypothetical C_{60} molecule as a purely theoretical possibility shortly thereafter.[7] Following the proposal of Kroto et al., Buckminsterfullerene immediately became the subject of intense theoretical study, and experimentalists vigorously sought evidence that C_{60} did indeed have the structure of a soccerball. This evidence proved difficult to come by in carbon cluster beam experiments, where the molecules are available in small quantities for short times.

Recently, Krätschmer, Fostiropoulos, and Huffman[8] reported the observation of four sharp lines in the IR spectrum of carbon dust. This led them to believe that carbon dust, produced by resistively heating graphite in a He atmosphere, contains a significant amount (1%) of C_{60}. We were soon able to directly confirm this belief using a surface analytical mass spectrometer,[9] and we began producing quantities of carbon dust on the order of tens of milligrams using the method of Krätschmer et al. We then found that the collected raw carbon dust could be purified by fractional distillation and that refined films consisting almost entirely of C_{60} and C_{70} could thereby be produced. The relative proportion of these two species was checked with use of the mass spectrometer and could be controlled by varying the sublimation temperature. Using such purified films we were able to measure vibrational Raman spectra of C_{60} and C_{70}, as reported elsewhere.[10] A preliminary comparison of both the available IR data[8] and these recent Raman data for C_{60} with vibrational spectra calculated for the soccerball structure already strongly suggests that this is likely to be the correct structure.

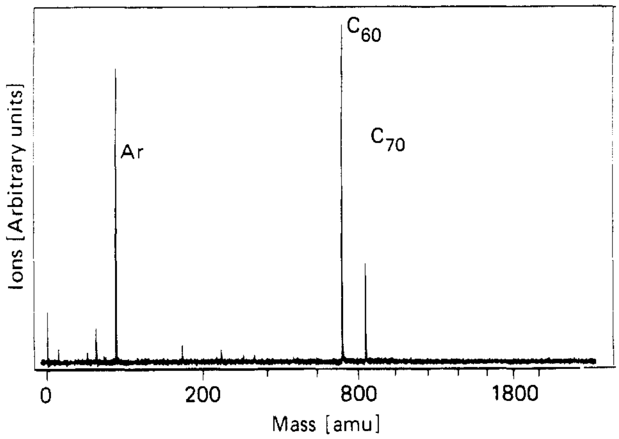

Figure 1. Time-of-flight mass spectrum of the C_{60}/C_{70} mixture used in the NMR experiment. A 10-μL drop of the CCl_4 solution was allowed to evaporate on a tantalum foil, and the spectrum was obtained with use of the surface analytical mass spectrometer. The horizontal axis is linear in time-of-flight and the corresponding (nonlinear) mass scale is indicated.

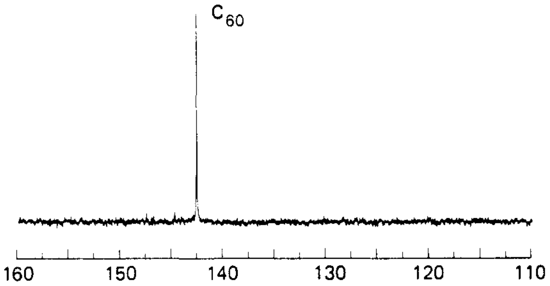

Figure 2. Aromatic region of the ^{13}C NMR spectrum of ~200 μg of C_{60}/C_{70} in CCl_4, without ^{1}H decoupling, obtained with a Bruker AM-500 NMR spectrometer operating at 125.7 MHz at 25 °C, with 13 000 scans over a 14 kHz bandwidth digitized into a 64 kword dataset; chemical shift referenced to CCl_4 at 96.1 ppm. The resonance at 142.5 ppm is assigned to C_{60}.

One particular aspect of the proposed soccerball geometry, *the exact equivalence of all 60 atoms implied by the I_h symmetry*, can be directly tested with NMR spectroscopy. The NMR spectrum of Buckminsterfullerene containing a single ^{13}C atom should consist of a single sharp line. In this communication we present NMR data which show that this is indeed the case, thus confirming the icosahedral symmetry of C_{60}.

In the experiments reported here, purified films of C_{60}/C_{70} were deposited on cooled suprasil slides by fractional sublimation of carbon dust at 600 °C. Part of the deposited material was dissolved in 1.6 mL of carbon tetrachloride. $Cr(ac)_3$ was added, to a concentration of 0.028 mM, to minimize saturation. The composition of the sample was determined by evaporating a 10 μL drop of the CCl_4 solution on a tantalum foil and analyzing the residual material with the surface mass spectrometer.[11] A

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* To whom correspondence should be addressed.

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