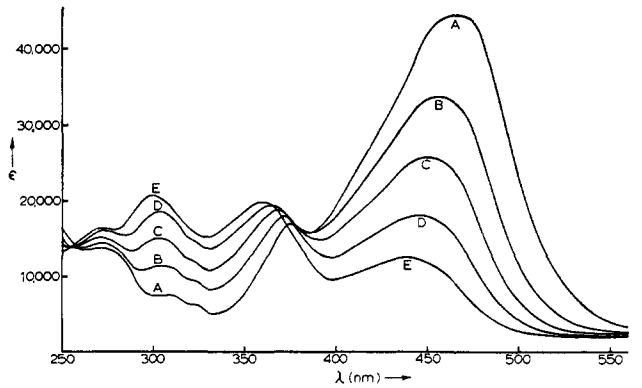

Figure 1. Absorption spectra of equimolar solutions of **3** in solvent mixtures of CH_2Cl_2–C_6H_{14} at room temperature. Volume % C_6H_{14} in CH_2Cl_2: A, 0; B, 52; C, 72; D, 84; E, 92.

shifting the equilibrium in favor of the dithiete (**4**). Similar effects were obtained in solvent mixtures C_2H_5OH–C_6H_6, C_2H_5OH–*n*-hexane, and CH_3CN–CCl_4.[14] The effect of light on the equilibrium **3** ⇄ **4** can be deduced from Figure 2. The position of the equilibrium in CH_2Cl_2, which has an equilibrium constant of $K(\mathbf{3}/\mathbf{4}) = 16$ at $-0.4°$, is approximately reversed after irradiation for 2 min at that temperature with the attainment of a photostationary state.[15] Furthermore the equilibrium returns to its original position, if the solution is allowed to stand in the dark at that temperature. All absorption spectra taken during the irradiation and thereafter go through an isosbestic point (at 385 nm), as one would expect for an equilibrium of this kind.

Kinetic and thermodynamic measurements were carried out by means of uv and nmr techniques between -3 and 43° in order to determine the activation parameters in CH_2Cl_2. It was shown that the tautomerization process cleanly follows reversible first-order kinetics, a fact that clearly excludes the reversible formation of any dimer. The rate constants k_1 (**4** → **3**) and k_{-1} (**3** → **4**) fit the Arrhenius equations. The values of the

$$k_1 = 4.32 \times 10^{10} \exp\left(-\frac{17.5 \text{ kcal mol}^{-1}}{RT}\right) \text{sec}^{-1}$$

$$k_{-1} = 2.29 \times 10^{13} \exp\left(-\frac{22.4 \text{ kcal mol}^{-1}}{RT}\right) \text{sec}^{-1}$$

equilibrium constants at different temperatures yield the enthalpy change for **4** → **3** as $\Delta H° = -4.9$ kcal mol^{-1} together with $\Delta S° = -12.5$ eu. The activation energy for the ring opening of **4** to **3** is about 15 kcal smaller than average values reported for the ring opening of cyclobutenes to butadienes.[16] This decrease is obviously mainly due to the difference in the bond energies between the C–C and the S–S bonds. For the ring closure 3 → 4 there are only few data available for comparison.[17] The small size of the activation energy,

(14) It seems likely that the observations of Saville and Steer[6] on monothiobenzil are not due to reversible polymerization of this compound, but originate from valence tautomerization to the oxathiete isomer. The isosbestic point at 470 nm appears to support this assumption.

(15) This was shown by irradiating a sample in an nmr tube at $-60°$ and following the ratio of the methyl peaks of the two isomers.

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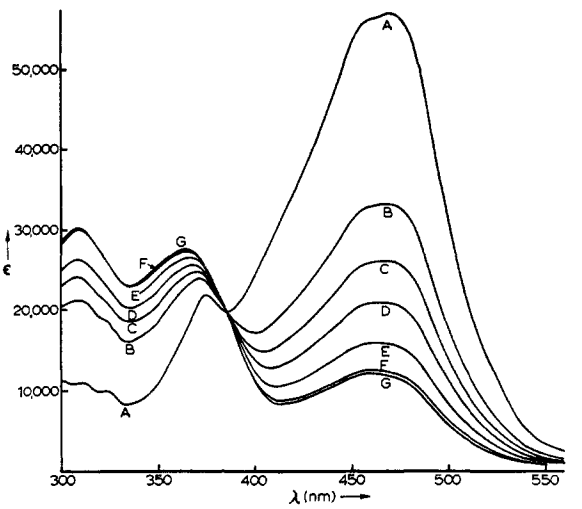

Figure 2. Spectral changes upon irradiation (λ >500 nm) of a degassed solution of **3** in CH_2Cl_2 at $-0.4°$. Total irradiation time (in sec): A, 0; B, 5; C, 10; D, 20; E, 45; F, 525; G, 3525.

however, suggests that the ring closure is facilitated by a considerable delocalization of the π electrons in the ring.

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Fluxional Behavior of $B_{11}H_{11}^{2-}$

Sir:

Isomerization of $B_nH_n^{2-}$ ions is generally believed to be a high-temperature phenomenon. We report here the spontaneous isomerization of $B_{11}H_{11}^{2-}$ and of $B_{11}H_7Br_4^{2-}$ ions in solutions at low temperatures in nmr time scales.

The $(Et_4N)_2B_{11}H_{11}$, prepared by known procedures,[1,2] was shown by tlc to have negligible traces of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. The $(Me_4N)_2B_{11}H_7Br_4$ was prepared under N_2 by adding dropwise 47.2 mmol of Br_2 in 150 ml of 1 *N* NaOH to 12.4 mmol of $Na_2B_{11}H_{11}$ in 50 ml of 1 *N* NaOH at 2°. After 4 hr at 2° and 20 hr at 25°, 45 ml of a 25% solution of Me_4NOH was added. The precipitate was fractionally recrystallized eight times from 0.1 *N* NaOH and EtOH. *Anal.* Calcd: C, 16.18; H, 5.26; B, 20.02; Br, 53.82; N, 4.72. Found: C, 16.01; H, 5.65; B, 19.57; Br, 53.86; N, 4.81. Also, $(Ph_4As)_2B_{11}H_{11}$ and $(Ph_4As)_2B_{11}H_7Br_4$ were prepared by adding $Ph_4As^+Cl^-$ to aqueous solutions of the sodium salts and then drying the precipitate.

The ^{11}B spectra of the $(alkyl)_4N^+$ salts in a DMF–acetone–methanol solution were taken at 32.1 MHz on a Varian XL-100 spectrometer with Fourier transform. The ^1H spectra of the Ph_4As^+ salts in perdeuteriodimethylformamide–methanol were obtained at 100 MHz on a Varian HA-100 with Fourier transform.

The ^{11}B spectrum of $B_{11}H_{11}^{2-}$ shows a doublet at 16.95 ppm [J(B–H) = 130 Hz] relative to $BF_3 \cdot O(Et)_2$.

(1) (a) F. Klanberg and E. L. Muetterties, *Inorg. Syn.*, **11**, 25 (1968); (b) F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966).

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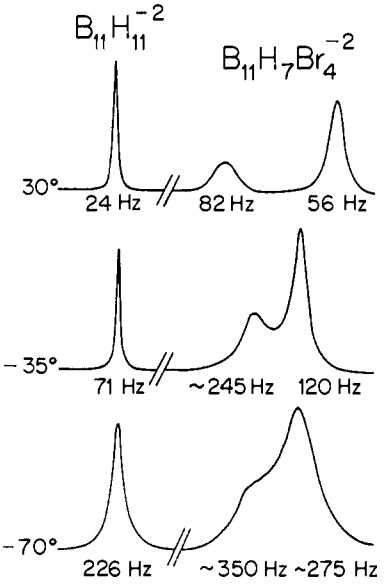

Figure 1. Variable temperature B^{11} nmr of $B_{11}H_{11}^{2-}$ (left) and $B_{11}H_7Br_4^{2-}$ (right) with ^1H decoupling. Half-widths are indicated below peak.[4] Spectral widths were expanded at lower temperature to enhance small broad spectral changes.

This doublet is collapsed to a singlet ($w_{1/2}$ = 24 Hz) at 30° upon ^1H decoupling (Figure 1, left), similar to decoupling effects[3] in $B_{12}H_{12}^{2-}$. At −90°, $w_{1/2}$ increases to 612 MHz, and the peak remains symmetrical. These half-widths show a linear correlation with typical solvent viscosities. The ^{11}B spectrum of $B_{11}H_7Br_4^{2-}$ ion shows a doublet at 17.81 ppm [J(B–H) = 141 Hz] and a (B–Br) singlet at 6.44 ppm. Upon ^1H decoupling this doublet becomes a singlet ($w_{1/2}$ = 56 Hz), which is in intensity ratio of 7:4 to the B–Br singlet ($w_{1/2}$ = 82 Hz) (Figure 1, right). Temperature broadening of both peaks follows the expected $1/T_2$ dependence.[4]

The ^1H spectra (not shown) are consistent with these results. At 30°, $B_{11}H_{11}^{2-}$ shows a broad quartet, with fine structure and a width of about 600 MHz. At −93°, ^1H is decoupled so that a single peak remains at 2.25 ppm relative to TMS. Similarly, $B_{11}H_7Br_4^{2-}$ shows at 30° a broad quartet with fine structure and a width of 720 Hz and at −93° a single peak at a δ of 2.45 ppm. At −73° the singlet in $B_{11}H_7Br_4^{2-}$ is sharp, while $B_{11}H_{11}^{2-}$ shows a broad hump, suggesting that the greater electric field gradients in the brominated ion decrease the ^{11}B quadrupole relaxation time thus broadening the boron resonance and decoupling the ^1H spectra at higher temperature.

Structures proposed, so far, for $B_{11}H_{11}^{2-}$, are either the C_{2v} structure of the isoelectronic carborane $B_9C_2H_{11}$, or the C_{5v} structure of an icosahedron having one apex missing.[1,5,6] The coordination and other environments of BH units are so different within either structure that it is most unlikely that the nmr equivalences found here are coincidental. Moreover, these two structures are very closely related, as shown in Figure 2. Very little motion of a BH unit is required to pass

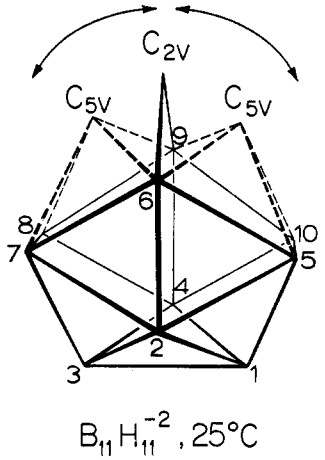

Figure 2. Proposed mechanism for isomerization of $B_{11}H_{11}^{2-}$ ion. The C_{5v} intermediate is probably never actually achieved in the rearrangement, which may also involve partly concerted processes in producing eventual equivalence of all B atoms. Atom 11 has not been labeled.

from C_{5v}, through C_{2v}, to another C_{5v} and to another C_{2v} structure. Such a process can be expected to have a low activation energy and to mix all boron atoms within the molecule. Moreover, this process accounts for the single ^{11}B boron environment in $B_{11}H_{11}^{2-}$ and for the two different ^{11}B boron environments (B–H and B–Br of ratio 7 to 4) in $B_{11}H_7Br_4^{2-}$ provided only that the characteristic time for the process is fast compared with the nmr time scale. Even at −90° the ^{11}B resonances developed no asymmetry, so that a low activation energy is required.

The C_{5v} structure for $B_{11}H_{11}^{2-}$ is to be regarded as highly idealized, since the central three-center bond theory[7] of the boranes gives no acceptable valence structure, and simplified molecular orbital theory[8] indicates an open valence shell. Either solvent interaction or distortion of the C_{5v} structure would remove this difficulty. No such difficulty exists for the C_{2v} structure for $B_{11}H_{11}^{2-}$, which can be described in terms of three distinct central three-center bonds to the 11th BH unit and the remaining framework bonds selected from those for $B_{10}H_{14}^{2-}$ to be compatible with these three bonds. From these simple bonding arguments we favor the C_{2v} structure, isomerizing through a structure distorted from the idealized C_{5v} model.

Low temperature isomerization has not been observed and would not necessarily be expected in the $B_{10}H_{10}CH^-$ ion and the $B_9C_2H_{11}$ isoelectronic analogs. Use of an open three-center bond $B_6C_{11}B_9$ at the 11 position in[9] $B_{10}H_{10}CH^-$ and of an open three-center bond $B_5C_6B_7$ and $B_8C_9B_{10}$ in $B_9C_2H_{11}$ may stabilize a C_{2v} valence structure having 0930 topology and single bonds 1–3, 2–6, and 4–9 (and central three-center bonds 1,2,5; 2,3,7; 3,4,8; and 1,4,10). This valence structure, not suitable for $B_{11}H_{11}^{2-}$, might localize carbon at position 11 in[10] $B_{10}H_{10}CH^-$ or at positions 6 and 9 in

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$C_2B_9H_{11}$. Nevertheless, a study of the nmr spectrum of $B_{10}H_{10}CH^-$ at higher temperatures might be interesting.

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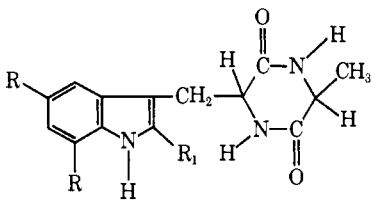
Monoisoprenylated *cyclo*-L-Alanyl-L-tryptophanyl. A Biosynthetic Precursor of Echinulin

Sir:

Biosynthetic studies in *Aspergillus amstelodami* indicate that mevalonic acid[1] and *cyclo*-L-alanyl-L-tryptophanyl[2] are *in vivo* precursors of echinulin (I). Partially isoprenylated peptide intermediates have not been isolated from the fungus or been shown to be *in vivo* precursors of echinulin. Recently, however, a partially purified enzyme from this fungus has been described[3] which transfers the isoprene unit from 3-methyl-2-butenyl 1-pyrophosphate to *cyclo*-L-alanyl-L-tryptophanyl (III) forming monoisoprenylated *cyclo*-L-alanyl-L-tryptophanyl (MICAT), tentatively identified as *cyclo*-L-alanyl-2-(1,1-dimethylallyl)-L-tryptophanyl (II). This



I, R = $-CH_2CH{=}C(CH_3)_2$; $R_1 = -C(CH_3)_2CH{=}CH_2$
II, R = H; $R_1 = -C(CH_3)_2CH{=}CH_2$
III, R = R_1 = H

paper describes *in vivo* studies which establish MICAT as a precursor of echinulin.

cyclo-L-Alanyl-L-tryptophanyl, *cyclo*-L-alanyl-L-[3-^{14}C]tryptophanyl, and [1-^{3}H]3-methyl-2-butenyl 1-pyrophosphate were prepared as previously described.[3] MICAT, singly labeled with tritium in the isoprene moiety and doubly labeled with tritium in the isoprene moiety and ^{14}C in the 3 position of the tryptophanyl moiety, were prepared enzymically using the above reagents and a partially purified enzyme from *A. amstelodami*, by a slight modification of the previously described methods.[3] The chromatographic mobilities and ultraviolet spectra of the isolated radioactive products were the same as those previously described for MICAT.

The utilization of ^{3}H-MICAT and ^{3}H,^{14}C-MICAT as precursors of echinulin was studied in growing surface cultures of *A. amstelodami* (ATCC 10065). Culture flasks containing 50 ml of Czapek-Dox broth supplemented with sucrose (30%) were inoculated with fungus and incubated at 30°. In two experiments, 2- to 3-day-old cultures were fed ^{3}H-MICAT dissolved in 0.25 ml of dimethyl sulfoxide (251,400 dpm, experiment 1; and 282,000 dpm, experiment 2), and then permitted to continue growing for 4 more days. In a third experiment, a 4-day-old culture was similarly fed ^{3}H,-^{14}C-MICAT (334,000 dpm, ^{3}H; and 12,500 dpm, ^{14}C) and permitted to continue growing for 3 more days. The fungal mats were harvested and dried, and the lipid-soluble metabolites were extracted with $CHCl_3$ as previously described.[4] The $CHCl_3$ extracts contained approximately 20% of the total radioactivity fed to the fungus. Most of the remaining radioactivity was shown to be present in the culture medium.

In each case the $CHCl_3$ extracts were concentrated and the metabolites chromatographed as previously described[4] on 10-g silica gel columns, using 250 ml each of benzene–ethyl acetate (8:2, v/v) and benzene–butanol (95:5, v/v) as eluents. The metabolites eluted in several ultraviolet absorbing peaks with echinulin emerging from the column in the benzene–butanol solvent as previously described.[4] Echinulin was identified by its ultraviolet spectrum and R_f values in several thin-layer chromatographic systems. Radioactivity was observed in the echinulin fraction in each case and represented 14, 11, and 5% of the total radioactivity fed to the fungus in experiments 1, 2, and 3, respectively.

Aliquots from the pooled chromatographic fractions containing echinulin (experiment 1) were subjected to thin-layer silica gel chromatography in three solvent systems, benzene–ethyl acetate (8:2, v/v), benzene–butanol (8:2, v/v), and benzene–ethanol (8:2, v/v), and gave R_f's of 0.00, 0.85, and 0.82, respectively. In each case, the only component observed on the fluorescent sheets chromatographed with an R_f value identical with that of authentic echinulin. Furthermore, analysis of the chromatographic sheets for radioactivity indicated in each solvent system that essentially all of the radioactivity cochromatographed with echinulin. *cyclo*-L-Alanyl-L-tryptophanyl and the MICAT in benzene–butanol (8:2, v/v) gave R_f's of 0.11 and 0.45, respectively, indicating that the fungal product chromatographs quite differently than these compounds.

In other control experiments, approximately 5×10^4 dpm of the ^{3}H-MICAT was mixed with either 33 mg of echinulin or a nonradioactive $CHCl_3$ extract of a fungal mat grown under the same conditions as those used in the feeding experiments. Silica gel column chromatography of these mixtures demonstrated no radioactivity in the isolated echinulin fractions. The ^{3}H-MICAT was removed from these columns by subsequent elution with ethanol.

Furthermore, a crude ^{3}H-labeled echinulin fraction (8500 dpm), prepared by differential solvent extraction[5] of a dried $CHCl_3$ extract from a culture fed ^{3}H-MICAT, was mixed with 30 mg of authentic echinulin and subjected to repeated recrystallizations from ethanol. Constant specific activity was obtained after the fourth recrystallization.

Experiments with doubly labeled MICAT were car-

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