ometry noted for the two homochelates at the ends of the series. The intense bands at the red end of the visible spectra are consistent with the metal to ligand charge-transfer designation determined for the tetrakis 8-quinolinol derivatives of tungsten(IV).[22] That is, the smaller aromatic picolinato ligands cause shifts to higher energies relative to the more highly conjugated quinolinolato ligands by about 0.06 μm^{-1} for each picolinato replacement.

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(29) The 2:1 doublet is at 2.42 and 2.47 ppm at 35 °C in CD_2Cl_2.
(30) The only exceptions to this among the numerous dodecahedral and antiprismatic possibilities are a few which violate Orgel's rule; cf. footnote 31 and ref 23 and 32.
(31) These results do not prove a rigid stereochemistry exists for the WP_nQ_{4-n} series. Flexible or nonrigid metal centers can cycle through various polytopes without ligand scrambling.[10] (Figure 1 of ref 3 shows such a nonscrambling cycle including the C_{2v} hendecahedron, the D_{4d} antiprism, and the D_{2d} dodecahedron.) The ground states for all of the WP_nQ_{4-n} species are expected to have oxygen atoms at the dodecahedral A positions and nitrogen atoms at the B positions in accord with Orgel's rule.[23,32] Logical low energy paths involving antiprismatic and/or hendecahedral intermediates either lead back to the initial dodecahedron or to dodecahedra with some nitrogen and oxygen atoms exchanged from the low energy positions. Continual cycling to the same low energy dodecahedron can produce the observed stereochemical integrity. Details to be submitted for publication.
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(33) The visible spectra were obtained as the bands emerged from the chromatographic column before any isomerization can occur.
(34) Theoretically, 11 WP_2Q_2 geometrical isomers exist which keep the nitrogens in the dodecahedral B positions and the oxygens in the dodecahedral A positions as anticipated from Orgel's rule. The remainining nine structures include four isomers derived from the parent C_2(*mmgg*) stereoisomer, three from D_2(*gggg*), and two from S_4(*gggg*).

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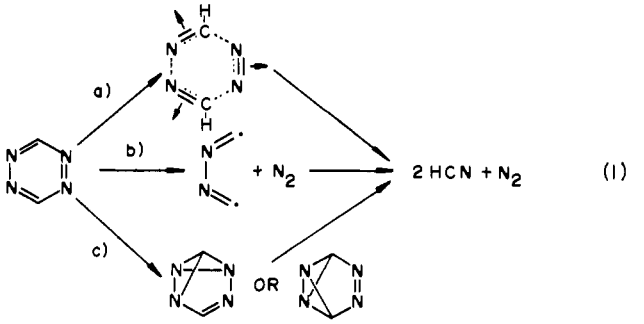
The Photochemical Decomposition of 1,4-s-Tetrazine-$^{15}N_2$

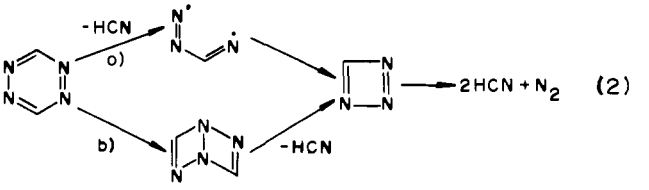
Sir:

Recently Hochstrasser and King[1] reported that *s*-tetrazine in mixed crystal systems undergoes isotopically selective photochemical decomposition from both the lowest n-π^* singlet and triplet state to yield, with near unit quantum efficiency,[2] stoichiometric quantities of nitrogen and hydrogen cyanide. No intermediate species were observed in this photolysis even when performed in organic crystals at 1.6 K.[1,3] These observations led us to investigate further the nature of this intriguing photochemical reaction. We wish to report here the preparation and state selective photochemical decomposition of the isotopic species 1,4-*s*-tetrazine-$^{15}N_2$. In addition, we draw attention to the potential of low temperature high resolution mixed crystal absorption spectroscopy as a novel nondestructive method for isotopic analysis.

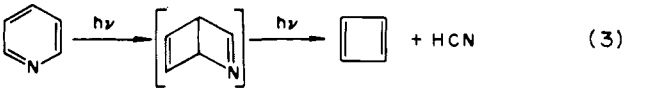
Two general reaction pathways are immediately discernible for this photoinduced reaction, the primary distinction being the occurrence or nonoccurrence of bonding between the nitrogen atoms disposed 1,4 in the tetrazine molecule. For example, excitation as shown in eq 1, could lead either via a concerted (1a) or stepwise (1b or 1c) process to N_2 and HCN without the advent of a 1,4-nitrogen bonded intermediate. Alternatively, decomposition involving 1,4-bonding could proceed through such cyclic intermediates as triazacyclobutadiene (eq 2).[4] Refinement of the latter pathway allows for HCN extrusion to occur either prior to or after 1,4-nitrogen bonding. Ample precedent for eq 2 arises from the recent observation at room temperature of "Dewar" pyridine upon ir-



(1)



(2)



(3)

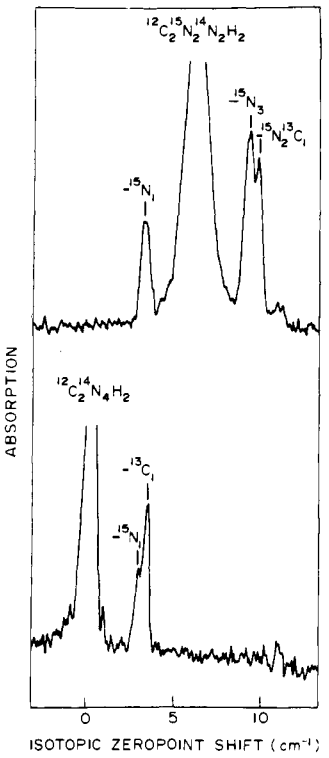


Figure 1.

radiation of pyridine in the liquid phase.[5] In addition, Chapman and co-workers[6] have demonstrated that cyclobutadiene is a secondary photochemical product of pyridine when irradiated at low temperature (8 K) in an argon matrix.[7]

To distinguish between reaction pathways (1) and (2), *s*-tetrazine labeled with nitrogen-15 specifically at the 1 and 4 positions was required. Photochemical decomposition of this species via either pathway would yield 1 equiv of HCN (mol wt 27) and 1 equiv of HCN (mol wt 28). The resultant nitrogen, on the other hand, would be entirely mol wt 29 from pathway 1, while pathway 2 would yield an isotopic mixture of N_2: 0.25 equiv of $^{14}N_2$ (mol wt 28), 0.5 equiv of $^{14}N^{15}N$ (mol wt 29), and 0.25 equiv of $^{15}N_2$ (mol wt 30). Mass analysis of the derived nitrogen would allow evaluation of the relative contribution pathways (1) and (2) make to the overall photochemical reaction.

Isotopically labeled 1,4-*s*-tetrazine-$^{15}N_2$ of high purity was prepared via the method of Spencer, Cross, and Wiberg[8] as modified by King[9] employing ethyl diazoacetate-$^{15}N_1$ available in high yield upon diazotization[10] of ethyl glycinate hydrochloride with nitrous acid generated from sodium nitrite-$^{15}N_1$ (99.5%).[11] Initial isotopic composition of the nitrogen-15 enriched *s*-tetrazine was determined by low temperature high resolution mixed crystal absorption spectroscopy. Optical quality single crystals of benzene were grown by the Bridgeman technique[12] from high purity benzene doped with the enriched *s*-tetrazine at ca. 10^{-5} mol per mole. Figure 1 displays at high resolution (ca. 0.15 cm^{-1}) the origin regions of the lowest energy singlet-singlet absorption spectra of *s*-tetrazine and 1,4-*s*-tetrazine-$^{15}N_2$ in benzene at 4.2 K. Clearly evident in Figure 1 are the transitions due to the isotopic species: *s*-tetrazine-$^{15}N_1$; -$^{15}N_2$; -$^{15}N_3$; -$^{15}N_2{}^{13}C_1$. The respective intensity ratios of 1.6:100:2.7:2.2 were calculated assuming a natural abundance of carbon-13 (e.g., 1.1%). These measurements were repeatable and accurate to 0.1% abundance. Confirmation of this analysis by high resolution mass spectrometry[14] establishes the utility of high resolution absorption spectroscopy for isotopic analysis. The relatively large amount of *s*-tetrazine-$^{15}N_3$ in the enriched sample (expect 0.75% from natural abundance) indicates, as expected,[10] that some isotopic exchange occurs during the diazotization step of the chemical synthesis.

State selective irradiations of 1,4-*s*-tetrazine-$^{15}N_2$ in the gas and solid phases were performed at room temperature with either a 1000-W Xe or high pressure Hg arc properly filtered to selectively excite either the $^3n\pi^*$ (7500–6000 Å), $^1n\pi^*$ (5800 Å), or $^1\pi\pi^*$ (3200–2500 Å) state. Approximately 1 mg of nitrogen-15 enriched *s*-tetrazine was photolyzed in each case. The photoproducts were subsequently fractionally distilled into a high resolution mass spectrometer. In every experiment the results were identical. The only species observed over a trap held at 77 K was $^{14}N^{15}N$ (*m/e* 29). No $^{15}N_2$ (*m/e* 30) (i.e., 1.5% or less) was observed. When the trap temperature was raised to 273 K, two isotopic species of HCN (*m/e* 27 and 28) were detected in approximately equal amounts. The small amount of tetrazine-$^{15}N_3$ (e.g., 2.7%) present in the labeled tetrazine sample was expected to lead to ca 1.3% of $^{15}N_2$ (*m/e* 30); however, this was not detected as the instrumentation[14] ignores peak intensities at the level of 1.5% or less.

From these results we conclude that 1,4-nitrogen bonding plays a negligible role in the overall photochemical decomposition of *s*-tetrazine. Second, the photochemical decomposition of *s*-tetrazine leads to the same products with the same isotopic distributions following excitation to either the singlet or triplet state. This result is consistent with the suggestion[1] that the dissociation of the triplet is spin-orbit induced. These results coupled with the absence of observable intermediates at 1.6 K and the fact that the reaction occurs equally efficiently in solids, liquids, and gas (i.e., there is little steric influence on te reaction) would seem to favor reaction processes 1a or 1b.[15] Finally, this study demonstrates for the first time that high resolution low temperature mixed crystal absorption spectroscopy has significant potential as an alternate accurate method for analysis of isotopic compositions on the nanogram level.

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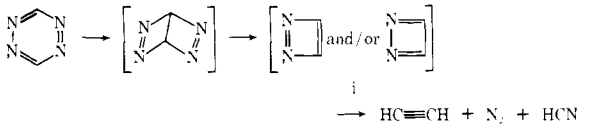
(4) A third reaction pathway involving 1,4-carbon–carbon bonding, as shown below, is formally possible but has been demonstrated to be unlikely. This pathway would be expected to yield at least to some extent acetylene in addition to N_2 and HCN. That is, it is unlikely that fragmentation of either diazacyclobutadiene (i) would lead solely to HCN. Careful analysis, by infrared spectroscopy, has indicated that less than 0.5% of acetylene relative to HCN is produced in the photolysis of *s*-tetrazine.



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(15) By process 1b we do not exclude the equivalent possibility of initial HCN extrusion.

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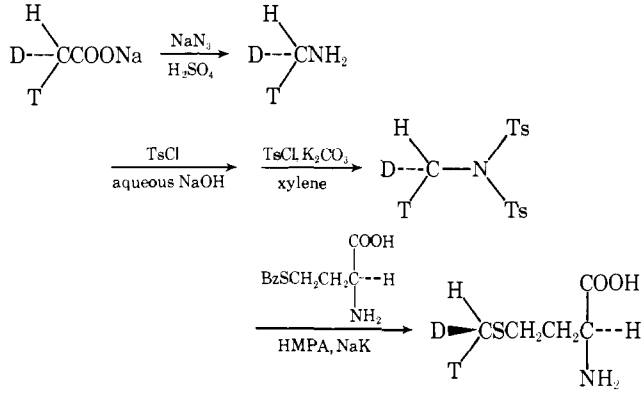
Synthesis of Methionine Carrying a Chiral Methyl Group and Its Use in Determining the Steric Course of the Enzymatic C-Methylation of Indolepyruvate during Indolmycin Biosynthesis

Sir:

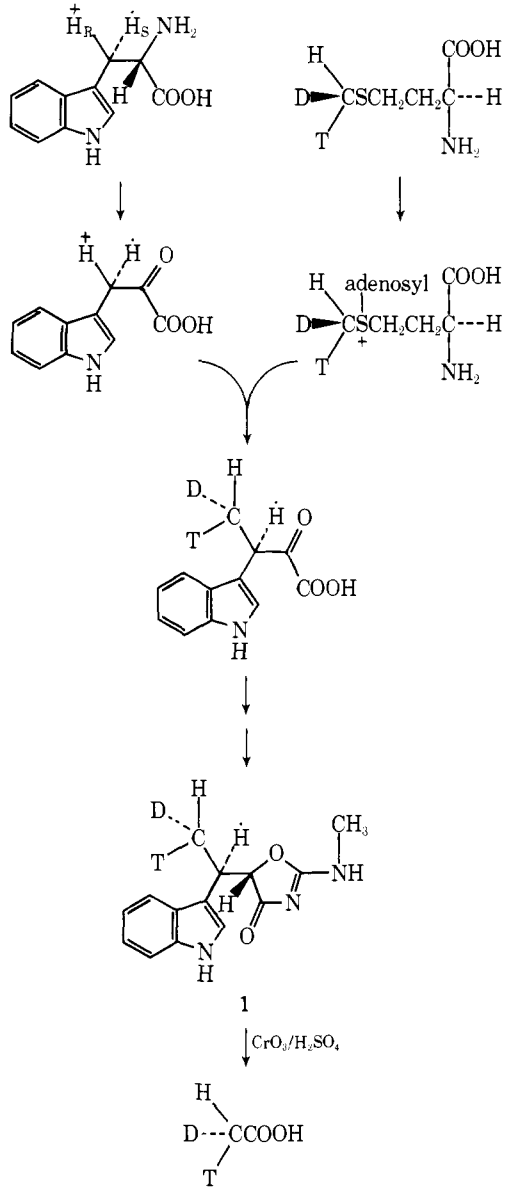
Transmethylation reactions involving the transfer of the methyl group of methionine are widespread in nature, but little is known about their detailed mechanism. This communication describes a synthesis of the two diastereomers of L-methionine carrying a chiral methyl group and the results of experiments using these substrates as methyl donors in the in vivo synthesis of the antibiotic, indolmycin (**1**).

The reaction sequence for the methionine synthesis is shown in Scheme I. The *S*- and *R*-[2-$^2H_1$,$^3H_1$]acetates needed as starting materials were prepared by using the glycolytic enzymes to synthesize *R*- and *S*-[3-$^2H_1$,$^3H_1$]pyruvates,[1,2] which were trapped as lactate using an excess of lactate dehydrogenase and NADH. Lactate was isolated by paper chromatography (Whatman 3MM, ethanol-NH_4OH-H_2O 8:4:17) and oxidized to acetate.[3] The chirality of the methyl group of these acetate samples and others described below was determined by the method of Cornforth et al.[4] and Arigoni et al.,[5] following

Scheme I



Scheme II



Eggerer's procedure.[4] In this procedure the acetate sample is enzymatically converted to malate which is then equilibrated with fumarase. During equilibration, malate samples synthesized from the *S*-isomer of acetate retain less than half of their tritium while samples synthesized from the *R*-isomer retain more than half of their tritium.

The first step in the synthesis of methionine is the Schmidt degradation of acetate to methylamine,[6] which is trapped as the hydrochloride and tosylated by heating with *p*-toluenesulfonyl chloride in 10% aqueous NaOH. The second tosyl group is introduced by refluxing the monotosylate, *p*-toluenesulfonyl chloride, and K_2CO_3 in anhydrous xylene. The key step in the sequence is the use of the ditosylimide function as a leaving group in the alkylation of the homocysteine anion with the chiral methyl group.[7,8] This reaction was performed, under an argon atmosphere, by treating a suspension of benzyl-L-homocysteine in HMPA with Na-K alloy, followed by addition of the ditosylimide and heating to 80 °C. Methionine was purified by ion exchange (Dowex 50W, 10% NH_4OH) and thin layer (silica gel 60 F-254, 1-butanol-acetic acid-H_2O 4:1:1) chromatography. The Schmidt reaction is known[9] to proceed with retention of configuration and the ditosylimide displacement should involve inversion of configuration, racemization being the only plausible alternative.[10] Thus, *S*-[2-