clude that the splitting is quite similar throughout the series, with perhaps a slight tendency to increase as the NNC angle increases.

Indirect support for our assignment of the pes of **1**(1) can be obtained by noting that in a certain sense our assignments appear to be consistent with the pes of 2,3-diazabicyclo[2.2.1]heptane.[6] Upon forming the hydrazine derivatives of **1**(*n*), the N–N bond would be expected to lengthen and the dihedral angle between the "lone pair" orbitals would increase from 0 to about 120°. Consequently the interaction of the "lone pair" orbitals would be less. This is, in fact, confirmed by the pes of the hydrazine derivative of **1**(1) which indicates a value of 1.81 eV for Δ^6 compared with the value of 2.95 eV reported here for **1**(1).

Because of its low extinction coefficient, the observed uv transition of **1**(*n*) (*cf.* Table II) is certainly of the n → π^* type. Recent *ab initio* calculations[16] indicate that for cis azo compounds the n → π^* transition energy decreases as ∠NNC increases, mainly because the n– level is destabilized while the π^* level remains approximately unchanged. Thus within a series of closely related molecules we can expect that the variation of IP_1 parallels the variation of the n → π^* transition energy. This is indeed the case for **1**(*n*) for which a reasonable correlation of λ_{max} (in eV) *vs.* IP_1 is observed (*cf.* Tables I and II); there is a small discrepancy for **1**(4) but slight changes in correlation energy and orbital reorganization effects prevent a strictly quantitative correlation between λ_{max} and IP_1.

Finally we would like to point out an interesting feature of the pes of all cis azo molecules that have been studied to date; the separation of the n– and π levels is remarkably constant (about 2.5 ± 0.2 eV) whereas the splitting of the n_+ and n– "lone pair" orbitals can be as small as 1.6 eV in 3,4-diazatricyclo[4.2.1.$0^{2,5}$]non-3-ene[15] or as large as 3.5 eV in diazirine.[2]

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Configuration of the β-Carbon Atoms of the β-Methyllanthionine Residues in Nisin

Sir:

β-Methyllanthionine occurs in yeast[1] and as a constituent of several interesting heterodetic polycyclic peptides, the structures of two of which have recently been elucidated.[2,3] Although the configurations of alanine and aminobutyric acid obtained after desulfurization have been determined,[2,3] the assignment at the β-carbon atom had to await comparison of the natural material with synthetic β-methyllanthionine of known configuration.

This has now been accomplished for the isomer occurring in nisin,[2] and several observations have been made pertaining to the problem in general.

Starting materials for the synthesis of the isomers of β-methyllanthionine are the diastereoisomeric pairs A and B of DL-β-methyl-*S*-benzylcysteine prepared by the addition of benzylmercaptan to the azlactone of benzoyldehydrobutyrine followed by fractional crystallization and hydrolysis of the products.[4] The configurational identities were determined by application of the cyanogen bromide reaction[5] to the *N*-acetyl-β-methyl-*S*-methylcysteines. The benzyl group was removed by reaction with anhydrous hydrogen fluoride (HF) for 1 hr at room temperature in the presence of anisole. After evaporation of the HF and washing with ethyl acetate, the amino acids were *S*-methylated by treatment with methyl-*p*-nitrobenzene sulfonate in 0.05 *M* phosphate buffer (pH 8.5) under nitrogen. The *S*-methyl derivatives were treated with a fourfold excess of acetic anhydride at the same pH, and sufficient 88% formic acid was added to give a 60% formic acid solution. Exposure to 3 equiv of cyanogen bromide at room temperature for 2 days resulted in the transformation of 50% of the acetyl-DL-β-methyl-*S*-methylcysteine A to 97% pure DL-*O*-acetyl-*allo*-threonine (Figure 1) while the amino acids B, correspondingly yielded DL-*O*-acetylthreonine of identical configurational purity.

The identity of the products was determined by comparison of their elution volumes from cation exchange resin columns (0.9 × 60 cm, 53°, 0.2 *N* sodium citrate buffer, pH 3.25) with those of authentic samples prepared from DL-threonine and DL-*allo*-threonine by treatment with 1 *N* HCl in glacial acetic acid and crystallization from alcohol–ether. Since an inversion of configuration at the β-carbon atom is expected in the cyanogen bromide reaction (Figure 1), the pair designated A must be the DL-threo amino acids, while B are the DL-allo isomers.

The β-methyllanthionines were obtained from the reaction of the β-methylcysteines with *N*-formyl-L-β-chloroalanine.[6] The latter was prepared by dissolving L-chloroalanine hydrochloride in anhydrous formic acid, adding 1 equiv of sodium bicarbonate and 20 equiv of preformed formic acetic anhydride[7] at 10° in two portions separated by a 2-hr interval. The mixture was lyophilized after 4 hr and the product allowed to react with the thiol amino acids in 0.05 *M* phosphate buffer (pH 8.5) under nitrogen. The formyl group was removed with 6 *N* HCl in 10 min at 100°.[8] Amino acid analysis indicated an initial 5% per day rate of formation of β-methyllanthionine. The only side reaction of significance, the formation of serine, proceeded at half that rate. The products from DL-*threo*-β-methylcysteine are not separated in the chromatographic system employed (peak II, Figure 2); those from DL-*allo*-β-methylcysteine are eluted at different effluent volumes (peaks I and I′, Figure 2).[9]

The isomer of β-methyllanthionine occurring in nisin[2] coelutes with the threo derivatives and must therefore have the L-*configuration at the β-carbon atom* since the α-carbon atom of the amino butyric acid moiety had previously been assigned the D configuration.[2]

Inasmuch as the assignment of configuration is based on properties of the amino acids obtained by acid hydrolysis, knowledge of the extent of racemization occurring under these conditions is necessary. Lanthionine is completely racemized under the conditions of acid hydrolysis.[2] Isolation of the isomers represented by peak I′ and treatment with 6 *N* HCl for 24 hr at 110° results in the transformation of 30% of the material to the isomers of peak I and 10% to the isomers of peak II. When the isomers of peak II are exposed to the same conditions, they are transformed to the extent of 10% to the isomers of peaks I and I′.

Evidently the α-carbon atom of the alanine moiety is subject to more extensive configurational change than that of the amino butyric acid portion. This is consistent with the occurrence of 0.5 residues of *allo*-β-methyllanthionine in hydrolysates of nisin which contains a total of four residues of the amino acid. Thus, only 63% of the amino acid in a hydrolysate retains the original configurations, while 27% is inverted at the alanine moiety alone, 3% at both the α-carbon atoms of the alanine and amino butyric acid portions, and 7% at the α-carbon atom of the amino butyric acid moiety only. In spite of this, β-methyllanthionine having the correct configuration at the α-carbon atoms[3] and showing the elution behavior of the threo compound[10] was isolated by the selective process of crystallization from a hydrolysate of subtilin.[11]

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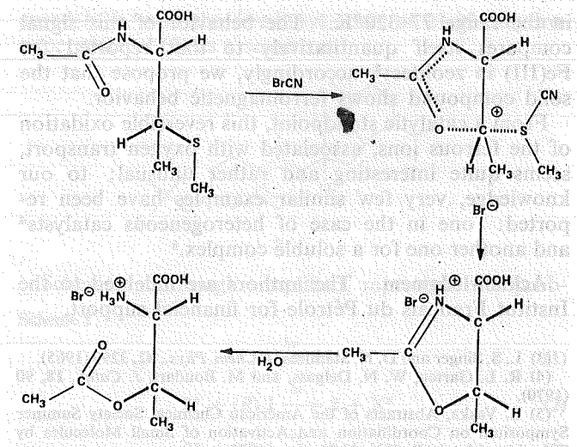

Figure 1. The reaction of *N*-acetyl-β-methyl-*S*-methylcysteine with cyanogen bromide.

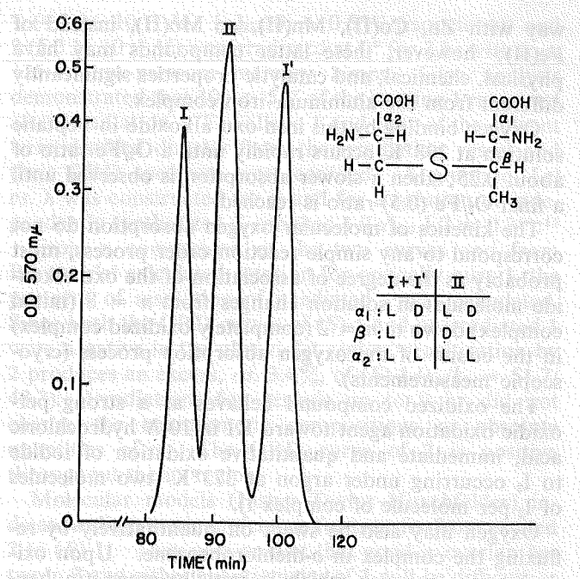

Figure 2. The separation of the isomers of β-methyllanthionine by ion exchange chromatography (column: 0.9 × 60 cm, 53°, 0.2 *N* sodium citrate buffer, pH 3.25). Isomers not shown in inset are enantiomers with the D-alanine moiety.

(8) This procedure gave 95% pure L-lanthionine in a trial synthesis wherein the undesired product of epimerization (*meso*-lanthionine) is easily detected by ion exchange chromatography.

(9) In a synthesis involving addition of DL-cysteine to benzoyldehydrobutyrineazlactone, the quantities of the isomers of peaks I, II, and I′ are in the proportion 1:2:1.

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$Fe[OAl(O\text{-}n\text{-}Bu)_2]_2$. A New Molecular Oxygen Activator

Sir:

We want to report the behavior of an oxo alkoxide of aluminum and iron(II) as a reversible molecular oxygen activator.

This amorphous compound, highly soluble in hydrocarbons, is obtained by a straight condensation reaction (at 500°K in decalin under argon atmosphere), according to eq 1. Its composition was established by

$$2Al(OR)_3 + Fe^{II}(CH_3COO)_2 \longrightarrow (OR)_2AlOFeOAl(OR)_2 + 2CH_3COOR \quad (1)$$

elementary analysis;[1] the Al/Fe ratio is found to be near 1.98 by complexometric titration (EDTA in acetate buffer after oxidation of Fe(II) into Fe(III)). The OR/Al ratio as determined by glc after hydrolysis of the complex equals 1.96. All these values are consistent with the expected ones for eq 1, *i.e.*, Al/Fe = OR/Al = 2. R may be a *n*-butyl, isopropyl, or isobutyl group. Other oxo alkoxides may also be prepared in the same

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way with Zn, Co(II), Mn(II), or Mo(II), instead of Fe(II); however, these latter compounds may have physical, chemical, and catalytic properties significantly different from the aluminum–iron complex.

Oxygen binding by this iron oxo alkoxide in heptane solution at 298°K occurs rapidly until a O_2/Fe ratio of about 0.25; then a slower absorption is observed until a final O_2/Fe (0.5) ratio is reached.

The kinetics of molecular oxygen absorption do not correspond to any simple reaction order process, most probably as the degree of association of the oxo alkoxide molecules in solution changes from $n = 8$ (initial complex) down to $n = 2$ (completely oxidized complex) in the course of the oxygen absorption process (cryoscopic measurements).

The oxidized compound behaves as a strong peroxidic oxidation agent toward KI in 10 *N* hydrochloric acid, immediate and quantitative oxidation of iodide to I_2 occurring under argon at 373°K (two molecules of I_2 per molecule of complex I).

Oxygen may also be swept off quantitatively by refluxing the complex in *o*-dichlorobenzene. Upon oxidation, the solution which is initially green (in heptane or other solvents) turns red; refluxing in $C_6H_4Cl_2$ yields back the initial green coloration and the process may be repeated several times.

By redox titration, Fe(II) is found to be the dominant species in the unoxidized complex, while, after O_2 absorption, Fe(III) is the only valence state as observed by a specific EDTA complexometric titration. This valency change of Fe is supported by uv–visible spectra which show a band at 950 nm in the unoxidized complex; this band, characteristic of the high-spin Fe(II) complexes and assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition,[2] disappears upon oxidation.

Supported by the former data, a reversible oxygen transport mechanism (eq 2) may be postulated.

$$\frac{2}{n}[(OR)_2AlOFeOAl(OR)_2]_n + O_2 \underset{C_6H_4Cl_2}{\overset{298°K}{\rightleftharpoons}} \underset{\displaystyle O}{\overset{\displaystyle (OR)_2AlOFeOAl(OR)_2}{|}} \underset{\displaystyle O}{|} \underset{\displaystyle (OR)_2AlOFeOAl(OR)_2}{|} \quad (2)$$

I

The reversibility of a mechanism such as eq 2 (with respect to Fe) has been ascertained over four complete redox cycles from epr data. No signal is detected for the unoxidized material at 298°K; hence, this species probably contains Fe(II) which is not detected by epr at this temperature. Upon oxidation, a broad resonance line (peak-to-peak line width = 1500 Oe) centered near $g = 2.3$ appears gradually. Internal calibration with respect to a known standard (Varian Strong Pitch) was used to evaluate the relative spectral intensities and to show that the epr signal was of the order of magnitude expected for the oxidized compound in solution at the used concentration level, hence ruling out impurity effects; this signal is assigned to Fe(III) species.

The epr signal of the oxidized solid compound has an intensity which is nearly independent of temperature in the range 77–320°K. The behavior of this signal compares itself quantitatively to that reported for Fe(III) in zeolites;[3] accordingly, we propose that the solid compound shows ferromagnetic behavior.

From a catalytic standpoint, this reversible oxidation of the ferrous ions, associated with oxygen transport, seems quite interesting and rather unusual; to our knowledge, very few similar examples have been reported: one in the case of heterogeneous catalysts[4] and another one for a soluble complex.[5]

Acknowledgment. The authors are indebted to the Institut Français du Pétrole for financial support.

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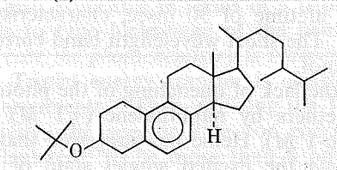
A General Method for the Determination of Steric Effects during Collisional Energy Transfer. Partial Photoresolution of Penta-2,3-diene

Sir:

Since an electronically excited sensitizer (P*) and a quencher (A) must be very close during collisional energy transfer, bulky groups close to the chromophores of P and A should be important in determining the efficiency of transfer. Demonstration of such effects has proved difficult[1] and only in a few cases have they been reported.[2,3] The main problem has been to separate a group's electronic pertubation on a chromophore (auxochromic effect) from its steric influence on the ease of approach of another molecule. We have devised a general method for the study of steric influences on collisional energy transfer which excludes auxochromic effects.[4] We report here its first application: the partial photoresolution of penta-2,3-diene (**1**).

Since the energy levels of any pair of enantiomeric allenes are the same, the rate constants for energy transfer from a nonchiral P to (*R*)- and (*S*)-**1** must be identical (*i.e.*, $k_r = k_s$). When P is optically active, k_r and k_s need not be equal. The collision complexes, [P···(*S*)-**1**]* and [P···(*R*)-**1**]* are diastereomeric and, in principal, chemically distinguishable. We have measured k_r/k_s with the *tert*-butyl ether of 21,22-dihydroneoergosterol (**2**) as a sensitizer.[5]



2

Scheme I, although simplified, represents the probable, important steps in the sensitized isomerization of **1** by **2**. At the photostationary state for **1**, eq 5 is

Scheme I

$$\mathbf{2} \xrightarrow{h\nu} \mathbf{2}^* \quad (1)$$

$$\mathbf{2}^* + (R)\text{-}\mathbf{1} \xrightarrow{k_r} \mathbf{2} + X^* \quad (2)$$

$$\mathbf{2}^* + (S)\text{-}\mathbf{1} \xrightarrow{k_s} \mathbf{2} + X^* \quad (3)$$

$$X^* \xrightarrow{k_x} \beta[(R)\text{-}\mathbf{1}] + (1 - \beta)[(S)\text{-}\mathbf{1}] \quad (4)$$

$$k_s/k_r = ([(R)\text{-}\mathbf{1}]/[(S)\text{-}\mathbf{1}])_{PSS}[(1 - \beta)/\beta] \quad (5)$$

valid. The ratio of [(*R*)-**1**]/[(*S*)-**1**] can be determined from the specific rotation of **1**, measured after prolonged sensitization by **2**, and from the absolute rotation of optically pure **1**, calculated by Brewster[6] to be $[\alpha]_{589}$ 174°. Subject to the provisions that X* is achiral and that it does not begin to decay to **1** until it separates from **2**, the decay ratio, $(1 - \beta)/\beta$, *must be* unity (*vide infra*).

The sequence for the $R \rightleftharpoons S$ isomerization of chiral allenes is thought to proceed from an antiplanar gound state and pass through one or both of two possible planar (achiral) excited states, *cis*-X* and *trans*-X*, which decay to regenerate the ground state.[7] Even if (*R*)- and (*S*)-**1** produce different ratios of *cis*-X*/*trans*-X* after excitation by **2**, eq 5 remains valid since *each* excited state must decay with equal probability to (*R*)- and (*S*)-**1**.[8]

In a typical experiment,[5] a 6-ml portion of a deoxygenated, argon-saturated isooctane solution of racemic **1** (4.3×10^{-2} *M*; $[\alpha]_{250}$ 0 ± 0.5°[11] (isooctane)) and **2** (5.3×10^{-2} *M*) was irradiated at 0° for 3 hr with four 125-W low-pressure mercury lamps. Glpc analysis demonstrated that 100 ± 5% of the starting **1** remained after irradiation. The allene **1** and part of the solvent were distilled directly from the irradiation vessel and their ORD spectrum was recorded. A graph of $[\alpha]$ *vs.* λ was constructed for it and for a solution of independently synthesized *S*-enriched **1** ($[\alpha]_{589}$ 1.7 ± 0.3°).[12]

From a comparison of the two curves and from Brewster's[6] calculated rotation for optically pure **1**, the per cent of resolution of irradiated **1** was calculated. Since both the ORD curves of (*S*)-**1** and of irradiated **1** were negative in the ultraviolet region, sensitization by **2** produces an excess, *ca.* 3.4%, of (*S*)-**1** (k_r/k_s = 51.7/48.3). Irradiations for periods up to 9 hr did not change the enantiomeric compositions or absolute quantities of **1**. The ORD curve of **2** is positive throughout the uv region.

Molecular models (Fisher–Taylor–Hirschfelder) indicate a slight steric preference for transfer from excited **2** to (*R*)-**1**. They also predict that good π overlap between **2** and either enantiometer of **1** will be difficult.

By the PPP method, Borden[7a] calculated E_s = 147 kcal/mol and E_t = 99 kcal/mol for the first excited singlet and triplet of antiplanar allene. This makes "vertical" energy transfer from a tetraalkyl-substituted phenyl chromophore (E_s = 105 kcal/mol,[13] E_t = 80 kcal/mol[14]) to **1** improbable. A reversible, stepwise addition of **1** to the phenyl chromophore of **2** is unlikely, also, since irradiation of benzene–allene solutions produces stable adducts.[15] Calculated energies for the planar excited states of allene[7a] (E_s = 94 kcal/mol, E_t = 62 kcal/mol) indicate that a "thermally activated" transfer[16] could occur. In fact, it is possible that an *electronically* excited state of **1** is not obtained during isomerization. Elucidation of the nature of the energy transfer step[17] and experiments with other allenes and optically active sensitizers are in progress and will be presented in a full paper.

While we have not mentioned the possible synthetic importance of this work it should be noted that with better selectivity, this method would offer a simple, one-step alternative to existing methods[10,12,18] for the resolution of allenes.

Acknowledgments. We wish to thank the Conselho Nacional de Pesquisas of Brazil, the National Academy of Sciences, the National Science Foundation, the Agency for International Development, and Atlantic Richfield of Brazil for generous financial support.

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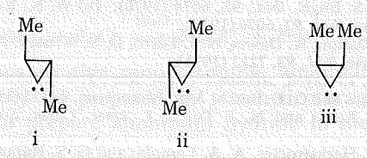
(8) It is possible,[9a] but improbable,[7b,9b] in this case that the ultimate precursors to the regeneration of **1** after its excitation are cyclopropylidenes, i–iii. Since i and ii are chiral, they could "decay" *via* a conrotatory opening to give an excess of (*R*)- or (*S*)-**1**.[10] However, if any point along the reaction, **1** → X* → **1**, includes a planar configuration, eq 5 is still valid. The work of Ward and Karafiath[7b] indicates that a planar configuration is obtained.



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