(m, 2 H), 4.65 (t, J = 2 Hz, 2 H), 6.41 (t, J = 1.9 Hz, 2 H).

1,2-Dibromo-7,7-dimethylenebicyclo[2.2.1]heptane. Catalytic hydrogenation was carried out with a Parr low-pressure hydrogenator under 75 psi initial pressure. A solution of 5,6-dibromo-7,7-dimethylenebicyclo[2.2.1]hept-2-ene (26.0 g, 93 mmol) in EtOAc (200 mL) was shaken at room temperature for 6 h in the presence of W-4 Raney Nickel[25] (prepared from 50% Ni-Al alloy). The reaction mixture was filtered and concentrated to give the title compound in quantitative yield, mp 75 °C after recrystallization from aqueous EtOH. ^{1}H NMR ($CDCl_3$): δ 0.59 (s, 4 H), 1.5-2.1 (m, 4 H), 2.10 (d, J = 7.9 Hz, 2 H), 4.78 (s, 2 H). Anal. Calcd for $C_9H_{12}Br_2$: C, 38.60; H, 4.31. Found: C, 38.51; H, 4.41.

7,7-Dimethylenebicyclo[2.2.1]hept-2-ene. Zn-Cu couple[26] (45 g) was added to a warm solution of 1,2-dibromo-7,7-dimethylenebicyclo[2.2.1]heptane (18.0 g, 65 mmol) in 95% EtOH (400 mL), and the mixture was refluxed for 5 h. The solid was filtered, and the filtrate was poured into H_2O (1.0 L). The mixture was extracted with pentane (2 × 50 mL), the combined extracts were washed twice with H_2O and dried over $MgSO_4$, and the pentane was removed with an efficient fractionating column. The residue was distilled to give 5.1 g (66%) of the title compound, bp 52-53 °C (30 Torr) ((lit.[24] bp 63 °C (60 Torr)).

7,7-Dimethylene-*exo*-2-acetoxy-*exo*-3-(chloromercurio)bicyclo[2.2.1]heptane. A solution of 7,7-dimethylenebicyclo[2.2.1]hept-2-ene (13.0 g, 108 mmol) and $Hg(OAc)_2$ (34.0 g, 105 mmol) in glacial AcOH (500 mL) was stirred at room temperature for 12 h, and then 900 mL of 2% aqueous NaCl was added. The solid that formed was filtered, washed with H_2O, air-dried, and recrystallized from EtOAc to give 26.0 g (75%) of the title compound, mp 97 °C. ^{1}H NMR ($CDCl_3$): δ 0.33-0.83 (m, 4 H), 1.00-1.90 (m, 4 H), 1.97 (s, 3 H), 2.45-2.65 (m, 2 H), 2.74 (d, J = 7.3 Hz, 1 H). Anal. Calcd for $C_{11}H_{15}CHgO_2$: C, 31.81; H, 3.64. Found: C, 31.82; H, 3.65.

7,7-Dimethylene-*exo*-3-deuterio-*exo*-bicyclo[2.2.1]heptan-2-ol and Tosylate 4. Reduction of 7,7-dimethylene-*exo*-2-acetoxy-*exo*-3-(chloromercurio)bicyclo[2.2.1]heptane (20.8 g, 50 mmol) with sodium amalgam and NaOD in D_2O according to the procedure of Jensen, Miller, Cristol, and Beckley[11] gave the crude alcohol, which was tosylated[12a] to give 6.6 g (45% for two steps) of 4, mp 59-60 °C. ^{1}H NMR ($CDCl_3$): δ 0.17-0.75 (m, 4 H), 1.00-2.00 (m, 7 H), 2.46 (s, 3 H), 4.61 (d, J = 7 Hz, 1 H), 7.67 (q, 4 H).

***exo*-2-Acetoxy-*exo*-3-(bromomercurio)bicyclo[2.2.1]hept-5-ene.** A solution of bicyclo[2.2.1]hepta-2,5-diene (20.2 g, 0.22 mol) and $Hg(OAc)_2$ (49.8 g, 0.16 mol) in AcOH (120 mL) was stirred at room temperature for 10 min and poured into 200 mL of 10% aqueous KBr. From the oil that soon separated, the aqueous AcOH was decanted and the oil was crystallized at -20 °C. The solid was filtered and washed with H_2O several times to give 65 g of crude product. Recrystallization from EtOAc (200 mL) gave 53.0 g (80%) of the title compound, mp 127 °C (lit.[24] mp 127-128 °C). ^{1}H NMR ($CDCl_3$): δ 1.78 (s, 2 H), 2.10 (s, 3 H), 2.75 (dd, J = 7.2 and 2.5 Hz, 1 H), 3.14 (s, 1 H), 3.33 (s, 1 H), 5.10 (d, J = 7.1 Hz, 1 H), 6.22 (d of q, J = 17.0 and 3.0 Hz, 2 H).

***exo*-3-Deuteriobicyclo[2.2.1]hept-5-en-2-ol and Tosylate 5.** Reduction of *exo*-2-acetoxy-*exo*-3-(bromomercurio)bicyclo[2.2.1]hept-5-ene (21.6 g 50 mmol) with sodium amalgam and NaOD in D_2O according to the procedure of Jensen, Miller, Cristol, and Beckley[11] gave the crude alcohol, which was tosylated[12a] to give 4.9 g (37% for two steps) of 5, mp 43 °C (lit.[27] mp 49-51 °C). ^{1}H NMR ($CDCl_3$) δ 1.47-1.70 (m, 2 H), 2.45 (s, 3 H), 2.81 (s, 1 H), 2.94 (s, 1 H), 4.49 (d, J = 6.8 Hz, 1 H), 6.04 (d of q, J = 36.5 and 3.2 Hz, 2 H), 7.51 (q, 4 H).

Elimination Reaction Procedure and Hydrocarbon Analyses. Solutions of potassium alkoxides in triglyme were prepared by reacting KH with the corresponding alcohol in triglyme under nitrogen.[7] For reactions of 0.125 M tosylate with 0.25 M potassium alkoxide and 0.25 M 18-crown-6 in triglyme at 60 °C, hydrocarbon products were removed from the reaction vessel with a slow nitrogen sweep[15] and were trapped and analyzed by GC and GC-MS as reported previously.[7] For reaction of 0.125 M 4 with 0.25 M potassium *tert*-butoxide in triglyme in the absence of 18-crown-6, the reaction was conducted at 80 °C.

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Supplementary Material Available: Proton NMR spectra of tosylates 4 and 5 (2 pages). Ordering information is given on any current masthead page.

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Solvolytic Stereoselective Dehalogenation of *vic*-Dihalides[1]

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The debromination of *vic*-dibromides has been a subject of investigation with diverse reducing agents[2] in different solvents under a variety of reaction conditions. Both stereospecific and stereoselective dehalogenations have been reported with various reagents, but little is known about the role of solvents in these reactions except that methanol[3] is reported to bring about methanolysis of *meso*-stilbene dibromide (eq 1). *meso*- and *dl*-stilbene dibromides (1) have invariably been chosen as model substrates, and varying amounts of (*Z*)-stilbene (2) have been reported from *dl*-1, unlike *meso*-1 which gives (*E*)-2 stereospecifically and stereoselectively.

$$\underset{\text{Meso- or dl-}}{\text{RCHBr CHBr R}} \xrightarrow{\text{Reagent, Solvent}} \underset{\text{E- or Z-}}{\text{RCH=CHR}} \qquad (1)$$

This is the first report on the quantitative debromination of *meso*- and *dl*-stilbene dibromides (1) and *meso*- and *dl*-dimethyl-2,3-dibromosuccinates (3) by dry *N*,*N*-dimethylformamide (DMF) at 155-160 °C under N_2 atmosphere to give the (*E*)-alkene in the *absence* of any reagent whatsoever. The debrominations were complete in 90 min, and even at 100 °C we observed 19% debromination of *meso*-1 in 60 min with DMF. Thus, we believe that some of the previous reports on debromination with different reagents in DMF,[2f,4b,c,5] especially at elevated temperature,

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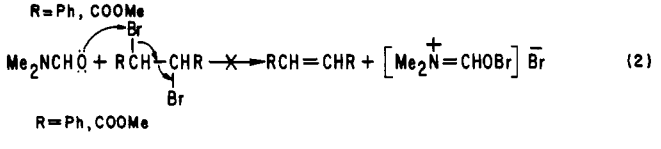
Table I. Reaction of *vic*-Dihalides with dry DMF under Nitrogen Atmosphere

substrate	solvent	time, min	product	% yield
meso-1	DMF	60	(*E*)-2	99[a]
dl-1	DMF	90	(*E*)-2	98[a]
meso-3	DMF	45	4	95[b]
dl-3	DMF	60	4	96[b]
meso-1	CH_3CN	90	*meso*-1	*c*
meso-1	THF	90	*meso*-1	*c*
meso-1	1,4-dioxane	90	*meso*-1	*c*
meso-stilbene dichloride	DMF	210	(*E*)-2	*d*
erythro-methyl cinnamate dibromide	DMF	60	(*E*)-methyl cinnamate	93[e]
benzalacetophenone dibromide	DMF	60	benzalacetophenone	83[e,f]
benzalacetone dibromide	DMF	60	benzalacetone	74[e,g]

[a] Relative yields determined by GLC. No (*Z*)-2 was detected. [b] Relative yields determined by GLC. No dimethyl maleate was detected. [c] Reactions carried out under reflux. GLC analyses of the reaction mixture showed no stilbenes. [d] GLC analyses showed 23% and 66% of (*E*)-2 after 60 and 210 min, respectively. [e] Isolated yield. [f] α-Bromobenzalacetophenone (13%) was also isolated. [g] α-Bromobenzalacetone (17%) was also detected.

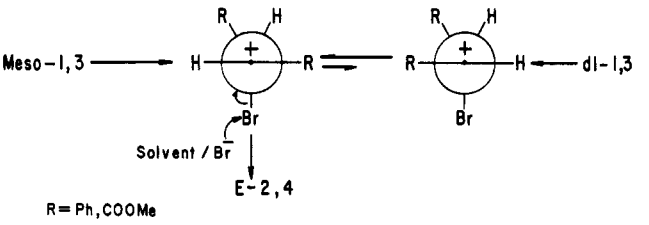
proceed mainly by the participation of the solvent alone. The reagent may, however, aid these dehalogenations. We have carried out a detailed investigation of these dehalogenations with DMF. Our results are summarized in Table I.

Our results (Table I) show that the elimination, in the conversion of *meso*- and *dl*-1 to (*E*)-2 and that of *meso*- and *dl*-3 to dimetheyl fumarate (4) exclusively, proceeds stereoselectively. The isomerization of (*Z*)-2 to (*E*)-2 during elimination has been ruled out by various independent experiments: (i) reaction of (*Z*)-2 with DMF at 155–160 °C as no traces of (*E*)-2 were detected even after 120 min; (ii) detection of *dl*-1[6] only in the isomerization of (*Z*)-2 to (*E*)-2 with bromine (equimolar) under above reaction conditions (~90 min), and (iii) isomerization of (*Z*)-2 to (*E*)-2 by continuous bubbling of dry HBr in the reaction mixture under the above reaction conditions not even 50% complete after 120 min.[7] Since the isomerization by Br_2 or HBr is not spontaneous, these observations suggest that the eliminations in question are stereoselective. This eliminates the possibility of an antiperiplanar (E_2) elimination where DMF acts as a two-electron reductant (eq 2) and also the elimination by an



S_N2 attack from the oxygen end of DMF on one of the carbons bearing halogen followed by an E_2 elimination (eq 3) as both of these pathways would lead to stereospecific

Scheme I



elimination contrary to our observations. The anti alignment in *meso*- and *dl*-1, though favored by orbital symmetry rules,[8] is opposed in the latter case conformationally by a free energy difference of 4.4 kcal/mol.[9] The stereoselective elimination via free radicals by single-electron transfer from DMF[10] is unlikely since no free radicals could be trapped by the hydrogen atom donors cyclohexene and cumene.

These eliminations are believed to be proceeding by slow ionization to a stable onium species, i.e., bromonium/carbonium ion pair or isolated carbonium ion which collapses to (*E*)-alkene. In the case of *dl*-1 or *dl*-3 the carbonium ion formed initially undergoes rapid C–C bond rotation, owing to conformational instability, to a more stable onium species (Scheme I). The absence of rate retardation by sodium bromide in the reaction of *meso*-1 in DMF under identical conditions implies irreversible ionization to an onium species. The participation by sodium bromide itself simultaneously cannot, however, be ruled out.[4b,e] The order of reactivity in E_1 elimination[11] I > Br > Cl > F also agrees with our observations since only 23% and 66% of dechlorination was observed after 60 and 210 min, respectively, in the reaction of *meso*-stilbene dichloride with DMF. The formation of intermediate onium species is further corroborated by (i) detection of trace amounts of α-bromostilbene in the reaction of *meso*-1 when repeated on a large scale (20 mmol) and confirmed by TLC and thin-layer cochromatography with the authentic sample, (ii) isolation of α-bromobenzalacetophenone (13%) and α-bromobenzalacetone (17%) besides the alkene in the reactions of benzalacetophenone dibromide and benzalacetone dibromide, respectively, and (iii) absence of any elimination (120 min) in the reaction of tolan dibromide with DMF under identical conditions. Nevertheless, no elimination was observed in the reaction of *meso*-1 with polar solvents, e.g., 1,4-dioxane, tetrahydrofuran, and acetonitrile.

Experimental Section

vic-Dibromides were prepared by the addition of bromine to the corresponding olefins. Dimethylformamide (BDH) was used after drying. Melting points were determined on a Labequip apparatus and are uncorrected. GLC analyses were done with SE-30 column (3 m) on a Shimadzu Model GC-9A using FID detector and nitrogen as the carrier gas. IR spectra were recorded on Shimadzu Model 435 spectrophotometer.

General Procedure for the Dehalogenation by DMF. A 10-mmol portion of the *vic*-dihalide was placed in a 100-mL round-bottomed flask mounted over a magnetic stirrer and fitted with a reflux condenser and mercury trap. A 50-mL portion of dry DMF was added to the flask, and the system was flushed with nitrogen for 15 min. The progress of the reaction was monitored by thin-layer chromatography. After complete disappearance of

(6) *dl*-1 is the starting material (entry 2, Table I), a study of which is the aim of this paper.

(7) However, in the debromination 1 with DMF only small amount of HBr, if any, may be present at such a high temperature. Hence, complete isomerization by HBr in 60–90 min under our reaction conditions is highly unlikely.

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the starting material, the contents of the flask were cooled to room temperature and poured into water (~300 mL). The product mixture was extracted with dichloromethane (3 × 25 mL), dried (anhydrous $MgSO_4$), and subjected to GLC analyses after concentration on a Buchi rotavapor. Only (*E*)-stilbene and dimethyl fumarate were detected from 1 and 3, respectively, and no trace of (*Z*)-alkene. The solvent was removed completely and the product dried under vacuum to yield (*E*)-alkene, confirmed by melting point, mixed melting point, and superimposable IR spectra.

The reaction mixtures from benzalacetophenone dibromide and benzalacetone dibromide were separated by column chromatography (silica gel, 100–200 mesh) with benzene as eluent to yield the corresponding olefin and the α-bromo olefin.

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Transition-Metal-Assisted Asymmetric Synthesis of Amino Acid Analogues. A New Synthesis of Optically Pure D- and L-Pyridylalanines

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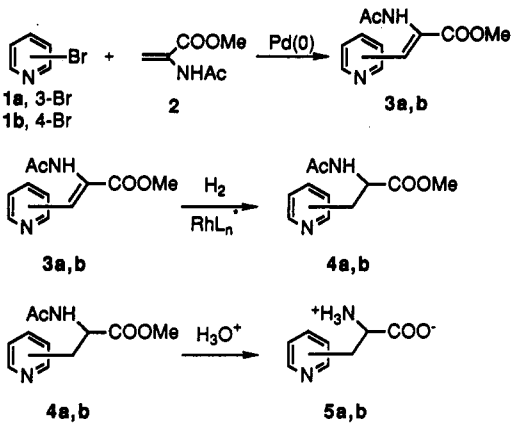
Pyridylalanines and substituted pyridylalanines, structural analogues of the naturally occurring amino acids histidine, phenylalanine, and tyrosine, exhibit a diverse range of effects when introduced into biological systems.[2] Pyridylalanines have been incorporated as histidine replacements in angiotensin II[3] and the N-terminal tetradecapeptide of ribonuclease A and ribonuclease S.[4] As enzyme substrates, the pyridylalanines are found to be antagonists of phenylalanine[5] and inhibitors of histidine decarboxylase.[6] Pyridylalanines have been studied as pharmaceutical agents and show antiinflammatory activity[7] and are components of both new antibacterial cepholasporins[8] and antiovulatory peptides.[9] As part of our program to use transition-metal catalysts in the synthesis of biologically active molecules, we report a new asymmetric route to both the D and L isomers of 3- and 4-pyridylalanine. To our knowledge, this is the first report of a direct asymmetric synthesis of these heterocyclic amino acid analogues. Although other methods have been reported for the synthesis of pyridylalanines,[10] the principal drawback to these approaches is that resolution is required to obtain the pure enantiomer. Our approach is shown in Scheme I. Treatment of 3- or 4-bromopyridine (**1a** or **1b**) in a nitrile solvent (6–8 mL/mmol of heteroaromatic bromide) with olefin **2** in the presence of 2–3 mol % of $Pd_2(dba)_3$, 8–12 mol % $P(o\text{-}tol)_3$, and 1.1 equiv of Et_3N for 18 h at 110°C under an inert atmosphere gives good yields of prochiral enamides **3a** or **3b**. The enamide is hydrogenated in the presence of a chiral Rh catalyst to give the optically active pyridylalanine precursors **4a** or **4b**. The free amino acids **5a** and **5b** are released by hydrolysis of **4**.

Scheme I



The key step in the process is the initial palladium-catalyzed coupling of **2** and the bromopyridine. The product enamides are normally prepared by conversion of an aromatic aldehyde to the corresponding azalactone using classical Erlenmeyer methodology,[11] followed by hydrolysis or reaction of the azalactone with an alkoxide. However, an Erlenmeyer approach for the synthesis of **4b** starting from 4-pyridinecarboxaldehyde was unsuccessful and gave instead only polymeric material.

The conditions used for the palladium-catalyzed coupling are important. Initial experiments showed that standard conditions reported by Heck[12] and others[13] are not successful for the preparation of **3** from the cross-coupling of **1** and **2**. At the high reactant concentrations

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