under way in this laboratory.

Concluding Remark. The present study establishes that the combination of micellized thiazolium ion and flavin remarkably facilitates the oxidation of aldehydes and α -keto acids, and both cofactors act as turnover catalysts. The finding provides a useful insight into the mechanism of pyruvate dehydrogenase. Also significant is that the reaction sequence is readily diverted to the oxidation reaction, leading to exploitation of a new class of synthetic procedures.

Experimental Section

Materials. N-Hexadecylthiazolium bromide (HxdT) and N-benzylthiazolium bromide (BzlT) were prepared from thiazole and the corresponding alkyl bromides. For HxdT: mp 77-79 °C; NMR (CDCl₃) δ 0.88 (3 H, t, CH₃), 1.24 (28 H, m, (CH₂)₁₄), 4.75 (2 H, t, N-CH₂), 8.19 (2 H, m, 4-H and 5-H), 10.90 (1 H, m, 2-H). Anal. Calcd for C₁₉H₃₆NSBr·H₂O: C, 55.88; H, 9.38; N, 3.43. Found: C, 55.52; H, 9.42; N, 3.38. For BzlT, mp 155-156 °C. Anal. Calcd for C₁₀H₁₀NSBr: C, 46.70; H, 3.94; N, 5.47. Found: C, 46.70; H, 3.93; N, 5.41.

Thiamine and TPP were kindly supplied from Kyowa Hakko Co. Ltd. and were used without further purification. Preparations of authentic samples for GLC and high-pressure LC analyses were described previously.4c

Methods of Flavin Oxidation and Product Analyses. An aqueous solution containing substrate, CTAB, HxdT, and MeFl was kept in the dark. The detailed reaction conditions are recorded in the tables. The solution was acidified with 1% HCl

to pH 1-2. In the oxidation of aromatic substrates [4-chlorobenzaldehyde and (4-chlorobenzoyl)formic acid], the final solution was extracted with chloroform. The chloroform layer was concentrated under reduced pressure and then analyzed by using high-pressure liquid chromatography (Shimadzu LC-3). In the oxidation of pyruvic acid, the aqueous solution was directly subjected to GLC analysis (Shimadzu GC-4CM).

Kinetic Measurements. The kinetic measurements of the flavin oxidation were carried out at 30 °C under anaerobic (N_2) conditions in 3 vol % of aqueous ethanol. A Thunberg cuvette was used to provide the anaerobic reaction conditions. The detailed procedure was described previously.4c The progress of the reaction was monitored spectrophotometrically by following the disappearance of MeFl at 448 nm.²²

Registry No. 4-Chlorobenzaldehyde, 104-88-1; 4-chlorobenzoic acid, 74-11-3; 4,4'-dichlorobenzoin, 4254-20-0; 4,4'-dichlorobenzil, 3457-46-3; (4-chlorobenzoyl)formic acid, 7099-88-9; pyruvic acid, 127-17-3; acetic acid, 64-19-7; acetaldehyde, 75-07-0; 2,4-dichlorobenzaldehyde, 874-42-0; benzaldehyde, 100-52-7; formaldehyde, 50-00-0; butyraldehyde, 123-72-8; octanol, 124-13-0; thiamine, 59-43-8; thiamine pyrophosphate, 582-37-6; cinnamaldehyde, 104-55-2; terephthalaldehyde, 623-27-8; methyl benzoate, 93-58-3; methyl cinnamate, 103-26-4; tert-butyl cinnamate, 14990-09-1; dimethyl terephthalate, 120-61-6; thiazole, 288-47-1; benzyl bromide. 100-39-0: hexadecyl bromide, 112-82-3; HxdT, 75066-49-8; MeFl, 21066-33-1; CTAB, 57-09-0; BzlT, 75066-50-1.

(22) Note Added in Proof. Recently a thiazolium-catalyzed ester synthesis was reported: Inoue et al. J. Chem. Soc., Chem. Commun. 1980, 549

Reaction of α -Azido Esters with Lithium Ethoxide: Synthesis of Dehydroamino Esters and α -Keto Esters

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 α -Azido esters 4 react with catalytic amounts of ethoxide in tetrahydrofuran/ethanol to evolve nitrogen and form dehydroamino esters 3. Acid hydrolysis gives α -keto esters 5 in good yields.

In an attempt to prepare enolate 1, ethyl 2-azidopropanoate was added to a solution of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at dry ice temperature. Nitrogen was evolved and the reaction mixture turned deep red. Hydrolytic workup gave an intractable tar and no GLC volatile products. Presumably, 1 is formed but spontaneously loses nitrogen to form imine anion 2, which, in the strongly basic reaction medium, undergoes further reaction (eq 1). In agreement with this,

$$\begin{array}{c} \overset{N_{3}}{\underset{l}{\overset{}}_{2}} CH_{3}CHCO_{2}Et + LDA \xrightarrow{THF} \left[\begin{array}{c} \overset{N_{3}}{\underset{-78 \ ^{\circ}C}{\overset{}}{\overset{}}} \left[\begin{array}{c} \overset{N_{3}}{\underset{l}{\overset{}}_{2}} CH_{3}CCO_{2}Et \right] \xrightarrow{-N_{2}} CH_{3}CCO_{2}Et \end{array} \right] \xrightarrow{1} 2$$

there are scattered reports in the literature of base-induced elimination of nitrogen from α -azido ketones¹ and acids² leading to imine-derived products. Prior to the completion of this work, Jarvis³ described the synthesis of nitriles from

 α -azido sulfur compounds via presumed imine intermediates.

It seemed likely that generation of anions analogous to 2 in a protic medium would allow isolation of the corresponding dehydroamino esters 3. Since α -azido esters 4 are readily obtained from the corresponding esters (eq 2), the overall sequence would provide a simple route to dehydroamino esters and, by hydrolysis, the corresponding α -keto esters 5 (eq 3). Accordingly, we have examined the

$$\operatorname{RCH}_{2}\operatorname{CO}_{2}\operatorname{Et} \xrightarrow{1. \operatorname{LDA}}_{2. \operatorname{Br}_{2}} \operatorname{RCHBrCO}_{2}\operatorname{Et} \xrightarrow{\operatorname{NaN}_{3}}_{\operatorname{DMF}} \operatorname{RCH}(\operatorname{N}_{3})\operatorname{CO}_{2}\operatorname{Et} (2)$$

$$4 \xrightarrow{\operatorname{Dose}}_{4^{+} \operatorname{Dose}} \operatorname{RCCC}_{2} \operatorname{E^{+}} \xrightarrow{\operatorname{H}_{2} \operatorname{C^{+}}}_{\operatorname{RCCC}_{2}} \operatorname{RCCC}_{2} \operatorname{E^{+}} (3)$$

reaction of α -azido esters with several weak bases with the results reported here.

3

5

Results and Discussion

THF solutions containing ethyl 2-azidopropanoate (4, R = Me) and triethylamine did not evolve nitrogen even at reflux temperatures. Reaction of 4 (R = Me) with

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Table I. Formation of α -Keto Esters from α -Azido Esters



^a Time for complete evolution of nitrogen at 25 °C. b GLC yields, determined with internal standard, unless otherwise noted. In all cases, removal of solvent left a residue of essentially pure ('H NMR analysis) α -keto ester. ^c Yield of distilled product.

aqueous sodium hydroxide/THF resulted in disappearance of starting ester by GLC analysis but no nitrogen was evolved.

Addition of 4 (R = Me) to 1 equiv of sodium ethoxide in ethanol at 25 °C gave slow (8 h) and quantitative evolution of nitrogen. Hydrolysis of the yellow reaction mixture gave minor amounts (<10%) of ethyl pyruvate (5, R = Me). Similar reactions conducted in THF solution were much faster, and reasonable rates (<15 min) could be achieved even with catalytic amounts (0.5–0.05 equiv) of ethanolic sodium ethoxide. These reaction mixtures turned light vellow and quenching gave 50-70% vields of 5 (R = Me). However, even with scrupulous protection from atmospheric oxygen and moisture, our stock solutions of ethanolic sodium ethoxide deteriorated rapidly. To obtain maximum yields of 5 it was necessary to use freshly prepared solutions of the alkoxide. Fortunately, lithium ethoxide served equally well and solutions of this base can be conveniently generated as needed by injection of nbutyllithium into small amounts of ethanol. Yields of α -keto esters obtained by adding azido esters to THF/ ethanol suspensions of lithium ethoxide are shown in Table I.

Attempts to isolate ethyl 2-iminopropanoate (6) by distillation of unhydrolyzed reaction mixtures were unsuccessful. The pot contents turned dark on heating and eventually formed a nonvolatile tar. However, careful evaporation of solvent at 25 °C from freshly prepared reaction mixtures gave a residue of essentially pure 6 as judged by ¹H NMR analysis. Alternatively, addition of triethylamine and acetyl chloride to the unhydrolyzed reaction mixture gave a 60% isolated yield of the corresponding N-acetyl derivative 7 (eq 4).

More simply, verification of dehydroamino ester formation was obtained by reaction of 4 with lithium ethoxide in CCl_4 /ethanol solution. Direct ¹ NMR analysis of the reaction mixtures indicated essentially quantitative formation of dehydroamino esters [3, R = Me, Et (a mixture of imino and enamino esters was formed), and Ph].

Both α -keto esters and dehydroamino esters are compounds of biological importance.^{4,5} The present procedure offers advantages in both simplicity and availability of starting materials over previously reported procedures.^{6,7}

Experimental Section

All solvents were distilled before use. Acetyl chloride, n-butyllithium, ethyl 2-bromopropanoate, ethyl 2-bromobutanoate, and 2-bromo-2-phenylacetic acid were obtained from Aldrich Chemical. Ethyl 2-bromo-3-methylbutanoate was prepared by the method of Rathke.⁸ 2-Bromo-3-phenylpropanoic acid was prepared by the method of Marvel⁹ and esterified by standard procedures. All reactions were conducted under argon atmosphere. Gas chromatographic data were obtained on a Varian 920 chromatograph equipped with a 4 ft \times 0.25 in. column packed with 10% Carbowax 20M terephthalate on Chromosorb G. ¹H NMR spectra were recorded on a Varian T-60 spectrometer and are reported in parts per million relative to Me₄Si. Infrared spectra were taken on a Perkin-Elmer 237 B spectrometer, using polystyrene as a reference. Mass spectra were obtained with a Finnegan 4000 GC/MS. Melting points are uncorrected. Yields of azides are not maximized and ranged from 50-85%

General Procedure for Preparation of Azides (4). Ethyl 2-Azidopropanoate¹⁰ (4, $\mathbf{R} = \mathbf{Me}$). Ethyl 2-bromopropanoate (65 mL. 0.50 mol) was added to a suspension of sodium azide (49 g, 0.76 mol) in 50 mL of dimethylformamide at 25 °C and stirred for 2.5 h. After addition of 200 mL of water, the solution was extracted with two 50-mL portions of CH_2Cl_2 . The combined organic layers were washed with 200 mL of water, dried (MgSO₄), and concentrated in vacuo. Distillation afforded 51.01 g (72%) of 4 (R = Me) as a clear, colorless oil: bp 36-40 °C (0.5 torr); ¹H NMR (CDCl₃) 4.18 (q, 2 H), 3.90 (q, 1 H), 1.42 (d), and 1.28 (t) (total 6 H); IR (neat) 2100 (s, CN₃), 1745 (s, C=O) cm⁻¹; mass spectrum, m/e 143 (M⁺), 73, 70, 56, 42.

Ethyl 2-azidobutanoate $(4, \mathbf{R} = \mathbf{E}t)$ was prepared as above: bp 38-40 °C (0.15 torr); NMR (CDCl₃) 4.20 (q, 2 H), 3.73 (t, 1 H), 1.82 (m, 2 H), 1.30 (t) and 1.00 (t) (total 6 H); IR (neat) 2100 (s, CN₃), 1745 (s, C=O) cm⁻¹; mass spectrum, m/e 157 (M⁺), 84, 73, 69, 56.

Ethyl α -azidoisovalerate¹¹ (4, R = (CH₃)₂CH) was prepared as above: bp 45-45.5 °C (0.35 torr); NMR (CDCl₃) 4.13 (q, 2 H), 3.57 (d, 1 H), 2.08 (m, 1 H), 1.27 (t) and 1.00 (dd) (total 9 H); IR (neat) 2090 (s, CN₃), 1730 (s, C=O) cm⁻¹; mass spectrum m/e171 (M⁺), 102, 70, 43.

Ethyl 2-azidophenylacetate¹² (4, $\mathbf{R} = \mathbf{Ph}$) was prepared as above: bp 85-88 °C (0.05 torr); NMR (CDCl₃) 7.28 (s, 5 H), 4.87 (s, 1 H), 4.08 (q, 2 H), 1.10 (t, 3 H); IR (neat) 2100 (s, CN₃) 1735 (s, C=O) cm⁻¹; mass spectrum, m/e 205 (M⁺), 163, 132, 104, 77, 51.

Ethyl 2-azido-3-phenylpropanoate¹³ (4, $\mathbf{R} = \mathbf{PhCH}_2$) was prepared as above: bp 107-107.5 °C (0.05 torr); NMR (CDCl₃) 7.10 (s, 5 H), 3.8-4.3 (m, 3 H), 2.85-3.10 (dd, 2 H), 1.15 (t, 3 H); IR (neat) 2100 (s, CN₃), 1700 (s, C=O) cm⁻¹; mass spectrum, m/e219 (M⁺), 191, 176, 91.

General Procedure for Preparation of Dehydroamino Esters (3). Ethyl 2-Iminopropanoate (3, R = Me). Ethanol (0.05 mL, 0.8 mmol) was added to n-butyllithium (1.6 M, 0.32 mL, 0.5 mmol) in hexane. The mixture was dissolved in 5 mL of CCl₄ at 25 °C. Ethyl 2-azidopropanoate (4, R = Me) was added dropwise and stirred at 25 °C until 125 mL (5 mmol) of N_2 was evolved (20 min). Benzene (0.22 mL, 2.5 mmol) was added, and the yield was determined by ¹H NMR¹⁴ analysis: yield 100%; ¹H NMR (CCl₄) 10.91 (br s, 1 H), 4.24 (q, 2 H), 2.29 (s, 3 H), 1.41 (t, 3 H).

Ethyl 2-iminobutanoate $(3, \mathbf{R} = \mathbf{E}t)$ was prepared as above: yield $100\,\%^{\,14}$ (mixture of imine and enamine); partial 1H NMR

⁽⁴⁾ α -Keto esters are the biological precursors to amino acids. See: Lehninger, A. L. "Biochemistry"; Worth: New York, 1975; Chapter 21.

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(CCl₄) for imine, 2.64 (q. 2 H); partial NMR (CCl₄) for enamine. 5.54 (q, 1 H, J = 7 Hz), 1.70 (d, 3 H, J = 7 Hz).

Ethyl 2-iminophenylacetate $(3, \mathbf{R} = \mathbf{Ph})$ was prepared as above: vield 100%;¹⁴ ¹H NMR (CCl₄) 10.5 (s, 1 H), 7.3-8.0 (m, 5 H), 4.20 (q, 2 H), 0.85 (t, 3 H).

N-Acetyl-2,3-dehydroalanine (7). Imine 3 (R = Me) was prepared as above. Triethylamine (0.77 mL, 5.5 mmol) was added and the solution cooled to 0 °C. Acetyl chloride (0.54 mL, 5.5 mmol) was added dropwise. The mixture was filtered, concentrated in vacuo, and the residue purified by bulb-to-bulb distillation, giving 0.42 g (58%) of pale yellow oil; ¹H NMR (CDCl₃) 8.20 (br s, 1 H), 6.58 (s, 1 H), 5.90 (br s, 1 H), 4.40 (q, 2 H), 2.27 (s, 1 H), 1.46 (t, 3 H).

General Procedure for Preparation of α -Keto Esters (5). Ethyl 2-Oxobutanoate (5, R = Et). Ethanol (0.05 mL, 0.8 mmol) was added to n-butyllithium (1.6 M, 0.32 mL, 0.5 mmol) in hexane. The mixture was dissolved in 5 mL of THF and stirred at 25 °C. Ethyl 2-azidobutanoate (0.76 mL, 5.0 mmol) was added dropwise. After 20 min at 25 °C, 125 mL (5 mmol) of N₂ had evolved, and the reaction was quenched with 2 mL of 3 N HCl. The solution was extracted with two 10-mL portions of ether. The combined organic layers were dried (K_2CO_3) and concentrated in vacuo. The yield was 86% as determined by GLC: ¹H NMR (CDCl₃) 4.13 (q, 2 H), 2.70 (q, 2 H), 1.23 (t, 3 H), 1.00 (t, 3 H); 2,4-DNP, mp 139–140.5 °C (lit.¹⁵ mp 141–142 °C); mass spectrum, m/e 310 (M⁺).

Ethyl pyruvate (5, $\mathbf{R} = \mathbf{Me}$) was prepared as above: yield 50%; ¹H NMR (CDCl₃) 4.31 (q, 2 H), 2.45 (s, 3 H), 1.50 (t, 3 H); 2,4-DNP, mp 154.5-155 °C (lit.¹⁶ mp 154.5-155 °C); mass spectrum, m/e 296 (M⁺).

Ethyl α -oxoisovalerate (5, R = (CH₃)₂CH) was prepared as above: yield 94%; NMR (CDCl₃) 4.25 (q, 2 H), 3.20 (m, 1 H),

(14) Yields based on integration of product peaks relative to benzene standard.

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1.35 (t, 3 H), 1.17 (d, 6 H); 2,4-DNP, mp 172.5-173.5 °C (lit.¹⁷ mp 171.5-172 °C); mass spectrum, m/e 324 (M⁺).

Ethyl phenylglyoxylate (5, $\mathbf{R} = \mathbf{Ph}$) was prepared as above: yield 91%; ¹H NMR (CDCl₃) 7.20-8.00 (m, 5 H), 4.37 (q, 2 H), 1.23 (t, 3 H); 2,4-DNP, mp 161-162.5 °C (lit.¹⁸ mp 162-163.5 °C); mass spectrum, m/e 358 (M⁺).

Ethyl phenylpyruvate (5, $R = PhCH_2$) was prepared as above. The residue was purified by bulb-to-bulb distillation. affording a 94% yield of clear, light yellow oil identified as the keto ester containing a small amount of enol:¹⁹ 1 H NMR (CDCl₃) of keto form, 7.25 (s, 5 H), 4.30 (q, 2 H), 4.15 (s, 2 H), 1.40 (t, 3 H); 2,4-DNP, mp 132.5-133 °C (lit.²⁰ mp 132.5-133 °C); mass spectrum, m/e 372 (M⁺).

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Registry No. 3 (R = Me), 75213-99-9; **3** (R = Et), 75214-00-5; **3** (R = Ph), 75214-01-6; 4 (R = Me), 71754-74-0; 4 (R = Et), 2571-38-2; 4 (R = (CH₃)₂CH), 75214-02-7; 4 (R = Ph), 75214-03-8; 4 (R = PhCH₂), 75214-04-9; 5 (R = Et), 15933-07-0; 5 (R = Me), 617-35-6; 5 (R = Me) 2,4-DNP derivative, 17767-38-3; 5 (R = $(CH_3)_2CH)$, 20201-24-5; 5 (R = Ph), 1603-79-8; 5 (R = Ph) 2,4-DNP derivative, 3602-40-2; 5 (R = PhCH₂), 6613-41-8; 5 (R = PhCH₂) 2,4-DNP derivative, 50838-93-2; 7, 23115-42-6; ethyl 2-bromopropanoate, 535-11-5; ethyl 2-bromobutanoate, 533-68-6; ethyl 2-bromo-3-methylbutanoate, 609-12-1; ethyl α -bromobenzeneacetate, 2882-19-1; ethyl a-bromobenzenepropanoate, 39149-82-1; lithium ethoxide, 2388-07-0; 5 (R = Et) 2,4-DNP derivative, 75214-05-0; 5 (R = $CH_3)_2CH$) 2,4-DNP derivative, 50838-92-1.

Synthesis of Triamantane

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Triamantane, the third member of the diamondoid hydrocarbon series, has been synthesized efficiently in five easy stages from norbornadiene. Acid-catalyzed rearrangement of the norbornadiene [4 + 4] dimer, binor S (5), either in solution using silver perchlorate or in the gas phase on silica gel, gives two hexacyclic olefins (13 and 14) suitable (without separation) for further elaboration: [4 + 2] cycloaddition with butadiene gives C_{18} adducts whose hydrogenated forms (26 and 27) are converted by aluminum chloride catalyzed rearrangement into triamantane in 60% yield. By use of isoprene instead of butadiene in the cycloaddition stage the synthesis can be modified to produce 9-methyltriamantane. The mechanism of the binor S rearrangement is discussed.

The diamondoid hydrocarbons adamantane $(1)^1$ and diamantane $(2)^{2,3}$ are best prepared by Lewis acid catalyzed rearrangement of tetrahydrodicyclopentadiene (3) and tetrahydrobinor S (4), respectively.^{4,5} These precursors

are readily available, the former from hydrogenation of cyclopentadiene dimer and the latter from hydrogenolytic opening of the cyclopropane rings of the [4 + 4] norbornadiene dimer, binor S (5).⁶ Although triamantane (6), the third member of the diamondoid series, has also been synthesized by rearrangement routes, the polycycles $(7)^7$

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