and cyclic voltammetric data for this species are consistent with the formation of a π-vinyl ether complex,[18] analogous to **2a**. Though the ^{1}H NMR of **2b** is similar to that of **2a**, these data clearly establish the formation of a different complex than that obtained from **1** in methanol. Taking into account the method of preparation, we conclude that the complex **2b** is $[Os(NH_3)_5(\eta^2\text{-}trans\text{-}CH_3CH{=}C(OCH_3)(CH_3))]^{2+}$ and assign **2a** to be the cis stereoisomer. A comparison of chemical shifts for these complexes with those reported for the free ligands further supports this assignment. Solutions of either **2a** or **2b** fail to show interconversion in acetone after several days.

When a DME solution of the enol **3a** is treated with 1 equiv of CH_3OTf (Aldrich), the major product formed is the *cis*-vinyl ether complex, **2a**. An NMR of the isolated product mixture in acetone-d_6 shows only trace amounts of the trans material. If it is assumed that nucleophilic attack by the enol occurs with retention of stereochemistry, the complex **3a** must also show a cis configuration.

When a DMF solution of **3a** is treated with 1 equiv of the oxidant $Fe(Cp)_2^+$, the organic ligand is surrendered over a period of several hours in the form of its tautomer 2-butanone. If pentaammineosmium(II) is generated in the presence of this species[19] a material is formed, **4**, which is readily characterized as the η^2-coordinated ketone complex $[Os(NH_3)_5(\eta^2\text{-}CH_3CH_2COCH_3)]^{2+}$. Microanalytical, electrochemical, and NMR data are in good agreement with that reported for the acetone analogue[20] in which a crystal structure confirms this bonding mode for ketones on pentaammineosmium(II).

With the hope of determining the thermodynamically favored tautomer of C_4H_8O on pentaammineosmium(II), several attempts were made to interconvert the enol (**3a**,**b**) and the ketone (**4**) complexes by acid or base catalysis without success. Noteworthy, however, is the resistance of these species toward deprotonation. A wet acetone-d_6 solution of **3a**,**b** was treated with an equivalent of Proton Sponge (pK_a 12.4) and allowed to stand 24 h after which time no reaction or deuterium exchange at the enol position was detected. This behavior is in contrast to that reported for the complex $PtCH_2(CHOH)(acac)Cl$ which acts as a moderate acid (pK_a = 3.5).[21] A methanol-d_4 solution of the ketone **4** with 1 equiv of NaOMe (ca. 1 mM) shows isotopic exchange only at the ammines over this time period. A summary of the chemistry described appears in Figure 1.

Pentaammineosmium(II) differs from the metal ions, such as Hg^{2+} and Pd^{2+}, which have commonly been used to activate alkynes for addition reactions,[1] in being less electrophilic, but much more given to back-bonding interactions. Why the kind of chemistry we have described is not more commonly observed for other metal centers answering to the same general description is a matter of some interest.

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(18) Characterization of **2b**: ^{1}H NMR (acetone-d_6, BPh_4^- salt) 1.46 (d, 3 H, CCH_3), 1.61 (s, 3 H, CCH_3), 3.42 (q, 1 H, CH), 3.53 (s, 3 H, OCH_3), 3.72 (b, 12 H), 4.82 (b, 3 H), (BPh_4^-: 6.77 (8 H), 6.92 (16 H), 7.33 (16 H)); CV (acetone; TBAH) $E_{1/2}$ = 0.54 V, NHE. Anal. Calcd for $C_{53}H_{65}OsON_5B_2$: C, 63.66; H, 6.55; N, 7.00. Found: C, 63.58; H, 6.73; N, 6.86.

(19) Synthesis of $[Os(NH_3)_5(\eta^2\text{-}CH_3CH_2COCH_3)](OTf)_2$ (**4**): A solution of $Os(NH_3)_5(OTf)_3$ (250 mg) and 2-butanone (15 mL) (Aldrich) was stirred with Mg (1.0 g, activated with I_2) for 1.5 h. The brilliant orange solution was filtered, reduced in volume to 1 mL, and then treated with Et_2O (10 mL). The resulting ppt was collected, washed with ether, and dried under vacuum. NMR (acetone-d_6) 5.43 (b, 3 H), 4.00 (b, 12 H), 2.16 (m, 1 H), 1.60 (s, 3 H), 1.25 (m, 1 H), 1.20 (m, 1 H); CV (DMF, 100 mV/s) TBAH) $E_{p,a}$ = 0.37 V; $E_{p,c}$ = −0.61 V, NHE. Anal. Calcd for $C_6H_{23}OsS_2F_6O_7N_5\cdot{}^1/_4Et_2O$ (as observed in NMR): C, 12.68; H, 3.69; N, 10.57; S, 9.67. Found: C, 12.35; H, 3.58; N, 10.34; S, 9.78.

(20) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223.

(21) Deprotonation of this Pt(II)–enol complex is accompanied by an isomerization in which the Pt coordinates to the enolate carbon. See ref 3 and 4.

Artificial Photosynthesis of β-Ketocarboxylic Acids from Carbon Dioxide and Ketones via Enolate Complexes of Aluminum Porphyrin

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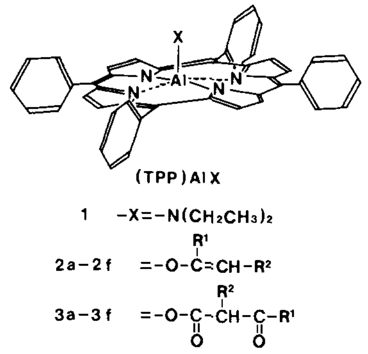
Photochemical fixation of carbon dioxide is of much interest in connection with biological photosynthesis by green plants as well as from the viewpoint of carbon resource utilization.[1] One of the important steps in the assimilation of carbon dioxide is the carboxylation of a carbonyl compound into ketocarboxylic acid, where the reaction proceeds via an enolate species as reactive intermediate. For example, in "four carbon (C_4)" pathway and "Crassulacean acid metabolism (CAM)" processes, pyruvate is converted with the aid of ATP into phosphoenolpyruvate, which is subsequently carboxylated to give oxaloacetate by the action of pyruvate carboxylase.[2] In relation to this interesting biological process, some artificial systems have been exploited for the synthesis of β-ketocarboxylic acid derivatives from carbon dioxide and ketones using nucleophiles such as metal carbonates, thiazolates, phenolates, alkoxides, and strong organic as well as inorganic bases,[3] which promote the enolization of ketones in the intermediate step.

We wish to report here a novel, visible light-induced fixation of carbon dioxide with the enolate complex of aluminum porphyrin, giving β-ketocarboxylic acid under mild conditions.

Typically, into a 50-mL round-bottomed flask fitted with a three-way stopcock containing a benzene-d_6 solution (7.5 mL) of $(TPP)AlOC(C_6H_5){=}CHCH_3$ (**2a**,[4] $R^1 = C_6H_5$, $R^2 = CH_3$; TPP: 5,10,15,20-tetraphenylporphinato) generated in 87% yield by the reaction of 1-phenyl-1-propanone (0.13 mmol) with $(TPP)AlN(C_2H_5)_2$ (**1**,[5] 0.12 mmol) under dry nitrogen and freed of the



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(1) (a) Vol'pin, M. E.; Kolomnikov, I. S. *Organomet. React.* **1975**, *5*, 313. (b) *Organic and Bio-organic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Kodansha: Tokyo, 1981. (c) *Organic Phototransformations in Nonhomogeneous Media*; Fox, M. A., Ed.; ACS Symposium Series 278; American Chemical Society: Washington, DC, 1985. (d) *Carbon Dioxide as a Source of Carbon*; Aresta, M., Forti, G., Eds.; D. Reidel Publishing Company: Dordrecht, 1987. (e) Willner, I.; Mandler, D.; Maidan, R. *Nouv. J. Chim.* **1987**, *11*, 109.

(2) (a) Hatch, M. D.; Slack, C. R. *Biochem. J.* **1966**, *101*, 103. (b) *Photosynthesis*; Govindjee, Ed.; Academic Press: New York, 1982.

(3) (a) Stiles, M. *J. Am. Chem. Soc.* **1959**, *81*, 2598. (b) Finkbeiner, H. L.; Stiles, M. *J. Am. Chem. Soc.* **1963**, *85*, 616. (c) Bottaccio, G.; Chiusoli, G. P. *Chem. Commun.* **1966**, 618. (d) Corey, E. J.; Chen, R. H. K. *J. Org. Chem.* **1973**, *38*, 4086. (e) Ito, T.; Takami, Y. *Chem. Lett.* **1974**, 1035. (f) Matsumura, N.; Asai, N.; Yoneda, S. *J. Chem. Soc., Chem. Commun.* **1983**, 1487. (g) Tirpak, R. E.; Olsen, R. S.; Rathke, M. W. *J. Org. Chem.* **1985**, *50*, 4877. (h) Hogeveen, H.; Menge, W. M. P. B. *Tetrahedron Lett.* **1986**, *27*, 2767.

(4) **2a**: ^{1}H NMR (C_6D_6, C_6H_6 (δ 7.40) as internal standard) 6.92 (t, p-H), 6.71 (t, m-H), 4.85 (d, o-H), 3.29 (q, CH), −0.73 (d, CH_3) (The stereochemistry of the enolate complex has been discussed in the following: Arai, T.; Murayama, H.; Inoue, S. *J. Org. Chem.* **1989**, *54*, 414). **2a**/MeIm: ^{1}H NMR (C_6D_6) δ 6.92 (t, p-H), 6.73 (t, m-H), 4.75 (d, o-H), 2.94 (q, CH), −0.79 (d, CH_3), 1.63 (s (br), N-CH_3 (MeIm)).

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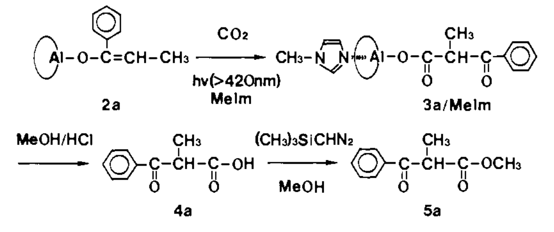
Scheme I



liberated diethylamine under reduced pressure was added 1-methylimidazole (MeIm, 0.20 mmol), and gaseous carbon dioxide was bubbled for 1 min with stirring magnetically at room temperature (~25 °C) under atmospheric pressure. Then, an aliquot of the reaction mixture was transferred from the flask into an NMR tube (5 mm-Φ), which was put in a water bath and exposed to a Xenon lamp (500 W, >420 nm) from the distance of 35 cm. In the ^1H NMR spectrum of the reaction mixture after 11.5-h irradiation, a new set of signals assignable to the β-ketocarboxylate complex (TPP)$AlO_2CCH(CH_3)COC_6H_5$/MeIm (**3a**/MeIm,[6] $R^1 = C_6H_5$, $R^2 = CH_3$) appeared at the expense of the initial enolate complex (TPP)$AlOC(C_6H_5)$=$CHCH_3$/MeIm (**2a**/MeIm[4]). The intensity of the new signals corresponded to 75% yield of **3a**/MeIm. In the ^{13}C NMR spectrum, two signals characteristic of the carbonyl carbons of **3a**/MeIm ($R^1 = C_6H_5$, $R^2 = CH_3$) appeared at δ 195.2 and 164.7 ppm ($C_6H_5\mathit{C}O$, $\mathit{C}O_2Al$). When carbon dioxide enriched in ^{13}C was employed for the above reaction, the ^1H NMR signals due to CH and CH_3 of **3a**/MeIm split into a double quartet and a double doublet due to the occurrence of ^1H–^{13}C coupling ($J(^1H–^{13}C)$ = 7.3 and 6.8 Hz, respectively), and the ^{13}C NMR signal at δ 164.7 ppm ($\mathit{C}O_2Al$) was enhanced. Upon treatment of the above reaction mixture with CH_3OH/HCl followed by careful extraction gave 2-benzoylpropanoic acid (**4a**),[7] which was subsequently methylated by trimethylsilyldiazomethane ($(CH_3)_3SiCHN_2$)[8] to afford methyl 2-benzoylpropanoate (**5a**)[7] in 57% isolated yield based on the β-ketocarboxylate complex.

Of particular interest to note is the fact that the irradiation by visible light was essential for the above reaction (Figure 1). In the reaction conducted in the dark, the yield of the β-ketocarboxylate complex, as determined by ^1H NMR, was only about 1% (12.5 h) under the same conditions (●, Figure 1b). The effect of light was much more explicitly shown by the light on–off experiment illustrated in Figure 1c, which demonstrates that the enolate complex as nucleophile is activated to react with carbon dioxide only when the light is "on". Another interesting observation was that the effect of visible light irradiation did not appear at all in the absence of 1-methylimidazole (MeIm). In relation to this observation, we have previously shown that the axial coordination of MeIm onto the vacant side of the aluminum porphyrin forces the structure of the N_4Al skeleton to change from a "sitting-atop" to a "square-planar".[9] Thus, the enhancement in the reactivity of the aluminum enolate species **2** as the result of the photoexcitation of the porphyrin moiety is pronounced when the central aluminum atom takes a square-planar position.

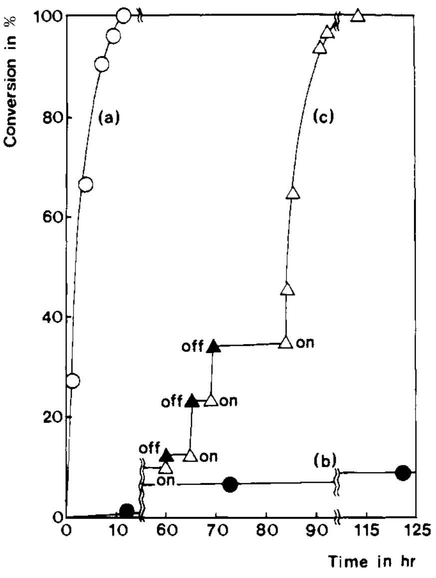


Figure 1. Reaction of carbon dioxide with (TPP)$AlOC(C_6H_5)$=$CHCH_3$ (**2a**) in the presence of 1-methylimidazole (MeIm) in C_6D_6 at room temperature (~25 °C) under the atmospheric pressure of carbon dioxide: (a) under irradiation (>420 nm), (b) in the dark ($[\mathbf{2a}]_0/[\mathrm{MeIm}]_0 = 1.4 \times 10^{-2}/2.7 \times 10^{-2}$ M), (c) light "on–off" condition ($[\mathbf{2a}]_0/[\mathrm{MeIm}]_0 = 1.0 \times 10^{-2}/2.7 \times 10^{-2}$ M). Time vs conversion relationship as determined by ^1H NMR signals at δ −0.79 (**2a**/MeIm, CH_3) and −0.44 (**3a**/MeIm, CH_3).

The photocarboxylation of various phenones could be similarly accomplished by the reaction of the corresponding (porphinato)aluminum enolates with carbon dioxide under mild conditions. For example, 1-phenyl-1-butanone, 1-phenyl-3-methyl-1-butanone, and 1-phenyl-1-pentanone were efficiently photocarboxylated to give the corresponding β-ketocarboxylate complexes (**3b**–**3d**/MeIm) in 89, 67, and 73% yield, respectively, with the complete consumption of the intermediate enolate complexes (**2b**–**2d**/MeIm). The enolate complexes (**2e**,**2f**) derived from aliphatic ketones such as 3-pentanone and 3,3-dimethyl-2-butanone in the presence of MeIm were reactive enough even without irradiation, so that the reaction with carbon dioxide to give the corresponding β-ketocarboxylate complexes (**3e**,**3f**/MeIm) was completed within 30 min.

The present study provides the first example of the artificial photosynthesis of β-ketocarboxylic acids directly from carbon dioxide and ketones via an aluminum enolate complex carrying light-absorbable porphyrin ligand.

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Supplementary Material Available: ^1H NMR spectral data of enolate complexes **2b**–**2f**, enolate complexes coordinated to MeIm **2b**–**2f**/MeIm, and β-ketocarboxylate complexes coordinated to MeIm **3b**–**3f**/MeIm (2 pages). Ordering information is given on any current masthead page.

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[5] Preparation of (TPP)$AlN(C_2H_5)_2$ (**1**): To a flask containing (TPP)$AlCH_3$ (0.3 mmol), prepared by the reaction of $TPPH_2$ and $Al(CH_3)_3$, was added 1.5 mL of a $(C_2H_5)_2NH$ solution of $LiN(C_2H_5)_2$ (0.25 M) under dry nitrogen, and the mixture was refluxed for 1 h and cooled to room temperature to give a crystalline precipitate, which was filtered, washed with *n*-hexane, and dried under reduced pressure at room temperature to afford **1** in 40–60% yield. ^1H NMR (C_6D_6) δ −1.3 to −1.4 (CH_2CH_3); ^{13}C NMR (C_6D_6, C_6H_6 (δ 128.0) as internal standard) δ 37.5 ($N\mathit{C}H_2$), 14.0 (CH_3).

[6] **3a**/MeIm: ^1H NMR (C_6D_6) δ 7.08 (t, p-H), 6.83 (t, m-H), 6.63 (d, o-H), 1.62 (q, CH), −0.44 (d, CH_3). The complex **3a**/MeIm could be separately obtained by the reaction of (TPP)$AlCH_3$ with $C_6H_5COCH(CH_3)CO_2H$ (prepared from $C_6H_5COCH_2CO_2C_2H_5$, Hope, E.; Perkin, W. H. *J. Chem. Soc.* **1909**, 2042), followed by the addition of 1-methylimidazole (MeIm).

[7] Isolation of **4a**: To the reaction mixture (60 mL) cooled with ice/water was added 30 mL of cold CH_3OH/concentrated HCl (2%), and the mixture was stirred for 30 min and evaporated to dryness. The ether-soluble fractions were extracted from the residue and shaken with aqueous $NaHCO_3$. The water layer was separated, neutralized with cold concentrated HCl, and subjected to repeated extraction with cold CH_2Cl_2, and the extracts combined were evaporated to dryness to leave **4a** as a pale yellow solid: ^1H NMR ($CDCl_3$, $CHCl_3$ (δ 7.28) as internal standard) δ 6–8.5 (br, CO_2H), 8.02 (d, o-H), 7.63 (t, p-H), 7.52 (t, m-H), 4.48 (q, CH), 1.55 (d, CH_3);[3g] ^{13}C NMR ($CDCl_3$) δ 196.2 ($C_6H_5\mathit{C}O$), 176.0 ($\mathit{C}O_2H$), 135.4, 133.9, 128.9 and 128.8 (C_6H_5), 47.4 (CH), 14.3 (CH_3). Treatment of the methanol solution of **4a** with $(CH_3)_3SiCHN_2$[8] gave **5a**: ^1H NMR (C_6D_6) δ 8.12 (d, o-H), 7.23–7.37 (m, m-H and p-H), 4.29 (q, CH), 3.45 (s, OCH_3), 1.62 (d, CH_3); ^{13}C NMR (C_6D_6) δ 195.2 ($C_6H_5\mathit{C}O$), 171.0 ($\mathit{C}O_2CH_3$), 136.4, 133.2, 128.82, and 128.76 (C_6H_5), 51.8 (OCH_3), 48.1 (CH), 13.9 (CH_3); EI-MS, *m/e* 192 (M^+), 161 ($C_6H_5COCH(CH_3)CO^+$), 105 ($C_6H_5CO^+$), 77 ($C_6H_5^+$); HRMS 192.0834, calcd for $C_{11}H_{12}O_3$ 192.0786.

[8] Hashimoto, N.; Aoyama, T.; Shioiri, T. *Chem. Pharm. Bull.* **1981**, *29*, 1475.

[9] Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1983**, *105*, 1304.