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Ytterbium Metal-Promoted Reaction of Ketimines with Carbon Dioxide

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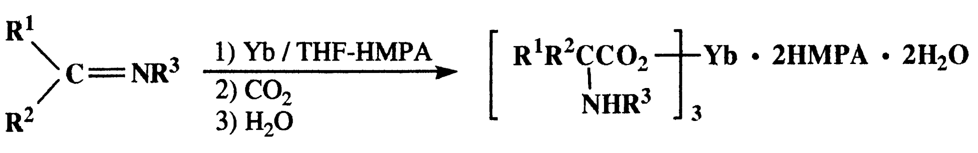
Ketimines are reduced by ytterbium metal and reacted with carbon dioxide to give Yb salts of α-amino acids in good yields.

We have previously demonstrated that diaryl ketones were umpoled by ytterbium metal and reacted with various electrophiles such as ketones, esters, and epoxides.1) On the treatment of imines with Yb metal, aldimines were changed to 1,2-diaminoethane derivatives, but in contrast ketimines were reduced to the corresponding amines.2) The latter result suggests a possiblity of umpolung of ketimines. We report herein a new and facile method for the synthesis of α-amino acids from ketimines and carbon dioxide.

Treatment of N-diphenylmethyleneaniline (**1a**) with Yb metal followed by CO_2 bubbling in THF-HMPA gave Yb salt of glycine derivative **2a** in 92% yield. The salt **2a** contains two equivalents of HMPA and water, which were difficult to be removed. IR spectrum of **2a** exhibits a characteristic absorption of P=O at 1141 cm^{-1} in addition to those of α-amino acid.3) ^1H-NMR was not able to measure because of trivalent Yb metal. The phenyl, C_2, and HMPA carbons were observed in ^{13}C-NMR spectra, but the carbonyl carbon was obscured. The salt **2a** was converted to the corresponding free amino acid **3a** 4) in 93% yield by the treatment with hydrochloric acid.5)

The result using other ketimines are summarized in Table 1. In all cases, HMPA and water were incorporated into the Yb salts,6) which is attributed to the high coordination numbers of the metal. Of the ketimines, diphenylmethyleneamine (1, R^1=R^2=Ph, R^3=H) did not react with



$$R^1R^2C{=}NR^3 \xrightarrow[\text{2) } CO_2\text{, 3) } H_2O]{\text{1) Yb / THF-HMPA}} [R^1R^2C(NHR^3)CO_2]_3Yb \cdot 2HMPA \cdot 2H_2O$$

1 **2**

CO_2 though reduction took place quantitatively. The carboxylation of the ketimines proceeded probably via metallaazirizine intermediates.$^{7)}$

A typical example is as follows; ketimine **1a** (257 mg,1 mmol) in THF (2 ml) was added to a slurry of activated Yb metal (173 mg,1 mmol) in THF-HMPA (2:1,3 ml) and stirred for 2 h at room temperature. Then CO_2 was passed through the resulting reddish black solution for 1 h. The reaction was quenched with water and the mixture was extracted with ether, dried, and concentrated in vacuo to give the salt **2a** (453 mg,92%).

Table 1. Synthesis of Yb salts of α-amino acids from ketimines **1** and CO_2

Ketimine	R^1	R^2	R^3	Product	Yield/%$^{a)}$
1a	Ph	Ph	Ph	**2a**	92
1b	Ph	Ph	C_6H_4Cl-p	**2b**	72
1c	Ph	Ph	C_6H_4OMe-p	**2c**	88
1d	Ph	Ph	C_6H_4Me-p	**2d**	83
1e	Ph	C_6H_4Cl-p	Ph	**2e**	74
1f	Ph	C_6H_4Me-p	Ph	**2f**	62
1g	C_6H_4Me-p	C_6H_4Me-p	Ph	**2g**	66
1h	C_6H_4Me-p	C_6H_4Me-p	C_6H_4Me-p	**2h**	84

a) Isolated yield.

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3) **2a**: mp 136.5-137 °C; IR (Nujol) 3372, 3339, 1639, 1141 cm^{-1}; ^{13}C-NMR ($CDCl_3$) δ 40.0 (HMPA), 58.0 (tert-C), 112.5, 114.8, 126.0, 126.4, 127.1, 136.9, 142.4. Anal. Found: C,58.81; H,5.81; N,8.53%. Calcd for $C_{72}H_{88}N_9O_{10}P_2Yb$: C,58.64; H,6.01; N,8.54%.
4) **3a**: mp 164-166.5 °C; IR (Nujol) 3055, 1627 cm^{-1}; ^1H-NMR (DMSO-d6) δ 6.42-7.63 (m); ^{13}C-NMR (DMSO-d6) δ 70.4 (tert-C), 115.2, 116.8, 127.0, 127.8, 141.3, 146.1, 173.6 (C=O). Anal. Found: C,79.07; H,5.69; N, 4.59%. Calcd for $C_{20}H_{17}NO_2$: C,79.18; H,5.64; N, 4.61%.
5) Similarly, **2g** was converted to **3g** in 83% yield.
6) The salts **2b**-**2h** gave similar spectral data to **2a** and satisfactory elemental analyses.
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