$CHNHCONHCH(CH_3)CH_2CH_3$, 98%; cyclo-$C_6H_{11}NHCONH$-cyclo-$C_6H_{11}$, 95%.

Unsymmetrical ureas can be conveniently prepared using 2-DPC by a two-step, one-pot procedure (eq. 4). 2-Pyridyl carbamates prepared from an equimolar mixture of 2-DPC and amines were treated with equimolar amounts of amines to afford the corresponding unsymmetrical ureas in high yields. The reaction of 2-pyridyl cabamates with amines required 4 h at room temperature. Some typical isolated yields of unsymmetrical ureas were: $C_6H_5CH_2NHCON(CH_2CH_2CH_3)_2$, 81%; $CH_3CH_2CH_2NHCON(n\text{-}C_4H_9)_2$, 80%; $CH_3CH_2(CH_3)CHNHCON(\text{cyclo-}C_6H_{11})_2$, 87%; cyclo-$C_6H_{11}NHCON(n\text{-}C_3H_7)_2$, 87%.

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# Catalytic Isomerization of Fumaronitrile to Maleonitrile with the Rhodium(I)-Perchlorato Compound $Rh(ClO_4)(CO)(P(C_6H_5)_3)_2$

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The isomerization of fumaronitrile (*trans*-NCCH = CHCN, FN) to maleonitrile (*cis*-NCCH = CHCN, MN) is catalyzed by iodine[1] and occurs when FN is treated with BuLi[2] or irradiated in the presence of a photosensitizer 1,2,3-triphenylpropene.[3]

**TABLE 1: Isomerization and Hydrogenation of FN with Related Rhodium(I) Complexes.[a]**

| Catalyst | Temp, °C | Reaction Time, h | Product, mmol | | |
|---|---|---|---|---|---|
| | | | MN[c] | SN[d] | FN |
| 1 | 25 | 48 | 0 | 0 | 10.0 |
| | 70 | 24 | 2.9 | 0.1 | 7.0 |
| | 70 | 48 | 4.4 | 0.1 | 5.5 |
| | 120[b] | 6 | 0 | 5.8 | 4.2 |
| | 120[b] | 12 | 0 | 8.4 | 1.6 |
| | 120[b] | 24 | 0 | 10 | 0 |
| 2 | 25 | 1 | 0 | 5.8 | 4.2 |
| | 25 | 2 | 0 | 8.6 | 1.4 |
| 3 | 25 | 48 | 0 | 0 | 10 |
| | 70 | 24 | 0 | 1.1 | 8.9 |
| | 70 | 48 | 0 | 2.0 | 8.0 |

[a] All experiments were carried out using 0.1 mmole of catalyst and 10 mmoles of FN (singlet, at 6.23 ppm relative to TMS in $C_6H_5Cl$) in 25 m*l* of monochlorobenzene under hydrogen ($P^{H_2}$ + vapor pressure of the solution = 1 atm). Product ananlyses were obtained by $^1H$-NMR spectroscopy at 60 MHz. [b] In a pressure bottle under hydrogen ($P_{H_2}$ + vapor pressure of the solution = 1 atm at room temperature before the reactor was heated). [c] Singlet at 6.16 ppm relative to TMS in $C_6H_5Cl$. [d] Singlet at 2.23 ppm relative to TMS in $C_6H_5Cl$.

No reports have been made thus far on the isomerization of FN to MN with transition metal complexes.

We wish to report the catalytic isomerization of FN to MN by the rhodium(I)-perchlorato compound Rh ($ClO_4$) (CO) ($P(C_6H_5)_3)_2$ (**1**). Chlorobenzene solution of complex **1** and FN at 70°C under hydrogen selectively produces MN until 44% of FN is converted into MN. (See the footnotes of Table 1 for experimental details.) This isomerization of FN to MN with **1** does not proceed any further even for prolonged time under the same experimental conditions. A small amount of the hydrogenation product, succinonitrile ($NCCH_2CH_2CN$, SN) is also produced at 70°C (see Table 1). In the absence of hydrogen, the isomerization of FN to MN with complex **1** does not occur at all at 70°C. At 120°C, however, complex **1** exclusively catalyzes the hydrogenation of FN to give SN in 100% yield (see Table 1).

In the same manner, attempts have been made to catalyze the isomerization of FN to MN with the related compounds, RhCl ($P(C_6H_5)_3)_3$ and RhCl (CO) ($P(C_6H_5)_3)_2$. (See the footnotes of Table 1 for experimental details.) No catalytic isomerization, however, has been observed (see Table 1).

It may be noteworthy to compare our date (FN : MN = 56 : 44) with those obtained from the photolytic isomerization in the presence of photosensitizer 1,2,3-triphenylpropene where the isomerization of FN to MN proceeded until the ratio (FN : MN = 60 : 40) was obtained.[3] Practically the same ratio (FN : MN = 57 : 43) was also predicted in the laser photolysis experiments in the presence of photosensitizer.[4] Further investigation is being undertaken for the mechanism of the

catalytic isomerization of FN to SN with 1.

## Experimental

$Rh(ClO_4)(CO)(P(C_6H_5)_3)_2$, $RhCl(P(C_6H_5)_3)_3$ and $RhCl(CO)(P(C_6H_5)_3)_2$ were prepared by the literature methods.[5-7] Proton NMR spectra were obtained on a Varian EM-360A (60 MHz) at 25°C.

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# Unusual Formation of L-Proline from L-Glutamic Acid Derivative

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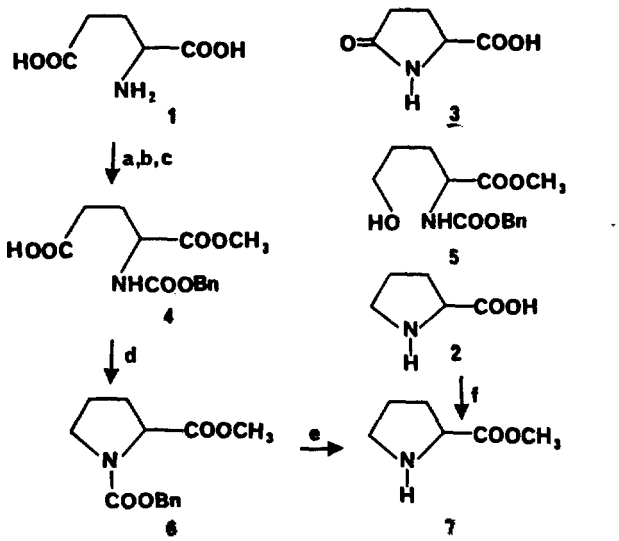
Numerous examples of chemical interconversion between L-glutamic acid (**1**) and L-proline (**2**) have been reported. For instance, reduction of L-pyroglutamic acid (**3**) derivatives[1] or reductive cyclization of L-glutamic acid γ-esters[2] yielded L-proline derivatives, while ruthenium tetroxide oxidation of protected L-proline afforded L-pyroglutamic acid derivatives[3]. Recently, in the course of our work on the synthesis of Δ¹-pyrroline-5-carboxylic acid derivatives[4] from L-glutamic acid, we have found that diborane reduction of N-benzyloxycarbonyl-L-glutamic acid α-methyl ester (**4**) surprisingly produced N-benzyloxycarbonyl-L-proline methyl ester (**6**) in moderate yield.

L-Glutamic acid (**1**) was transformed into N-benzyloxycarbonyl-L-glutamic acid α-methyl ester (**4**) in straight manner[5,6,7] (see SCHEME). To prepare the alcoholic compound **5** by reduction of the free carboxylic acid **4**, the compound **4** was treated with excess diborane in THF at rt for 6 hrs. TLC analysis showed the formation of two products, of which the less polar, major one was isolated by column chromatography (silica, Kieselgel 60, 70-230 mesh, eluant; 1:1 $CHCl_3$-EtOAc).

The oily product thus obtained in 40% yield had following ir and H-nmr spectral data: ir (neat); 1730, 1680 $cm^{-1}$ (strong absorption); H-nmr ($CDCl_3$) ; δ 7.35 (*s*, 5H, phenyl), 5.10 (*s*, 2H, $-CH_2-$ of benzyl), 4.56-4.25 (*m*, 1H, -CH-), 3.62 (*s*, 3H, $-OCH_3$), 3.70 (broad *s*, 2H, $-CH_2-$), 2.20-1.76 ppm (*m*, 4H, two $-CH_2-$).

Since the desired alcoholic product **5** has two deuterium exchangeable protons, the product was subjected to deuterium exchange nmr analysis, but no significant spectral change was observed. Attempted acetylation ($Ac_2O$, Py) or oxidation ($CrO_3 \cdot 2$ Py, $CH_2Cl_2$) of the product was not also successful. These




a; ClCOOBn, $K_2CO_3$, toluene-$H_2O$, rt, 12 hr, 85%, b; $Ac_2O$, rt, 3 hr, 78%, c; $CH_3OH$, $(cyclohexyl)_2NH$, rt, 3 hr, $H_2SO_4$, 81%, d; $B_2H_6$, THF, rt, 6 hr, 40%, e; $H_2$, 50 psi, Pd-C, $CH_3OH$, rt, 8 hr, 80%, f; $CH_3OH$, HCl, reflux, 12 hr, 90%

results thus excluded the alcoholic compound **5** as the possible reduction product.

The above spectral and chemical data, however, are in full agreement with the assigned structure **6**, N-benzyloxycarbonyl-L-proline methyl ester. Two protons at δ 3.70 ppm in H-nmr spectrum could be assigned to the methylenic protons adjacent to nitrogen and the remaining four protons at δ 2.20-1.76 ppm those of the other two methylene units. To confirm the structure of the reduction product further, the product **6** was hydrogenolized with hydrogen over Pd-C. H-Nmr