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.

Acknowledgement. We wish to thank the Korea Science and Engineering Foundation and the Korean Ministry of Education for their financial supports.

References

(1) G. E. Ficken, R. P. Linstead, E. Stephen, and M. Whally, *J. Chem. Soc.*, 3879, 1958.
(2) G. Helling and D. Woehrle, *Makromol. Chem.*, **179**, 101, 1978 and the references therein.
(3) P. C. Wong and D. R. Arnold, *Can. J. Chem.*, **57**, 1037, 1979.
(4) P. C. Wong, *Can. J. Chem.*, **60**, 339, 1982.
(5) J. Peone, Jr. and L. Vaska, *Angew. Chem. Int. Edit.*, **10**, 511, 1971.
(6) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, 1711, 1966.
(7) D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Syntheses*, **11**, 99, 1968.

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

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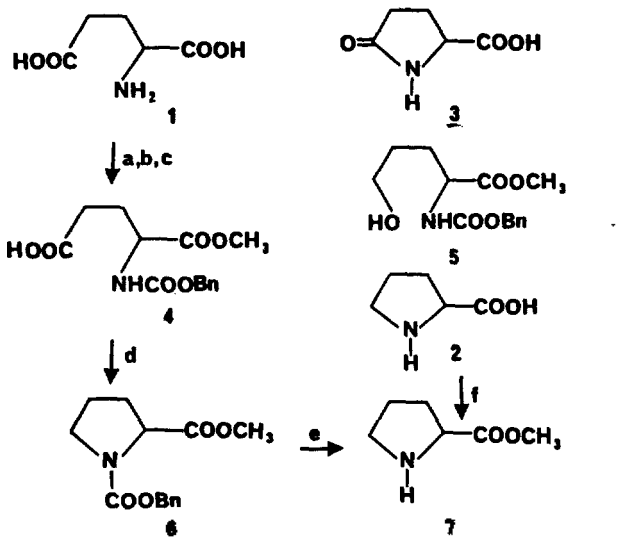
Numerous examples of chemical interconversion between L-glutamic acid (**1**) and L-proline (**2**) have been reported. For instance, reduction of L-pyroglutamic acid (**3**) derivatives[1] or reductive cyclization of L-glutamic acid γ-esters[2] yielded L-proline derivatives, while ruthenium tetroxide 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

spectral data of the hydrogenolyzed product were exactly matched with those of authentic L-proline methyl ester (7), unambigueously prepared from L-proline and methanol. Optical rotation of the hydrogenolized product ($[\alpha]_D^{24} = -32.6°$) was also in full agreement with that of L-proline methyl ester (7) ($[\alpha]_D^{24} = -32.9°$, methanol, lit[6]., $[\alpha]_D^{24} = -34°$).

From the above results, it was confirmed that diborane reduction of N-benzyloxycarbonyl-L-glutamic acid α-methyl ester (4) undoubtedly afforded N-benzyloxycarbonyl-L-proline methyl ester (6), although its mechanism could not be clearly understood.

References

(1) (a) R. Buyle, *Chem. & Ind.*, 380 (1966); (b) H. J. Monterio, *Synthesis*, 137 (1974) and references cited therein.

(2) M. Tanaka, T. Kishi and S. Kinoshita, *Nippon Nogei Kaishi*, **34**, 782, 972 (1960).

(3) S. Yoshifugi, H. Matsumoto, K. Tanaka and Y Nitta, *Tetrahedron Lett.*, **21**, 2963 (1980).

(4) H. J. Strecker, *J. Biol. Chem.*, **235**, 2045 (1960).

(5) E. Klieger and H Gibian, *Ann. Chem.*, **649**, 183 (1961).

(6) M. Bergmann and L. Zervas, *Ber.*, **65**, 1192 (1932).

(7) E. Klieger and H. Gibian, *Ann. Chem.*, **655**, 195 (1962).

(8) J. Buckingham, Ed., "Dictionary of Organic Compounds", 5th Ed., Vol. 5, p. 4773, Chapman and Hall, New York, 1982.

n–*n* Orbital Interaction Involving *anti*-Hückel σ-Aromaticity

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(*Received October 6, 1984*)

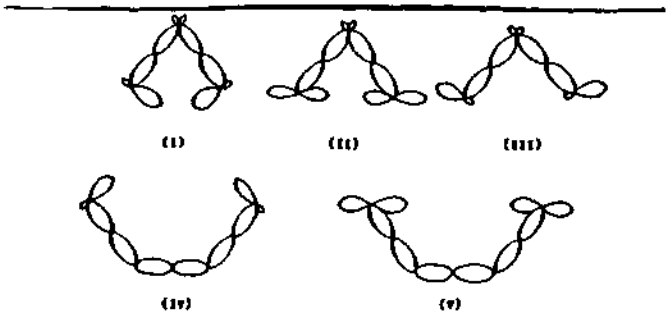
Interactions between two nonbonding orbitals, n_1 and n_2, are normally dissected into two varieties, *i.e.*, through-space (TSI) and through-bond (TBI) interactions.

We wish here to report the third kind of interaction which becomes important only in cases where the two orbitals can overlap significantly. In this type of interaction both TSI and TBI are involved and the two overlapping nonbonding orbitals are considered to constitute terminal hybrid AOs within a cyclic form of σ conjugative chain. In the frontier orbital approach,[2] the energy change, δE_i, involved in an interaction between the two terminal hybrid AOs, n_1 and n_2, is due mainly to the corresponding perturbation of the HOMO, ψ_i, of the chain.[3]

$$\delta E_i = \nu_i \int \psi_i P \psi_i \mathrm{d}\tau = \nu_i c_{i1} c_{i2} \beta_{12} \qquad (1)$$

where ν_i is the number of electrons occupying the HOMO, c_{i1} and c_{i2} the AO coefficients of n_1 and n_2 in the HOMO, and β_{12} is the resonance integral between the two orbitals. In the simple theory of σ conjugation[4] (C-approximation),[1c,5] the AO coefficients are determined by an HMO calculation, while the sign of β_{12} depends on the symmetry adapted orbitals; β_{12} will be negative (overlap integral S_{12} will be positive) for $n_+ (= n_1 + n_2)$ and β_{12} will be positive ($S_{12}<0$) for $n_- (= n_1 - n_2)$ level.

In the diradicals or diamines with even number of intervening sigma bonds between n_1 and n_2 (N = even),[1c] the product of terminal AO coefficients of the HOMO has a negative sign,[6,8] $c_{i1} \cdot c_{i2} < 0$. Thus for an N= even system having a crowded structure with significant overlap between two terminal nonbonding lobes, δE_i will be negative, *i.e.*, stabilizing, if β_{12} is positive corresponding to a negative overlap, $S_{12}<0$. Therefore the *anti*-symmetric combination of orbitals, n_-, having positive β_{12} will be stabilizing and symmetric combination, n_+, will be destabilizing. The level order will thus become n_- below n_+ level which is the reverse of the normal level order for N = even cases.[1c,9] Since the reversal of the sign of one β to positive ($S<0$) brings stabilization, the system has an *anti*-Hückel or Möbius type σ aromaticity[3,10]; an N = even system with a crowded a structure having significantly overlapping terminal nonbonding lobes forms an *anti*-Hückel or Möbius system[6] so than n_- level has



σ-aromatic whereas n_+ level has σ-antiaromatic[3] structure.

Various levels of MO calculations[1,7] gave in fact the level order of n_- below n_+ for outward pyramidalized trimethylene diradicals, (I).[7]

This reversal of level order has been a puzzle[1] and no ready explanation has yet been found. It is clear that this level order reversal in (I) is due to the third type of *n*–*n* orbital interaction, in which both the direct overlap between the two nonbonding orbitals (TSI) and the σ-conjugative and hyperconjugative interactions of the nonbonding orbitals with the CC bonds forming framework σ orbitals (TBI)[1c] are involved. This type of coupling term involving both contributions has been known to exist,[1c,7] but the nature of the interaction was not explicitly