

Hydrogenolysis and Homologation of Linear and Branched Pentenes on Ru/SiO₂ Catalysts: Implication in the Mechanism of C–C Bond Formation and Cleavage on Metal Surfaces

Eloy Rodriguez,^{1a} Michel Leconte,^{1a} Jean Marie Basset,^{*1a} Katsumi Tanaka,^{1b} and Ken-Ichi Tanaka^{1c}

Contribution from the Institut de Recherches sur la Catalyse, Laboratoire Propre du CNRS, Conventionné à l'Université Claude Bernard, Lyon I, 2, Avenue Albert Einstein, 69626 Villeurbanne Cédex, France, Research Institute for Catalysis, Hokkaido University, Kita-Ku, Sapporo 060, Japan, and Institute for Solid State Physics, University of Tokyo, 7-22-1 Roppongi, Minato-Ku, Tokyo 106, Japan.
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Abstract: Hydrogenolysis and homologation of 1-pentene to butenes and hexenes take place simultaneously and at the same rate over a Ru/SiO₂ catalyst at 110 °C, suggesting that these two reactions are mechanistically related. ¹³C labeling experiments indicate that C–C cleavage occurs at the double bond of 1-pentene-1-¹³C leading to unlabeled 1-butene and labeled hexenes. The product distribution in the hydrogenolysis of 1-pentene, 2-pentenes, 3-methyl-1-butene, 2-methyl-2-butene, and 2-methyl-1-butene is accounted for by a carbene-olefin mechanism, which can therefore be considered as a reasonable common path for the formation and cleavage of carbon-carbon bonds on metal surfaces.

The hydrogenolysis of saturated hydrocarbons over heterogeneous transition-metal catalysts converts an alkane, in the presence of H₂, to lower chain hydrocarbons (plus methane).²⁻⁶ The hydrogenolysis of olefinic hydrocarbons on the same metallic catalysts, in the presence of H₂, leads to lower olefins and paraffins plus methane.^{6,7} Interestingly, the hydrogenolysis of olefins is accompanied by the formation of the next higher olefins (homologation reaction).^{7,8} It has been suggested by Pettit and co-workers⁶ that hydrogenolysis of hydrocarbons is mechanistically related to the Fischer-Tropsch synthesis in terms of C–C bond formation and C–C bond cleavage. Evidence was also given for a mechanistic similarity between paraffin⁹ and olefin⁸ homologation and the Fischer-Tropsch synthesis. We present evidence here that olefin hydrogenolysis to lower olefins and olefin homologation to higher olefins are also mechanistically related, which seems to indicate that, on a metal surface, formation or cleavage of C–C bonds would obey the same elementary steps. The proposed mechanism involves a carbene-olefin intermediate.

Results and Discussion

When a mixture of pentene/H₂/argon (pentene/H₂ = 1/1) is allowed to flow over a Ru/SiO₂ catalyst (at 250 °C and atmospheric pressure), hydrogenation and isomerization of the olefin are observed. Besides, formation of unsaturated and saturated hydrocarbons ranging from C₁ to C₇ occurs. Hydrogenolysis and homologation occur regardless of the isomer (1-pentene, 2-pentene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene). Conversions¹⁰ were found to vary proportionally to contact time.

(1) (a) Institut de Recherches sur la Catalyse. (b) Research Institute for Catalysis. (c) Institute for Solid State Physics.

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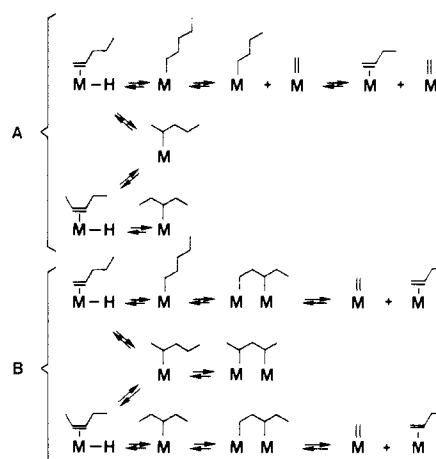
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(10) Conversions are expressed as the molar ratio of the C₁-C₇ products to the C₅ starting olefin and vary between 0.05% and 0.5% (differential conditions); concerning the hydrogenolysis reaction (formation of C₁-C₄ hydrocarbons), the catalytic activities depend slightly on the linear or branched structure of the pentene (0.9 × 10⁻³ mol of C₁-C₄ × h⁻¹ × g⁻¹ catalyst for 1-pentene and 2-pentene; 0.75 × 10⁻³ mol of C₁-C₄ × h⁻¹ × g⁻¹ catalyst for methylbutenes).

Scheme 1: Formation of 1-Butene from 1-Pentene or 2-Pentene (Carbene-Deinsertion Mechanism A; Metallacycle Mechanism B).



The molar distributions of unsaturated and saturated hydrocarbons from C₁ to C₄ obtained for high-space velocities (10³ × h⁻¹ < GSV < 10⁴ × h⁻¹) are roughly independent of the contact time. At 250 °C, the major products of the hydrogenolysis of pentenes (linear or branched) are methane and C₄ hydrocarbons; a small amount (10-20%) of C₂ + C₃ hydrocarbons (with C₂ ≤ C₃) is produced (Figure 1). The percentage of olefins in the C₂-C₄ hydrocarbons is about 65-75% for a pentene/H₂ ratio of 1/1 but can reach 90% for a pentene/H₂ ratio of 3/1.

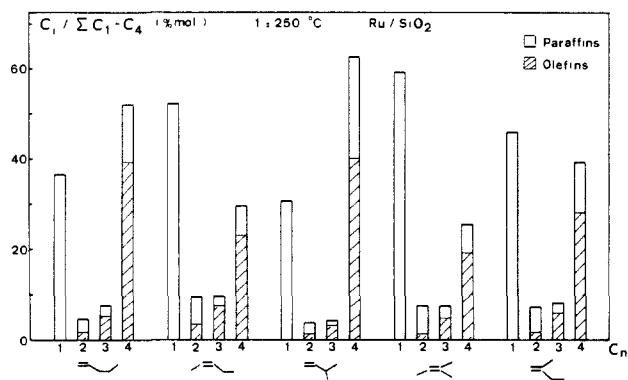
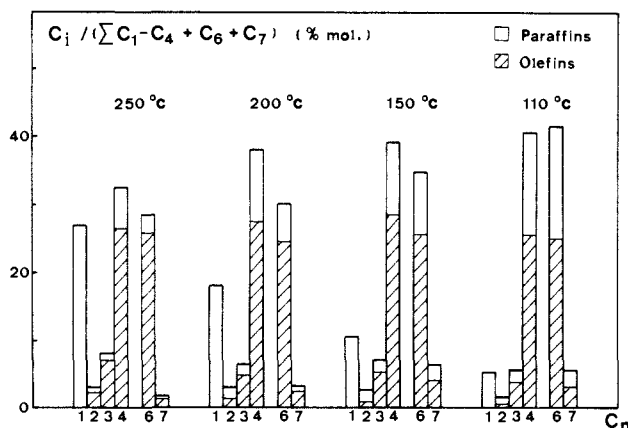
The C₁-C₇ distribution as a function of reaction temperature indicates that the proportion of CH₄ decreases with decreasing temperature (Figure 2; case of 1-pentene). At 110 °C, the major products of hydrogenolysis-homologation of 1-pentene are C₄ and C₆ hydrocarbons, with only ca. 5% CH₄ being formed.

The results of Figures 1 and 2 suggest that on a Ru/SiO₂ catalyst, in the presence of H₂, a C₅ olefin undergoes cleavage of mainly a terminal C–C bond leading to C₄ and C₁ fragments.¹¹ The C₄ fragments give butenes and butanes, and the C₁ fragments either lead to methane after hydrogenation or react with C₅ to

(11) The formation of C₂-C₃ hydrocarbons in roughly equal amounts suggests the possibility of a cleavage reaction, C₅ → C₃ + C₂. But we cannot exclude successive reactions of the type C₅ → C₄ + C₁, C₄ → C₃ + C₁, C₃ → C₂ + C₁, C₂ → 2C₁, which may perturbate the amounts of C₂ and C₃ and also increase the proportion of C₁.

Table I. ^{13}C Distribution (in Olefins from C_4 to C_6) in the Hydrogenolysis-Homologation of 1-Pentene- l - ^{13}C (48%) + 1-Pentene- l - ^{12}C (52%)

product	^{13}C distribution, %						
	$^{13}\text{C}_0$	$^{13}\text{C}_1$	$^{13}\text{C}_2$	$^{13}\text{C}_3$	$^{13}\text{C}_4$	$^{13}\text{C}_5$	$^{13}\text{C}_6$
1-butene	95.2	4.8	0	0	0		
isobutene	42.2	33.5	20.1	4.2	0		
<i>trans</i> -2-butene	94.7	5.3	0	0	0		
<i>cis</i> -2-butene	94.8	5.2	0	0	0		
1-pentene	52.0	48.0	0	0	0	0	
<i>trans</i> -2-pentene	52.0	48.0	0	0	0	0	
<i>cis</i> -2-pentene	52.0	48.0	0	0	0	0	
hexenes	54.3	37.4	8.3	0	0	0	0

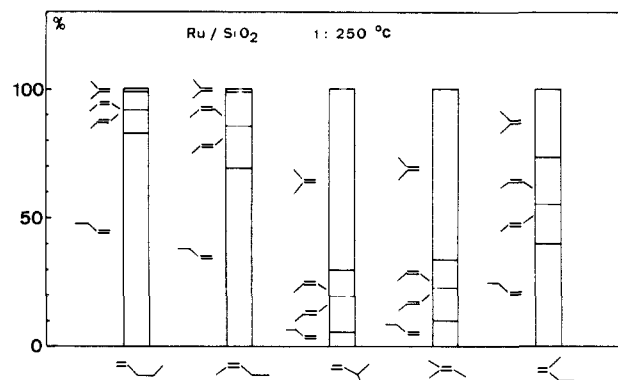
**Figure 1.** Product distributions (olefins + paraffins from C_1 to C_4) in the hydrogenolysis of pentene isomers ($\text{C}_3\text{H}_{10}/\text{H}_2 = 1/1$).**Figure 2.** Product distributions (olefins + paraffins from C_1 to C_7) in the hydrogenolysis and homologation of 1-pentene at various temperatures ($\text{C}_3\text{H}_{10}/\text{H}_2 = 1/1$).

give C_6 (and with C_6 to give C_7). At low temperature, there is almost no hydrogenation of the C_1 fragment, and it is quite logical to observe that the amount of C_6 is close to the amount of C_4 (no buildup of carbonaceous residue¹²). In any case, all these reactions of cleavage and formation of C-C bonds seem to occur simultaneously and at the same rate on the surface (at low contact time).

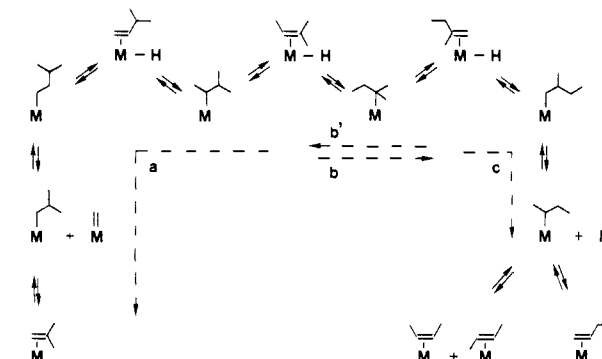
In order to verify this hypothesis, labeling experiments were carried out in a closed glass circulation system with a 48/52 mixture of 1-pentene- l - ^{13}C and 1-pentene- l - ^{12}C . At 110 °C, and after 5 min of reaction time, the conversion to C_4 is 0.68%¹³ and the product distribution (Table I) exhibits the following features: the linear butenes are mainly unlabeled, whereas hexenes are both labeled and unlabeled ($^{13}\text{C}_0$ - C_6 , $^{13}\text{C}_1$ - C_6 , $^{13}\text{C}_2$ - C_6). The results confirm that the labeled 1-pentene- l - ^{13}C is cleaved at the double bond to give unlabeled linear butenes.^{14,15} Simultaneously, the

(12) As suggested also by the fact that there was roughly no decrease of activity with reaction time.

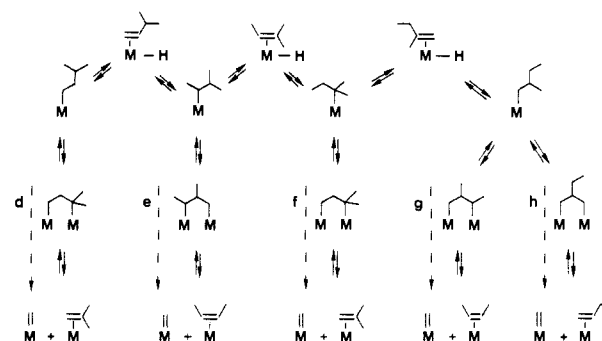
(13) Composition of the C_4 products (%): *n*-butane, 4.3; 1-butene, 36.2; isobutene, 7.2; *trans*-2-butene, 37.7; *cis*-2-butene, 14.5. Composition of the C_5 products (%): *n*-pentane, 6.1; 1-pentene, 13.6%; *trans*-2-pentene, 60.3; *cis*-2-pentene, 20.0.

**Figure 3.** Distribution of butenes produced from the hydrogenolysis of the five pentene isomers.

Scheme II: Formation of Butenes from Methylbutenes (Carbene-Deinsertion Mechanism A).



Scheme III: Formation of Butenes from Methylbutenes (Metallacycle Mechanism B).



labeled $^{13}\text{C}_1$ fragment can be incorporated into both unlabeled and labeled 1-pentene to give $^{13}\text{C}_1$ - C_6 and $^{13}\text{C}_2$ - C_6 .¹⁶

(14) It should be noticed that significant double-bond migration of 1-pentene is observed after the reaction, suggesting a possibility of isomerization up to the formation of 1-pentene-5- ^{13}C . Since more than 90% of the linear butenes are unlabeled, it is suggested that these three stepwise double-bond migrations leading to 1-pentene-5- ^{13}C are slower than hydrogenolysis.

The distribution of the C₄ olefinic hydrocarbons has been studied with unlabeled pentenes in a flow system at very low conversion. It depends on the nature of the pentene isomer, which supplies supplementary mechanistic information (Figure 3). Hydrogenolysis of 1-pentene or 2-pentene gives roughly the same distribution of C₄ olefinic isomers, with 1-butene as the major product, 2-butene in smaller amounts (which may be formed, in part, by secondary isomerization of 1-butene), and no isobutene (<0.5%). This result may be explained by both a carbene-deinsertion mechanism A and a mechanism involving metallacyclic intermediates B (Scheme I).¹⁷

Branched C₅ olefins give different results from linear olefins (Figure 3). Hydrogenolysis of 2-methyl-2-butene gives a distribution of C₄ isomers comparable with that obtained with 3-methyl-1-butene: isobutene as the major product (65–70%), 20–25% of 2-butene, and only a small amount of 1-butene. In contrast, 2-methyl-1-butene gives linear butenes as the major products with 2-butene and 1-butene in comparable amounts.

Let us consider the product distribution in light of the carbene-deinsertion mechanism A (Scheme II).¹⁷ When starting from 3-methyl-1-butene and 2-methyl-2-butene, the formation of isobutene in major amounts can be applied by the more favored reaction path a, which involves only primary and secondary metal-alkyl intermediates. The reaction path b + c would be more difficult due to the sterically unfavored tertiary metal-alkyl intermediate.¹⁸

When starting from 2-methyl-1-butene, reaction path c should be favored with respect to b' + a, with formation of larger amounts of 2-butene and 1-butene. However, one should obtain the same ratios of 2-butenes/1-butene with the three branched C₅, which is not the case since these ratios are, respectively, 4.0, 2.1, and 0.80 for 3-methyl-1-butene, 2-methyl-2-butene, and 2-methyl-1-butene.

Let us consider now the product distribution in the light of the metallacycle mechanism B (Scheme III).¹⁷ The main difference

between mechanism B and mechanism A is the formation of a metallacycle from a metal-alkyl via a γ -H abstraction as it occurs, e.g., with neopentyl complexes of platinum.¹⁹ Once the metallacycle is formed, a metathesislike mechanism occurs. The preferential formation of isobutene when starting from 3-methyl-1-butene and 2-methyl-2-butene and the preferential formation of linear butenes from 2-methyl-1-butene can be explained on the same basis as in mechanism A. But the variation of the ratio 2-butene/1-butene with the nature of the C₅ isomer is now easily accounted for by the simultaneous occurrence of two reaction paths leading to 2-butene (e and g): with 2-methyl-1-butene, the 2-butene/1-butene ratio close to unity is explained by the major and equiprobable reactions paths g and h; with the olefins 3-methyl-1-butene and 2-methyl-2-butene, the higher 2-butene/1-butene ratio is explained by the possibility of another reaction path (e) leading to 2-butene.

Conclusion

From the data and the discussion presented above, a number of interesting conclusions may be drawn:

Hydrogenolysis and homologation of pentenes to butenes and hexenes take place simultaneously and at the same rate over a Ru/SiO₂ catalyst, suggesting that these two reactions are mechanistically related as already suggested by Pettit.⁶

Labeling experiments confirm that the terminal olefin is cleaved at the double bond to yield a labeled C₁ fragment, which is incorporated in the starting terminal alkene to produce the higher homologue; at low temperature, this C₁ fragment is only slightly hydrogenated to methane.

Two mechanisms can be proposed to explain both C–C bond formation and cleavage: (i) a carbene insertion-deinsertion mechanism to (from) a metal-alkyl fragment^{6,20,21} and (ii) a carbene-olefin mechanism via dimetallacyclopentane intermediates.^{22–27} The carbene-olefin pathway, already proposed for olefin homologation,^{7,28,29} seems to account very well also for the product distribution in the hydrogenolysis of various isomers of pentenes³⁰ and can therefore be considered as a reasonable common path for the formation and cleavage of carbon-carbon bonds on metal surfaces.^{9,31–40} These elementary steps can be invoked

(15) A small amount of isobutene (7% of C₄) was also found in the C₄ products. This formation of isobutene in the hydrogenolysis of linear pentenes was observed only when experiments were carried out in a batch system with recycling device. In such circumstances side reactions were more important. The reason why isobutene had a fairly high degree of ¹³C₁ and ¹³C₂ labeling is because the ¹³C₁ fragments may react with propene to give isobutene. Propene may be unlabeled or ¹³C₁-labeled, since it may be formed both by C₄ → C₃ + C₁ and C₅ → C₃ + C₂ reactions; then, its reaction with ¹³C₁ fragments will give [¹³C₁]- or [¹³C₂]isobutene.

(16) One could be tempted to interpret the labeling experiments in detail, assuming simple hypotheses. However this approach proved to be very difficult due to the fact that a variety of side reactions can occur during homologation and hydrogenolysis: The expected ¹³C₀/¹³C₁/¹³C₂ distribution in the hexenes should be ca. 25/50/25, assuming an equal amount of unlabeled and labeled CH₂ fragments. Due to the possible successive reactions unlabeled C₄ → C₃ + C₁ and C₃ → C₂ + C₁, the amount of unlabeled CH₂ is probably much higher than 50%, increasing the amount of unlabeled hexenes and decreasing the amount of doubly labeled hexenes. The expected ¹³C₀/¹³C₁ ratio in the hexenes should be lower than (or equal to) unity if one assumes that the ratio of unlabeled to monolabeled 1-pentene is strictly unity (regardless of the ratio ¹³CH₂/¹²CH₂). In fact it is very likely that not only the ratio ¹³CH₂/¹²CH₂ is far from unity (due to successive degradation), but also it is likely that unlabeled to labeled surface C₅ fragment ratio is not strictly unity. (For example, assuming ¹³CH₂/¹²CH₂ = 0.2/0.8 and ¹³C¹²C₄/¹²C₅ = 0.4/0.6, the calculated unlabeled/monolabeled/dilabeled distribution in the hexenes is 6/5.5/1, whereas the observed value is 6.5/4.5/1). Other figures assuming different hypotheses can lead to expected results close to experimental ones. One should mention that detailed interpretation of the labeling experiments carried out here cannot be done due to the presence of too many side reactions. Consequently, regarding the labeling experiments, the only significant result is that 1-pentene labeled in a terminal position can give monolabeled or doubly labeled hexene, which can be formed only by the addition of labeled C₁ to a 1-pentene fragment. In fact, in order to have a deeper approach to the mechanism, it was necessary to study in detail the distribution of isomers.

(17) For clarity, the possible reaction paths leading to C₂ and C₃ hydrocarbons (by C₅ → C₃ + C₂ or C₄ → C₃ + C₁ and C₃ → C₂ + C₁) have not been drawn. But formation of C₂ and C₃ hydrocarbons may equally well be explained on the basis of the same mechanisms. Coupling of carbenes to give olefin or homolytic cleavage of olefin to carbenes constitute a possible alternative mechanism. However, we have no evidence of carbene coupling; especially when working with internal C₅ olefins, no drastic increases of C₂ and C₃ olefins were noticed in comparison with terminal C₅ olefins.

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(30) It has been suggested by one reviewer that both mechanisms are operative; the metallacycle mechanism would apply to branched olefins, whereas the carbene insertion-deinsertion mechanism would be operative with unbranched olefins. This is a possibility that we cannot reject, but it seems more simple to invoke a single mechanism, since it explains the results obtained with both branched and unbranched olefins.

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not only in olefin homologation and hydrogenolysis but also in alkane hydrogenolysis and isomerization and in the Fischer-Tropsch synthesis.

Experimental Section

1. Materials. 1-Pentene, 2-pentene, 3-methyl-1-butene, 2-methyl-2-butene, and 2-methyl-1-butene (Fluka) were used as received.

1-Pentene-*l*-¹³C was obtained by a methylene exchange of 1-pentene with ¹³C-labeled ethylene (ca. 2/1 ratio) on a SnMe₄-treated MoO₃/TiO₂ catalyst at room temperature;⁴¹ 48% ¹³C-labeled and 52% unlabeled 1-pentene were produced in the reaction. The mixture was purified by column separation and vacuum evaporation to remove water. Hydrogen was purified by passage through a Pd thimble at 400 °C.

2. Catalysts. For the experiments in a flow system the Ru/SiO₂ catalyst was prepared by adsorbing Ru₃(CO)₁₂ (Johnson Matthey) from a hexane solution onto silica (Aerosil 200 Degussa) that had been pre-treated at 500 °C under 10⁻⁴ Torr for 16 h. The cluster was then decomposed overnight under flowing H₂ at 300 °C. The final metal content was 1.0%, and the average particle size determined by electron microscopy was ca. 15 Å.

For the labeling experiments the Ru/SiO₂ catalyst was prepared by reducing RuCl₃ supported on SiO₂ (Merck, Kieselgel 60) with 200 Torr

H₂ at 400 °C for 2 h in a closed circulation system with a glass loop maintained at -196 °C; the final metal content was 2.8 atom %.

3. Catalytic Reactions. Flow System. The reactor was a dynamic microreactor working at atmospheric pressure. The reagents were a mixture of pentene/H₂/argon. Pentene was introduced in a saturator, the temperature of which was stabilized at 0 °C, and the flow rate of the olefin was regulated by the flow of argon. Typically, the flow rates of argon and hydrogen were such that the final reaction mixture corresponded to pentene/H₂ = 1/1 (molar ratio).

The experiments were carried out according to the following procedure: the catalyst Ru/SiO₂ (ca. 200 mg) introduced in the reactor was heated at the reaction temperature under a flow of pure hydrogen; then the mixture pentene/H₂/argon was allowed to flow over the catalyst (10³ × h⁻¹ < GSV < 10⁴ × h⁻¹) for 10 mn before the products of the reaction were analyzed by gas-phase chromatography.

Separation and analysis of the products were carried out with a fid gas-phase chromatograph Intersmat IGC 120 FB. Hydrocarbons from C₁ to C₄ were separated by employing a 1/8 in. × 6 m squalane (7%)/alumina column. Hydrocarbons from C₅ to C₇ were separated employing a set of two columns including a 1/8 in. × 4.5 m SE 30/Chromosorb column and a 1/8 in. × 2 m DC 550/Chromosorb column.

Labeling Experiments. The reaction was carried out by introducing 1-pentene (48% ¹³C; 40 Torr) in the presence of H₂ (4 Torr) on the Ru/SiO₂ (20 mg) at 110 °C in a closed glass circulation system with a volume of 260 mL, equipped with greaseless stop valves to prevent absorption of reactant and product gases.

The product distribution in the 1-pentene reaction was determined by means of an on-line gas chromatograph with fid detector (Shimadzu GC 4), fitted with a 13-m stainless steel column (3 mm i.d.) packed with Sebacitrile 25% on Uniport C. The distribution of ¹³C in each product was analyzed by mass spectrometry (Hitachi RMU-6) with low-ionization voltage (10–12 V) to prevent fragmentation. Products of 1-pentene homologation were concentrated in a sampling loop and separated by means of a column, then each product was trapped by a gas-collecting equipment.

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Asymmetric Synthesis with Chiral β -Lactams. α -Substituted Aromatic α -Amino Acids and Their Derivatives through Highly Stereoselective Alkylations

Iwao Ojima,* Hauh-Jyun C. Chen, and Kazuaki Nakahashi¹

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794. Received April 1, 1987.

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Abstract: A novel route to optically pure α -alkylated aromatic α -amino acids and their dipeptide derivatives was developed through the asymmetric alkylation at the C-3 position of a chiral β -lactam **1** followed by the reductive cleavage of the alkylated β -lactams **2**. The stereochemical course of the reaction is effectively controlled by the chiral center at the C-4 position of the β -lactam. This novel asymmetric alkylation was successfully applied for the synthesis of (*S*)- α -methyl-DOPA via a chiral β -lactam **4**, which was synthesized by the asymmetric [2 + 2] cycloaddition of a chiral ketene to an imine.

Recently the significance of nonproteinogenic amino acids has been recognized in connection with the design and synthesis of enzyme inhibitors as potential pharmaceutical drugs and also for the study of enzymic reaction mechanisms.^{2–6} Among those

nonproteinogenic amino acids, α -substituted α -amino acids provide a challenging synthetic problem for chemists, since the α -substituted α -amino acids have chiral quaternary carbons, and thus, conventional enzymic optical resolution technology cannot be applied effectively; viz., no racemization can take place at the chiral α -carbons, and thus, D-isomers cannot be recycled to the optical resolution process. Therefore, the asymmetric synthesis of optically

(1) Research Fellow, on leave from Fuji Chemical Industries, Ltd., 530 Chokeiji, Takaoka, Toyama, Japan, 1984–1986.

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