tioned preparation of *exo*-**3**, followed by hydroboration.

As the exo selectivity is expected in the concerted insertion that will take place on the sterically less hindered exo face of norcaranylidene carbenoid (Scheme I, a),[10] the present stereochemical outcome clearly indicates that the endo-selective insertion into the α-C–H bond of alkoxides proceeds by a mechanism different from that for the exo-selective concerted insertion.[11] In the previous report,[3] we demonstrated a novel stepwise mechanism, hydride abstraction–recombination mechanism, in the insertion by alkylidenemethylene carbenoid into the α-C–H bond of alkoxides. The present characteristic endo selectivity is reasonably explained in terms of the hydride abstraction from the α position of alkoxides by norcaranylidene carbenoid on its exo face, followed by the recombination of the resulting *endo*-norcaranyl anion with the carbonyl compound (Scheme I, b).[12] The mechanism is further supported in the reaction of **2c** (eq 3) by the formation of 1-methylcyclohexanol, a product from the intermediate carbonyl compound trapped by MeLi.

We noted in a separate study that the hydride abstraction by carbenoids predominates when the concerted insertion is sterically retarded.[3] The minor products *exo*-**3** and *exo*-**4** formed in the reactions of primary alkoxides **2a** and **2b** are produced supposedly through a concerted mechanism, but this mechanism is completely suppressed in the reaction of sterically demanding secondary alkoxide **2c** where an exclusive endo selectivity was attained.

The present study as well as our latest report[3] shows that the hydride abstraction is a common reaction of carbenoids. A highly electrophilic character of carbenoids exhibited in the hydride abstraction supports the current view that carbenoids are electron deficient at carbon.[13-15]

Registry No. 1, 2415-79-4; **2a**, 22379-62-0; **2b**, 2245-69-4; **2c**, 54637-77-3; **3**, 100971-67-3; **4**, 103499-75-8; **5**, 103499-76-9; **6**, 103499-77-0; **7**, 6537-04-8; PhCHO, 100-52-7; $PhCH_2CHO$, 122-78-1; 1-methylcyclohexanol, 590-67-0; 7-bromo-7-lithionorcarane, 57640-05-8; 7-benzoylnorcarane, 31152-14-4; norcaranylidene carbenoid, 91781-43-0.

Supplementary Material Available: A general reaction procedure and ^1H NMR (200 MHz), IR, and mass spectral data of the insertion products (3 pages). Ordering information is given on any current masthead page.

(10) For the theoretical study on the transition-state geometry of the C–H insertion reaction, see: Jug, K.; Mishra, P. C. *Int. J. Quantum Chem.* **1983**, *23*, 887 and references cited therein.

(11) A radical chain/electron-transfer mechanism similar to that proposed for an aryl halide–methoxide system (Bunnett, J. F.; Wasmer, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 6721) seems unlikely in the present reaction: the involvement of norcaranylidene radical anion (or its adduct with a carbonyl compound) in the chain cannot explain the characteristic endo selectivity.

(12) For the conformational stability of cyclopropyllithium, see: (a) Applequist, D. E.; Peterson, A. H. *J. Am. Chem. Soc.* **1961**, *83*, 862. (b) Walborsky, H. M.; Impastato, F. J.; Young, A. E. *Ibid.* **1964**, *86*, 328.

(13) Draisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5035.

(14) (a) Seebach, D.; Siegel, H.; Gabriel, J.; Hassig, R. *Helv. Chim. Acta* **1980**, *63*, 2046. (b) Seebach, D.; Hassig, R.; Gabriel, J. *Ibid.* **1983**, *66*, 308.

(15) Mareda, J.; Rondon, N. G.; Houk, K. N.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 6997 and references cited therein.

Akira Oku,* Yasunari Yamaura, Toshiro Harada

Department of Chemistry
Kyoto Institute of Technology
Matsugasaki, Sakyo-ku
Kyoto 606, Japan

Received April 1, 1986

((9-Fluorenylmethyl)oxy)carbonyl (Fmoc) Amino Acid Chlorides. Synthesis, Characterization, and Application to the Rapid Synthesis of Short Peptide Segments

Summary: Fmoc amino acid chlorides are described as stable, easily synthesized coupling agents and shown to be useful in a novel method of rapid, repetitive peptide synthesis.

Sir: Although protected amino acid chlorides have been known as coupling agents since the earliest days of peptide synthesis, they have never been widely used except in special circumstances.[1] Protecting groups stable enough to survive conversion to an acid chloride are generally difficult to deblock. We point out that with the development of the Fmoc amino-protecting group,[6] there is no longer a need to avoid the use of acid chlorides. Under appropriate conditions coupling occurs without loss of chirality at the carboxylic acid site. A convenient method of coupling involves a two-phase system with a mild inorganic base in the aqueous layer to minimize contact with the acid chloride. Coupling is completed within a few minutes. Simple coupling reactions in homogeneous solution are also possible.

Table I lists the Fmoc amino acid chlorides synthesized to date. Following reaction with thionyl chloride, recrystallization from CH_2Cl_2–hexane gives analytically pure samples of the acid chlorides which can be stored indefinitely in a dry atmosphere. Prior to use samples may, if desired, by analyzed for any residual acid content via a simple HPLC technique: addition to dry methanol followed by immediate injection onto a C_{18} column reveals the ratio of acid chloride (as methyl ester) and free acid.

These new acid chlorides have been used in a novel technique for the rapid solution synthesis of short peptide segments. Traditional solution methods are often tediously slow. Improvements have long been sought and several

(1) A recent authoritative review[2] on coupling methods pronounced the use of amino acid chlorides in peptide coupling as obsolete. In our view, far from being obsolete, amino acid chlorides are now among the most convenient reagents for peptide bond formation following the stepwise strategy considering ease of access, low cost, shelf stability, and speed of reaction with amino acid and peptide esters. Fmoc amino acid chlorides were previously used for the preparation of polymeric active esters, or, prepared in situ, in order to synthesize otherwise difficultly obtainable amides. [Cohen, B. J. Ph.D. Dissertation, Weizmann Institute of Science, Rehovot, Israel, 1979; Pass, S.; Amit, B.; Patchornik, A. *J. Am. Chem. Soc.* **1981**, *103*, 7674.]. The fear of racemization attending the use of ordinary protected amino acid chlorides[3-5] is not borne out. Kunz and Bechtolsheimer[3] have also recommended resurrection of the use of acid chlorides in peptide coupling, especially in the case of hindered substrates. For the [[2-(triphenylphosphonio)ethyl]oxy]carbonyl system, special interactions involving the phosphonium cation were invoked to account for the observed lack of racemization. Our work and that of others[4,5] shows that no special structural elements are needed to avoid racemization.

(2) Jones, J. H. In *The Peptides*; Gross, E., Meienhofer, J., Eds.; Academic Press: New York, 1979, Vol. 1, p 65.

(3) (a) Bechtolsheimer, H.-H.; Kunz, H. *Angew. Chem., Int. Ed. Engl* **1982**, *21*, 630. (b) Kunz, H.; Bechtolsheimer, H.-H. *Liebigs Ann. Chem.* **1982**, 2068.

(4) For additional examples of the use of chiral protected amino acid chlorides, see: (a) Cupps, T. L.; Boutin, R. H.; Rapoport, H. *J. Org. Chem.* **1985**, *50*, 3976. (b) Nordlander, J. E.; Njoroge, F. G.; Payne, M. J.; Warman, D. *J. Org. Chem.*, **1985**, *50*, 3481. (c) Nordlander, J. E.; Payne, M. J.; Njoroge, F. G.; Balk, M. A.; Laikos, G. D.; Vishwanath, V. M. *J. Org. Chem.* **1984**, *49*, 4107.

(5) Under very mild conditions even *tert*-butoxycarbonyl and benzyloxycarbonyl systems have been used successfully. See: (a) Losse, G.; Wehrstedt, K.-D. *Z. Chem.* **1981**, *21*, 148. (b) Matsuda, F.; Itoh, S.; Hattori, N.; Yanagiya, M.; Matsumoto, T. *Tetrahedron* **1985**, *41*, 3625.

(6) Carpino, L. A.; Han, G. Y. *J. Am. Chem. Soc.* **1970**, *92*, 5748; *J. Org. Chem.* **1972**, *37*, 3404.

0022-3263/86/1951-3732$01.50/0

Table I. Fmoc Amino Acid Chlorides[a]

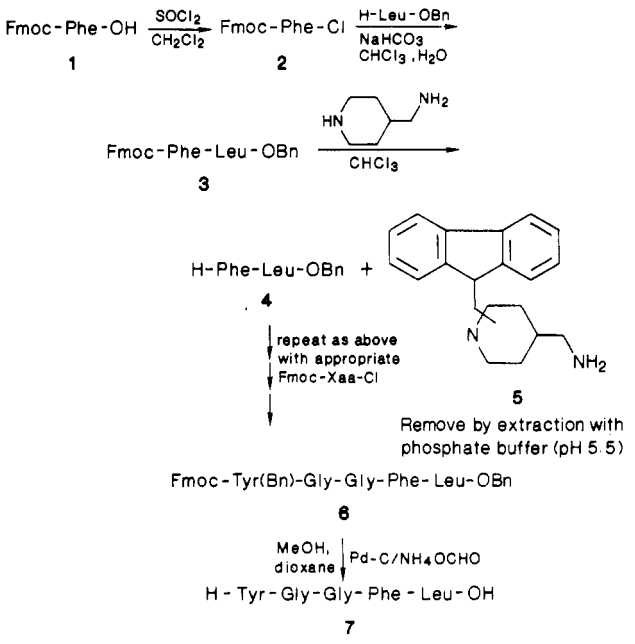
compound	yield (%)[b]	mp (°C)	optical rotation, $[\alpha]_D$, t (°C)	t_R (flow rates)[c]
Fmoc-Gly-Cl	95.4	108–9		8.50/10.25 (1)
Fmoc-Ala-Cl	80.6	112–4	+4.03 (c 1, CH_2Cl_2), 24	5.00/6.20 (2)
Fmoc-Ile-Cl	87.3	103–4	+2.43 (c 1, CH_2Cl_2), 24	9.90/13.45 (2)
Fmoc-Pro-Cl	78.6	93–4	−39.9 (c 1, CH_2Cl_2), 24	6.35/8.45 (2)
Fmoc-Val-Cl	85.3	111–2	+5.5 (c 1, CH_2Cl_2), 24	8.05/10.75 (2)
Fmoc-Met-Cl	90.3	118–9	−9.76 (c 1, CH_2Cl_2), 24	6.45/8.10 (2)
Fmoc-Cys(Bn)-Cl	95.2	104–5	−13.5 (c 1, CH_2Cl_2), 26	13.50/17.60 (2)
Fmoc-Lys(Z)-Cl	88.3	67–8	+0.53 (c 4, CH_2Cl_2), 23	8.85/12.35 (2)
Fmoc-Phe-Cl	95.8	120–1	+15.7 (c 1, CH_2Cl_2), 24	8.95/11.45 (2)
Fmoc-D-Phe-Cl	92.5	119–20	−15.5 (c 1, CH_2Cl_2), 24	8.25/10.50 (2)
Fmoc-Leu-Cl	96.0	80–1	−4.24 (c 2, CH_2Cl_2), 30	8.50/11.05 (2)
Fmoc-Tyr(Bn)-Cl	91.2	114–5	+16.5 (c 1, CH_2Cl_2), 24	10.45/13.95 (4)
Fmoc-Ser(Bn)-Cl	90.8	96–8	+11.1 (c 1, CH_2Cl_2), 21	7.95/10.40 (2)
Fmoc-Asp(Bn)-Cl	89.3	50–3	+7.9 (c 1, CH_2Cl_2), 21	7.10/8.65 (2)

[a] Fmoc amino acids were prepared by acylation via Fmoc-N_3 (compare ref 6) for 24–70 h. Physical constants and spectral data agreed with published values. For a representative example of conversion to the acid chloride, a solution of 0.3 g (0.88 mmol) of Fmoc-Val-OH in 5 mL of CH_2Cl_2 was treated with 1.05 g (8.8 mmol) of $SOCl_2$ and the mixture refluxed for 15 min under N_2. In other cases up to 1–2 h of refluxing was necessary for complete reaction. In the presence of 0.1 equiv of DMF as catalyst, complete conversion to the acid chloride occurs within 1 h at room temperature. Solvent and excess $SOCl_2$ were removed in vacuo and the residue was dissolved in 1 mL of CH_2Cl_2. Addition of 10 mL of hexane precipitated pure Fmoc-Val-Cl. [b] Yields given are of the pure isolated chlorides following recrystallization from CH_2Cl_2–hexane. HPLC analysis of the recrystallized valine derivative showed 95.36% acid chloride along with 1.25% of the free acid. Prior to crystallization, HPLC analysis indicated 96.30% acid chloride and 0.36% acid. Other minor unidentified impurities were visible in the HPLC traces of this and all other derivatives. [c] Retention times (flow rates) are given in min (mL/min) for the residual free acid and derived methyl ester, respectively, obtained upon addition of the acid chloride to excess dry methanol. Analysis must be completed immediately due to subsequent Fischer esterification of the free acid in the methanolic HCl solution. For example, a mixture initially analyzing for 92.07% Fmoc-Gly-Cl (as Me ester) and 7.93% Fmoc-Gly-OH came to equilibrium after 2 h with a measured content of 99.62% Fmoc-Gly-OMe and 0.35% Fmoc-Gly-OH. For a solution containing 11.37% Fmoc-Val-OH, 52 h were required to come to equilibrium (0.36% acid). Analyses were carried out on a Waters Z-Module Radial Compression Unit (C_{18} column, 0.8 × 10 cm, 10 μm) with eluant consisting of 65% MeOH/35% H_2O (0.1% trifluoroacetic acid).

fast repetitive methods have been developed for which the time period for one complete cycle is 2.6–6 h.[7] None has yet been widely adopted.

Since deblocking is rapid and liberates the amino function in a form directly ready for the next step, syntheses involving Fmoc protection require only a fraction of the time needed with acid-sensitive protection. By carrying out the initial coupling reaction and subsequent deblocking step in a water-immiscible solvent such as $CHCl_3$, CH_2Cl_2, or $ClCH_2CH_2Cl$, one can effect further savings in time by removal of excess reagents and byproducts by simple aqueous extractions. In order to maintain high yields, a 10% or greater excess of Fmoc amino acid chloride is taken over the initial ester or growing peptide ester. Removal of excess acid chloride is then achieved by addition of *N*-methylpiperazine.[8] The resulting amide is extracted with dilute hydrochloric acid. Following separation of layers, deblocking is effected by a large excess of 4-(aminomethyl)piperidine. After 5–30 min (depending on the solvent), deblocking is complete and a quick wash with water removes the excess deblocking agent. Aside from the desired peptide ester, only the dibenzofulvene adduct of 4-(aminomethyl)piperidine remains in the organic phase.[9] As a difunctional strong base, the adduct (**5**, precise structure not specified) is readily removed quantitatively without disturbing the free peptide ester by extraction with a phosphate buffer of pH 5.5. The reaction time for one cycle is only 10–45 min, the remainder of the period being taken up in phase separation, the time for which varies with the particular sequence. The method is outlined in Scheme I.

Scheme I



Without stopping at intermediate stages,[11] the Fmoc-

(7) Kisfaludy, L. In The Peptides; Eds. Gross, E., Meienhofer, J., Eds. Academic Press: New York, 1980; Vol. 2, Part A, p 418. See also: (a) Nozaki, S.; Muramatsu, I. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2165. (b) Dölling, R.; Kaufmann, K.-D. *J. Prakt. Chem.* **1984**, *326*, 171.

(8) *N*-Methylpiperazine is also an effective deblocking agent for the Fmoc group. However, the amount and time needed to scavenge the acid chloride is insufficient to cause extensive premature deblocking. Should deblocking occur, any derived byproducts would be washed out prior to the next coupling step. Alternatively, 4-(aminomethyl)piperidine can be added immediately following addition of *N*-methylpiperazine. Indeed, some protected amino acid *N*-methylpiperazides are only inefficiently extracted by hydrochloric acid. Following deblocking, extraction, even by phosphate buffer, is rapid. Our current preferred practice is to dispense completely with the use of *N*-methylpiperazine, add 4-(aminomethyl)piperidine directly, and omit the hydrochloric acid extraction. Cycle times are shorter and yields are higher. Experimental details will be presented in a full paper which will also cover applications of our technique to longer peptides.

(9) A small, noninterfering amount of dibenzofulvene remains in the solution as evidenced by TLC, NMR, and UV analysis. The presence of the hydrocarbon is thought to be due to the existence of an equilibrium[10] involving its adduct with the deblocking amine.

(10) Compare: Carpino, L. A.; Mansour, E. M. E.; Knapczyk, J. *J. Org. Chem.* **1983**, *48*, 666.

protected leucine enkephalin **6** was synthesized on a 10-mmol scale within 3–4 h. Total deblocking of the protected pentapeptide by catalytic transfer hydrogenation[12-14] using palladium–carbon and ammonium formate in dioxane–methanol (1:1) gave, in an overall yield of 50–55%, leucine enkephalin **7**[15] which was isolated by filtration, evaporation of solvent, and trituration with ether to remove 9-methylfluorene. Elemental and amino acid analyses, spectral data, and comparison with an authentic sample confirmed the structure of the peptide.

As a test for racemization, a new method[17] was applied which sums the loss of optical activity throughout a complete cycle involving preparation of the Fmoc-protected amino acid (phenylalanine), conversion to its acid chloride, peptide coupling (leucine methyl ester), deblocking by means of 4-(aminomethyl)piperidine, and subsequent N-benzoylation. Overall racemization at the phenylalanine residue, obtained by measuring the ratio of D,L and L,L diastereomers of *N*-benzoylphenylalanylleucine methyl ester using HPLC on silica gel was found to be less than 0.1%.

Acknowledgment. We are indebted to the National Institutes of Health (GM-09706) for support of this work.

Registry No. FMOC-Gly-OH, 29022-11-5; FMOC-Ala-OH, 35661-39-3; FMOC-Ile-OH, 71989-23-6; FMOC-Pro-OH, 71989-31-6; FMOC-Val-OH, 68858-20-8; FMOC-Met-OH, 71989-28-1; FMOC-Cys(Bn)-OH, 53298-33-2; FMOC-Lys(Z)-OH, 86060-82-4; FMOC-Phe-OH, 35661-40-6; FMOC-D-Phe-OH, 86123-10-6; FMOC-Leu-OH, 35661-60-0; FMOC-Tyr(Bn)-OH, 71989-40-7; FMOC-Gly-Cl, 103321-49-9; FMOC-Ala-Cl, 103321-50-2; FMOC-Ile-Cl, 103321-51-3; FMOC-Pro-Cl, 103321-52-4; FMOC-Val-Cl, 103321-53-5; FMOC-Met-Cl, 103321-54-6; FMOC-Cys-(Bn)-Cl, 103321-55-7; FMOC-Lys(Z)-Cl, 103321-56-8; FMOC-Phe-Cl, 103321-57-9; FMOC-D-Cl, 103321-58-0; FMOC-Leu-Cl, 103321-59-1; FMOC-Tyr(Bn)-Cl, 103321-60-4; H-Leu-OBn, 1738-69-8; FMOC-Phe-Leu-OBn, 103321-61-5; H-Phe-Leu-OBn, 63649-15-0; FMOC-Tyr(Bn)-Gly-Gly-Phe-Leu-OBn, 88099-29-0; H-Tyr-Gly-Gly-Phe-Leu-OH, 58822-25-6.

(11) In a typical cycle, to 10 mL of a 0.1 M solution in $CHCl_3$ of the amino acid ester or the peptide ester obtained in a previous step was added 1.1 equiv of the next amino acid chloride in 5–10 mL of $CHCl_3$ along with 10 mL of 10% $NaHCO_3$. After vigorously stirring for 1–10 min, the organic phase was separated, and 0.1–0.5 mL of *N*-methylpiperazine[8] was added with brisk stirring followed by immediate extraction with 5% HCl. To the organic phase was added 3–5 mL of 4-(aminomethyl)piperidine and after 10–30 min the organic phase was extracted twice with 15-mL portions of water or saturated NaCl solution followed by two to four 15-mL portions of 10% phosphate buffer (pH 5.5) to give an organic phase ready for addition of the next amino acid. In case additional organic solvent is added to aid layer separation, the volume of the solution is reduced before continuing.

(12) Anwer, M. K.; Spatola, A. F. *Synthesis* **1980**, 929. See also: Carpino, L. A.; Tunga, A. *J. Org. Chem.* **1986**, *51*, 1930.

(13) Atherton, E.; Bury, C.; Sheppard, R. C.; Williams, B. J. *Tetrahedron Lett.*, **1979**, 3041.

(14) Martinez, J.; Tolle, J. C.; Bodanszky, M. *J. Org. Chem.* **1979**, *44*, 3596.

(15) Obtained as tiny white needles on crystallization from methanol: mp 158 °C: $[\alpha]^{25}_D$ −22.8° (*c* 0.8, DMF); lit.[12] mp 155–158 °C lit.[16] mp 206 °C dec; lit.[16] $[\alpha]^{25}_D$ −23.4° (*c* 1, DMF). Anal. Calc for $C_{28}H_{37}N_5O_7 \cdot H_2O$: C, 58.63; H, 6.85; N, 12.21. Found: C, 58.34; H, 6.89; N, 12.19. Amino acid analysis: Tyr 1.05 (1), Gly 2.06 (2), Phe 1.05 (1), Leu 1.00 (1). HPLC: Waters C_{18}-Radialpak (CH_3OH, 1 mL/min): t_R 4.80 min, ref (Chemical Dynamics): 4.81 min. Also obtained in analytically pure form were all acid chlorides in the table and the following precursors and intermediates: (a) Fmoc-Tyr(Bn)-OH, mp 164–166 °C. $[\alpha]^{25}_D$ −15.8° (*c* 1, DMF); (b) Fmoc-Phe-Leu-OBn, mp 154–155 °C $[\alpha]^{25}_D$ −24.7° (*c* 1, DMF); (c) Fmoc-Tyr(Bn)-Gly-Gly-Phe-Leu-OBn, mp 178 °C, $[\alpha]^{25}_D$ −16.9° (*c* = 0.9, DMF). The protected tripeptide [Fmoc-Gly-Phe-Leu-OBn, mp 130 °C $[\alpha]^{25}_D$ −11.5° (*c* = 1, DMF), 80% yield] and the corresponding tetrapeptide [Fmoc-Gly-Gly-Phe-Leu-OBn, mp 163–164 °C, $[\alpha]^{25}_D$ −8.2° (*c* 1, DMF) 63% yield] were also made in single repetitive sequences.

(16) Bower, J. D.; Guest, K. P.; Morgan, B. A. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2488.

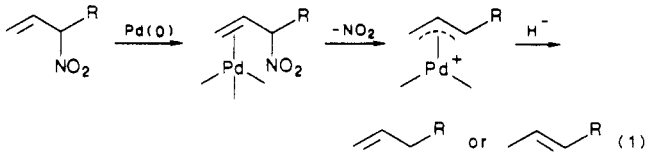
(17) For another application of the method, see: Carpino, L. A.; Rice, N. W.; Mansour, E. M. E.; Triolo, S. A. *J. Org. Chem.* **1984**, *49*, 836.

Louis A. Carpino,* Beri J. Cohen
Kenton E. Stephens, Jr., S. Yahya Sadat-Aalaee
Jien-Heh Tien, Denton C. Langridge
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01003
Received February 7, 1986

Regioselective Removal of Allylic Nitro Groups via Hydride Transfer

Summary: Allylic nitro groups are regioselectively removed by hydride-transfer reaction in the presence of a catalytic amount of a palladium catalyst.

Sir: Aliphatic nitro groups serve as activating groups for carbon–carbon bond-forming reactions and their use in organic synthesis depends upon the ease of removal of this activating group. The most important transformation is the replacement of the C–N bond with a C–H bond. In general, reduction of nitro compounds by hydride ion results in bond breaking of a N–O bond rather than a C–N bond.[1] Recently this difficulty has been overcome by radical denitration using tributylstannane and this process is becoming an important synthetic method.[2] However, it is very difficult to control the regiochemistry of denitration of allylic nitro compounds by radical method, where migration of the double bond is a serious problem. In this paper we report a regioselective method for denitration of allylic nitro compounds. The procedure relies on activation by initial complexation with Pd(0) derivatives followed by nitrite ion expulsion and subsequent hydride attack on the resulting π-allyl complex as in eq 1.[3] Various kinds of hydride ion sources appear to be effective and the process is catalytic in the palladium complex.



The results are summarized in Tables I and II. Although reductive replacement of allylic oxygen, sulfur, and selenium functional groups by hydride via catalytic activation by a palladium(0) complex is a well-known reaction,[4] the present denitration is the first example of replacement of the nitro group by hydrogen via hydride transfer. Compared to radical denitration with Bu_3SnH,[5] regiose-

(1) Smith, P. A. S. *The Chemistry of Open-Chain Nitrogen Compounds*, Vol. I and II; W. A. Benjamin Inc.; New York, 1966.

(2) Ono, N.; Miyake, H.; Tamura, R.; Kaji, A. *Tetrahedron Lett.* **1981**, *22*, 1075. Ono, N.; Miyake, H.; Kamimura, A.; Hamamoto, I.; Tamura, R.; Kaji, A. *Tetrahedron* **1985**, *41*, 4013. Ono, N.; Kamimura, A.; Miyake, H.; Hamamoto, I.; Kaji, A. *J. Org. Chem.* **1985**, *50*, 3692 and references therein.

(3) Tamura, R.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 3727. Ono, N.; Hamamoto, I.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1982**, 821.

(4) Hutchins, R. O.; Learn, K.; Fulton, R. P. *Tetrahedron Lett.* **1980**, *21*, 27. Hutchins, R. O.; Learn, K. *J. Org. Chem.* **1982**, *47*, 4382. Matsushita, H.; Negishi, E. *J. Org. Chem.* **1982**, *47*, 4161. Kotake, H.; Yamamoto, T.; Kinoshita, H. *Chem. Lett.* **1982**, 1331.

(5) Radical denitration of the nitro compound of entry 5 gives a mixture of 1-alkene and 2-alkene, whose ratio is 15:85, and this ratio is not affected by the reaction conditions.[2]

0022-3263/86/1951-3734$01.50/0