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Palladium-Catalyzed Selective Hydrogenolysis of Alkenylcyclopropanes Having Two Electron Withdrawing Groups Using Ammonium Formates

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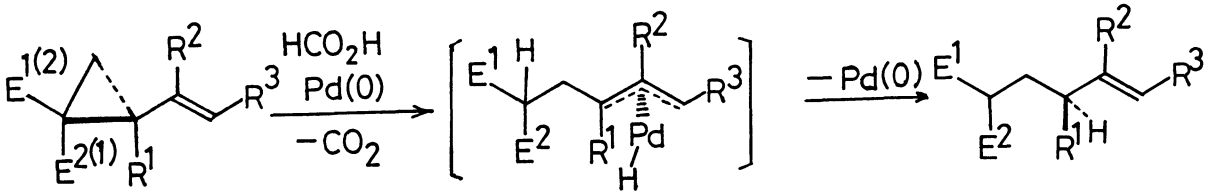
Selective hydrogenolysis of vinyl- or 2-(methoxycarbonyl)-ethenylcyclopropanes having two electron withdrawing groups was carried out using palladium-phosphine catalysts with ammonium formates. The reaction proceeded with inversion of stereochemistry.

Cyclopropanation reaction followed by ring-opening reaction is a useful synthetic method. Although a variety of stereoselective ring opening reactions of alkenylcyclopropanes are known,[1] selective hydrogenolysis is difficult.[2] Several ring opening reactions of alkenylcyclopropanes having two electron withdrawing groups with palladium-phosphine complexes to form π-allylpalladium complexes have been reported.[3] We have reported that terminal allylic compounds are easily converted to 1-olefins with ammonium formates in the presence of Pd(0)-Bu_3P catalysts via π-allylpalladium intermediate.[4] So we have expected that selective hydrogenolysis of alkenylcyclopropanes is possible with ammonium formates in presence of palladium catalysts. We wish to report here a selective hydrogenolysis of alkenylcyclopropanes with HCO_2H using palladium catalysts (Scheme 1).



1 3 2

Scheme 1.

The reactions of alkenylcyclopropanes (**1a**-**1d**) with ammonium formate in the presence of palladium catalyst are summarized in Table 1. In a typical experiment, the vinylcyclopropane **1a** (2 mmol) was added to a solution of $Pd_2(dba)_3CHCl_3$ (0.05 mmol), n-Bu_3P (0.4 mmol) and HCO_2NH_4 (4 mmol) in dry dioxane (10 cm^3), and the mixture was refluxed for 2.5 h to give the 1-olefin **2a** in 95% yield after chromatographic purification on SiO_2 using hexane-AcOEt as an eluent. No formation of 2-olefin was observed. Other vinylcyclopropanes, **1b** and **1c**, were also converted to the terminal olefins, **2b** and **2c**, in 71% and 88% yields respectively. The reaction of the α,β-unsaturated ester **1d** gave the (*E*)-α,β-unsaturated ester **2d** (IR (neat) 970 cm^{-1}) selectively in 77% yield. The observed stereoselectivity is similar fashion to that obtained from other allylic compounds reported previously.[4,5]

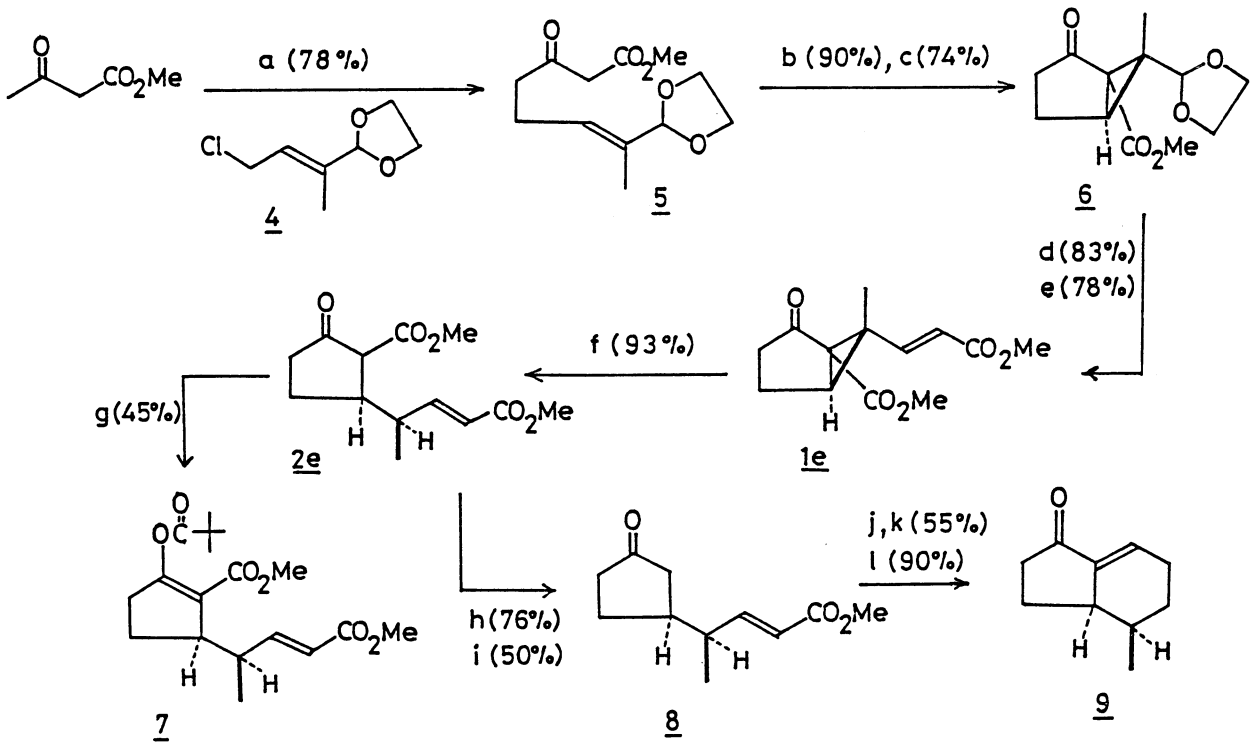
The stereochemistry of this reaction was studied using the bicyclic alkenylcyclopropane **1e** (Scheme 2). γ-Alkylation reaction of methyl acetoacetate using its dianion with (*E*)-1-chloro-4,4-ethylenedioxy-3-methyl-2-butene **4**[6] gave the β-keto ester **5**. Reaction of the β-keto ester **5** with TsN_3 followed by cyclopropanation using Cu powder in boiling toluene gave the bicyclo[3.1.0]hexanone **6**. Deacetalization of **6** was carried out using 5 mol% of $PdCl_2(CH_3CN)_2$ in acetone[7] followed by Emmons-Horner-Wittig reaction to give the bicyclic diester **1e**.[8] Hydrogenolysis of **1e** was carried out with HCO_2H-Et_3N (1:1) using 1/2 $Pd_2(dba)_3CHCl_3$-n-Bu_3P (1:1) (5 mol%) in boiling dioxane for 1 h to give the cyclopentanone **2e** in 93% yield.[9]

Table 1. Palladium-Catalyzed Hydrogenolysis of Alkenylcyclopropanes **1**[a]

Cyclopropane	Product	Yield/%[b]
1a (E^1=E^2=CO_2Me, R^1=R^2=R^3=H)	**2a**	95
1b (E^1=E^2=CO_2Me, R^1=R^3=H, R^2=CH_3)	**2b**	71
1c (E^1=CO_2Me, E^2=COMe, R^1=R^2=R^3=H)	**2c**	88
1d (E^1=E^2=R^3=CO_2Me, R^1=R^2=H)	**2d**	77

a) The reactions were carried out using 5 mol% of 1/2 $Pd_2(dba)_3CHCl_3$-n-Bu_3P (1:4) in boiling dioxane for 2.5 h. b). Isolated yield.

The cyclopentanone 2e was converted to its enol pivaloyl ester 7, whose ^{13}C NMR spectrum showed that the product was a single stereoisomer.[10] The cyclopentanonedicarboxylate 2e was converted to the indanone 9 in order to elucidate the relative stereochemistry of the methyl substituent in 2e. Hydrolysis of the esters followed by decarboxylation and subsequent esterification gave the mono ester 8. Reduction of 8 with $LiAlH_4$ in THF followed by oxidation with pyridinium chlorochromate gave the keto aldehyde, which was cyclized in an acidic condition to give the bicyclic enone 9. Protons of the methyl group of 9 appeared in δ 0.81 ppm as a doublet (J=7 Hz) (lit.[11] trans 9 δ 0.78; cis isomer δ 1.05), indicating trans stereochemistry shown as 9 in Scheme 2. Thus, the palladium-catalyzed hydrogenolysis of 1e to 2e proceeded with inversion (1→2 shown in Scheme 1). We have clarified that the hydride attacks intramolecularly from the palladium side (3→2) in the palladium catalyzed hydrogenolysis with ammonium formates.[5] Therefore, this stereochemistry indicates that cyclopropane ring opening by palladium-phosphine complexes proceeds with inversion by S_N2 manner (1→3), which is similar to the oxidative addition of Pd(0) to other allylic compounds.[12]



a: NaH, n-BuLi, THF, 4; b: TsN_3, Et_3N, CH_3CN; c: Cu, $PhCH_3$; d:$PdCl_2(CH_3CN)_2$, acetone; e: NaH, $(CH_3O)_2P(O)CH_2COOCH_3$, THF; f: $Pd_2(dba)_3CHCl_3$, n-Bu_3P, HCOOH, Et_3N, dioxane; g: $(CH_3)_3CCOCl$, Et_3N, HMPA, THF; h: 10%-KOH, $PhCH_2NEt_3Cl$, ether, then 3N-HCl reflux; i: CH_3OH, H_2SO_4; j: $LiAlH_4$, THF; k: PCC, CH_2Cl_2; l: 3N-HCl, THF.

Scheme 2.

Alkenylcyclopropanes can be obtained easily and the hydrogenolysis with HCO_2H is stereoselective. So this method is useful for synthesis of various natural products having ring and side chain chiral centers, such as steroids, pseudoguaianolides and iridoids.[13] Further synthetic application of this method is in progress.

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8) Spectral data: **1e** ^{1}H NMR (CCl_4) δ 1.10 (m, 1H), 1.30 (s, 3H), 2.10-2.80 (m, 4H), 3.70 (s, 6H), 5.70 (d, J=16 Hz, 1H), 6.60 (d, J=16 Hz, 1H). HRMS Found: 252.0970, Calcd for $C_{13}H_{16}O_5$ 252.0998. **2e** ^{1}H NMR (CCl_4) δ 1.10 (d, d=6 Hz, 3H), 2.00-3.00(m, 7H), 3.67 (s, 3H), 3.75 (s, 3H), 5.80 (d, J=16 Hz, 1H), 6.75 (dd, J=8 and 16 Hz, 1H). **7**; ^{1}H NMR ($CDCl_3$) δ 1.10 (d, J=6 Hz, 3H), 1.30 (s, 9H), 2.0-3.0 (m, 6H), 3.66 (s, 3H), 3. 67 (s, 3H), 5.65 (d, J=16 Hz, 1H), 6.80 (dd, J=16 and 8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.7 (q), 21.5 (t), 26.8 (q), 32.3(t), 37.9 (d), 38.9 (s), 47.3 (d), 50.9 (q), 51.2 (q), 119.1 (s), 121.0 (d), 150.4 (d), 160.7 (s), 163.6 (s), 166.7 (s), and 175,5 (s); IR (neat) 2950, 1750, 1715, 1695, and 1650 cm^{-1}.
9) It should be noted that the ratio of palladium and phosphine for hydrogenolysis of **2e** seems to be crucial. When excess phosphine was used, a mixture of unindentified products was obtained.
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