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PALLADIUM-CATALYZED REARRANGEMENT OF α-CYANOALLYLIC ACETATES APPLICATION TO A NEW SYNTHETIC METHOD FOR FURANS

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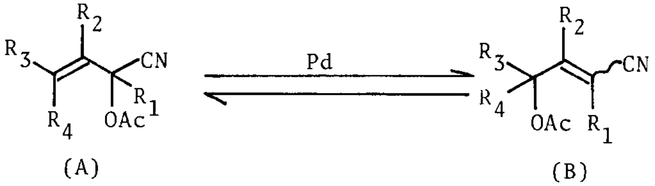
Summary: Various types of α-cyanoallylic acetates were undergone the palladium-catalyzed rearrangement to give the γ-acetoxy-α,β-unsaturated nitriles in high yields. These rearranged acetates were conveniently transformed into the furan derivatives often encountered in natural products by the reduction using diisobutylaluminum hydride.

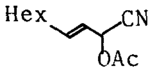
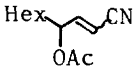
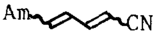
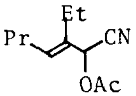
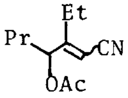
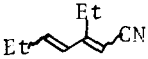
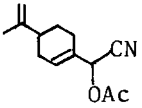
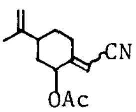
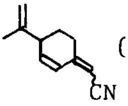
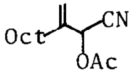
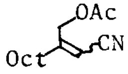
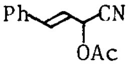
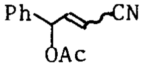
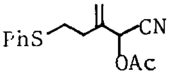
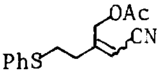
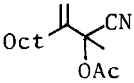
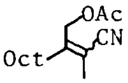
Palladium-catalyzed rearrangement of the allylic acetates is one of the useful methods for allylic oxygen interconversion due to its mild reaction conditions. An detailed investigation of this rearrangement involving a kinetic consideration has been carried out by Henry.$^{1)}$ The recent study aimed at synthetic utilities of this reaction has also been reported.$^{2)}$ We have reported that the α-cyanoallylic acetate was smoothly converted to a dienenitrile by the palladium-catalyzed reaction ($Pd(OAc)_2$-PPh_3) and the reaction was applied to a simple synthesis of pellitorine.$^{3)}$ In this communication, we wish to report that the palladium catalysts equilibrate the various α-cyanoallylic acetates (A⇌B) under mild and neutral conditions as represented by the following equation.



The method consists simply of stirring α-cyanoallylic acetates at room temperature in THF containing a catalytic amount of tetrakis(triphenylphosphine)-palladium(0) except for a case. The typical experimental procedure is exemplified by the synthesis of 4-acetoxy-4-phenyl-crotononitrile. A mixture of 2-acetoxy-4-phenyl-3-butenenitrile (2.0 g, 10 mmol), $Pd(PPh_3)_4$ (1154 mg, 1 mmol) in THF (15 ml) was stirred at room temperature for 12 hr under a nitrogen atmosphere. The product was isolated by column chromatography (silica gel) to give the rearranged acetate (1.43 g, 71%).

Some examples of the palladium-catalyzed transformation are given in Table I.

Table I Palladium-catalyzed rearrangement of α-cyanoallylic acetates.4)

Entry	Substrate	Conditions a)		Conversion (%) c) Rearranged (%) d)		Diene (%) d)	
		Time (hr)	Catalyst b)				
1		2.0	$PdCl_2(CH_3CN)_2$		(55) (50)		(0)
2	"	0.5	$Pd(PPh_3)_4$	"	(100) (55)	"	(40)
3		0.5	$Pd(PPh_3)_4$		(100) (75)		(20)
4		1.0	$Pd(PPh_3)_4$		(100) (65)		(25)
5e)		2.0	$Pd(OAc)_2$-PPh_3		(100) (90)		(0)
6	"	2.0	$Pd(PPh_3)_4$	"	(100) (91)		(0)
7		12.0	$Pd(PPh_3)_4$		(95) (71)		(0)
8		1.5	$Pd(PPh_3)_4$		(100) (83)		(0)
9		1.0	$Pd(PPh_3)_4$		(100) (93)		(0)

a: Carried out at room temperature using THF as the solvent.

b: $PdCl_2(CH_3CN)_2$; 10 mol%, $Pd(PPh_3)_4$; 10 mol%, $Pd(OAc)_2$-PPh_3; 10 mol% and 20 mol% were used, respectively.

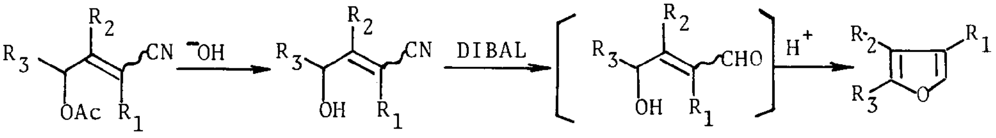
c: Determined by gas chromatography (SE-30, 3mm x 3m).

d: Isolated yields by column chromatography (silica gel).

e: Carried out in refluxing THF.

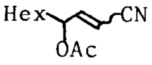
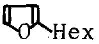
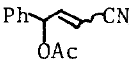
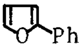
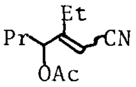
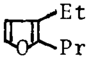
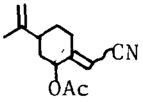
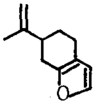
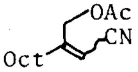
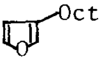
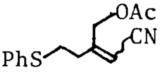
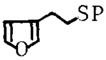
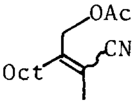
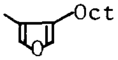
In entry 1, $PdCl_2(CH_3CN)_2$ catalyst effectively equilibrated the acetate in ca. 1:1 ratio without formation of a dienenitrile, although the elimination of HOAc was possible in this case. When this $PdCl_2(CH_3CN)_2$ catalyst was used for other substrates (entries 2-9), the starting α-cyanoallylic acetates were recovered unchanged. Although the $Pd(OAc)_2$-PPh_3 catalytic system showed no catalytic activity at room temperature, it smoothly promoted the rearrangement at reflux temperature (entry 5). Use of this catalyst for the substrates in entries 1, 3, and 4 at refluxing temperature of THF gave the dienenitriles as the sole product. $Pd(PPh_3)_4$ was a suitable catalyst for all the cases, but in entries 2, 3, and 4 the reaction proceeded with the inevitable formation of the dienenitriles. In order to get the rearranged products efficiently in these cases, it was neccessary to quench the reaction within 0.5 hr. In the cases where the elimination could not occurred (entries 6, 8, and 9), the complete rearrangements were observed within 2 hr at room temperature.

We have found that the rearranged acetates obtained by this reaction are new and good synthons of furan derivatives often present in natural products. The corresponding γ-hydroxy-α,β-unsaturated nitriles were undertaken the reduction by diisobutylaluminum hydride followed by the treatment with dilute hydrochloric acid to give the furan derivatives in satisfactory yields as shown in the following scheme.



A typical example is as follows: 3-Acetoxymethyl-2-undecenenitrile (2.37 g, 10 mmol) was hydrolyzed (1N NaOH, dioxane), and the resulting alcohol was purified by a short column chromatography (silica gel, hexane-ether 5:1). The 3-hydroxymethyl-2-undecenenitrile (1.81 g, 9.3 mmol) thus obtained was treated with diisobutylaluminum hydride (10 ml, 22.3 mmol, 2.2 mol solution of hexane) in ether at ice-salt bath temperature (-10 °C) for 1 hr. The mixture was poured into ice cold 1N HCl, and was taken up with ether. The ethereal solution was concentrated to give the oil, which was again diluted with ether and stirred with 1N HCl for 2 hr at room temperature. After the usual work-up, the product was isolated by a short column chromatography (silica gel, hexane as eluent) to give 3-octyl furan (1.34 g, 7.44 mmol, 74% based on the acetate). Some examples are shown in Table II.

Table II Transformation of the γ-acetoxy-α,β-unsaturated nitriles to furan derivatives[a)]

Entry	Substrate	Furans (%)[b)]	Entry	Substrate	Furans (%)[b)]
1		 (70)	2[c)]		 (40)
3		 (68)	4		 (61)
5		 (74)	6		 (72)
7		 (76)			

a: The γ-hydroxy-α,β-unsaturated nitriles were isolated. The direct reduction of the acetates and subsequent acid cyclization gave lower yields.

b: Isolated yields by silica gel column chromatography.

c: The corresponding hydroxy nitrile could not be obtained. So the direct reduction by DIBAL gave good result.

Application of this method to natural product synthesis will be reported shortly.

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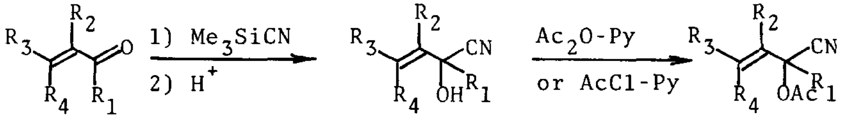
References and Note

1) P. M. Henry, J. Am. Chem. Soc., 94, 5200 (1972).
2) (a) L. E. Overman and F. M. Knoll, Tetrahedron Lett., 321 (1979).
(b) P. A. Grieco, T. Takigawa, S. L. Bongers, and H. Tanaka, J. Am. Chem. Soc., 102, 7587 (1980).
3) T. Mandai, J. Goto, J. Otera, and M. Kawada, Chem. Lett., 313 (1980).
4) The α-cyanoallylic acetates were prepared as follows:



cf. reference 3.

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