A New Preparative Method for α,β-Unsaturated Nitriles by the Palladium-catalysed Decarboxylation–Dehydrogenation of Allyl α-Cyanocarboxylates

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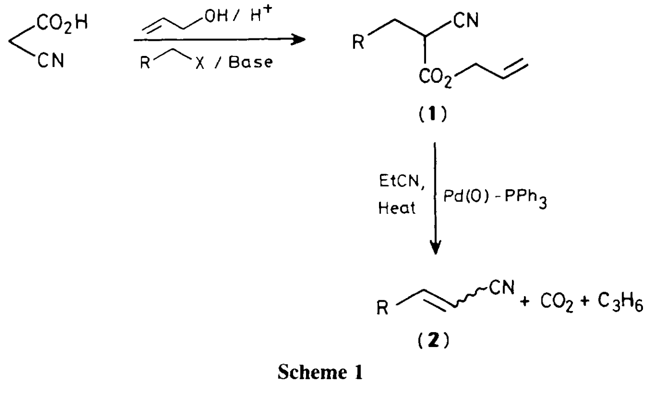
Allyl α-cyanocarboxylates, derived from cyanoacetic acid, were converted into α,β-unsaturated nitriles in the presence of a palladium catalyst.

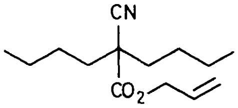
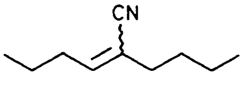
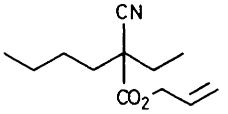
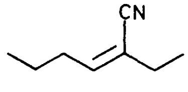
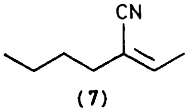
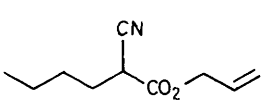
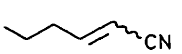
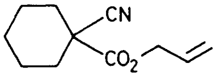
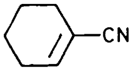
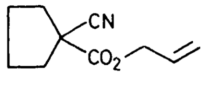
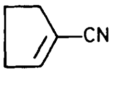
α,β-Unsaturated nitriles are important synthetic intermediates and their efficient preparative methods are highly desirable. The established method is based on the dehydration of cyanohydrins,[1] but the method requires toxic sodium cyanide. During our work on the development of new preparative methods for α,β-unsaturated compounds,[2—7] we found that allyl α-cyanocarboxylates can be converted into α,β-unsaturated nitriles by the palladium catalysed intramolecular decarboxylation–dehydrogenation. The reaction can be expressed by Scheme 1.

As shown in Table 1, various allyl α-cyanocarboxylates were converted into the corresponding α,β-unsaturated nitriles in good yields. From allyl 2-cyanohexanoate (**8**), two isomeric products were obtained in a ratio of 5:3 and separated by preparative g.l.c. Careful studies of their n.m.r. spectra revealed that the major product has the (*E*)-configuration.[8] In the reaction of dialkylated allyl cyanoacetate such as (**3**), the (*Z*)-product was obtained with nearly 90% selectivity. When the allyl α-cyanocarboxylate, substituted with two different alkyl groups such as (**5**), was subjected to the palladium catalysed reaction, two isomers (**6**) and (**7**) were obtained without regioselectivity.



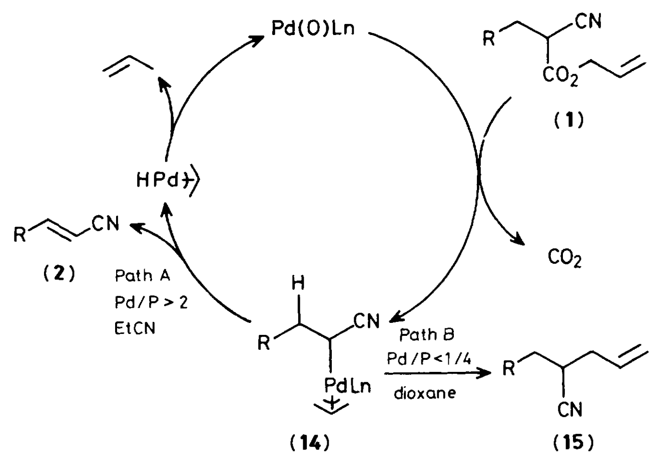
Scheme 1

Table 1. Preparation of α,β-unsaturated nitriles.

Substrate	Product	% Yield
 (3)	 (4) (Z):(E) = 8:1[b]	78[a]
 (5)	 (6)	48[b]
	 (7)	33[b]
 (8)	 (9) (E):(Z) = 5:3[b]	65[c]
 (10)	 (11)	81
 (12)	 (13)	78

[a] ^{1}H N.m.r. ($CDCl_3$) chemical shifts of vinyl proton; Z isomer 6.13 (t, J 7.5 Hz); E isomer 6.33 (t, J 7.6 Hz). [b] Calculated by g.l.c. analysis. [c] ^{1}H N.m.r. ($CDCl_3$) chemical shifts of vinyl protons; E isomer 5.32 (dt, J 16.3 and 1.5 Hz), 6.72 (dt, J 16.3 and 6.9 Hz); Z isomer 5.30 (dt, J 10.8 and 1.1 Hz), 6.46 (dt, J 10.8 and 7.6 Hz), ref. 3.

Generally, the reaction was carried out in the following way; a solution of allyl α-cyanocarboxylate (1 mmol), PPh_3 (0.05 mmol), and $Pd_2(dba)_3{\cdot}CHCl_3$ (0.1 mmol, dba = dibenzylidene acetone) in propionitrile (5 ml, dried over P_2O_5) was refluxed for 1—3 h under argon. After the reaction was complete (g.l.c. analysis), the resultant mixture was filtered through Florisil. Pure α,β-unsaturated nitrile was isolated by column chromatography on silica gel or preparative g.l.c. In this reaction, use of dry solvent is essential. Otherwise, saturated nitriles were sometimes obtained by the protonation of the intermediate (**14**). As we have reported previously, the phosphine-free palladium catalyst is effective for the dehydrogenation reaction.[2] However, the phosphine ligand has a stabilizing effect on the Pd(0) species, and addition of a small amount of phosphine ligand sometimes enhances turnover and reactivity of the catalyst. In the present reaction, we found that addition of PPh_3 is effective (Pd/P > 2). It should be pointed out that the molar ratio of palladium to phosphine ligand is crucial.[2] When the reaction was carried out in the presence of an excess of phosphine ligand (Pd/P < 1/4), the decarboxylation–allylation to give γ,δ-unsaturated nitrile (**15**) takes place predominantly (dioxane, 100 °C, 60—80%. Path B in Scheme 2).[9]



Scheme 2

Similar to the reaction of allyl β-ketocarboxylates[3,9,10] and alkenyl allylcarbonates,[4] the reaction can be explained by the following mechanism. Oxidative addition of allyl α-cyanocarboxylates (**1**) to the Pd(0) complex, followed by decarboxylation affords (α-cyanoalkyl)(π-allyl)palladium complex (**14**). Then elimination of the β-hydrogen (Path A) gives α,β-unsaturated nitriles (**2**) and propene, and regenerates the Pd(0) catalyst. Contrary to our expectation that allyl esters having electron withdrawing groups at the α-position such as allyl malonates or allyl α-nitrocarboxylates should undergo decarboxylation–dehydrogenation, corresponding α,β-unsaturated compounds were obtained in low yields (0—20%) under similar conditions.

In conclusion, the present reaction offers a facile preparative method for α,β-unsaturated nitriles from allyl α-cyanocarboxylates.†

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† Allyl α-cyanocarboxylates were prepared from methyl cyanoacetate by alkylation with corresponding alkyl bromides (K_2CO_3, reflux in acetone), followed by transesterification with allyl alcohol (reflux in allyl alcohol with a catalytic amount of toluene-*p*-sulphonic acid).