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ALLYL ETHYL CARBONATE / PALLADIUM (0), A NEW SYSTEM FOR THE ONE STEP CONVERSION OF ALCOHOLS INTO ALLYL ETHERS UNDER NEUTRAL CONDITIONS

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Abstract : Alcohols are converted in a one-step procedure into allyl ethers under neutral conditions, using allyl ethyl carbonate in the presence of a catalytic amount of palladium (0). Anomeric hydroxyls are selectively allylated in the presence of other hydroxyl groups.

Allyl groups have been found to be of general use as temporary hydroxyl-protecting groups in sugar chemistry [1-3]. The successful application of the allyl group in carbohydrate chemistry is mainly due to its relative stability during glycosidation or deblocking procedures which lead to the removal of other protecting groups.

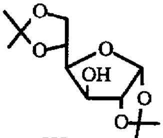
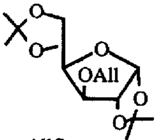
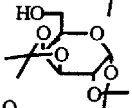
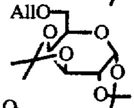
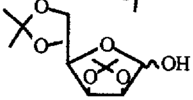
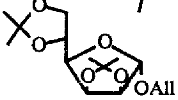
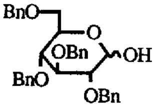
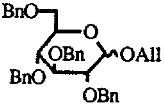
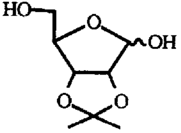
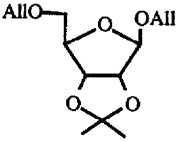
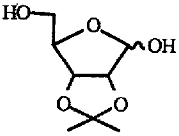
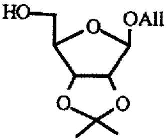
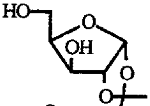
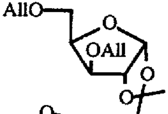
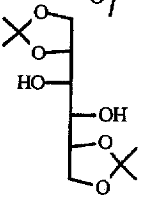
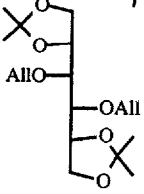
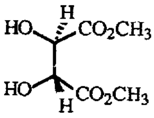
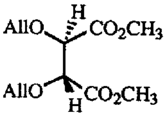
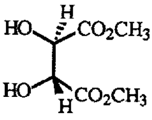
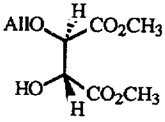
An allyl ether can be synthesised by treatment of a free hydroxyl group with 3-halopropene in the presence of base [1]. Compounds containing base labile groups can be allylated using allyltrichloro-acetamidate [4]. Allylation of alcohols or polyols is also feasible starting from intermediate trialkyltin oxides or dialkylstannylidenes [5]; in the latter case, specific monoalkylation of carbohydrates has been observed [6,7]. More recently, a neutral two-step allylation procedure was introduced by Guibé [8] and developed by Tsuji [9] in which an allylcarbonate obtained from an alcohol was subjected to palladium(0) catalyzed decarboxylation to afford an allyl ether derivative.This procedure has also been applied in carbohydrate chemistry [10,11].

During our programme directed towards the application of organometallic reagents in carbohydrate chemistry, we found that a neutral one-step allylation procedure involving alcohols and especially carbohydrates was possible, using allyl ethyl carbonate **1** as the allylating reagent in the presence of a catalytic amount of palladium (0) (eq. 1).

$$\text{R-OH} \xrightarrow[\text{Pd (0) / THF / 65° C}]{\text{CH}_2\text{=CH-CH}_2\text{OCO}_2\text{Et } \mathbf{1}} \text{R-O-CH}_2\text{CH=CH}_2 \qquad \text{(eq. 1)}$$

As can be seen from Table I, allyl ethers are formed in consistently high yields using this procedure.

Table I. Synthesis of allyl ethers using allyl ethyl carbonate **1** in the presence of Pd (0) [a].

Entry	Substrate		[**1**]/[substrate]	Product		Yield % [b]
1		**2**	2		**3**	74
2		**4**	3		**5**	92
3		**6**	2		**7**	94 [c]
4		**8**	2		**9**	94 [d]
5		**10**	6		**11**	84 [e]
6		**10**	1.2		**12**	70 [e]
7		**13**	6		**14**	95
8		**15**	4		**16**	97
9		**17**	4		**18**	75
10		**17**	1.1		**19**	50

[a] General Procedure :
Under argon, to a stirred solution of $Pd_2(dba)_3$ [12] (0.025 mmoles) and dppb [12] (0.1mmole) in 2 ml of dry THF was added the alcohol (1 mmole) and the allyl ethyl carbonate **1** in 2 ml of dry THF. After stirring the solution at 65 °C for 4 h, the solvent was evaporated and the crude product chromatographed on silica gel to give the pure O-allylated compound.

[b] All yields refer to chromatographically purified product.All compounds gave appropriate ^1H and ^{13}C NMR, IR and combustion analysis data. Bn = benzyl ; All = allyl.

[c] Only the α anomer is observed.

[d] As a mixture of α and β anomers (40:60).

[e] Only the β anomer is observed.

A secondary alcohol like **2** is very easily converted into an allyl ether using two equivalents of allyl ethyl carbonate **1** (entry 1). For achieving high yields in derivatising primary alcohols like in compound **4**, 3 equ. of **1** are needed (entry 2).

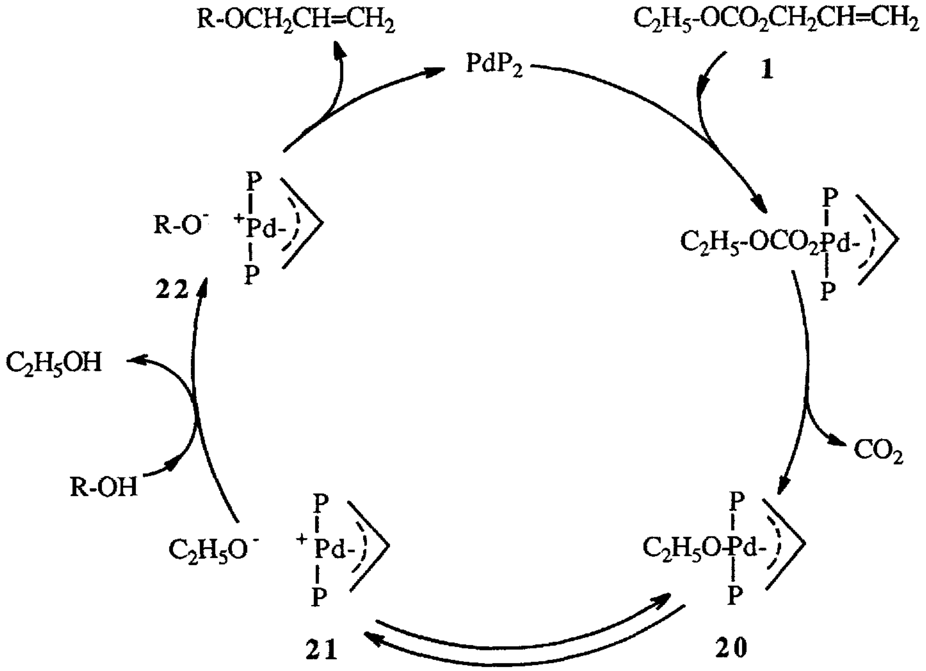
Anomeric hydroxyls reacted quantitatively giving,for the mannofuranose derivative **6** only the α anomer **7** (entry 3), and for the glucofuranose derivative **8**, the allyl ether **9** as a mixture of α and β anomers (40:60) (entry 4). The configurations at the anomeric center of the products were assigned, respectively, by comparison with results obtained by Schmidt [13] in the case of the mannose derivative **7** and, alternatively, by ^{13}C NMR spectra (observation of the γ gauche effect) for the glucose derivative **9**.

Dihydroxyl compounds are also converted to allyl ethers and give the corresponding bis derivatives (entries 5, 7-9). It is interesting to compare the yield and the ease of the preparation of the bis-allylated mannitol **16** with the preceding synthesis of this compound [14]. There is also some discrimination between a primary and an anomeric hydroxyl; the use of only 1.2 equ. of allyl ethyl carbonate **1** allowed the formation of only the mono allylated sugar **12** with a chemical yield of 70%; this is due probably to the more acidic nature of the anomeric hydroxyl.

Functionalised compounds like the hydroxy ester **17** are also easily allylated under our conditions (entry 9). Here again, using only one equ. of allyl ethyl carbonate gives the mono allylated compound **19** with 50% yield, and no trace of the bis-allylated substrate **18** (entry 10).

As suggested by Scheme 1, the reaction proceeds by the following mechanism. Oxidative addition of allyl ethyl carbonate **1** to Pd(0) species, followed by decarboxylation gives the (π-allyl)-palladium ethylate complex **20**, which is in equilibrium with the cationic one **21**. Subsequent exchange of the ethoxide with the alkoxide gives the new cationic alkoxide complex **22** and the allylation reaction then takes place.

In conclusion, a very simple one-step procedure for the allylation of alcohols under neutral conditions has been discovered, and although most of the examples shown are taken from the carbohydrate series, we have no doubt that it could be extended to a greater variety of functionalised alcohols.



Scheme 1

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