Pergamon

Tetrahedron, Vol. 53, No. 51, pp. 17501-17512, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)10198-3

A Study of $Pd(II)Cl_2$/CuCl catalysed Wacker reaction for the deprotection of Prop-2-enyl and Prop-1-enyl Ethers

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Abstract: $Pd(II)Cl_2$ (1 mole equivalent)/CuCl/DMF-H_2O/O_2/2h catalysed oxidation of various prop-2-enyl ethers **1a-12a** is reported to result in the formation of Wacker ketones **1b,3b,5b,6b,9b,11b,12b** (12-51%), hydrolysis products **2c,4c-7c,9c-12c** (12-43%) and η^2-vinyl complexes of palladium chloride **2d,4d,7d,8d** (52-94%) respectively. The corresponding prop-1-enyl ethers **2e,4e-12e** under similar conditions react with a catalytic amount of $Pd(II)Cl_2$ (0.2 mole equivalent) rapidly (15-20 min.) to give exclusively hydroxy compounds **2c,4c-12c** respectively in good yields (75-97%). © 1997 Elsevier Science Ltd.

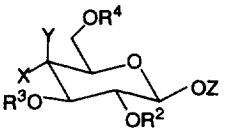
Oxidation of alkenes by use of $Pd(II)Cl_2$ was first reported more than 100 years ago by Philips in 1894[1]. Modern palladium chemistry developed very rapidly after an ingenious Wacker process has been invented in 1958 for the industrial production of acetaldehyde from ethylene using $Pd(II)Cl_2$ and CuCl as catalysts[1,2]. Vibrant research in the application of Wacker reaction is evident from recent developments such as use of formamide microemulsions[3], polymer supported catalysts[4] and electrochemical methods[5]. Many useful reactions have been discovered specially in the application of this unique reaction of palladium to organic synthesis and mechanism of Wacker reaction has also been well studied[6]. Utility of Wacker reaction to oxygen functionalised terminal olefin substrates has been reported to result in the formation of ketones and or aldehydes without any regioselectivity[7]. Exclusive non-Markonikov addition of $Pd(II)Cl_2$ has been directed and the resultant aldehyde intramolecularly trapped by a hydroxyl group to obtain *bis*-furanoside chirons[8]. Application of this finding has also been utilized by us as a key step in the total synthesis of 5(S)-goniofufurone[9]. $Pd(II)Cl_2$ and Pd(O) catalysed chemistry has also been used for the deprotection of acyclic, cyclic and aromatic prop-1-enyl ethers mainly due to its utility as a protecting group in organic synthesis. Thus, prop-2-enyl ethers have earlier been deprotected in a two step reaction sequence involving first isomerisation to prop-1-enyl ether by use

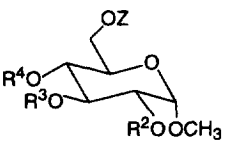
of either a base (KO^tBu)[10] or under neutral conditions with $(Ph_3P)_3RhCl$[11] or $[Ir(COD)(PMePh_2)_2]$-PF_6[12] followed by acidic hydrolysis with 0.1N HCl at 60°C or $HgCl_2$-HgO-H_2O[13] or I_2-H_2O[14]. Prop-2-enyl ethers have also been deprotected under acidic conditions in a single step by use Pd-C-MeOH-TsOH or $ClSO_3H$ at reflux[15], SeO_2-HOAc at reflux[16], $PdCl_2$-NaOAc-HOAc at 60°C[17], $Pd(Ph_3P)_4$-HOAc at 60°C[18], $SmCl_3$[19], $AlCl_3$-N,N-dimethylaniline-$SnCl_4$[20] and NBS-CCl_4-NaOH[21]. Zirconacene[22], a two step photo chemical method[23] and $Pd(NH_3)_2Cl_2$[24] have also been reported for the deprotection. Reaction of aromatic prop-2-enyl ethers with $PdCl_2$ has largely been described in patented literature[25] to result in intramolecular migration (Claisen rearrangement) of propenyl group and use of $PdCl_2(PhCN)_2$[26] affects isomerisation to yield prop-1-enyl aromatic ethers under non-hydrolytic conditions. Deprotection of phenyl prop-2-enyl ether by $Pd(Ph_3P)_4$[27] in THF at 25°C has also been reported. Contrary to the deprotection, formation of prop-1-enyl ethers of saccharide derivatives by reaction of saccharide alcohol and allyl carbonate by use of Pd(O) has also been reported[28]. We were the first group to report the deprotection of prop-1-enyl ethers under Wacker conditions[29].

Due to the increased use of prop-2-enyl protecting group specially in oligosaccharide chemistry[30] we decided to undertake a detailed study to understand the Wacker reaction for de-O-allylation of diverse substrates such as aliphatic, cyclic functionalised and aromatic prop-2-enyl and their corresponding prop-1-enyl ethers, to find conditions to retain the acid sensitive protecting groups and interglycosidic linkages intact.

Reaction of allyl ether **1a**[31] with $PdCl_2$(0.2 mole equivalent) under Wacker reaction conditions [N,N-dimethylformamide(DMF)-H_2O-CuCl-O_2] resulted in the isolation of the expected keto compound **1b** in good yield exclusively (Table 1) and was characterised from ^{1}H-NMR spectrum, the corresponding benzyl ether derivative **2a**[32] under similar reaction conditions however resulted in the formation of **2c**[33] and **2d** along with the recovery of **2a**. Use of mole equivalent of $PdCl_2$ instead, resulted in the complete conversion of **2a** to obtain an inseparable mixture of **2c** and **2d** (see experimental). Change of solvent to acetone-water (10:1)[34] to obtain more of **2c** was not possible. A quick chromatography of the reaction mixture gave reasonably pure **2d**[35] (68%) which was characterised from ^{1}H-NMR as η^2-vinyl palladium complex from the upfield shift of vinylic protons (3H) to δ 4.30-4.7 (merged), there was no change in the chemical shift of 1'-H (2H) protons. Such stable η^2-vinyl palladium complexes have been earlier prepared for allyl ethers[36]. Reactivity of the acetyl substituted allyl derivative **3a**[37] with catalytic amount of $PdCl_2$ (0.2 mole equivalent) was identical to **1a** resulting in the formation of keto compound **3b** in 81% yield. Analogous to **2a**; **4a**[38,39] also resulted in the formation of **4c**[32] and **4d**.Thus, anomeric allyl glycopyranosides having electron withdrawing substituents **1a** and **3a** favoured the formation of Wacker ketones **1b** and **3b** respectively, whereas the electron rich benzyl ether substituted pyranosides **2a** and **4a** did not indicate any definite pathway for the reaction, except that major products **2d** and **4d** respectively were η^2-vinyl palladium complexes. Differences in the reactivity of electron rich and deficient pyrano- and furanosides possessing a leaving group at the anomeric center has earlier been observed in saccharide chemistry and termed as 'Armed-Disarmed' effect by Fraser-Reid[40], that was found for

anomeric substituted n-pentenyl[40], phenylthio[41], and pyridyl-2-thioglycosides[42] and now for allyl glycosides. When other than anomeric substituted prop-2-enyl ether such as **5a** was reacted it gave the keto and the hydrolysis products **5b** and **5c**[43].





1 $R^2 = R^3 = R^4 = Ac$, X = OAc, Y = H **a)** $Z = CH_2\text{-}CH{=}CH_2$

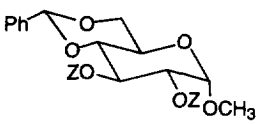
2 $R^2 = R^3 = R^4 = Bn$, X = OBn, Y = H **b)** $Z = CH_2COCH_3$

3 $R^2 = R^3 = R^4 = Ac$, X = H, Y = OAc **c)** Z = H

4 $R^2 = R^3 = R^4 = Bn$, X = H, Y = OBn **d)** Z = Pd-Π^2 vinyl complex

e) Z = (Z) CH=CHCH$_3$

5 $R^2 = R^3 = R^4 = Bn$



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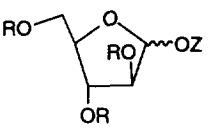
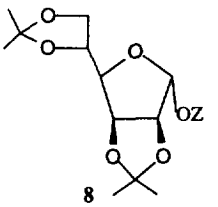


7 $R^2 = R^3 = R^4 = Bn$



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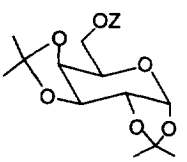

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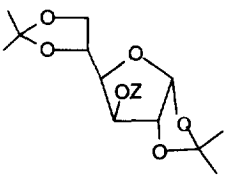

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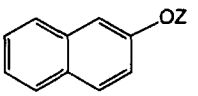

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Applicability of this reaction was next attempted on sterically hindered prop-2-enyl ethers, thus **6a** gave inseparable mixture of Wacker ketone **6b** (24% by ^1H NMR) and hydroxy product **6c**[44] (46% by ^1H NMR). Benzyl ether substituted furanoside derivative **7a** exhibited reactivity analogous to **2a** and **4a** resulting in the formation of **7c**[45] and η^2-vinyl palladium complex **7d**. In order to check the course of Wacker reaction on glycoside substrates without aromatic substituents, isopropylidene derivative **8a**[28,46] was reacted to obtain exclusively the η^2-vinyl palladium complex **8d** in 94% yield. Due to the formation of stable π-complexes these reactants **2a**,**4a**,**7a** and **8a** consumed mole equivalent of $PdCl_2$. 6-O-Allyl isopropylidene derivative **9a**[24] in a similar reaction analogous to **5a** gave **9b** and **9c**[47]. However, 3-O-prop-2-enyl substituted 'diacetone glucose' **10a**[28b] gave 39% of ketone **10b** along with hydroxy compound **10c**[48] in 66% yield. Thus, it was rather difficult to generalise the product formation. We decided to look at the reactivity of aromatic prop-2-enyl ether **11a**[49] and aliphatic prop-2-enyl ether **12a** also. **11a** gave the ketone **11b** and hydrolysis product **11c** in almost equal ratio, formation of isomerised products was not observed in all these reactions. **12a** analogous to

11a gave **12b** and **12c** in equal ratio. Hence, we concluded that de-O-allylation by Wacker reaction conditions does not lead to any single product for utility in organic synthesis except for **1a** and **3a**, where Wacker ketones **1b** and **3b** are obtained.

Table 1 : Palladium chloride/CuCl/O_2 catalysed deprotection of prop-2-enyl **1a-12a** and prop-1-enyl ethers **2e,4e-12e**

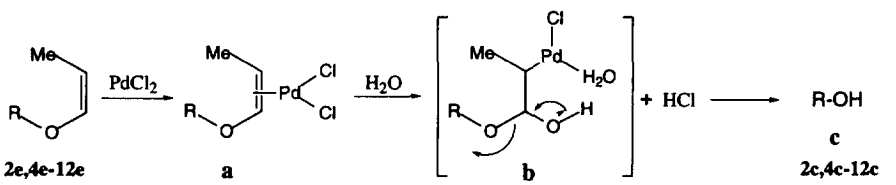
Substrate	% yield of isolated products		
	Wacker ketone **b**	hydrolysis products **c**	π^2-Pd complexes **d**
1a	82	-	-
2a (2e)	-	15 (85)	68
3a	81	-	-
4a (4e)	-	12 (86)	52
5a (5e)	30	32 (75)	-
6a (6e)	24[+]	46[+] (75)	-
7a (7e)	-	26 (76)	42
8a (8e)	-	- (90)	94
9a (9e)	42	35 (97)	-
10a (10e)	-	66 (81)	-
11a (11e)	51	43 (89)	-
12a (12e)	52	45 (90)	-

[*]2a,4a-12a were reacted with 1 mole equivalent of $PdCl_2$ and CuCl and 1a, 3a,2e,4e-12e with 0.2 mole equivalent

[+]inseparable mixture

We continued with our studies on the Wacker reaction of the corresponding prop-1-enyl ethers **2e**, **4e-12e** (Table 1). **2a**, **4a-12a** were isomerised with KO^{t}Bu in dry dimethylsulfoxide at 140°C to obatin their corresponding prop-1-enyl ethers **2e**, **4e-12e** respectively. Reaction of **2e**, **4e-12e** with catalytic amount of

$PdCl_2$ (0.2 mole equivalent) in DMF-H_2O (10:1), CuCl (0.2 mole equivalent) with bubbling of oxygen rapidly (10-15 min.) reacted to give exclusively the desired hydroxy compounds **2c**, **4c-12c** respectively in good yields (75-95%) that were fully characterisedby comparison of physical data with that of authentic samples. Hydrolysis of prop-1-enyl ethers can be explained (Scheme 1) based on completely regioselective hydroxypalladation of electron rich enol ether **a** with $PdCl_2$ to form the intermediate **b** which being a hemiacetal spontaneously breaks down to give the alcohol **c**. This mechanism is consistent with the formation of hydroxy products **2c,4c** and **8c** from **2e, 4e and 8e** where stereochemistry at the anomeric center is retained due to cleavage of the enol ether carbon. Acid sensitive protecting groups such as benzylidene and acetals remained unaffected indicating the mildness of the reaction.



Scheme 1

In conclusion, de-O-allylation by use of $PdCl_2$ under Wacker reaction conditions leads to the formation of all possible products, formation of the products could not be predicted except in case of anomeric glycopyranosides with electron withdrawing substituents where exclusive Wacker ketones have been obtained. Whereas the corresponding benzyl ether and isopropylidene substituted substrates gave mostly η^2-vinyl palladium complexes. However, a similar reaction of enol ethers with catalytic amount of $PdCl_2$ gave hydroxy compounds, resulting in the finding of a new, mild method of deprotection that adds to the arsenal of deprotecting allyl ethers via enol ethers.

Acknowledgement : SRL thanks Council of Scientific Industrial Research, New Delhi for the financial assistance in the form of a Junior Research Fellowship.

Experimental

^{1}H-NMR spectra were measured with a Varian Gemini (200 MHz) spectrometer, with tetramethylsilane as internal standard for solutions in deuteriochloroform. ^{13}C-NMR spectra were taken with a Varian Gemini (50 MHz) spectrometer with $CDCl_3$ as internal standard (δ_c 77.0) for solutions in deuteriochloroform. Optical rotations were measured with a JASCO DIP-370 instrument and $[\alpha]_D$ values are in units of 10^{-1} deg cm^2 g^{-1}. IR spectra were taken with a Perkin-Elmer 1310 spectrometer. Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40°C in vacuuo. Melting points were determined on a Fischer-John's melting point apparatus and are uncorrected. Chemical ionization mass spectra were taken on a VG 70-70H mass spectrometer using acetone as the CI reagent. LSIMS spectra were ran on a Micromass AUTOSPEC-M unit using Cs^+ ions as the primary beam for bombardment.

Preparation of O-allyl ethers 5a-12a : To a solution of hydroxy compounds **5c-12c** (1 mmol) in dry N,N-dimethylformamide (DMF) (1-2 ml) at 0°C was added hexane washed NaH (1.2 mmol) and stirred for 15 min. Allyl bromide (1.1 mmol) was added dropwise to the above reaction mixture and contents were brought to room temperature and stirred for 1-2 h until t.l.c. (hexane-ethyl acetate, 5:1) indicated completion of the reaction from the formation of a faster moving spot. Reaction was quenched by addition of methanol (0.5 ml), diluted with chilled water (350 ml), extracted into diethyl ether, dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator to obtain the O-allyl ethers **5a-12a** in 75-80% yield. They have been purified by filtering on a bed of SiO_2 by eluting with [hexane-ethyl acetate] (4:1).

Preparation of enol ethers 2e,4e-12e : To a solution of O-allyl ethers **2a,4a-12a**)(1 mmol) in dry DMSO (2 ml) was added KO^{t}Bu (0.5 mmol) and heated to 140°C in an oil bath for 2-3 h until t.l.c. (hexane-ethyl acetate, 10:1) indicated completion of the reaction from the appearence of a slightly faster moving spot. Reaction mixture was cooled to room temperature, diluted with water (250 ml), extracted into diethyl ether, dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator to obtain **2e,4e-12e** in 80-90% yields and were filtered on a small bed of SiO_2 by eluting with [hexane-ethyl acetate] (10:1) for further reactions.

A typical experimental procedure for the reaction of O-allyl ethers 1a-12a with $PdCl_2$, CuCl in DMF, water and oxygen : To a homogenous solution of O-allyl ethers **1a-12a** (0.5 mmol) in DMF-H_2O (10:1) (2 ml) was added $PdCl_2$ (0.5 mmol), CuCl (0.5 mmol) and oxygen was bubbled for about 1 to 2 h until t.l.c. indicated complete disappearence of the substrates. Reaction mixture was diluted with water (200 ml), extracted into diethyl ether (200 ml). Organic phase was separated and washed with water, dried (Na_2SO_4) and concentrated to obtain the keto compounds **1b,3b,5b,6b,9b,11b,12b**, hydroxy compounds **2c,4c,5c-7c,9c-12c** and palladium complexes **2d,4d,7d,8d** that were separated by column chromatography (SiO_2, hexane-ethyl acetate, 8:1) for characterisation,whereever possible.

A typical experimental procedure for the $PdCl_2$ catalysed deprotection of enol ethers 2e,4e-12e : To a homogenous solution of enol ethers **2e,4e-12e** (1 mmol) in DMF-H_2O (10:1) (2 ml) was added catalytic amount of $PdCl_2$ (0.2 mmol) and CuCl (0.2 mmol) and oxygen was bubbled at room temperature for about 15-20 min. When t.l.c. indicated (hexane-ethyl acetate, 4:1) disappearence of the substrate and appearence of slower moving spot, the reaction mixture was diluted with water (250 ml). Organic phase was separated, washed with water (200 ml), dried (Na_2SO_4) and concentrated to obtain the hydroxy compounds **2c,4c-12c** in good yields (75-97%) and were fully characterised by comparison of physical data with that of the authentic samples.

General procedure for obtaining 2,3,4,6-Tetra-O-benzyl-α/β-D-gluco-(2c), -α/β-D-galacto-pyranoside (4c) and 2,3,5-tri-O-benzyl-α/β-D-arabinofuranoside (7c).- Reaction of **2e,4e** and **7e** (0.28 g, 0.5 mmol) severally with $PdCl_2$ (22 mg, 0.1 mmol) and CuCl (5.5 mg, 0.1 mmol) in DMF-H_2O (10:1) (1 ml) while bubbling oxygen gave after usual work up **2c,4c** and **7c** respectively in good yield (75-85%) as a syrup containing more of β-anomer for **2c** and **4c** (α/β ratio 1:4 by ^{1}H-NMR). Since **7e** was itself a mixture of α/β it gave **7c** also in the same ratio of 1:2. On standing and depending upon the time taken for work up **2c** and **4c** gradually equilibrated to more stable α-anomers. **2c** and **4c** had comparable ^{1}H-NMR and t.l.c. with that of authentic samples.

General procedure for obtaining η^2-$PdCl_2$ complexes 2d,4d,7d and 8d.- Reaction of **2a,4a,7a** and **8a** (0.5 mmol) severally with $PdCl_2$ (0.5 mmol), CuCl (0.5 mmol) in DMF-H_2O (10:1) (2 ml) at room temperature for 30 min. resulted in the formation of **2c** and **2d**, **4c** and **4d**, **7c** and **7d** as inseparable mixture

and **8d** respectively in 42-98% yields. **2d,4d,7d** and **8d** had the same rf value on t.l.c. as their corresponding hydroxy glycosides **2c,4c,7c** and **8c** respectively. Since they do not acetylate on reaction with Ac_2O/Py they were ruled out as hydroxy compounds. Formation of η2-$PdCl_2$ complexes was evident from the upfield shift of vinylic protons of **2a,4a,7a** and **8a** from δ 5.0-5.9 (3 H) to δ 4.1-4.7 (3 H) in **2d,4d,7d** and **8d**, other protons remained nearly unchanged. These products on standing and chromatography did not yield any homogenous material for characterisation. Presence of palladium in these substrates was confirmed by colour test with 1% dimethyl glyoxime, which gave orange-yellow colour precipitate of palladium dimethyl glyoximate.

2-Oxopropyl 2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside (1b).- Reaction of **1a**[31] (0.1 g, 0.24 mmol) with $PdCl_2$ (0.04 g, 0.24 mmol) and CuCl (0.02 g, 0.24 mmol) while bubbling oxygen gave **1b** (0.08 g) in 82% yield as a syrup, $[\alpha]_D$ -25.0° (c 1.0, $CHCl_3$) ; IR (neat) : 1710 and 1717 cm^{-1} ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.03, 2.05, 2.09 x 2, 2.18 (15 H, 5s, OCOCH_3), 3.6 - 3.75 (1 H, m, 5'-H), 4.0 - 4.4 (4 H, m, 6',1-H), 4.57 (1 H, d, $J_{1,2}$ 8.7 Hz, 1'-H), 4.95-5.35 (3 H, m, 2'-4'-H); Anal. calcd. for $C_{17}H_{24}O_7$: C, 62.95; H, 7.46. Found : C, 62.85; H, 7.39%.

Prop-1-(*Z*)-enyl 2',3',4',6'-tetra-O-benzyl-β-D-glucopyranoside (2e).- Reaction of **2a**[32] (0.5 g, 0.98 mmol) with K^{t}BuO (0.05 g, 0.48 mmol) in dry DMSO (4 ml) gave **2e** (0.41 g) in 82% yield as a syrup, $[\alpha]_D$ 17.5° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.65 (3 H, dd, J 1.65 Hz, J 7.2 Hz, CH_3), 3.85-3.5 (2 H, m, 6'-H), 4.1-3.9 (1 H, m, 5'-H), 5.05-4.35 (13 H, m, Ph CH_2 x 4, 1'-4'-H, 2-H), 6.04 (1 H, d, J 5.0 Hz, 9.5 Hz, 1-H), 7.05-7.5 (20 H, m, Ar-H); Anal. calcd. for $C_{37}H_{40}O_6$: C, 76.52; H, 6.94. Found : C, 76.49; H, 6.82%.

Prop-2-enyl 2',3',4',6'-tetra-O-acetyl-β-D-galactopyranoside (3a).- Reaction of β-D-galactose pentaacetate (3.9 g, 10 mmol) in dry dichloromethane (20 ml) at 0°C was added allyl alcohol (0.7 ml, 10.7 mmol), BF_3-etherate (6.4 ml, 15 mmol) and stirred at room temperature 4 h. Reaction mixture was quenched with anhydrous K_2CO_3 (0.5 g) and filtered to remove the insoluble salts. Organic phase was diluted with CH_2Cl_2 (200 ml) washed with water (2x100 ml), dried over Na_2SO_4 and concentrated to yield a thick syrup which contained anomeric mixture of **3a** (1:4). It was separated by column chromatography (SiO_2, 60-120 mesh), (hexane-ethyl acetate, 8:1) to obtain analytically pure **3a** (1.62 g) in 50% yield as a syrup, $[\alpha]_D$-11.2° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.0, 2.08 x 2, 2.18 (12 H, 3s, OCOCH_3), 3.89 (1 H, m, 5'-H), 4.0-4.32 (4 H, m, 1,6'-H), 4.52 (1 H, d, $J_{1',2'}$ 7.5 Hz, 1'-H), 5.0 (1 H, dd, $J_{2',3'}$ 10.0 Hz, $J_{3',4'}$ 3.0 Hz, 3'-H), 5.05-5.4 (4 H, m, 2',4',3-H), 5.75-6.0 (1 H, m, 2-H); Anal. calcd. for $C_{17}H_{24}O_6$ · C, 62.95; H, 7.46. Found : C, 62.83; H, 7.41%.

2-Oxopropyl 2',3',4',6'-tetra-O-acetyl-β-D-galactopyranoside (3b).- Reaction of **3a**[37] (0.1 g, 0.24 mmol) with $PdCl_2$ (8 mg, 0.04 mmol) and CuCl (4 mg, 0.04 mmol) while bubbling oxygen gave **3b** (0.08 g), in 82% yield as a syrup, $[\alpha]_D$ 4.0° (c 1.0, $CHCl_3$) ; IR (neat) : 1710 cm^{-1} ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.03, 2.06, 2.09, 2.11, 2.2 (15 H, 5s, 4 x OCOCH_3, COCH_3), 3.68 (1 H, m, 5'-H), 4.0- 4.35 (4 H, m, 1,6'-H), 4.67 (1 H, d, $J_{1',2'}$ 8.0 Hz, 1'-H), 4.95-5.3 (3 H, m, 2'-4'-H); Anal. calcd. for $C_{17}H_{24}O_7$: C, 62.95; H, 7.46. Found : C, 62.81; H, 7.39%.

Prop-1-(*Z*)-enyl-2',3',4',6'-tetra-O-benzyl-β-D-galactopyranoside(4e).- Reaction of **4a**[38] (0.5 g, 0.98 mmol) with K^{t}BuO (0.05 g, 0.48 mmol) in dry DMSO (4 ml) gave **4e** (0.4 g) in 81% yield as a syrup, $[\alpha]_D$ 3.2° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.65 (3 H, dd, J 5.5 Hz, J 1.0 Hz, CH_3), 3.4-3.6 (2 H, m, 6'-H), 3.8 - 3.95 (1 H, m, 5'-H), 4.30 - 5.0 (13 H, m, PhCH_2 x 4, 1'-4',1-H), 6.18 (1 H, dd,

J 7.5 Hz, 2-H), 7.1-7.45 (20 H, m, Ar-H); Anal. calcd. for $C_{37}H_{40}O_6$: C, 76.52; H, 6.94. Found : C, 76.39; H, 6.81%.

Methyl 2,3,4-tri-O-benzyl-6-O-(prop-2'-enyl)-α-D-glucopyranoside (5a).- Reaction of **5c**[43] (0.1 g, 0.21 mmol) with allyl bromide (0.03 g, 0.2 mmol) and NaH (0.01 g, 0.2 mmol) gave **5a** (0.11 g) in 97% yield as a syrup, $[\alpha]_D$ 19.9° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 3.39 (3 H, s, OCH_3), 3.5-4.15 (8 H, m, OCH_2, 2-6-H), 4.55-5.4 (9 H, m, 3 x OCH_2Ph, $=CH_2$, 1-H), 5.8-6.0 (1 H, m, vinylic), 7.2-7.45 (15 H, m, Ar-H); Anal. calcd. for $C_{31}H_{36}O_6$: C, 73.78; H, 7.19. Found : C, 73.69; H, 7.09%.

Methyl 2,3,4-tri-O-benzyl-6-O-(2'-oxopropyl)-α-D-glucopyranoside (5b).- Reaction of **5a** (0.1 g, 0.2 mmol) with $PdCl_2$ (0.04 g, 0.24 mmol) and CuCl (0.02 g, 0.24 mmol) with oxygen bubbling gave **5b** (0.03 g), in 30% yield as a syrup, $[\alpha]_D$ 3.6° (c 1.0, $CHCl_3$) ; IR (neat) : 1717 cm^{-1} ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.12 (3 H, s, CH_3CO), 3.39 (3 H, s, OCH_3), 3.4 - 4.1 (8 H, m, OCH_2CO, 2-6-H), 4.5-5.05 (7H, m, 3 x OCH_2Ph, 1-H), 7.2-7.5 (15 H, m, Ar-H); Anal. calcd. for $C_{31}H_{36}O_7$: C, 71.43; H, 6.88. Found : C, 71.33; H, 6.79% and **5c**[43] (0.028 g), in 32% yield.

Methyl 2,3,4-tri-O-benzyl-6-O-[prop-1'-(Z)-enyl]-α-D-glucopyranoside (5e).-
Reaction of **5a** (0.1 g, 0.2 mmol) with K^{t}BuO (0.01 g, 0.1 mmol) in dry DMSO (1 ml) gave **5e** (0.09 g) in 90% yield as a syrup, $[\alpha]_D$ 2.8° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.6 (3 H, dd, J 6.6 Hz, J 2.1 Hz, $=CHCH_3$), 3.39 (3 H, s, OCH_3), 3.45-4.05 (5 H, m, 2-4,6-H), 4.35-4.45 (1 H, m, 5-H), 4.5-5.0 (8 H, m, $=CH$ CH_3, 3 x OCH_2Ph, 1-H), 5.95 (1 H, dd, J 6.7 Hz, J 2.1 Hz, 1'-H), 7.2-7.5 (15 H, m, Ar-H); Anal. calcd. for $C_{31}H_{36}O_6$: C, 73.78; H, 7.19. Found : C, 73.67; H, 7.10%.

Methyl 2,3-Di-O-[prop-1'-(*E/Z*)-enyl]-4,6-O-benzylidene-α-D-glucopyranoside (6e).- Reaction of **6a**[24] (0.5 g, 1.6 mmol) with K^{t}BuO (0.18 g, 1.6 mmol) in dry DMSO (4 ml) gave **6e** (0.48 g) in 96% yield as a syrup, $[\alpha]_D$ 56.2° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.45-1.65 (6 H, m, 2 x=$CHCH_3$), 3.43 (3 H, s, OCH_3), 3.5-4.5 (8 H, m, 2-6-H, 2 x 2'-H), 4.78 (1 H, d, $J_{1,2}$ 4.0 Hz, 1-H), 5.51 (1 H, s, $PhCHO_2$), 6.04, 6.15 (2 H, 2 x dd, J 5.4 Hz, J 1.0 Hz, 1'-H), 7.29-7.5 (5 H, m, Ar-H); Anal. calcd. for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found : C, 66.18; H, 7.17%.

Prop-2-enyl-2',3',5'-tri-O-benzyl-α/β-D-arabinofuranoside (7a).- Reaction of **7c** (0.4 g, 0.95 mmol) with allyl bromide (0.15 g, 1.14 mmol) and NaH (0.04 g, 1.90 mmol) gave **7a** (0.35 g) in 79% yield as a syrup, $[\alpha]_D$ -21.5° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 3.5-3.7 (2 H, m, 5'-H), 3.85-4.3 (5 H, m, 2'-4'-H, 1-H), 4.4-4.65 (6 H, m, 3 x OCH_2Ph), 5.1 (1 H, s, 1'-H), 5.12-5.4 (2 H, m, 3-H), 5.8-6.1 (1 H, m, 2-H), 7.29-7.45 (15 H, m, Ar-H); Anal. calcd. for $C_{29}H_{32}O_5$: C, 75.63; H, 7.00. Found : C, 75.59; H, 6.91%.

2,3,5-Tri-O-benzyl-α/β-D-arabinofuranoside (7c).-Acidic hydrolysis of allyl 2,3,4-tri-O-benzyl-α/β-D-arabinofuranoside gave **7c** as a syrup, $[\alpha]_D$ 3.4° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 3.1 (1 H, br s, OH), 3.4-3.6 (2 H, m, 5-H), 3.85-4.2 (3 H, m, 2-4-H), 4.35-4.7 (6 H, m, 3 x OCH_2Ph), 5.2-5.4 (1 H, m, 1-H α/β), 7.29-7.4 (15 H, m, Ar-H); Anal. calcd. for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71. Found : C, 74.19; H, 6.61%.

Prop-1-enyl-(*E/Z*)-2',3',5'-tri-O-benzyl-α/β-D-arabinofuranoside(7e).- Reaction of **7a** (0.5 g, 1.08 mmol) with K^{t}BuO (0.06 g, 0.54 mmol) in dry DMSO (4 ml) gave **7e** (0.45 g) in 90% yield as a syrup,

$[\alpha]_D$ -25° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.58 (3 H, dd, J 6.0 Hz, J 1.0 Hz, =CHCH_3), 3.45-3.65 (2 H, m, 5'-H), 3.85-4.3 (3 H, m, 2'-4'-H), 4.35 - 4.7 (7 H, m, 3 x OCH_2Ph, 2-H), 5.17 (1 H, s, 1'-H), 6.09 (1 H, dd, J 6.0 Hz, J 1.0 Hz, 1-H), 7.29-7.4 (15 H, m, Ar-H); Anal. calcd. for $C_{29}H_{32}O_5$: C, 75.63; H, 7.00. Found : C, 75.57; H, 6.89%.

2,3:5,6-Di-O-isopropylidene-1-O-(prop-2'-enyl)-α-D-mannofuranoside (8a).- Reaction of **8c**[46] (0.5 g, 1.92 mmol) with allyl bromide (0.3 g, 2.3 mmol) and NaH (0.09 g, 3.84 mmol) gave **8a** (0.48 g) in 86% yield as a syrup, $[\alpha]_D$ 54.0° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz $CDCl_3$): δ 1.60, 1.70, 1.79, 1.82 (12 H, 4s, 2 x $O_2C[CH_3]_2$), 4.18-4.43 (5 H, m, OCH_2, 4,6-H), 4.63-4.78 (1 H, m, 5-H), 4.92 (1 H, d, $J_{2,3}$ 5.5 Hz, 2-H), 5.08 (1 H, dd, $J_{3,4}$ 3.6 Hz, 3-H), 5.32 (1 H, d, J $_{2',3'cis}$ 11.2 Hz, 3'-H), 5.61 (1 H, d, $J_{2',3'\ trans}$ 17.1 Hz, 3'-H), 6.2 (1 H, ddd, $J_{1',2'}$ 5.85 Hz, 2'-H); Anal. calcd. for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05. Found : C, 59.84; H, 7.93%.

2,3:5,6-Di-O-isopropylidene-1-O-[prop-1'-(*Z*)-enyl]-α-D-manofuranoside (8e).- Reaction of **8a** (0.2 g, 0.66 mmol) with K^{t}BuO (0.05 g, 0.33 mmol) in dry DMSO (2 ml) gave **8e** (0.14 g) in 70% yield as a syrup, $[\alpha]_D$ 11° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.32, 1.39, 1.45, 1.48 (12 H, 4s, 2 x $O_2C[CH_3]_2$), 1.55 (3 H, dd, J 6.4 Hz, J 1.2 Hz, =CHCH_3), 3.85-4.0 (2 H, m, 6-H), 4.08 (1 H, t, $J_{3,4} = J_{4,5}$ 6.8 Hz, 4-H), 4.3-4.4 (1 H, m, 5-H), 4.55 (1 H, dq, $J_{1',2'} = J_{2',3'}$ 6.4 Hz, 2'-H), 4.7 (1 H, d, $J_{2,3}$ 7.2 Hz, 2-H), 4.8 (1 H, dd, 3-H), 5.12 (1 H, s, 1-H), 6.07 (1 H, dd, 1'-H); Anal. calcd. for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05. Found : C, 59.91; H, 7.94%.

1,2:3,4-Di-O-isopropylidene-6-O-(2'-oxopropyl)-α-D-galactopyranoside (9b).- Reaction of **9a**[24] (0.2 g, 0.63 mmol) with $PdCl_2$ (0.13 g, 0.75 mmol) and CuCl (0.07 g, 0.75 mmol) while bubbling oxygen gave **9b** (0.05 g), in 42% yield as a syrup, $[\alpha]_D$ -62.0° (c 1.0, $CHCl_3$) ; IR (neat) : 1647 cm^{-1} ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.31 x 2, 1.4, 1.52 (12 H, 3s, 2 x $O_2C[CH_3]_2$), 2.15 (3 H, s, COCH_3), 3.55 (1 H, dd, $J_{6,6}$ 17.8 Hz, $J_{5,6}$ 6.7 Hz, 6-H), 3.69 (1 H, dd, $J_{5,6}$ 4.9 Hz, 6-H), 3.9-3.98 (1 H, m, 5-H), 4.05 (2 H, 2d, J $_{gem}$ 10.0 Hz, 1'-H), 4.1-4.3 (2 H, m, 2-4-H), 4.54 (1 H, dd, $J_{2,3}$ 8.1 Hz, $J_{3,4}$ 2.0 Hz, 3-H), 5.47 (1 H, d, $J_{1,2}$ 4.9 Hz, 1-H); Anal. calcd. for $C_{15}H_{24}O_7$: C, 56.95; H, 7.65. Found : C, 56.88; H, 7.59% and **9c**[47] (0.057 g) in 35% yield.

1,2:3,4-Di-O-isopropylidene-6-O-[prop-1'-(*Z*)-enyl]-α-D-galactopyranoside (9e).- Reaction of **9a**[24] (0.25 g, 0.79 mmol) with K^{t}BuO (0.04 g, 0.39 mmol) in dry DMSO (3 ml) gave **9e** (0.17 g) in 77% yield as a syrup, $[\alpha]_D$ 9.0° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.38 x 2, 1.4, 1.49 (12 H, 3s, 2 x $O_2C[CH_3]_2$), 1.55 (3 H, dd, $J_{1',3'}$ 1.0 Hz, $J_{2',3'}$ 5.0 Hz, =CHCH_3), 3.6-4.4 (6 H, m, 2-6-,2'-H), 4.55 (1 H, dd, $J_{2,3}$ 6.75 Hz, $J_{3,4}$ 4.0 Hz, 3-H), 5.45 (1 H, d, J 5.5 Hz, 1-H), 5.9 (1 H, dd, J $_{1',2'}$ 5.0 Hz, 1'-H); Anal. calcd. for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05. Found : C, 59.89; H, 7.94%.

1,2:5,6-Di-O-isopropylidene-3-O-[prop-1'-(*Z*)-enyl]-α-D-glucofuranoside (10e).- Reaction of **10a**[28b] (0.4 g, 1.32 mmol) with K^{t}BuO (0.74 g, 0.66 mmol) in dry DMSO (4 ml) gave **10e** (0.35 g) in 79% yield as a syrup, $[\alpha]_D$ -8.0° (c 1.0, $CHCl_3$) ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.29, 1.32, 1.4, 1.47 (12 H, 4s, 2 x $O_2C[CH_3]_2$), 1.55 (3 H, dd, $J_{2',3'}$ 6.7 Hz, J $_{1',3'}$ 1.8 Hz, =CHCH_3), 3.9-4.6 (7 H, m, 2-6-H,2'-H), 5.88 (1 H, d, $J_{1,2}$ 3.6 Hz, 1-H), 6.01 (1 H, dd, $J_{1',2'}$ 5.6 Hz, 1'-H); Anal. calcd. for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05. Found : C, 59.85; H, 7.97%.

2'-Naphthyl prop-2-enyl ether (11a).- To a solution of **11c** (4 g, 0.02 moles) in acetone (15 ml) was

added K_2CO_3 (11.49 g, 0.08 moles) and allyl bromide (3.12 ml, 0.03 moles). Reaction mixture was stirred at room temperature for 3 h until a faster moving spot appeared in TLC (hexane-ethyl acetate 10:1). The reaction mixture was filtered to remove K_2CO_3 and salts, washed with acetone (25 ml) and concentrated to obtain a syrup which was purified by column chromatography (SiO_2, hexane-ethyl acetate 15:1) to obtain **11a** as a syrup (5.0 g) in 98% yield. ^{1}H-NMR (200 MHz, $CDCl_3$): δ 4.65 (2 H, d, $J_{1,2}$ 5.0 Hz, 1-H), 5.35 (1 H, dd, $J_{2,3}$ 10.0 Hz, $J_{3,3}$ 1.0 Hz, 3-H), 5.5 (1 H, dd, $J_{2,3\ trans}$ 17.0 Hz, 3-H), 6.1 (1 H, ddt, 2-H), 7.1-7.9 (7 H, m, Ar-H); M+ 184, Anal. calcd. for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found : C, 84.67; H, 6.48%.

3-(2'-Naphthyloxy)-2-oxopropane (11b).- Reaction of **11a** (0.2 g, 1.08 mmol) with $PdCl_2$ (0.2 g, 1.08 mmol) and CuCl (0.1 g, 1.08 mmol)while bubbling oxygen gave **11b** (0.1 g), in 51% yield as a syrup, IR (neat) : 1731 cm^{-1} ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 2.35 (3 H, s, CH_3), 4.63 (2 H, s, 1-H), 7.0-7.9 (7 H, m, Ar-H); M+ 200; Anal. calcd. for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found : C, 77.89; H, 5.98% and 11c (0.067 g) in 43% yield that was comparable with the authentic sample of β-napthol.

2'-Naphthyl prop-1-(*E/Z*)-enyl ether (11e).- Reaction of **11a** (1 g, 5.4 mmol) with K^{t}BuO (0.3 g, 2.7 mmol) in dry DMSO (10 ml) gave **11e** (0.94 g) in 94% yield as a syrup, ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.7-1.9 (3 H, m, CH_3), 4.85-5.05 (1 H, m, 2-H), 5.3-5.6 (1 H, m, 1-H), 6.45-6.6 (1 H, m, 3'-H), 7.1-7.9 (6 H, m, 1',4'-8'-H); M+ 184; Anal. calcd. for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found : C, 84.67; H, 6.48%.

1'-*n*-Dodecenyl prop-2-enyl ether (12a).- Reaction of **12c** (0.5 g, 3.1 mmol) with allyl bromide (0.54 g, 4.0 mmol) and NaH (0.15 g, 6.24 mmol) in DMF gave **12a** (0.51 g) in 83% yield as a syrup, ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.9 (3 H, t, J 5.5 Hz, CH_3), 1.2-1.7 (20 H, m, 2'-11'-H), 3.4 (2 H, t, $J_{1',2'}$ 5.5 Hz, 1'-H), 3.95 (2 H, dd, $J_{1,2}$ 5.45 Hz, $J_{1,3}$ 2.25 Hz, 1-H), 5.17 (1 H, dd, $J_{2,3cis}$ 11.2 Hz, $J_{3,3}$ 2.2 Hz, 3-H), 5.25 (1 H, dd, $J_{2,3\ trans}$ 18.0 Hz, 3-H), 5.8-6.0 (1 H, ddt, 2-H); Anal. calcd. for $C_{15}H_{30}O$: C, 79.5; H, 13.36. Found : C, 78.6; H, 13.27%.

1'-*n*-Dodecenyl 2-oxo-propyl ether (12b).- Reaction of **12a** (0.2 g, 1.08 mmol) with $PdCl_2$ (0.19 g, 1.08 mmol) and CuCl (0.1 g, 1.08 mmol) while bubbling oxygen gave **12b** (0.104 g), in 52% yield as a syrup, IR (neat) : 1710 cm^{-1} ; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.9 (3 H, t, J 5.5 Hz, CH_3), 1.15-1.7 (20 H, m, 2'-11'-H), 2.15 (3 H, s, $COCH_3$), 3.48 (2 H, t, $J_{1',2'}$ 5.5 Hz, 1'-H), 3.95 (2 H, s, 1-H); M+ 242; Anal. calcd. for $C_{15}H_{30}O_2$: C, 74.32; H, 12.48. Found : C, 74.27; H, 12.41% and 12c(0.09g) in 45% yield and was comparable to the authentic sample of n-dodecanol.

1'-*n*-Dodecenyl prop-1-(Z)-enyl ether (12e).- Reaction of **12a** (0.3 g, 1.86 mmol) with K^{t}BuO (0.1 g, 0.9 mmol) in dry DMSO (5 ml) gave **12e** (0.25 g) in 86% yield as a syrup, ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.8 (3 H, t, J 5.5 Hz, CH_3), 1.0-1.40 (20 H, m, 2'-11'-H), 1.45-1.6 (3 H, m, =CHCH_3), 3.57 (2 H, t, J 5.9 Hz, 1'-H), 4.2 (1 H, dq, J 6.3 Hz, J 1.6 Hz, 2-H), 5.78 (1 H, dq, $J_{1,3}$ 1.8 Hz, $J_{1,2}$ 6.3 Hz, 1-H); M+ 226; Anal. calcd. for $C_{15}H_{30}O$: C, 79.57; H, 13.36. Found : C, 79.49; H, 13.29%.

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(*Received in UK* 2 *September* 1997; *revised* 14 *October* 1997; *accepted* 16 *October* 1997)