SHORT PAPER

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Palladium(0)-catalysed cyclisation of functionalised allenyl ethers with hypervalent iodonium salts†

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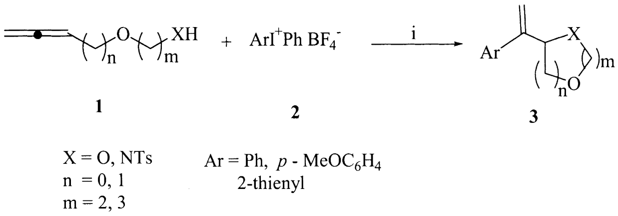
The palladium(0)-catalysed coupling and cyclisation of allenyl alcohols and allenyl amines with hypervalent iodonium salts afforded cyclised heterocyclic acetals and morpholines under mild conditions.

Keywords: palladium-catalysed cyclisation, allenyl ethers, hypervalent iodonium salts

Recently, palladium-catalysed cyclisations have received much attention as a method for the preparation of oxygen- and nitrogen-containing heterocycles. Walkup *et al.*[1] have reported that γ-hydroxyallenes or 4,5–hexadienoic acid reacted with arylpalladium halides generated from palladium(0) and aryl halides to form cyclised tetrahydrofurans and butyrolactones. Gallagher,[2] Hiemstra,[3] and Ibuka[4] also showed that γ-allenic amines undergo heteroatom cyclisation with aryl halides in the presence of palladium(0) to give the substituted pyrrolidinones or azacyclobutanes. We have reported[5,6] palladium(0) –catalysed cyclisations of allenyl amines, allenyl alcohols, allenyl carboxylic acid, and allenyl *N*–tosylcarbamates with hypervalent iodonium salts to form oxygen– and nitrogen containing heterocycles. In our effort to extend this type of cyclisation, we have investigated palladium(0)–catalysed cyclisations of allenyl alcohols and amines to form cyclised heterocyclic acetals and morpholine derivatives (Scheme 1).



Scheme 1 Reagents and conditions: i. $Pd(PPH_3)_4$(5 mol%), K_2CO_3(2.5 equiv), CH_3CN, 60°C, 2h

The results of the palladium(0)-catalysed cyclisation of allenyl alcohol and amine derivatives are shown in Table 1. The allenyl alcohol **1a**[7] reacted with diphenyliodonium tetrafluoroborate(**2a**) in the presence of $Pd(PPh_3)_4$ (5 mol %) and K_2CO_3(2 equiv) in CH_3CN at 60°C for 2 h to afford the cyclised acetal **3a** in 79% yield (entry 1 in Table 1). Of the bases tested, (K_2CO_3, Na_2CO_3, and $KHCO_3$), K_2CO_3 was the best choice. Under the same conditions treatment, the 2-thienylphenyliodonium salt **2b** gave with **1a** the 2-thienyl-substituted acetal **3b** in 63% yield as a major product along with **3a** (18%), which is easily separable by column chromatography (entry 2).

For the *p*-methoxyphenyl(phenyl)iodonium tetrafluoroborate(**2c**) the coupled and cyclised compound **3c** was produced (entry 3). When allenyl alcohol **1b** was employed as substrate with **2a**, the six membered acetal **3d** was obtained in 54% yield (entry 4). Similarly, compound **1b** was readily coupled with **2b** to furnish the 2-thienyl-substituted acetal **3e** in 59% yield with **3d** as a minor and separable compound (entry 5). However, the coupling of **1b** with **2c** provided the coupled and cyclised product **3f** as a sole product in 61% yield (entry 6). This cyclisation was applied to the allenyl amine **1c**. The compound **1c** was readily coupled with **2a** to give the substituted morpholine **3g** in 74% yield (entry 8). Finally, the reaction of allenyl amine **1c** with **2c** afforded the coupled morpholine **3h** as a sole product in 73% yield (entry 9).

In summary, palladium(0)-catalysed coupling and cyclisation of allenyl alcohols and allenyl amines with hypervalent iodonium salts to afford heterocyclic acetals and morpholines was accomplished under mild conditions.

Experimental

Typical procedure: Preparation of 2-(1-phenylvinyl)[1,3]dioxolane (**3a**). To a stirred solution of the allenyl ether **1a** (100 mg, 1.00 mmol) in acetonitrile(10 ml) was added tetrakis(triphenylphosphine)palladium(0) (57.7 mg, 5 mol %) with potassium carbonate(345 mg, 2.50 mmol) followed by diphenyliodonium tetrafluoroborate (**2a**) (441 mg, 1.20 mmol) at 60°C. The reaction mixture was stirred for 2 h and quenched with saturated NH_4Cl solution (5 ml) and then extracted with ether (3 × 30 ml). The organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (EA/hexanes = 1 : 4, $R_f = 0.71$) to give 2-(1-phenylvinyl)[1,3]dioxolane (**3a**) (98.5 mg, 79%); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.48–7.31 (m, 5H), 5.67 (s, 1H), 5.60 (s,1H), 5.52 (d, 1H, *J* = 1.5Hz), 4.01 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 65.2, 104.2, 116.6, 127.3, 127.9, 128.4, 138.1, 145.0; MS (EI): *m*/*e* (relative intensity) = 176 (M^+), 103 (18), 77 (23), 73 (100, base peak), 51 (11), 45 (21);.HRMS cald. for $C_{11}H_{12}O_2$: 176.0837 found: 176.0840.

2-(1-Thiophen-2-yl-vinyl)-[1,3]dioxolane (**3b**): TLC, SiO_2, EtOAc/hexanes 1 : 4, $R_f = 0.69$. ^1H NMR ($CDCl_3$, 500MHz) δ 7.22 (m, 2H), 7.00 (dd, 1H, *J* = 3.5, 11Hz), 5.64 (d, 1H, *J* = 1Hz), 5.61 (d, 1H, *J* = 0.5Hz), 5.47 (s, 1H), 4.07 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 65.3, 103.9, 115.0, 127.3, 138.7, 140.0; MS (EI): *m*/*e* (relative intensity) = 183 (M^+), 181(19), 108(26), 73(100), 65(11), 45(24); HRMS cald. for $C_9H_{10}O_2S$: 196.0558 found: 196.0559.

2-[1-(4-Methoxy-phenyl)-vinyl]-[1,3]dioxolane (**3c**): TLC, SiO_2, EtOAc/hexanes 1 : 4, $R_f = 0.59$. ^1H NMR ($CDCl_3$, 500MHz) δ 7.44 (dd, 2H, *J* = 2.5, 6.7Hz), 6.87 (dd, 2H, *J* = 2.5, 9Hz), 5.64 (d, 1H, *J* = 0.5Hz), 5.51 (t, 1H, *J* = 1Hz), 5.46 (d, 1H, *J* = 1Hz), 4.02 (m, 4H), 3.801 (d, 3H, *J* = 1Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 55.3, 65.2, 104.2, 113.9, 115.1, 128.4, 130.5, 144.2, 159.4 MS (EI): *m*/*e* (relative intensity) = 207(M^+), 90(11), 89(14), 77(18), 73(100), 63(12), 45(39); HRMS cald. for $C_{12}H_{14}O_3$: 206.0943 found: 206.0936.

2-(1-Phenyl-vinyl)-[1,3]-dioxane (**3d**): TLC, SiO_2, EtOAc/hexanes 1 : 4, $R_f = 0.59$. ^1H NMR ($CDCl_3$, 500MHz) δ 7.50 (m, 2H), 7.30 (m, 3H), 5.60 (t, 1H, *J* = 1Hz), 5.52 (d, 1H, *J* = 1.5Hz), 5.33 (s, 1H), 4.23 (m, 2H), 3.90 (m, 2H), 2.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 67.5, 101.9, 116.0, 127.0, 127.8, 128.2, 138.2, 145.6 MS (EI): *m*/*e* (relative intensity) = 190(M^+), 104(16), 103(37), 87(100), 77(26), 59(11); HRMS cald. for $C_{12}H_{14}O_2$: 190.0994 found: 190.0973.

2-(1-Thiophen-2-yl-vinyl)-[1,3]dioxane (**3e**): TLC, SiO_2, EtOAc/hexanes 1 : 4, $R_f = 0.59$. ^1H NMR ($CDCl_3$, 500MHz) δ 7.51 (m, 2H), 7.31 (m, 1H), 5.61 (s, 1H), 5.52 (s, 1H), 5.33 (s, 1H), 4.25 (m, 2H), 3.92 (m, 2H), 2.22 (m, 1H), 1.40 (m, 1H) ^{13}C NMR ($CDCl_3$, 125 MHz): δ 67.4, 101.7, 114.0, 125.0, 125.2, 127.2, 139.3, 140.5;

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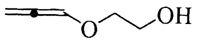
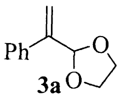
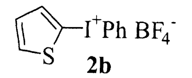
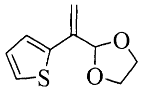
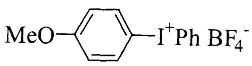
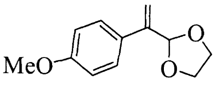
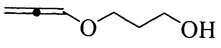
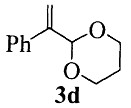
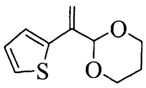
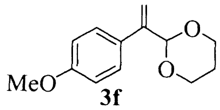
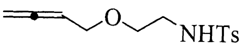
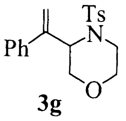
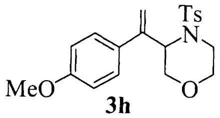
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Palladium(0)-catalysed cyclisation of allenyloxy ethers with hypervalent iodonium salts[a]

Entry	Substrate	Iodonium salt	Product	Isolated yield/%
1	 **1a**	$Ph_2I^+ BF_4^-$ **2a**	 **3a**	79
2	**1a**	 **2b**	 **3b** + **3a**(18)	63
3	**1a**	 **2c**	 **3c** + **3a**(11)	61
4	 **1b**	**2a**	 **3d**	54
5	**1b**	**2b**	 **3e** + **3d**(13)	59
6	**1b**	**2c**	 **3f**	61
7	 **1c**	**2a**	 **3g**	74
8	**1c**	**2c**	 **3h**	73

[a]All the reactions were performed in CH_3CN at 60°C in the presence of $Pd(Ph_3P)_4$ (5 mol %) and K_2CO_3(2.5 equiv) for 2 h.

MS (EI): *m/e* (relative intensity) = 196 (M^+), 103(19), 87(100), 77(14), 59(13); HRMS cald. for $C_{10}H_{12}O_2S$: 182.0402 found: 182.0403.

2-[1-(4-Methoxy-phenyl)-vinyl]-[1,3]dioxane (**3f**): TLC, SiO_2, EtOAc/hexanes 1 : 4, R_f = 0.39. ^{1}H NMR ($CDCl_3$, 500MHz) δ 7.40 (m, 2H), 6.80 (m, 2H), 5.50 (d, 1H, *J* = 1.5Hz), 5.45 (d, 1H, *J* = 1.5Hz), 5.30 (s, 1H), 4.20 (m, 2H), 3.90 (m, 2H), 3.80 (m, 3H), 2.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 25.9, 55.3, 67.5, 102.3, 113.7, 114.6, 128.2, 145.0, 159.4; MS (EI): *m/e* (relative intensity) = 221(M^+), 219(26), 132(30), 87(100), 59(11); HRMS cald. for $C_{13}H_{16}O_3$: 206.0943 found: 206.0936.

3-(1-Phenyl-vinyl)-4-(toluene-4-sulfonyl)-morpholine (**3g**): TLC, SiO_2, EtOAc/hexanes 1 : 4, R_f = 0.53. ^{1}H NMR ($CDCl_3$, 500MHz) δ 7.48 (t, 2H, *J* = 1.5Hz), 7.30–7.20 (m, 7H), 5.37 (f, 2H), 4.96 (d, 1H, 3Hz), 4.00 (d, 1H, *J* = 12Hz), 3.75 (m, 1H), 3.62 (m, 1H), 3.49 (m, 1H), 3.41 (m, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.7, 41.4, 55.3, 66.5, 68.2, 117.7, 127.4, 127.5, 127.9, 128.7, 129.8, 137.5, 140.7, 143.6, 145.3 MS (EI): *m/e* (relative intensity) = 345(M^+), 130(10), 128(16), 115(24), 102(32), 91(100), 84(14), 77(24), 65(21), 63(18), 54(13), 51(24); HRMS cald. for $C_{19}H_{21}NO_3S$: 343.1242 found: 343.1243.

3-[1-(4-Methoxy-phenyl)-vinyl]-4-(toluene-4-sulfonyl)-morpholine (**3h**): TLC, SiO_2, EtOAc/hexanes 1 : 4, R_f = 0.48. ^{1}H NMR ($CDCl_3$, 500MHz) δ 7.50 (d, 2H, *J* = 8Hz), 7.20 (m, 2H), 7.18 (d, 2H, *J* = 8Hz), 6.80 (m, 2H), 5.30 (d, 2H, *J* = 2Hz), 4.91 (d, 1H, *J* = 2.5Hz), 3.99 (d, 1H, *J* = 2Hz), 3.75 (m, 1H), 3.64 (m, 1H), 3.51 (m, 1H), 3.40 (m, 2H), 2.39 (s, 3H) ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.5, 29.7, 41.3, 55.2, 66.3, 68.0, 113.7, 116.5, 126.2, 128.3, 129.5, 132.8, 137.4, 143.3, 144.49; MS (EI): *m/e* (relative intensity) = 377(M^+), 239(12), 217(13), 176(23), 155(13), 144(13), 139(11), 117(18), 115(12), 102(12), 91(100), 84(23), 77(15), 65(19), 63(26), 54(11), 51(15); HRMS cald. for $C_{20}H_{23}NO_4S$: 373.1348 found: 373.1347.

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References

1 (a) R.D. Walkup, L. Guan, M.D. Moser, S.W. Kim, and Y.S. Kim, *Synlett*, 1993, 88; (b) R.D. Walkup, L. Guan, Y.S. Kim, and S.W. Kim, *Tetrahedron Lett.*, 1995, **36**, 3805.
2 I.W. Davis, D.I.C. Scopes, and T. Gallagher, *Synlett*, 1993, 85.
3 (a) W.F.J. Karstens, F.P.J.T. Rutjes, and H. Hiemstra, *Tetrahedron Lett.*, 1997, **38**, 6275; (b) F.P.J.T. Rutjes, K.C.M.F. Tjen, L.B. Wolf, W.F.J. Karstens, H.E. Schoemaker, H. Hiemstra, *Org. Lett.*, 1999, **1**, 717.
4 M. Anzai, A. Toda, H. Ohno, Y. Takemoto, N. Fujii, and T. Ibuka, *Tetrahedron Lett.*, 1999, **40**, 7393.
5 S-K. Kang, T-G. Baik, A.N. Kulak, *Synlett*, 1999, 324.
6 S-K. Kang, T-G. Baik, and Y. Hur, *Tetrahedron*, 1999, **55**, 6863.
7 I. Kadota, M. Kawada, V. Gevorgyan, and Y. Yamamoto, *J. Org. Chem.*, 1997, **62**, 7439.