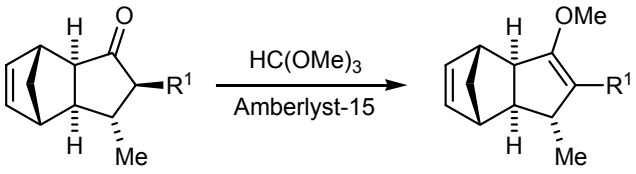
Eur. J. Org. Chem. **2006** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2006 · ISSN 1434–193X

SUPPORTING INFORMATION

Title: Synthesis of Highly Functionalized Pentalenes via Intermolecular Pauson–Khand Reaction
Author(s): Armand Becheanu, Angelika Baro, Sabine Laschat,* Wolfgang Frey
Ref. No.: O200500966

Protection of the keto function

As we first anticipated that the reducing agent in the follow-up reaction of derivatives **1** might interfere with the ketone moiety, it was protected by acetalization prior to ozonolysis. Surprisingly, treatment of ketones **1** with trimethyl orthoformate and acidic ion exchange resin Amberlyst-15 at room temperature[1] yielded the corresponding enol ethers **2** regardless of the substituent R^1.



1a–e **2a–e**

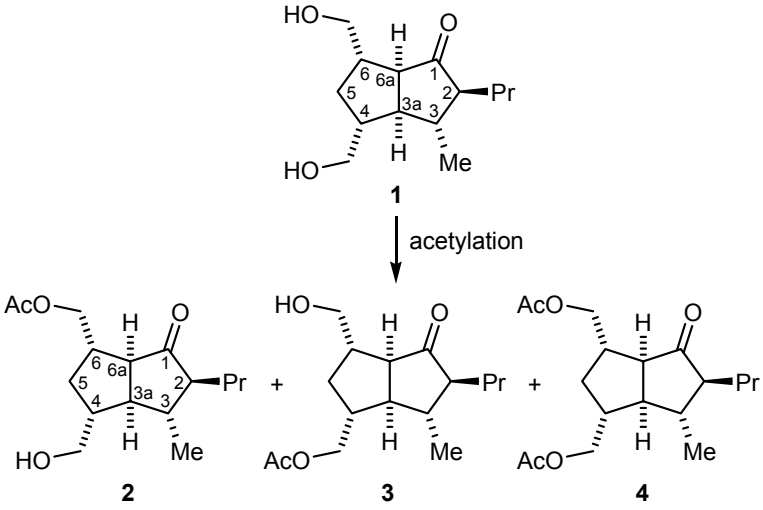
2	**a**	**b**	**c**	**d**	**e**
R^1	Pr	Bu	C_5H_{11}	C_6H_{13}	Ph
yield	64%	83%	68%	49%	86%

Typical procedure for the enolization: 3-methoxy-1-methyl-2-propyl-3a,4,7,7a-tetrahydro-1H-4,7-methanoindene (2a): A mixture of **1a** (1.07 g, 5.23 mmol), trimethyl orthoformate (2.85 mL, 2.78 g, 26.15 mmol) and Amberlyst-15 (250 mg) was stirred under inert gas atmosphere at room temperature for 12 h (tlc control). Then Amberlyst-15 was filtered off, the filtrate concentrated and the residue chromatographed on SiO_2 (pentane/Et_2O 60:1, R_f = 0.78) to give **2a** (727 mg, 3.33 mmol, 64 %) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.4 Hz, 3H, 3'-H), 1.02 [d, *J* = 7.0 Hz, 3H, (C-5)C*H*$_3$], 1.19–1.31 (m, 1H, 2'-H_a), 1.31–1.35 (m, 1H, 10-H_a), 1.38–1.48 (m, 1H, 2'-H_b), 1.52–1.55 (m, 1H, 10-H_b), 1.64 (dddd, *J* = 1.0 Hz, *J* = 1.6 Hz, *J* = 2.7 Hz, *J* = 7.7 Hz, 1H, 6-H), 1.80 (ddddd, *J* = 0.9 Hz, *J* = 2.4 Hz, *J* = 5.3 Hz, *J* = 8.8 Hz, *J* = 13.9 Hz, 1H, 1'-H_a), 2.05–2.11 (m, 1H, 5-H), 2.15 (ddd, *J* = 7.3 Hz, *J* = 9.0 Hz, *J* = 13.8 Hz, 1H, 1'-H_b), 2.53–2.55 (m, 1H, 7-H), 2.65–2.68 (m, 1H, 2-H), 2.76–2.78 (m, 1H, 1-H), 3.60 (s, 3H, OC*H*$_3$), 6.04 (dd, *J* = 2.9 Hz, *J* = 5.7 Hz, 1H, 8-H), 6.08 (dd, *J* = 3.0 Hz, *J* = 5.7 Hz, 1H, 9-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (C-3'), 20.7 (C-2'), 21.2 [(C-5)*C*H$_3$], 26.5 (C-1'), 41.1 (C-5), 42.0 (C-10), 44.2 (C-1), 47.7 (C-7), 48.2, 48.7 (C-2, C-6), 56.4 (O*C*H$_3$), 124.3 (C-4), 136.8, 137.2 (C-8, C-9), 151.3 (C-3) ppm. FT-IR (ATR): nu(tilde) = 2956 (s), 2930 (s), 2867 (s), 2838 (s), 1682 (s), 1454 (s), 1327 (m), 1234 (s), 1123 (s), 1087 (s), 1038 (s), 718 (s), 697 (vs) cm^{-1}. GC-MS (EI): *m/z* (%) = 218.2

(7) [M^+], 152.1 (100), 123.1 (86), 110.1 (12), 91.0 (4), 66.0 (2), 55.0 (2), 41.0 (2). HRMS (EI): calcd. for $C_{15}H_{22}O$ 218.1671, found 218.1671 [M^+].

[1] S. A. Patwardhan, S. Dev, *Synthesis* **1974**, 348–349.

Acetylation of keto diols – assignment of the ^{1}H NMR spectra



In the following a comment is given concerning the assignment of the constitution in mono acetates **2** and **3**.

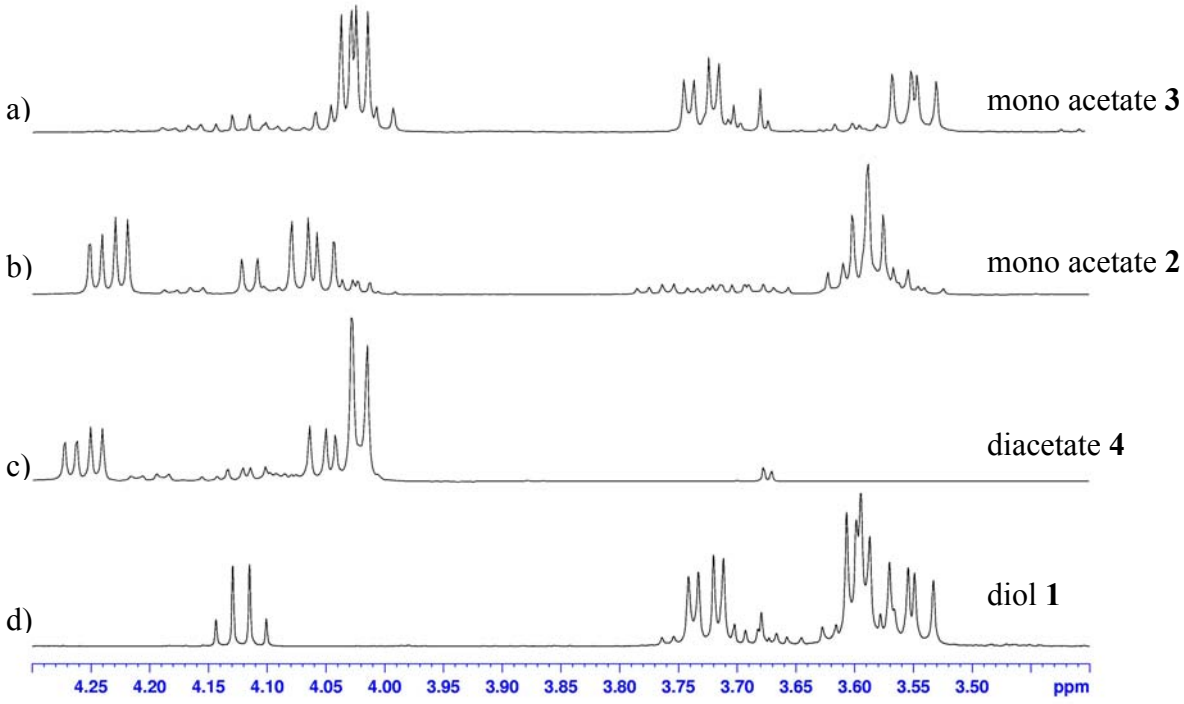


Figure. ^{1}H NMR spectra of diol **1**, mono acetates **2**, **3** and diacetate **4**. It must be noted that all compounds undergo epimerization in $CDCl_3$.

The signals of the bicyclooctane protons were assigned by C,H-COSY and H,H-COSY measurements. Upon comparison of the spectra of diacetate **4** and diol **1** (Figure c and d) it is clearly visible that acetylation results in a down field shift of both methylene signals 6-CH_2 and 4-CH_2 by about 0.4 ppm. Therefore we conclude that the ^{1}H NMR spectrum in Figure b) belongs to the (C-6)acetoxymethyl derivative **2** and the spectrum in Figure a) to (C-4)acetoxymethyl derivative **3**. While the diastereotopic protons of one methylene unit are well separated, the corresponding protons of the other methylene group are only poorly resolved and display a pronounced roof effect. The reason for the different spectroscopic behaviour of the methylene groups is presumably due to the carbonyl group at C-1. The diastereotopic 6-CH_2 protons are strongly influenced by the anisotropy of the C=O group, thus resulting in large chemical shift difference, whereas no such influence is present in the vicinity of the 4-CH_2 protons.

Diol 1: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.2 Hz, 3H, 3'-H), 1.18 (d, *J* = 6.5 Hz, 3H, C*H*$_3$), 1.20–1.37 (m, 2H, 2'-H$_a$, 5-H$_a$), 1.38–1.52 (m, 2H, 1'-H$_a$, 2'-H$_b$), 1.52–1.59 (m, 1H, 1'-H$_b$), 1.60–1.69 (m, 1H, 3-H), 1.95–2.01 (m, 1H, 2-H), 2.03–2.19 (m, 4H, 3a-H, 4-H, 5-H$_b$, 6-H), 2.62 (t, *J* = 9.1 Hz, 1H, 6a-H), 3.55 [dd, *J* = 8.0 Hz, *J* = 10.7 Hz, 1H, (C-6)C*H*$_a$OH], 3.60 [dd, *J* = 4.0 Hz, *J* = 5.6 Hz, 2H, (C-4)C*H*$_2$OH], 3.73 [dd, *J* = 4.1 Hz, *J* = 10.6 Hz, 1H, (C-6)C*H*$_b$OH] ppm.

Diacetate 4: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.0 Hz, 3H, 3'-H), 1.17 [d, *J* = 6.4 Hz, 3H, (C-3)C*H*$_3$], 1.20–1.31 (m, 2H, 2'-H$_a$, 5-H$_a$), 1.33–1.48 (m, 2H, 1'-H$_a$, 2'-H$_b$), 1.53–1.67 (m, 2H, 1'-H$_a$, 3-H), 1.87–1.93 (m, 1H, 2-H), 2.02 (dt, *J* = 4.1 Hz, *J* = 9.1 Hz, 1H, 3a-H), 2.06 (s, 3H, C*H*$_3$COO), 2.08 (s, 3H, C*H*$_3$COO), 2.10–2.19 (m, 2H, 4-H, 5-H$_b$), 2.22–2.31 (m, 1H, 6-H), 2.56 (t, *J* = 9.4 Hz, 1H, 6a-H), 4.02 [d, *J* = 6.4 Hz, 2H, (C-4)C*H*$_2$], 4.05 [dd, *J* = 6.9 Hz, *J* = 10.9 Hz, 1H, (C-6)C*H*$_a$], 4.26 [dd, *J* = 5.0 Hz, *J* = 10.9 Hz, 1H, (C-6)C*H*$_b$] ppm.

Mono acetate 2: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.2 Hz, 3H, 3'-H), 1.17 [d, *J* = 6.4 Hz, 3H, (C-3)C*H*$_3$], 1.22–1.31 (m, 2H, 2'-H$_a$, 5-H$_a$), 1.34–1.48 (m, 2H, 1'-H$_a$, 2'-H$_b$), 1.53–1.68 (m, 2H, 1'-H$_b$, 3-H), 1.89 (ddd, *J* = 1.4 Hz, *J* = 5.9 Hz, *J* = 11.2 Hz, 1H, 2-H), 2.00–2.15 (m, 6H, 3a-H, 4-H, 5-H$_b$, C*H*$_3$COO), 2.22–2.32 (m, 1H, 6-H), 2.53 (td, *J* = 9.2 Hz, *J* = 1.1 Hz, 1H, 6a-H), 3.57 (dd, *J* = 6.5 Hz, *J* = 10.5 Hz, 1H, C*H*$_a$OH), 3.61 (dd, *J* = 6.5 Hz, *J* = 10.5 Hz, 1H, C*H*$_b$OH), 4.06 (dd, *J* = 7.1 Hz, *J* = 10.9 Hz, 1H, C*H*$_a$OOC), 4.24 (dd, *J* = 5.2 Hz, *J* = 10.9 Hz, 1H, C*H*$_b$OOC) ppm.

Mono acetate 3: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.1 Hz, 3H, 3'-H), 1.17 [d, *J* = 6.4 Hz, 3H, (C-3)C*H*$_3$], 1.22–1.33 (m, 2H, 2'-H$_a$, 5-H$_a$), 1.36–1.52 (m, 2H, 1'-H$_a$, 2'-H$_b$), 1.53–1.70 (m, 2H, 1'-H$_b$, 3-H), 1.97–2.02 (m, 1H, 2-H), 2.04–2.16 (m, 6H, 3a-H, 4-H, 5-H$_b$, C*H*$_3$COO), 2.18–2.25 (m, 1H, 6-H), 2.63 (t, *J* = 8.7 Hz, 1H, 6a-H), 3.55 (dd, *J* = 8.2 Hz, *J* = 10.6 Hz, 1H, C*H*$_a$OH), 3.73 (dd, *J* = 4.2 Hz, *J* = 10.6 Hz, 1H, C*H*$_b$OH), 4.01 (dd, *J* = 6.1 Hz, *J* = 9.8 Hz, 1H, C*H*$_a$OOC), 4.03 (dd, *J* = 5.4 Hz, *J* = 9.8 Hz, 1H, C*H*$_b$OOC) ppm.