Carbohydrate Research, 254 (1994) 311-316
Elsevier Science B.V., Amsterdam

Note

Synthesis and characterisation of hexacarbonyldicobalt complexes derived from 2-propynyl and 3-butynyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosides

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(Received May 25th, 1993; accepted September 4th, 1993)

Metal-containing carbohydrate derivatives of the main group elements and complexes, coordinated via oxygen atoms, with transition elements are well documented[1], but organometallic compounds of carbohydrates with transition metals are rare and stereotyped; the latter are mainly *C*-glycosyl complexes containing [C-Mn(CO)$_5$][2], [C-Co(dmgH)$_2$py][3](dmg = dimethylglyoxime; py = pyridine), [C-Fe(CO)$_2$(η^5-C$_5$H$_5$)][4], and [C-Pt(PPh$_3$)$_2$Br][5] entities. In this note, we describe the synthesis and characterisation of hexacarbonyldicobalt complexes derived from hex-2-enopyranosides with pendant alkynyl-containing substituents.

The outcome of this study stemmed from our desire to elaborate the Pauson–Khand reaction (eq *1*)[6] to carbohydrate derivatives, with particular regard to achieving further examples of intramolecular type reactions[7] (see eq *2*). It is reported that 2,5-dihydrofurans and 2,3-dihydropyrans undergo the intermolecular Pauson–Khand reaction[8], but there are no reports of intramolecular processes of such ring systems. In this work, the choice of di-*O*-acetyl derivatives in the hex-2-enopyranoside series (**2**) provided a proximal acetoxy substituent which could, in principle, provide a neighbouring group effect[9a]. It may also be noted that the organocobalt complexes that are postulated[9b] to mediate Pauson–Khand reactions (eq *1*) have never been isolated and characterised.

2,3-Dideoxyhexenopyranosides (**1a–d**) were prepared from tri-*O*-acetyl-D-glucal and the appropriate alcohol in the presence of boron trifluoride etherate[10]. Two compounds prepared in this work (**1a,b**) have been recently reported in preliminary communications but full analytical and spectral properties were not provided[11,12]. Compounds **1a–d** show characteristic chemical shifts and coupling constants for the ring protons (see selected data in Table I); large couplings $J_{2,3} \sim 10$ Hz and $J_{4,5} \sim 9.5$ Hz are observed. Additional features of interest are small long-range couplings ($J \sim 2.5$ Hz) from the alkyne proton of **1a** and **1b** to the

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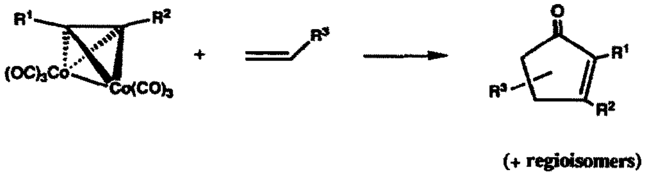

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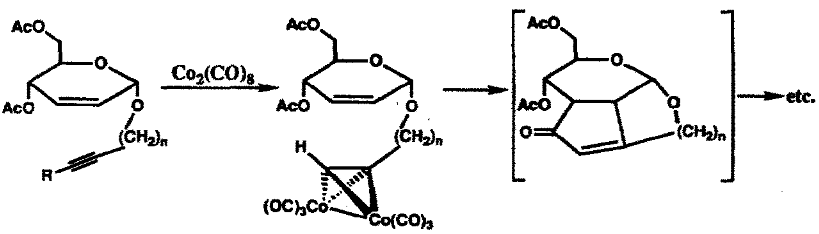

(2)

1

	n	R
a	1	H
b	2	H
c	1	Me
d	2	Me

2

	n
a	1
b	2

propargylic methylene hydrogens, and characteristic parameters for diastereotopic protons (H-1′a, H-1′b) at C-1′ of the aglycon side-chain, depending on chain length (e.g., $J_{1'a,1'b}$ ca. 9.7 Hz for **1b** and **1d**, but H-1′a and H-1′b fortuitously equivalent for **1a** and **1c**. Hex-2-enopyranosides (**1a**,**b**) were treated with octacarbonyldicobalt (1 mol equiv) in diethyl ether to give hexacarbonyldicobalt complexes (**2a**,**b**) as analytically pure red oils in good yields after chromatography. IR spectra in solution showed characteristic νCO bands of metal-coordinated carbon monoxide (e.g., for **2a** at 2093, 2052, and 2027 cm^{-1}) consistent with the presence of Co_2C_2 tetrahedrane units in a structure of type $Co_2(C_2RR')(CO)_6$[13]. ^{1}H NMR spectra (200 MHz) of the complexes indicate that complexation of the metal has little effect on chemical shifts of ring protons compared to values in the free ligand. The chemical shifts of alkyne protons show the anticipated downfield shift (e.g., 2.47 to 6.05 ppm from **1a** to **2a**, respectively). The two diastereotopic propargylic methylene protons of **2a** also suffer a slight downfield shift (of 4.28 to $\sim$4.8 ppm from **1a** to **2a** but, in contrast to those of **1a**, occur at different resonance frequencies and exhibit a strong geminal coupling [$J(H^AH^B)$ 14 Hz]; clearly, the bulky nature of the $Co_2(CO)_6$ moiety has a pronounced effect in influencing the rotamer population in respect of O–(C-1′) bond rotation. Interestingly, the 80-MHz resonance of this AB system in **2a** exhibits an additional 1-Hz doublet coupling to the alkyne proton which cannot be resolved at 200 MHz; this difference in resolution may arise from chemical shift anisotropy caused by incomplete motional averaging in solution, giving greater broadening of resonances observed at higher frequencies.

Attempts to promote intramolecular Pauson–Khand reactions of **2a,b** (e.g., in solution under CO atmosphere or on SiO_2[14]) were unsuccessful. New carbonyl-containing organic products and labile red–violet organocobalt complexes were isolated, but could not be fully characterised. Despite these difficulties, there is encouragement to investigate Pauson–Khand reactions on carbohydrate-derived enynes, and also to study related processes promoted by Pd[15]- and Zr[16]-organometallics.

EXPERIMENTAL

Organometallic reactions were carried out under an atmosphere of dry N_2 using standard Schlenk techniques. Solvents (benzene, diethyl ether, and petroleum ether) were dried and distilled before use from sodium benzophenone. ^1H NMR spectra were recorded for solutions in $CDCl_3$ at 200.13 and 80.13 MHz on Bruker WP 200 SY and WP 80 spectrometers, respectively. IR spectra were recorded on a Perkin–Elmer 580 instrument and calibrated against polystyrene.

*General synthesis of 2,3-dideoxy-α-*D-erythro-*hex-2-enopyranosides* (**1a–d**)[10].—Tri *O*-acetyl-D-glucal (2.0 g, 7.35 mmol), the appropriate alcohol (12.3 mmol), boron trifluoride etherate (0.4 mL), and dry benzene (8 mL) were stirred at room temperature for 45 min. The product was neutralised by careful addition of Na_2CO_3, the mixture was filtered, and then evaporated to dryness under reduced pressure. The β anomers of **1a–d** were removed as follows: compound **1a** was purified by trituration with EtOH, whereas **1b–d** were chromatographed {silica gel, 1:1 diethyl ether–petroleum ether (bp 40–60°C) eluant}. Selected comparative ^1H NMR data are collected in Table I; other spectral parameters are as follows.

*2-Propynyl 4,6-di-O-acetyl-2,3-dideoxy-α-*D-erythro-*hex-2-enopyranoside* (**1a**). ^1H NMR: δ 2.06 (s, 3 H, CH_3CO), 2.09 (s, 3 H, CH_3CO), 2.47 (t, 1 H, $J_{3',1'}$ 2.4 Hz, H-3′), 4.28 (d, 2 H, H-1′); EIMS: *m/z* 213 (rel abund. 15%), 166 (38), 153 (13), 124 (100), 111 (29), 85 (68). Anal. Calcd for $C_{13}H_{16}O_6$: C, 58.2; H, 6.0%. Found: C, 58.1; H, 6.3%.

*3-Butynyl 4,6-di-O-acetyl-2,3-dideoxy-α-*D-erythro-*hex-2-enopyranoside*. (**1b**). ^1H NMR: δ 1.93 (t, 1 H, $J_{4',2'}$ 2.7 Hz, H-4′), 2.07 (s, 3 H, CH_3CO), 2.11 (s, 3 H, CH_3CO), 2.45 (dt, 2 H, $J_{2',1'a} = J_{2',1'b} = 6.85$ Hz, H-2′), 3.61 (dt, 1 H, $J_{1'a,1'b}$ 9.7 Hz, H-1′a), 3.79 (dt, 1 H, H-1′b); EIMS: *m/z* 213 (73), 180 (38), 153 (21), 138 (100), 126 (21), 111 (100), 97 (24), 86 (52), 84 (42). Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.8: H, 6.4%. Found: C, 59.8; H, 6.3%.

*2-Butynyl 4,6-di-O-acetyl-2,3-dideoxy-α-*D-erythro-*hex-2-enopyranoside* (**1c**). ^1H NMR: δ 1.87 (t, 3 H, *J* 2.5 Hz, H-4′), 2.09 (s, 3 H, CH_3CO), 2.12 (s, 3 H, CH_3CO),

TABLE I

Selected ^{1}H NMR spectra data for 2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosides (**1a–d**)

Compound	Mp (°C)	Yield (%)	Sugar ring protons [a]										
			H-1	H-2	H-3	H-4	H-5	H-6a,6b [b]	$J_{2,3}$	$J_{2,4}$	$J_{4,5}$	$J_{3,4}$	$J_{6a,6b}$
1a	64-66	51	5.21	5.89	5.80	5.30	4.05	4.18	10.3	1.4	9.6	2.7	12.1
1b	(oil)	31	5.00	5.79 [c]	5.23	4.06	4.13	10.2	1.2	9.4	2.6	[d]	
1c	(oil)	46	5.25	5.92	5.87	5.34	4.09	4.21	10.2	1.4	9.6	2.6	13.9
1d	(oil)	34	5.08	5.88 [c]		5.32	4.14	4.22	10.2	1.2	9.6	2.5	~12

[a] Figures listed are for chemical shifts (δ) with respect to Me_4Si, with coupling constants (J, Hz). [b] Mean chemical shift of H-6a,6b, AB system ($J_{5,6a}$ 5 Hz; $J_{5,6b}$ 2.6 Hz). [c] Mean chemical shift of H-2/H-3, AB system. [d] Obscured by overlapping bands.

4.28 (distorted q, 2 H, *J* 2.5 Hz, H-1′); EIMS: *m/z* 111 (7), 55 (8). Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.8: H, 6.4%. Found: C, 59.7; H, 6.7%.

*3-Pentynyl 4,6-di-O-acetyl-2,3-dideoxy-α-*D-erythro*-hex-2-enopyranoside* (**1d**). ^{1}H NMR: δ 1.78 (t, 3 H, *J* 2.5 Hz, H-5′), 2.09 (s, 3 H, CH_3CO), 2.12 (s, 3 H, CH_3CO), 2.46 (m, 2 H, $J_{2',1'a} = J_{2',1'b} = 7.0$ Hz, H-2′), 3.64 (dt, 1 H, $J_{1'a,1'b}$ 9.6 Hz, 3.84 (dt, 1 H, H-1′b). Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.8: H, 6.8%. Found: C, 60.5; H, 6.5%.

Synthesis of hexacarbonyldicobalt complexes (**2a,b**) *derived from hex-2-enopyranosides* (**1a,b**).—The appropriate acetylene derivative (**1a,b**; 3 mmol) was added to a solution of octacarbonyldicobalt (3.1 mmol) in diethyl ether (60 mL) and the mixture was stirred for 12 h at room temperature. Filtration, evaporation to dryness under reduced pressure, and column chromatography of the residue under an atmosphere of N_2 [silica gel, 10:1 petroleum ether (bp 60–80°C)–diethyl ether eluant] gave **2a,b** as red oils (94 and 65%, respectively).

Compound (**2a**). IR: ν_{max} (petroleum ether, bp 60–80°C) 2093 (m), 2052 (s), 2027 (s, with shoulder) [νCO, $Co_2(CO)_6$], 1755 cm^{-1} (νCO, ester); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.09 (s, 3 H, CH_3CO), 2.10 (s, 3 H, CH_3CO), 4.05–4.32, (m, 3 H, H-5 and H-6a,6b), 4.70 (d, 1 H, $J_{1'a,1'b}$ 14 Hz, H-1′a), 4.91 (d, 1 H, H-1′b), 5.30 (m, 2 H, H-1 and H-4), 5.87–5.95 (d, 2 H, *J* 10 Hz, H-2 and H-3), 6.05 (s, 1 H, H-3′); ^{1}H NMR (80 MHz, $CDCl_3$): δ as above, but additional multiplicity observed in respect of the resonances at δ 4.70 (dd, 1 H, *J* 0.7 and 14.0 Hz) and 4.91 (dd, 1 H, *J* 0.7 and 14.0 Hz); FABMS: *m/z* 470 ($M^{+\cdot}$ − 3 CO), 442 ($M^{+\cdot}$ − 4 CO), 386 ($M^{+\cdot}$ − 6 CO). Anal. Calcd for $C_{19}H_{16}Co_2(CO)_{12}$: C, 41.2: H, 2.9; Co, 21.3%. Found: C, 40.9; H, 2.6; Co, 20.9%.

Compound (**2b**). IR: ν_{max} (petroleum ether, bp 60–80°C) 2103, 2055, 2040, 2018 [νCO, $Co_2(CO)_6$], 1755 cm^{-1} (νCO, ester); ^{1}H NMR (80 MHz $CDCl_3$): δ 2.1 (s, 6 H, 2 CH_3CO), 3.15 (approx. t, 2 H, $J_{2',1'a} \approx J_{2',1'b} \approx 6.5$ Hz, H-2′), 3.70 (dt, 1 H, $J_{1'_a,1'_b}$ 10 Hz, H-1′a), 4.05 (dt, 1 H, H-1′b), 4.06 (m, 1 H, H-5), 4.2 (m, 2 H, H-6a,6b), 5.07 (m, 1 H, H-1), 5.3 (m, 1 H, H-4), 5.85 (m, 2 H, H-2 and H-3), 6.05 (s, 1 H, H-4′); FABMS: *m/z* 484 ($M^{+\cdot}$ − 3 CO), 456 ($M^{+\cdot}$ − 4 CO), 400 ($M^{+\cdot}$ − 6 CO). Anal. Calcd for $C_{20}H_{18}Co_2O_{12}$: C, 42.3: H, 3.2; Co, 20.8%. Found: C, 42.3; H, 3.2; Co, 20.8%.

ACKNOWLEDGMENTS

We thank The Carnegie Trust for the Universities of Scotland for a Research Scholarship (to ABR), and Professor R.J. Ferrier for helpful discussions.

REFERENCES

1 See, for example, *Carbohydr. Chem.*, 22–24 (1990–1992) Chapters 17.
2 P. DeShong, G.A. Slough, and V. Elango, *Carbohydr. Res.*, 171 (1987) 342–345.
3 A. Ghosez, T. Göbel, and B. Giese, *Chem. Ber.*, 121 (1988) 1807–1811.
4 G.L. Trainor, *J. Organomet. Chem.*, 282 (1985) c43–c45.
5 Y. Nagel and W. Beck, *Z. Naturforsch., Teil B*, 40 (1985) 1181; *Chem. Abstr.*, 105 (1986) 79243.

6 P.L. Pauson and I.U. Khand, *Ann. NY Acad. Sci.*, 295 (1977) 2–14.

7 See, for example, S.W. Brown, and P.L. Pauson, *J. Chem. Soc., Perkin Trans.* 1, (1990) 1205–1209; P. Magnus, M.J. Slater, and L.M. Principe, *J. Org. Chem.*, 54 (1989) 5148–5153; E.G. Rowley and N.E. Schore, *ibid.*, 57 (1992) 6853–6861; M.E. Krafft, R.H. Romero, and I.L. Scott, *ibid.*, 57 (1992) 5277–5278; M.E. Krafft and C.A. Julians, *ibid.*, 57 (1992) 5106–5115.

8 D.C. Billington, W.J. Kerr, and P.L. Pauson, *J. Organomet. Chem.*, 328 (1987) 223–227.

9 (a) See, for example, M.E. Krafft, *J. Am. Chem. Soc.*, 110 (1988) 968–970. (b) See, for example, P. Magnus and D.P. Becker, *ibid.*, 109 (1987) 7495–7498.

10 R.J. Ferrier and N. Prasad, *J. Chem. Soc., C*, (1969) 570–575.

11 Y. Chapleur and N. Moufid, *J. Chem. Soc., Chem. Commun.*, (1989) 39–40.

12 N. Moufid and Y. Chapleur, *Tetrahedron Lett.*, 32 (1991) 1799–1802.

13 G. Bor, S.F.A. Kettle, and P.A. Strangehellini, *Inorg. Chim. Acta*, 18 (1976) L18–L20.

14 V.A. Smit, S.O. Simonyan, V.A. Tarasov, G.S. Mikaelian, A.S. Gybin, I.I. Ibragimov, R. Caple, D. Froen, and A. Kraeger, *Synthesis*, (1989) 472–476.

15 See, for example, R. Keese, R. Guidetti-Grept, and B. Herzog, *Tetrahedron Lett.*, 33 (1992) 1207–1210; G.J. Engelbrecht and C.W. Holzapfel, *ibid.*, 32 (1991) 2161–2164.

16 See, for example, E. Negishi, S.J. Holmes, J.M. Tour, J.A. Miller, F.E. Cederbaum, D.R. Swanson, and T. Takahashi, *J. Am. Chem. Soc.*, 111 (1989) 3336–3346; T.V. RajanBabu, W.A. Nugent, D.F. Taber, and P.J. Fagan, *ibid.*, 110 (1988) 7128–7135.