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Note

Synthesis of some 1,2-bis(acetylphenylhydrazone) derivatives

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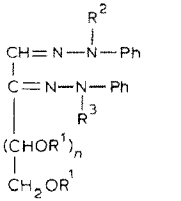
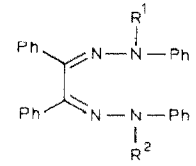
Chelated hydrazone derivatives (1-acetylphenylhydrazone-2-phenylhydrazones, and α-oxophenylhydrazones) are resistant to acetylation with acetyl chloride–pyridine (or *N,N*-dimethylaniline) or hot acetic anhydride but, on treatment with acetic anhydride–trifluoroacetic acid or acetic anhydride–zinc chloride, they give[1] 1,2-bis(acetylphenylhydrazones) and α-oxoacetylphenylhydrazones, respectively.

Analogous syntheses and the characterisation of L-*erythro*- (**4a**) and D-*threo*-(tri-*O*-acetyl)pentosulose 1,2-bis(acetylphenylhydrazone) (**4b**), D-*arabino*- (**4c**) and L-*xylo*-(tetra-*O*-acetyl)hexosulose 1,2-bis(acetylphenylhydrazone) (**4d**), and benzil bis(acetylphenylhydrazone) (**7**) are now reported (Tables I and II).



	R^1	R^2	R^3			
1	H	H	H	**a**	L-*erythro*	($n = 2$)
2	Ac	H	H	**b**	D-*threo*	($n = 2$)
3	Ac	Ac	H	**c**	D-*arabino*	($n = 3$)
4	Ac	Ac	Ac	**d**	L-*xylo*	($n = 3$)
				e	D-*lyxo*	($n = 3$)



	R^1	R^2
5	H	H
6	Ac	H
7	Ac	Ac

EXPERIMENTAL

General methods. — Melting points (uncorrected) were determined on a

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TABLE I

PREPARATION AND PHYSICAL DATA OF **2a,d 3a, 4a–d,** AND **7**

Product	*Starting material*	*Method of acetylation*	*Yield (%) [crude (pure)]*	*M.p. (deg.) (solvent of recrystn)*	$[\alpha]_D^{23}$ [a] *(deg.)*	*Formula*	*Analysis: found (calc.)*
2a	**1a**[2,3]	Ac_2O–Py[b,c]	94 (70)	137[d] (EtOH–H_2O)	+8.5[d]	$C_{23}H_{26}N_4O_6$	N, 12.32 (12.33)
2d	**1d**[2]	Ac_2O–Py[b,c]	95 (81)	80–82[e] (EtOH–hexane)	−80[e]	$C_{26}H_{30}N_4O_8$	C, 59.80 (59.30) H, 5.86 (5.74) N, 10.56 (10.64)
3a	**2a**	AcCl–Me_2NPh[g]	85 (78)	121 (EtOH)	−17	$C_{25}H_{28}N_4O_7$	C, 60.47 (60.47) H, 5.50 (5.68) N, 11.53 (11.29)
4a	**3a**	Ac_2O–TFA[f,g,h] (*b*)	(52)	amorphous	−22	$C_{27}H_{30}N_4O_8$	N, 10.45 (10.40) *m/z* 539 (M^+; 538.54)
4b	**2b**[5]	Ac_2O–TFA[g,h] (*b*)	(39)	amorphous	+53	$C_{27}H_{30}N_4O_8$	C, 60.53 (60.21) H, 5.65 (5.62) N, 10.23 (10.40) *m/z* 538 (M^+; 538.54)
4c	**2c**[6,7]	Ac_2O-TFA[g,h] (*b*)	(36)	amorphous	+72.5	$C_{30}H_{34}N_4O_{10}$	C, 58.86 (59.01) H, 5.66 (5.61) N, 9.22 (9.18) *m/z* 610 70 (M^+; 610 60)
4d	**2d**	Ac_2O–TFA[g,h] (*b*)	(41)	70–74 (MeOH)	+38	$C_{30}H_{34}N_4O_{10}$	N, 8 98 (9.18) *m/z* 611 (M^+; 610.60)
	2d	Ac_2O-$ZnCl_2$[g,h] (*a*)	(30)	75–76 (MeOH)	+37		
7	**5**[8]	Ac_2O–$ZnCl_2$[g] (*a*)	86 (62)	182–183 (EtOAc)	—	$C_{30}H_{26}N_4O_2$	C, 75.19 (75.93) H, 5.38 (5.52) N, 11.45 (11 81)
	6[9]	Ac_2O-$ZnCl_2$[g] (*a*)	94 (45)	178 (EtOAc)	—		

[a]Chloroform (*c* 1). [b]According to the known method[4]. [c]The reaction mixture was poured into ice and water, and a solution of the precipitated gum in benzene was washed successively with aqueous $KHSO_4$, water, aqueous $NaHCO_3$, and water, dried ($MgSO_4$), and then concentrated. The residue was crystallised from the solvents given. [d]D-Enantiomer[5]: amorphous, $[\alpha]_D$ −21° (*c* 0.5, chloroform) [e]Lit [4]: amorphous, "m.p." 75–80°, $[\alpha]_D^{15}$ −70° (*c* 0 3, chloroform). [f]Trifluoroacetic acid [g]See ref. 1. [h]After column chromatography on Kieselgel 40 (Merck) using 95:5 chloroform–acetone, the product was crystallised from the solvent given, or a solution in acetone was concentrated to dryness *in vacuo*.

TABLE II

U.V., I.R. AND ^{1}H-N.M.R. DATA FOR **2a, 2d, 3a, 4a–e,** AND **7**

Compound	λ_{max}^{MeOH}	λ_{min}^{MeOH}	ν_{max}^{KBr} (cm^{-1})			*δ (p.p.m.)*						
	[nm (log ε)]		*NH*	$\nu_{C\text{-}O}$	$\nu_{CO\text{-}N}$	*NH*	*H-1*	*H-3* ($J_{3,4}$ *Hz*)	*H-4* ($J_{4,5}$ *Hz*)	*H-5*	*H-6*	CH_3CO
2a			3299	1745	—	12.34s	7.52s	5.75–5.60m[a]		4.56–4.32m[a]		2.13, 2.10 2.04
2d			3307	1754	—							
3a				1745[c] 1740	1695	12.28s	[b]	5.51m[a]		4.40–4.14m[a]		2.63, 2.03 1.94, 1.88
4a	234 (3.98) 286 (4.13)	254 (3.97)					6.62s	6.19d (~5)	5.67m	4.63–4.28m[a]		2.48, 2.21 2.19, 2.10 2.08
4b	240 (3.99) 284 (4.12)	254 (3.96)					6.56s	6.17d (4.5)	5.80–5.72m	4.49–4.15m[a]		2.50, 2.18 2.15, 2.07 2.06
4c	236 (4.03) 285 (4.17)	256 (4.00)		1746	1700		6.51s	6.17d (2.5)	5.78dd (10)	5.45–5.37m	4.40–4.21m[a]	2.55, 2.20 2.15, 2.11 2.07, 2.05
4d	236 (4.05) 287 (4.17)	258 (4.01)		1756 1750	1703		6.50s	6.28d (6)	5.90dd (4.5)	5.49–5.41m	4.45–3.97m[a]	2.52, 2.23 2.17, 2.11 2.10, 2.06
4e[d]	237 (4.08)[c] 286 (4.26) 320 (3.97)[c]	255 (4.08) 310 (4.04)[c]		1748 1733	1702 1695		6.58s	6.20d (9)	5.80dd (2)	5.57mc	4.38–3.96m[a]	2.57, 2.18 2.12 (6 H) 2.06, 2.02
7	255 (4.11) 273 (4.01)[c] 325 (3.89)[c]	240 (4.09) 295 (3.97)[c]		—	1702 1699 1693							1.94 (6 H)

[a] 2 H [b] Among the signals for Ar-H. [c] Shoulder. [d] Ref. 1.

Kofler block. U.v. spectra were recorded (for solutions in methanol) with a Unicam SP 800 spectrophotometer, i.r. spectra (KBr discs) with a Perkin–Elmer 283 B spectrophotometer, and 200-MHz ^{1}H-n.m.r. spectra (for solutions in $CDCl_3$, internal Me_4Si) with a Bruker WP SY spectrometer. Mass spectra (70 eV) were obtained using a VG-7035 GC/MS/DS instrument (ion current, 0.1 mA; direct insertion technique). Optical rotations were measured with a Schmidt and Haensch visual polarimeter (1-dm path-length). Solution were concentrated *in vacuo* at $\gtrsim$45° (bath).

Methods of acetylation[1]. — (*a*) The starting material (2–5 mmol) was stirred with acetic anhydride (10 mL) containing anhydrous zinc chloride (1 g) until dissolution was complete. The solution was kept for 16–48 h at room temperature, and then (for the more-soluble sugar derivatives, after concentration) poured into ice and water. A solution of the crude product in chloroform was treated with fuller's earth and activated carbon, and then concentrated. The residue was crystallised from the solvents given (Table I).

(*b*) A solution of the starting material (~1 mmol) in acetic anhydride (10 mL) and trifluoroacetic acid (0.9 mL) was kept for 24 h at room temperature, then concentrated, and poured into ice and water. After the addition of sodium hydrogencarbonate, the product was dissolved in chloroform and processed as described in (*a*).

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