SYNTHESIS, STEREOCHEMISTRY, AND EPIMERIZATION OF METHYL 4,6-*O*-BENZYLIDENE-2,3-DICYANO-2,3-DIDEOXY-β-D-HEXOPYRANO-SIDES HAVING THE *allo*, *altro*, *gluco*, and *manno* CONFIGURATIONS*

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ABSTRACT

The reaction of methyl 4,6-O-benzylidene-2,3-dideoxy-3-nitro- β -D-erythro-hex-2-enopyranoside with hydrogen cyanide in the presence of catalytic amounts of potassium cyanide afforded the title compounds. The reaction is shown to involve the probable addition of hydrogen cyanide to an intermediate 2-cyano-hex-2-enopyranoside, followed by epimerization. The stereochemistry of this reaction and the epimerization of the products are described.

INTRODUCTION

We have shown¹ that the reaction of the nitro alkene 1 with hydrogen cyanide in the presence of a catalytic amount of potassium cyanide gives the nitro cyanide 2 and cyano alkene 3. A similar reaction of the α anomer of 1 also afforded the corresponding nitro cyanide and cyano alkene². Paulsen and Greve³ independently prepared 2 and 3 from the nitro alkene 1 and hydrogen cyanide, in the presence of triethylamine as a catalyst.

In general, the reactivity of cyano alkenes is much lower than that of the corresponding nitro alkenes. Thus treatment of 3 with hydrazoic acid in the presence or absence of sodium azide resulted only in the recovery of 3, whereas similar treatment of the corresponding 2-nitro alkene afforded addition products⁴. Likewise, Davison and Guthrie⁵ reported that methyl 4,6-O-benzylidene-3-cyano-2,3-dideoxy- α -D-*erythro*-hex-2-enopyranoside is inert to diethylamine. However, dicyano compounds (4-7) are formed, instead of 2 and 3, when an aqueous solution of potassium cyanide is passed through a column of cation-exchange resin and the eluate added directly to a stirred solution of 1 in acetonitrile at 32°. We have now investigated this reaction in detail, and report here the preparation and structural elucidation of these dicyano compounds, the most plausible reaction-path for their

^{*}Stereochemistry of Nucleophilic Addition Reactions: Part X.

formation, the stereochemistry of addition of hydrogen cyanide to the cyano alkene 3. and the epimerization of the dicyano products.

RESULTS AND DISCUSSION

When compound 1 in acetonitrile was treated with a solution, prepared by passing an aqueous solution of potassium cyanide through a column of cation-exchange resin (Amberlite IR-120, H^-), for 6 h at 32°, a mixture of dicyano compounds was formed. The *allo* isomer 4 was isolated by fractional crystallization. The *manno* isomer 6, having the lowest R_F value in t.l.c. [10:1 (v/v) benzene-ethyl acetate], was separated as a syrup by column chromatography on silica gel with benzene as eluant. Isolation of the *altro* (5) and *gluco* (7) isomer in admixture with 4 was difficult: both fractional crystallization and separated by column chromatography failed. The *altro* isomer 5 was, however, separated by column chromatography from a mixture consisting mainly of 4 and 5. The *gluco* isomer 7 was isolated by crystallization of the mixture obtained by epimerization of the *manno* isomer 6 with diethylamine, as described later.



The i.r. spectra of these dicyano products showed no nitro-group absorptions, but the cyano-group band was present at ~ 2250 cm⁻¹. Elemental analysis indicated the molecular formula $C_{16}H_{16}N_2O_4$. The configuration and conformation of each compound was determined from ¹H-n.m.r. data. The H-2 signal was assigned by spin-decoupling with irradiation of the H-1 signal. Although the H-3 signals of compounds 4 and 5 in chloroform-*d* were almost overlapped by the methoxyl signal, they were assigned unequivocally by comparison with the spectra of the 3-deuterated derivatives of 4 and 5, prepared from the 3-C-deuterated cyano alkene (3a). The $J_{1,2}, J_{2,3}$, and $J_{3,4}$ coupling constants were 8.2, 3.8, and 3.0 Hz for the *allo* isomer 6; and 7.5, 10.6, and 10 Hz for the *gluco* isomer 7. As shown in Table I, both the H-1 and H-5 signals of 4 and 5 appeared at lower field than those of 6 and 7, suggesting that the axial cyano group at C-3 exerts a deshielding effect. The equatorial protons at both C-2 and C-3 resonated at lower field than the corresponding axial protons.

When the reaction of 1 was terminated after 10 min, the cyano alkene 3 and the *allo* isomer 4 were formed as major products (Table II, expt. 3). Furthermore, a mixture of the nitro cyanide 2 and the cyano alkene 3 was obtained when the reac-

TABLE I

Compd.	H-I	H-2	H-3	H-4	H-5	Н-6а	Н-6е	PhCH	ОМе
4	4.91(d)	3.07(q)	~ 3.67	~ 3.91(q)	~ 3.96	~ 3.67(t)	4.37(q)	5.57(s)	3.64(s)
	$J_{1,2}$ 8.2,	$J_{2,3}$ 3.8,	$J_{3,4}$ 3.0, J	4.5 9.0, J _{5,64}	9.0, J _{5,6e}	3.2, J _{64,60}	9.0		
5	4.89(d)	3.44(t)	~ 3.65	3.99(q)	~4.00	3.96(t)	~ 4.39(q)	5.61(s)	3.60(s)
	$J_{1,2}$ 2.4.	$J_{2,3}$ 2.4,	J _{3,4} 4.8, J	4.5 9.0, J5.64	9.0, J _{5.6e}	^b , J _{6a.6e} 9.0			
6	4.38(d)	3.41(g)	3.15(a)	3.99(a)	3.1-3.5	3.83(t)	4.31(a)	5.61(s)	3 52(s)
	$J_{1,2}$ 2.2.	$J_{2,3}$ 4.1.	$J_{3,4}$ 10.7.	J4.5 8.9. J5 64	$10.4. J_{5}$	60 4.4. Jan	to 10.4	2.01(3)	2.32(3)
7	4 59(d)	3.04(a)	3 19(1)	3 5-3 7	~ 345	3 78(t)	4 36(a)	5 59(c)	3 58(0)
	$J_{1,2}$ 7.5,	$J_{2,3}$ 10.6	$J_{3,4}$ 10, .	J4,5 10, J5,6a	$10, J_{5,6e}$	5.0, $J_{6a,6e}$]	10	5.57(3)	5.50(3)

CHEMICAL SHIFTS (δ)^{*a*} and first-order coupling constants (Hz) at 100 MHz in Chloroform-*d*

"Me₁Si as internal standard. "Value uncertain.

tion was conducted for 10 min at 0° (expt. 1). Therefore, the reaction was performed under a variety of conditions and the relative product-ratios were determined on the basis of integration of the H-1 and methoxyl-group signals*. As shown in Table II, formation of the dicyano compounds seems to involve successive formation of the nitro cyanide and cyano alkene intermediates. In support of this idea, similar treatment of the nitro cyanide 2 or the cyano alkene 3 afforded the dicyano compounds (expts. 11–15). When the cyano alkene 3 was treated with hydrogen cyanide in the absence of potassium cyanide, the starting material was recovered quantitatively. In addition, treatment of 3 with potassium cyanide without addition of hydrogen cyanide gave a colored solution from which almost no products could be extracted with dichloromethane. Therefore, both hydrogen cyanide and potassium cyanide are required for these reactions. Even a catalytic amount of potassium cyanide was found to promote the reaction, giving an ~2:1 mixture of 4 and 5 (expt. 14).

Extensive studies of nucleophilic-addition reactions to the nitro alkene 1 and its α anomer have led to the conclusion that a nucleophile enters predominantly at C-2 from the side of the molecule opposite the anomeric methoxyl group⁶. These findings were explained in terms of steric hindrance, stereoelectronic control, and electrostatic interaction¹. Only limited data⁻ were available, however, concerning the stereochemistry of the subsequent protonation, because the nitro group almost always adopts the (more-stable) equatorial orientation; it is impossible to determine from the product whether or not the reaction is kinetically controlled. On the other hand, the present reaction afforded all possible isomers, and therefore we investigated this reaction in some detail. In contrast to the reaction with the nitro alkene 1, cyanide ion exclusively entered compound 3 from the side *cis* to the adjacent sub-

^{*}Although the H-1 signal of 6 almost overlapped the H-6e signals of 4 and 5, the product ratios were fairly precise, because the spectra were compared with those of mixtures consisting of pure compounds in almost the same ratios.

TABLE II

REACTION OF	: 1, 2,	OR 3	WITH	HYDROGEN	CYANIDE,	AND	EPIMERIZATION	OF	THE	DICYANO	COMPOUN	1DS
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27 7 4 days 30 H — — 2 1	5 5
28 4 8 days 30 I — — 2 1	2 2
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"Reaction conditions: A: An aqueous solution of potassium cyanide (98 mg) was poured into a column of Amberlite IR-120 (500 mg), and then water (0.5 mL) and acetonitrile (3 mL) were added. The cluate was added to the acetonitrile solution (3 mL) of 1 (147 mg). B: Similar conditions to A, but the scale was halved. C: To the solution of 2 or 3 (30 mg) in acetonitrile (1 mL) and water (0.1 mL) was added potassium cyanide (6.5 mg). D: To the solution of 3 (13.5 mg) in acetonitrile (0.5 mL) containing ~ 1 equiv. of hydrogen cyanide was added potassium cyanide (0.32 mg). E: Similar conditions to D, but the amount of potassium cyanide was 3.2 mg. F: An aqueous solution of potassium cyanide (0.05 mL, 0.32 mg) was added to the acetonitrile solution (1 mL) of the starting material (0.05 mmol) containing 2 equiv. of hydrogen cyanide. G: Similar conditions to F, but the amount of potassium cyanide. G: Similar conditions to F, but the amount of potassium cyanide was decreased to 0.08 mg. H: Similar conditions to F, but the amounts of potassium cyanide and water were 0.16 mg and 0.04 mL, respectively. I: To a solution of starting material (15 mg, 0.05 mmol) in acetonitrile (1 mL)-water (0.04 mL) was added diethylamine (0.1 mL). G: Similar conditions to I, but the solvent was benzene (1 mL). ^bThe ratios were determined by n.m.r. spectroscopy; t and — indicate trace and none detected, respectively. ^cRetention of deuterium at C-3.



stituent (O-4, expts. 16 and 20). Such a selective axial approach of cyanide ion may be rationalized on the basis of stereoelectronic control. Thus the initial intermediate (8) should have a more stable, stereoelectronically acceptable, chair conformation. It would be anticipated that subsequent protonation from the opposite side of the cyano group at C-3 would be favored, because steric hindrance between the incoming proton source and the linear cyano group should be operative, although it seems not to be significant. In fact, control experiments, where epimerization of the dicyano products (4-7) was negligible (expts. 21-24), demonstrated that protonation occurs predominantly from the axial side to give the *allo* (4) and *altro* (5) isomers in the ratio of $\sim 2:1$, as judged from n.m.r. spectroscopy (expts. 20).

From the foregoing considerations, the manno (6) and gluco (7) isomers should arise by epimerization of the initially formed allo (4) and altro (5) isomers. When this reaction was monitored by n.m.r. spectroscopy, compounds 6 and 7 increased with increase of reaction time.

As expected, the *altro* isomer 5 was epimerized more readily than the *allo* isomer 4 (expts. 17–18). When the *manno* isomer 6 was treated with hydrogen cyanide in the presence of small amounts of potassium cyanide in acetonitrile-water for 4 days at room temperature, a mixture of 4, 5, 6, and 7 in the approximate ratio of 2:1:5:5 was obtained (expt. 26). This appears to be the equilibrium mixture, because the same result was obtained from the *gluco* isomer 7 (expt. 27). Thus, the thermodynamic stability of the dicyano compounds decreased according to the sequence: *manno* ~ *gluco* > *allo* > *altro*. Therefore, the commonly expressed belief that the *manno* isomer is much less stable than the *gluco* isomer in β -D-hexopyranosides⁸ is not correct for the dicyano compounds.

When the dicyano compounds 4 and 6 were treated with diethylamine in acetonitrile-water for 8 days at 30°, epimerization occurred to give a mixture of 4, 5, 6, and 7, but no evidence for formation of cyano alkenes was obtained from the

n.m.r. spectra (expts. 28–29). On the other hand, similar treatment of 4 on 6 with diethylamine in benzene for 6 days afforded a mixture of 4 and 5 in the ratio of 2:1, and a mixture of 6 and 7 in the ratio of 1:1, respectively, showing that only H-2, being more acidic⁹ than H-3, was abstracted under these conditions.

EXPERIMENTAL

General methods. — Melting points were determined in capillaries and are uncorrected. I.r. spectra were recorded for potassium bromide discs with a Hitachi 215 i.r. spectrophotometer. N.m.r. spectra were determined in chloroform-d with tetramethylsilane as the internal standard with either a JNM-PS-100 (Jeol) or a Varian EM-360 spectrometer. Column chromatography was conducted on silica gel (C-300, Wakogel, Japan). T.l.c. was performed with Merck (Darmstadt) Silica Gel GF₂₅₄. Solutions were evaporated under diminished pressure.

Methyl 4,6-O-benzylidene-2-cyano-2,3-dideoxy-3-deuterio- β -D-erythro-hex-2enopyranoside (3a). — To a solution of 1 (ref. 10) (146 mg, 0.5 mmol) in acetonitrile (4 mL) were successively added potassium cyanide (2 mg), a solution of hydrogen cyanide (0.2 mL) in oxolane (2 mL), and deuterium oxide (0.5 mL). The mixture was stirred for 2 h at room temperature (~25°) and then evaporated to give a solid residue. Without further purification, the residue was dissolved in acetone (5 mL)deuterium oxide (0.7 mL) and to this solution was added triethylamine (0.3 mL). The mixture was kept for 15 h and then evaporated. Recrystallization of the residue from ethanol afforded 97 mg (71°) of 3a, the structure of which was confirmed by n.m.r. spectroscopy.

Attempts to prepare adducts from the cyano alkene 3 and hydrazoic acid. — To a solution of 3 (13.7 mg, 0.05 mmol) in acetonitrile (0.4 mL) and water (0.05 mL) were added sodium azide (3.3 mg, 0.05 mmol) and a solution of hydrazoic acid (0.1 mL, 0.16 mmol) in chloroform. The mixture was stirred for 30 min at room temperature and evaporated to a solid. The solid was washed with water to afford 13.4 mg of 3, the n.m.r. spectrum of which was identical with that of an authentic sample.

Similar treatment of 3 with hydrazoic acid for 18 h in the absence of sodium azide also resulted in the recovery of 3.

Preparation of compounds 2 and 3 with use of a column of cation-exchange rcsin. — An aqueous solution (0.5 mL) of potassium cyanide (198 mg) was placed on a column (6×10 mm) of cation-exchange resin (Amberlite IR-120, H⁺, 0.5 g), and the column was washed successively with water (0.5 mL) and acetonitrile (3 mL). The eluate was added directly to a stirred solution of 1 (147 mg, 0.5 mmol) in acetonitrile (3 mL) at ~4° (cooled with ice-water). After 30 min, the mixture was evaporated to give a solid mixture of 2 and 3 in the ratio of 2:1, as judged from n.m.r. spectroscopy. Recrystallization from ethanol afforded two kinds of crystals; the first crop was compound 2 (89.6 mg, 56%), and the second, 3 (37 mg, 27%). These compounds were identical (n.m.r. spectra) with authentic samples.

Isolation of dicyano compounds by column chromatography. — Treatment of 1 (293 mg), potassium cyanide (396 mg), and cation-exchange resin (1 g) as before, at 48° for 2.5 h, afforded a light-brown syrup (350 mg). The crude product (510 mg) was chromatographed on silica gel (14×3 cm) with benzene as eluant, and the eluate was fractionated (5-mL portions) with a fraction collector; fractions 107–117 gave 63 mg of 5: 118–123, 25 mg of 5 together with small amounts of 7; 124–132, a mixture of 4 and 5 (54 mg, in the ratio 4:1); 133–223, 210 mg of 4: and the last portion, 105 mg of 6.

Most convenient method for preparation of dicyano compounds: (a) The allo isomer 4. — To a solution (3.2 mL) of 3 (87 mg, 0.32 mmol) in acetonitrile were added an acetonitrile solution (0.8 mL) containing hydrogen cyanide (0.6 mmol) and an aqueous solution of potassium cyanide (0.25 mL, 1 mg) at 30°. The mixture was stirred at that temperature for 2.5 h and then evaporated to a solid, the n.m.r. spectrum of which showed the presence of 4 and 5 in the ratio of 2:1 together with small proportions of 6 and 7. Recrystallization from ethanol afforded 25 mg of 4, m.p. 205-206°, $[\alpha]_D^{22} - 36.4°$ (c 1, chloroform): v_{max} 2247 cm⁻¹: R_r 0.48 [10:1 (v/v) toluene-acetonitrile].

Anal. Calc. for C₁₆H₁₆N₂O₄: C, 63.99: H, 5.37: N. 9.33. Found: C, 63.77: H, 5.36; N, 9.32.

The filtrate was concentrated and chromatographed on silica gel with benzene as eluant: the first fraction was 5 (12 mg), the second a 1:4 mixture of 5 and 4 (25 mg), the third a mixture of 4, 5, and 7 (1:2.5:1.2; 15 mg), and the last, 6 (5 mg).

(b) The altro isomer 5. — To a solution of the allo isomer 4 (105 mg) in benzene (7 mL) was added 0.7 mL of diethylamine. The mixture was kept for 6 days at room temperature and then 20 mL of benzene was added. The organic layer was successively washed with 0.2 whydrochloric acid and water, dried over sodium sulfate, and then evaporated to a solid whose n.m.r. spectrum showed the presence of 4 and 5 in the ratio of 2:1. The residue was chromatographed on silica gel with benzene as eluant: the first fraction (28 mg) was 5, m.p. 192–192.5°, $[\alpha]_D^{22} - 28.7°$ (c 1, chloroform): $v_{max} 2248 \text{ cm}^{-1}$: $R_F 0.52$ [10:1 (v/v) toluene–acetonitrile].

Anal. Calc. for $C_{16}H_{16}N_2O_4$: C, 63.99: H, 5.37; N, 9.33. Found: C, 63.71: H, 5.42; N, 9.31.

The second fraction was a mixture of 4 and 5 (3:1, 20 mg), the third was 4 (40 mg), and the last was 6 (6 mg).

(c) The manno isomer 6. — The nitro alkene 1 (147 mg), potassium cyanide (198 mg), and cation-exchange resin (0.5 g) were treated as already described. The mixture was stirred for 66 h at 30°. The crude product was chromatographed on silica gel with benzene as eluant to give 73 mg (36%) of 6 as a syrup, $[\alpha]_D^{22} - 193^\circ$ (c l, chloroform); $v_{max} 2250 \text{ cm}^{-1}$; $R_F 0.32$ [10:1 (v/v) toluene-acetonitrile].

Anal. Calc. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 63.98; H, 5.50; N, 9.15.

Together with 6, a mixture of dicyano compounds (81 mg) was obtained.

(d) The gluco isomer 7. — To a solution of the manno isomer 6 (105 mg) in

benzene (7 mL) was added 0.7 mL of diethylamine. Processing similar to that described for the preparation of 5 gave a syrup whose n.m.r. spectrum showed the presence of 6 and 7 in the ratio of 1:1. Crystallization from ethanol afforded 30 mg of 7, m.p. 224–225° (dec.), $[\alpha]_D^{22} -65°$ (c 0.3, chloroform); v_{max} 2250 cm⁻¹; R_F 0.53 [10:1 (v/v) toluene–acetonitrile].

Anal. Caic. for C₁₆H₁₆N₂O₄: C, 63.99; H, 5.37; N, 9.33. Found: C, 63.71; H, 5.30: N, 9.33.

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