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Conversion of 2-Diazohexose Sugar Derivatives into Five-Carbon Acetylenic and Enol Ester Derivatives[1] ‡

Yvonne Gelas-Mialhe[2] and Derek Horton*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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Ethyl 4,6-*O*-benzylidene-2-deoxy-2-diazo-D-*arabino*-hexonate (1) decomposed spontaneously with loss of nitrogen to give the 3-oxo-2-deoxy ester **4**, which on acetylation gave an enol acetate derivative **5**. Treatment of either the diazo derivative 1 or its diacetate **2** with potassium hydroxide in isopropyl alcohol, with subsequent acetylation, gave the product of chain degradation with formation of an acetylenic sugar derivative, 4-*O*-acetyl-3,5-*O*-benzylidene-1,2-dideoxy-D-*erythro*-pent-1-ynitol (**3**). Thermolysis of the acetylated diazo derivative **2** gave a mixture of the enol 3-acetate **5** and the *E* and *Z* isomers of the corresponding enol 2-acetate (**6** and **7**). The transformations observed evidently proceed through carbenoid intermediates, and the reactions may be related to previously observed photochemical transformations and alkali-catalyzed degradations of (*N*-nitroso)acetamido sugars to acetylenic products.

1-Diazo derivatives of sugars having a stabilizing carbonyl group at the adjacent position are useful as synthetic intermediates for higher-carbon ketose sugars[3] and similarly stabilized 2-diazo sugar derivatives have been prepared[4] and their reactivity studied.[5] Nonterminal diazo sugar derivatives lacking an adjacent carbonyl group but possessing considerable stability have also been prepared by pyrolysis of arylhydrazone salts[6] and by treatment of hydrazone precursors with lead tetraacetate.[7] Transient diazo intermediates have been proposed[8] in the base-catalyzed, one-carbon chain degradation[9] of 2-(*N*-nitroso)acetamido sugar derivatives to chain-terminal acetylene products. The present work was undertaken (1) to test the hypothesis[8] of the intervention of a 2-diazo intermediate in the transformation of a 2-(*N*-nitroso)acetamidohexose derivative into a 5-carbon acetylene and (2) to assess the course of thermal decomposition of 2-diazo sugar derivatives as a potential net route for transformation of 2-amino-2-deoxy sugar precursors into the corresponding 2-deoxy-3-keto sugar analogues. Compounds of the latter type are of interest in their own right,[10] provide potential intermediates for synthesis of 3-substituted 2-deoxy sugars of various types,[11] and offer a potential route for transforming such compounds as aminocyclitol antibiotics[12] into structurally modified analogues of altered biological activity.

Oxidation[13] of 2-amino-2-deoxy-D-glucose hydrochloride to the aldonic acid, followed by conversion[4] into the ethyl ester 4,6-benzylidene acetal and subsequent cautious nitrosation with sodium nitrite–aqueous acetic acid acid[5,14] gave a yellow precipitate of ethyl 4,6-*O*-benzylidene-2-deoxy-2-diazo-D-*arabino*-hexonate (1) that, if filtered off and dried, was stable for several months when stored at room temperature. Isolation by dichloromethane extraction[5] gave crystalline 1 having the same physical characteristics as those previously reported,[5] but the product thus isolated was unstable at room temperature; it evolved nitrogen and underwent complete decomposition during a period of 4 days. The crystalline diacetate[5] (**2**) was readily prepared from 1 and was stable on storage.

An ethereal solution of the diazo ester 1 was treated at room temperature with an excess of potassium hydroxide in isopropyl alcohol for 1 h and the product was acetylated with acetic anhydride–pyridine. These conditions are the same as those used to convert acetylated 2-deoxy-2-(*N*-nitroso)acetamidohexoses in high yield,[8,9] and acetylated alkyl 2-deoxy-2-(*N*-nitroso)acetamidohexonates[8] in moderate (~30%) yield, into 3,4,5-triacetoxy-1-pentynes retaining the stereochemical configuration at C-3 and C-4 of the amino sugar precursor. The major product from the reaction of 1 was obtained in high yield and was isolated crystalline (the net isolated yield was decreased by the necessity of chromatographic purification to remove more polar side products). This crystalline product was identified as the C_5 acetylene derivative 4-*O*-acetyl-3,5-*O*-benzylidene-1,2-dideoxy-D-*erythro*-pent-1-ynitol (**5**) on the basis of its ^1H NMR spectrum (see Table I), which was essentially first order at 60 MHz in both chloroform-*d* and benzene-d_6 and was fully supportive of a pure, single product having the structure assigned. Infrared absorptions characteristic of a terminal, acetylenic group were observed, and the mass spectrum showed a significant molecular-ion peak (*m*/*e* 246) together with fragment ions readily reconciled with the assigned structure **3** (see Experimental Section for details).

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‡ Dedicated to Professor M. S. Newman on the occasion of his 70th birthday.

Table I. ^{1}H NMR Data[a] for Compounds 3–7

Compd	Registry no.	Solvent	H-1 ($J_{1,3}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5e ($J_{5e,5a}$)	H-5a ($J_{5a,6a}$)	H-6e ($J_{5a,6e}$)	H-6a ($J_{6a,6e}$)	Ph	PhC*H* (s)	OAc (enol) (s)	OAc (s)	$CH_2CH_3CH_2CH_3$	
			Chemical shifts of protons[b] in δ (1st order couplings, Hz, in parentheses)													
3	65915-35-7	$CDCl_3$	2.55 d (2.2)		4.60 dd (9.8)	5.20 m_6 (5.2)	4.52 dd (10.8)	3.65 t (10.0)[c]			7.40–7.80 m	5.60		2.17		
3		C_6D_6	2.02 d (2.1)		4.35 dd (9.8)	5.37 m_6 (5.6)	4.30 dd (10.8)	3.20 t (10.4)[c]			7.10–7.80 m	5.20		1.65		
4	65915-36-8	$CDCl_3$		3.65 s[d]			← 3.45–4.35 m →				7.1–7.5 m	5.45			4.12 q	1.17 t
5	65915-37-9	$CDCl_3$		6.15 s		4.42 d (10)		5.15 m_6 (10)	4.55 q (5.2)	3.70 t (10.4)	7.40–7.80 m	5.68	2.28	2.10	4.23 q	1.28 t
5		C_6D_6		6.21 s								5.41	2.00	1.70		
6	65915-38-0	$CDCl_3$			6.05 d (8.8)	5.58 t (9.6)		5.02 m_6 (10.0)	4.50 q (4.8)	3.87 t (10.5)	7.60–7.80 m	5.77	2.28	2.10	4.40 q	1.38 t
6	65915-39-1	C_6D_6			6.05 d (8.9)	5.72 t (9.2)		5.20 m_6 (10.0)	4.35 q (5.1)	3.60 t (10.0)	7.20–7.80 m	5.55	1.82	1.68	4.05 q	0.92 t
7		$CDCl_3$			6.60 d (8.0)		← 3.40–5.40 m →				7.60–7.80 m	5.68	2.30	2.05	4.32 q	1.30 t
7		C_6D_6			6.79 d (8.4)		← 3.20–5.40 m →				7.20–7.80 m	5.42	1.90	1.78	3.95 q	0.82 t

[a] Determined at 60 MHz. [b] Multiplicities: d, doublet; t, triplet; q, quartet; m_x, multiplet of x lines. [c] $J_{4,5a}$. [d] 2-Proton singlet.

Base-catalyzed decomposition of the acetylated diazo ester **2**, with subsequent acetylation of the product, likewise gave the crystalline acetylenic derivative **3**.

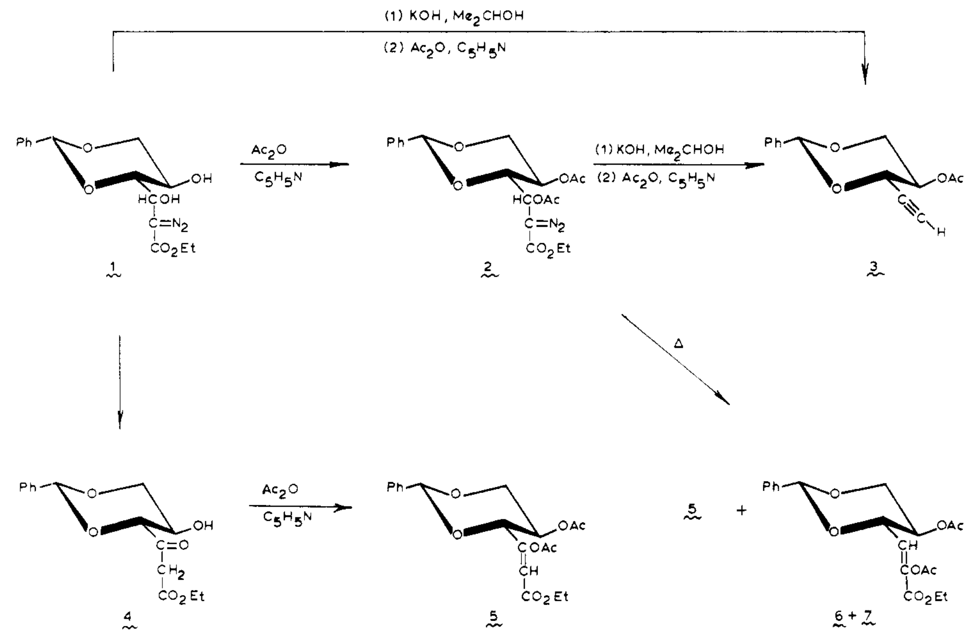
The foregoing observed conversions of the diazo derivatives **1** (or **2**) into the acetylene **3** support the idea[8] that the base-catalyzed degradation of 2-(*N*-nitroso)acetamido sugars to acetylenes in nonaqueous media takes place through a 2-diazo intermediate; in aqueous media the *N*-nitroso derivatives of 2-acetamido sugars undergo[15] conversion into 2,5-anhydroaldose groups with concomitant cleavage of glycosidic substituents.[16] Both of these reactions are useful in the sugar field; the route to acetylenic products is a useful complement to methods[17] involving ethynylation of aldehydo sugar derivatives, and the aqueous decomposition mode is of value for specific[16] fragmentation of such acetamido sugar-containing molecules as glycosaminoglycans,[18] and specific, immunological-determinant oligosaccharides of glycoproteins[19] and lipopolysaccharides.[20]

The diazo derivative **1**, as obtained by dichloromethane extraction, decomposed either in solution or in the dry state. The reaction was monitored by TLC and by disappearance of the diazo-group absorption (2119 cm^{-1}) in the infrared. Decomposition was complete after 48 h at ~25 °C and a principal, fast-migrating, reaction–product **4** was separated by chromatography on silica gel from two slower-migrating side products; it was obtained in 57% yield as an oil. Its IR spectrum showed hydroxyl (3450 cm^{-1}) and two separate carbonyl-group absorptions (1669 and 1739 cm^{-1}) and its NMR (Table I) and mass spectra (see Experimental Section) supported the assigned structure of ethyl 4,6-*O*-benzylidene-2-deoxy-D-*erythro*-hex-3-ulosonate (**4**). The presence of a 2-proton singlet at δ 3.65 (chloroform-*d*) indicated that the compound had an "isolated" methylene group at C-2; an alternative formulation as a 3-deoxy-2-keto ester would have led to multiplicity in this signal. Presumably the conversion of **1** into **4** involves loss of nitrogen and subsequent migration of H-3 to an incipient carbene at C-2 to generate the 2-ene-3-ol that subsequently ketonizes to the observed 2-deoxy-3-ketone **4**.

Acetylation of **4** with pyridine–acetic anhydride gave a mixture of two diacetylated products, presumably the geometric isomers of the structure **5**; these were separated by preparative TLC and the major one was obtained crystalline and analytically pure in 31% yield. The IR data were indicative of the enol ester structure, and cleavage of the molecular ion (*m/e* 378) between C-3 and C-4 leads to the observed fragments at *m/e* 221 and 157; further spectral details are recorded in the Experimental Section. The NMR spectrum (Table I) in chloroform-*d* was fully first order and afforded direct evidence for structure **5**; the low-field position (δ 2.28) of one of the acetyl-group signals is as expected for an enol acetate. The observation of a sharp singlet for H-2 at δ 6.15 provides clear indication that the compound has the 2-enol 3-acetate structure **5**; the proton of the enolic group would have shown the effect of vicinal coupling had the compound been the alternative 2-enol 2-acetate. It is not possible to specify with certainty the precise geometric isomerism about the C═C bond that is adopted in this crystalline isomer of **5**; attempted calculations from the chemical shift of H-2 (see later) gave ambiguous results.

The foregoing sequence of self-decomposition of **1** to give **4**, and subsequent conversion into the enol 3-acetate **5**, demonstrates a practical, net conversion of a 2-amino sugar precursor into a 2-deoxyaldos-3-ulosonic acid system.

The thermal decomposition of the acetylated diazo ester **2** was studied by heating the dry compound for 1 h at 100 °C. A mixture of three products was formed, although only two components were observed by TLC and required careful separation by preparative TLC. The faster migrating com-



ponent was found to be a single compound, isomeric with the enol acetate **5**, and it was formulated as one of the two geometric isomers (**6** or **7**) of the corresponding 2-enol 2-acetate. It showed IR absorptions similar to those observed for **5** and displayed a molecular ion (*m/e* 378) the same as that given by **5**, but distinct differences were evident in the fragmentation pattern (see Experimental Section). The NMR spectrum (Table I) provided clear differentiation of this product from **5**; the same general features were present, including a characteristic signal for the methyl protons of the enol acetate group, but the vinylic proton signal (a singlet in the spectrum of compound **5**) was observed as a wide doublet exhibiting coupling of ~9 Hz with H-4. This evidence permits assignment of the 2-enol 2-acetate structure, although it does not establish directly which one of the two possible geometric isomers (**6** or **7**) is this faster migrating component.

The slower migrating component (R_f 0.28) was found from its NMR spectrum to be a mixture of two products, the 2-enol 3-acetate **5** already described plus the geometric isomer (**7** or **6**) of the faster migrating component of the thermolysis product; the two products were present in ~7:13 ratio. The mixture having R_f 0.28 showed *m/e* 378 as the molecular ion, plus a series of fragment ions that comprised essentially the sum of the fragments observed in the separate spectra of **5** and the faster migrating (R_f 0.32) 2-enol 2-acetate. The NMR spectrum of the slower migrating component, after subtraction of all peaks assignable to compound **5**, allowed assignment of the remaining signals to the isomeric 2-enol 2-acetate (Table I); the wide, 1-proton doublet in the alkenic region (δ 6.60 in chloroform-*d*) again indicates that this signal arises from H-3, showing strong coupling to H-4, in the 2-enol 2-acetate structure.

The chemical shifts of the vinylic-proton doublets in the isomers **6** and **7** may be used for tentative attribution of geometrical isomerism by following the method of Matter et al.[21-23] for estimating these shifts in chloroform-*d* by means of the equation $\delta = 5.25 + Z_{\text{cis}} + Z_{\text{trans}} + Z_{\text{gem}}$, where the Z values are shielding constants of substituents in the locations specified. Using the published[22] values for these shielding constants, the calculated δ values for the vinylic (H-3) proton would be 6.09 ppm for the *E* isomer and 6.43 for the *Z* isomer. For the faster migrating (R_f 0.32) isomer **6**, the observed chemical shift of H-3 is 6.05 ppm, suggesting that it is the *E* isomer, whereas the shift of H-3 in the slower migrating 2-enol 2-acetate **7** is 6.60 ppm, suggesting that it is the *Z* isomer. For compound **5**, the observed shift (δ 6.15) differs considerably from values (5.40 and 5.68 ppm) calculated[21-23] for either geometric isomer.

The three products (**5**, **6**, and **7**) from thermolysis of **2** were formed in the approximate ratio of 20, 45, and 35%, showing that the carbene formed by loss of nitrogen from **2** undergoes stabilization by 3 → 2 migration of the 3-acetoxyl group more readily than 3 → 2 migration of H-3.

Experimental Section

Preparation of Ethyl 4,6-*O*-Benzylidene-2-deoxy-2-diazo-D-*arabino*-Hexonate (1). To a stirred solution of ethyl 2-amino-4,6-*O*-benzylidene-2-deoxy-D-gluconate hydrochloride (5.2 g, 15 mmol) in water (75 mL) at 0 °C was added sodium nitrite (4.2 g), and then acetic acid (2.5 mL) was added dropwide while maintaining the solution at 0 °C. A yellow precipitate appeared almost immediately. Stirring was continued for 40 min and the mixture was then extracted with dichloromethane. The dried (magnesium sulfate) extract was evaporated at 30 °C and the crystalline residue obtained was identical by IR spectrum, TLC, and other constants with the diazo derivative **1** already reported.[5]

The product thus isolated was not stable; it became pasty after several hours at room temperature, evolved nitrogen and was totally decomposed (TLC) after 96 h. To obtain a stable product, the yellow precipitate was filtered off instead of being extracted by dichloromethane. The solid was dried by lyophilization to give anhydrous **1** that could be kept for several months without special precautions. Possibly, traces of salts retained by precipitated **1** exerted a protective effect.

Acetylation of the stable, precipitated form of **1** with acetic anhydride–pyridine as already described[5] for the solvent-extracted preparation gave the diacetate **2**, identical with the product already reported.[5] This product was stable on storage at room temperature.

Base-Catalyzed Conversion of 1 (or 2) Into 3,5-*O*-Benzylidene-1,2-dideoxy-D-*erythro*-pent-1-ynitol, Isolated as Its 4-Acetate 3. A solution of **1** (642 mg, 2.0 mmol) in dry ether (100 mL) was stirred magnetically at ~25 °C and a solution of potassium hydroxide (560 mg) in isopropyl alcohol (20 mL) was added dropwise, with continued stirring, for 1 h. The solvents were evaporated off in vacuo and to the residue was added pyridine (20 mL) and acetic anhydride (4 mL); the mixture was stirred for 12 h at ~25 °C. Ice and water were added and the solution was extracted with dichloromethane. The extract was washed with water, dried (magnesium sulfate), and evaporated. There was obtained a brown oil that by TLC (1:1 petroleum ether–ethyl acetate) contained a major product, R_f 0.85, and slower migrating material. The principal product was separated by chromatography on a column of silica gel with the TLC solvent as eluent to give the pure acetylenic sugar **3** as a solid: yield 150 mg (30%); mp 102 °C; $[\alpha]_D{}^{20}$ −10.3° (*c* 0.9, dichloromethane); $\nu_{\text{max}}^{\text{KBr}}$ 3275 (≡CH), 3000, 2850, 2100 (C≡C), 1750 cm^{-1} (broad, C=O); *m/e* 246 (5, M$^{+}\cdot$), 245 (6.5), 221 (0.1, M$^{+}\cdot$ − HC≡C·), 187 (0.1, M$^{+}\cdot$ − ·OAc), 186 (4, M$^{+}\cdot$ − AcOH), 169 (1, M$^{+}\cdot$ − ·C$_6$H$_5$), 150 (2), 149 (29, PhCH=O$^+$CH$_2$CHO), 140 (0.1, M$^{+\cdot}$ − PhCHO), 124 (2, M$^{+\cdot}$ − PhCO$_2$H), 116 (1), 115 (12, 221 − PhCHO), 109 (1), 108 (1), 107 (36, PhC$^+$HOH, 149 → 107, m* 77, calcd 76.8), 106 (7, PhCHO$^{+\cdot}$), 105 (62, Bz$^+$), 91 (12, C$_7$H$_7$$^+$), 90 (1), 89 (0.5), 86 (3, AcOCH=CH$_2$$^{+\cdot}$), 82 (7), 81 (1), 79 (3), 78 (2), 77 (10, Ph$^+$), 55 (0.5), 53 (0.5), 52 (0.5), 51 (3), 50 (1), 44 (2), 43 (100, Ac$^+$). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.29; H, 5.69. Found: C, 68.62; H, 5.78.

When the same procedure was repeated with the diacetate **2**, the acetylenic derivative **3** was also obtained, identical in all respects with the preceding product.

Decomposition of 1 to Give Ethyl 4,6-*O*-Benzylidene-2-deoxy-D-*erythro*-hex-3-ulosonate (4). The diazo derivative **1** (400 mg), as isolated by extraction with dichloromethane, decomposed either in solution or in the dry state after evaporation of dichloromethane. The progress of the reaction was monitored by observing the progressive disappearance of the diazo-group absorption in the infrared (at 2119 cm^{-1}) and by TLC (4:1 dichloromethane–ether). The starting material **1** (R_f 0.17) was progressively replaced by a major product having R_f 0.54, together with a second product having R_f 0.22, and traces of a third product, R_f 0.27. At room temperature, the decomposition of **1** in dichloromethane was complete after 48 h; the progress of the reaction did not appear substantially altered according to whether the solution had been dried (magnesium sulfate or sodium sulfate) or not. The major product (R_f 0.54) was isolated by chromatography on a column of silica gel eluted with the TLC solvent and isolated as a colorless oil identified as **4:** yield 200 mg (57%) $[\alpha]_D$ +6.1 (*c* 1.15, dichloromethane); ν_{max}^{film} 3448 (OH), 2985, 2857, 1739 (C=O), and 1669 cm^{-1}; *m/e* 294 (0.4, M$^{+\cdot}$), 293 (0.4), 276 (0.2, M$^{+\cdot}$ − H$_2$O), 250 (0.6, BzOCH$_2$COCH$_2$CO$_2$Et$^{+\cdot}$), 249 (3.7, M$^{+\cdot}$ − EtO·), 248 (0.7), 234 (0.7), 192 (1), 168 (0.7, M$^{+\cdot}$ − PhCHO), 180 (10), 179 (100, PhCH=O$^+$CH$_2$CHOHCHO), 150 (3), 149 (25, PhCH=O$^+$CH$_2$CHO), 145 (2, 250 − PhCO·), 143 (2, 250 − Ph$\dot{C}$HOH), 115 (2, EtO$_2$C-CH$_2$CO$^+$), 108 (5), 107 (72, PhC$^+$HOH), 106 (40, PhCHO$^{+\cdot}$), 105 (135, PhCO$^+$), 102 (1, 179 − Ph·, m* 58.5, calcd 58.2), 92 (6), 91 (72, C$_7$H$_7$$^+$), 86 (15, 115 − Et·), 84 (21, 102 − H$_2$O), 79 (25), 78 (8), and 77 (32, Ph$^+$).

Ethyl 3,5-Di-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-D-*erythro*-hex-2-enonate (5). The foregoing product (**4**, 200 mg) in pyridine (10 mL) was treated with acetic anhydride (2 mL) for 24 h at ~25 °C and the mixture was then poured into water. The product was isolated by extraction with chloroform. The crude product on TLC (2:1 petroleum ether–ethyl acetate) showed two components, R_f 0.32 and 0.28, the latter being preponderant. Preparative TLC gave the pure major product as a crystalline solid: yield 80 mg (31%); mp 88–90 °C; $[\alpha]_D$ −20.4° (*c* 1.2, dichloromethane); ν_{max}^{KBr} 3030, 2950, 2850, 1775, 1745, 1720 (C=O), and 1675 cm^{-1} (C=C); *m/e* 378 (0.1, M$^{+\cdot}$), 377 (0.2), 336 (0.2 M$^{+\cdot}$ − C$_2$H$_2$O), 335 (0.1, M$^{+\cdot}$ − Ac·), 318 (0.5, M$^{+\cdot}$ − AcOH), 276 (1, EtO$_2$CCH=COAc$\dot{C}$HO$^+$=CHPh), 273 (2), 272 (17, M$^{+\cdot}$ − PhCHO), 230 (2, 272 − C$_2$H$_2$O), 227 (4, 272 − EtO·), 221 (3, PhCH=O$^+$CH$_2$CHOAcCHO), 213 (1, 272 − AcO·), 212 (1, 272 − AcOH, m* 165.5, calcd 165.2), 187 (2), 186 (0.3, EtO$_2$CCH=COAc-CHO$^{+\cdot}$), 185 (7, 186 − H·), 177 (2.5), 171 (4), 170 (30, 272 − AcO-CH$_2$CHO, m* 106.2, calcd 106.2), 167 (2), 162 (3, 221 − AcO·), 157 (5, EtO$_2$CCH=C$^+$OAc), 149 (13, PhCH=O$^+$CH$_2$CHO), 145 (7), 124 (3), 116 (11), 115 (75, 221 − PhCHO), 107 (14, PhC$^+$HOH), 106 (6, PhCHO$^{+\cdot}$), 105 (32, Bz$^+$), 91 (7, C$_7$H$_7$$^+$), 87 (6), 77 (6.5, Ph$^+$), 43 (100, Ac$^+$). Anal. Calcd for $C_{19}H_{22}O_8$: C, 60.32; H, 5.82. Found: C, 59.93; H, 6.05.

Thermal Decomposition of Diazo Ester 2 to give Ethyl (*E*)- and (*Z*)-2,5-*O*-Diacetyl-4,6-*O*-benzylidene-3-deoxy-D-*erythro*-hex-2-enonates (6 and 7) and the 3-*O*-Acetyl Isomer 5. The diazo ester **2** (170 mg) in a Pyrex tube was heated in an oil bath for 1 h at 100 °C (evolution of nitrogen), whereupon TLC (2:1 petroleum ether–ethyl acetate) showed that the starting ester had disappeared and had been replaced by components having R_f 0.32 and 0.28, in approximately equal proportion. Resolution by preparative TLC gave the pure component having R_f 0.32 whose NMR spectrum indicated it to be a single compound (**6** or **7**, most probably the *E* isomer; see Discussion); it was obtained as an oil: yield 46 mg (28%); $[\alpha]_D{}^{20}$ −30° (*c* 0.5, dichloromethane); ν_{max}^{film} 3030, 2950, 2850, 1750 (strong, C=O), 1670 cm^{-1} (C=C); *m.e* 378 (0.5, M$^{+\cdot}$), 336 (1, M$^{+\cdot}$ − CH$_2$CO), 318 (1, M$^{+\cdot}$ − AcOH), 276 [2.5, EtO$_2$CC(OAc)=CHCH$_2$OCCOPh], 272 (5, M$^{+\cdot}$ − PhCHO), 230 (11, 272 − CH$_2$CO), 229 (78, M$^{+\cdot}$ − 149), 227 [9, EtO$_2$CC(OAc)=CHCH=CHOAc$^{+\cdot}$ − ·CH$_3$], 223 (1.5), 221 (1.5, AcOCHCH$_2$OCHPhOCH$^+$), 200 (1), 188 (6.5), 187 (69, 229 − CH$_2$CO), 185 [2, EtO$_2$CC(OAc)=CHC≡O$^+$], 170 (4, 272 − AcO-CH$_2$CHO), 157· [7, EtO$_2$CC(OAc)=CH$^+$], 149 (73, PhCH=O+-CH$_2$CHO), 145 (62), 115 (7, 221 − PhCHO), 107 (32, PhC$^+$HOH), 106 (6, PhCHO$^{+\cdot}$), 105 (21, PhCO$^+$), 91 (13, C$_7$H$_7$$^+$), 84 (4, 157 − · CO$_2$Et), 77 (8, Ph$^+$), 43 (100, Ac$^+$).

The homogeneous product, R_f 0.28, yield 40 mg (25%), was an oil, $[\alpha]_D{}^{20}$ −62° (*c* 0.25, dichloromethane), ν_{max}^{film} 3000, 2950, 2850, 1770, 1740, and 1675 cm^{-1}, shown by its NMR spectrum to comprise a *mixture of the enol ester 3-acetate* **5** *already described plus a second* compound (**7** or **6**, most probably the *Z* isomer; see Discussion) in ~7:13 ratio. For this second enol ester 2-acetate **7** (or **6**) the estimated $[\alpha]_D{}^{20}$ was −84° (dichloromethane). The mass spectrum [*m/e* 378 (0.5, M$^{+\cdot}$)] was essentially a composite of those observed for **5** and the faster migrating isomer (**6**) of **7**.

The net composition of the product of thermolysis of **2** was approximately 20% **5** (R_f 0.28), 45% **6** (R_f 0.32), and 35% **7** (R_f 0.28), as *estimated by NMR spectral integration of the original mixture of* reaction products.

Registry No.—**1**, 35926-81-9; **2**, 35813-11-7; ethyl 2-amino-4,6-*O*-benzylidene-2-deoxy-D-gluconate hydrochloride, 40149-90-4.

References and Notes

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