

The Photochemistry of Ketones derived from Carbohydrates. Part 8.¹ Type I Cleavage of 1,2:4,5-Di-*O*-isopropylidene- β -*D*-erythro-2,3-hexodiulose-2,6-pyranose: a Synthesis of *D*-Ribulose from *D*-Fructose

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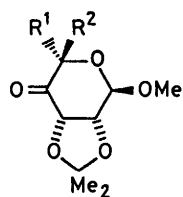
Solutions of di-*O*-isopropylidene- β -*D*-erythro-2,3-hexodiulose-2,6-pyranose (8) in various solvents decarbonylate upon irradiation with u.v. light to give an anomeric mixture of 1,2:3,4-di-*O*-isopropylidene-*D*-ribulose (10) and (11), accompanied by variable amounts of the unstable olefin (12) and the aldehyde (13). Compound (13) was found to be a thermal breakdown product from the olefin (12). The photoproduct yields were sensitive to the solvent polarity. The furanose derivatives (10) and (11) were produced with a 1.2 : 1.0 ratio in 30, 35, and 45% yields in methyl cyanide, benzene, and *n*-hexane, respectively. The *D*-ribulose derivatives (10) and (11) were produced on a preparative scale, isolated free from (12) and (13) by distillation, and hydrolysed to *D*-ribulose.

EARLIER we showed that solutions of pyranos-2-(or 4)-ulose derivatives are photodecarbonylated when irradiated with u.v. light. The C-5 epimeric 4-ulose derivatives (1) and (2) ring-contracted to furanosides (3)² whereas the anomers (4) and (5) of the 2-ulose derivative gave furanosides (6) and olefin (7).³ It is our intention to investigate the dependence of this photoreaction upon structure and also where possible, to exploit it for synthetic purposes.

could be induced then useful *D*-ribulose derivatives would result.

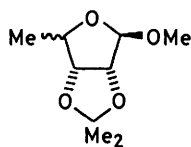
RESULTS AND DISCUSSION

U.v. irradiation of a solution of ulose (8) in benzene with a 450-W medium-pressure lamp gave four products (a), (b), (c), and (d), which were detectable by g.l.c. with R_d values 0.40, 0.59, 0.87, and 1.00, respectively, on Carbowax columns. On SE30 columns compounds (a)

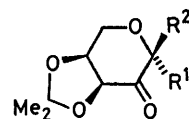


(1) $R^1 = \text{Me}, R^2 = \text{H}$

(2) $R^1 = \text{H}, R^2 = \text{Me}$

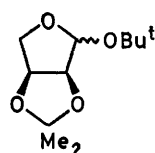


(3)

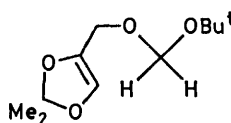


(4) $R^1 = \text{OBu}^t, R^2 = \text{H}$

(5) $R^1 = \text{H}, R^2 = \text{OBu}^t$



(6)



(7)

Although pyranosid-2-ulose derivatives are readily available, derivatives of this class, which are suitable for photochemical studies, are not so abundant since it is essential that the α -carbon atom in the aglycone does not carry a hydrogen atom. Hydrogen atoms at this site are abstracted in a Norrish Type II⁴ reaction by the carbonyl group at C-2.⁵ We overcame this problem in our earlier studies³ by using *t*-butyl glycoside derivatives. In this paper we turned our attention to the 3-ulose derivative (8) which possesses the cyclic ketone structure related to that of a pyranos-2-ulose, and contains no hydrogen atoms sterically accessible to the excited carbonyl group. This compound was of particular interest since it is readily available⁶ from an inexpensive *D*-fructose precursor and if ring-contraction

and (b) had identical retention times and so did compounds (c) and (d). Consequently analysis on the latter stationary phase gave an over-simplified picture of the reaction.⁷

In several separate experiments in benzene the yields of (b) and (d), based upon the amount of (8) which had undergone reaction, were consistently 19 and 16% respectively, whereas the amounts of (a) and (c) formed were variable, being dependent upon the period of irradiation. The yield of the former reached a maximum of 40% and the latter *ca.* 10%, when 50% of (8) had undergone reaction. Compounds (a) and (c) were both destroyed upon prolonged irradiation. Furthermore it was noted that the amounts of (b) and (d) remained constant after u.v. irradiation had ceased, whereas the

TABLE I

The 100 MHz n.m.r. parameters for the α - and β -anomers of 1,2:3,4-di-*O*-isopropylidene-D-ribulose [(11) and (10)] in CDCl₃^a

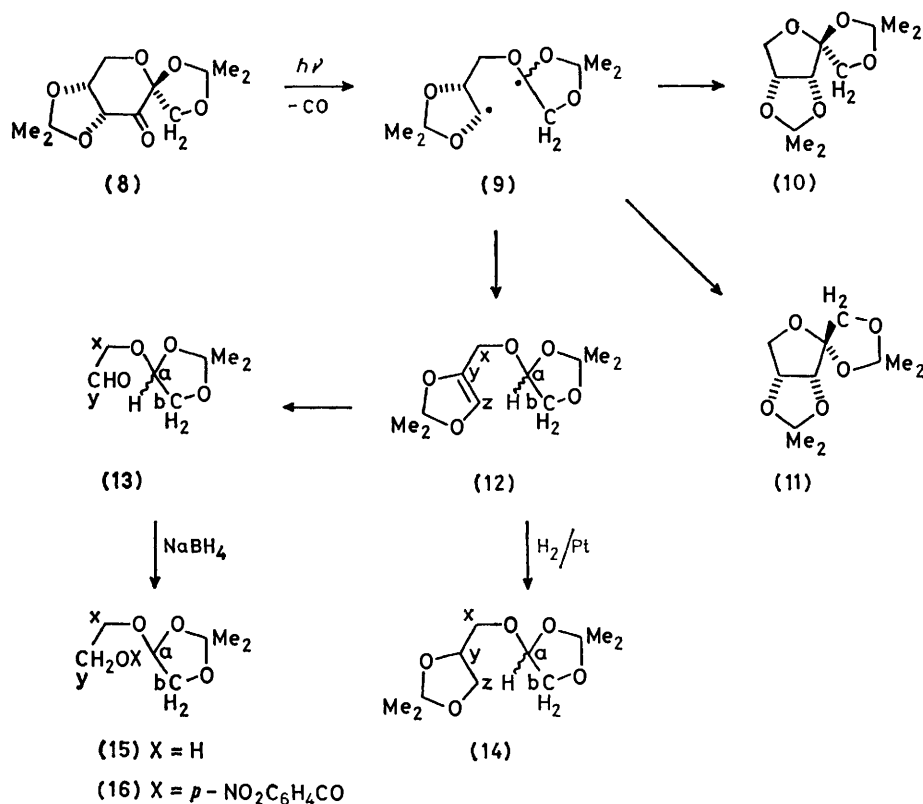
Compound	H-1	H-1'	H-3	H-4	H-5	H-5'	Me ₂ C
(b) [<i>i.e.</i> (10)]	4.24 (d, <i>J</i> _{1,1'} 8.5)	4.02 (d, <i>J</i> _{1',1} 8.5)	4.52 (d, <i>J</i> _{3,4} 6.0)	4.82 (ddd, ^b <i>J</i> _{4,3} 6.0, <i>J</i> _{4,5'} 1.0)	3.86 (dd, ^b <i>J</i> _{5,5'} 10.0, <i>J</i> _{5,4} 3.0)	3.91 (dd, <i>J</i> _{5',5} 10.0, <i>J</i> _{5',4} 1.0)	1.44 (s), 1.40 (s), 1.36 (s), 1.30 (s)
(d) [<i>i.e.</i> (11)]	4.01 (d, <i>J</i> _{1,1'} 8.5)	3.99 (d, <i>J</i> _{1',1} 8.5)	4.55 (d, ^b <i>J</i> _{3,4} 6.5)	4.75 (ddd, ^b <i>J</i> _{4,3} 6.5, <i>J</i> _{4,5'} 3.5, <i>J</i> _{4,5} 4.5)		3.98 (m)	1.53 (s), 1.46 (s), 1.39 (s), 1.32 (s)

^a Chemical shifts δ /p.p.m., *J* in Hz. ^b Double-resonance studies confirmed these coupling patterns.

concentration of (c) decreased and the concentration of (a) underwent an erratic increase.

The four products were initially isolated by collection from g.l.c., which was straightforward for compounds (b) and (d); for compounds (a) and (c), however, collection had to be made at -70°C under anhydrous conditions, because of their instability.

than (b) indicating the α -configuration (11) for the former and the β -configuration (10) for the latter. This was confirmed by the ¹H n.m.r. spectra. The two C-1 protons of isomer (d), and one of them from isomer (b) gave signals in the region δ 4.02–3.99, whereas the remaining C-1 proton from (b) appeared at lower field (δ 4.24). Models of (10) and (11) show that of the four



Compounds (b) ($[\alpha]_D^{21} -110^\circ$, Me₂CO) and (d) ($[\alpha]_D^{21} -5.7^\circ$, CHCl₃) had the same empirical formula, C₁₁H₁₈O₅ [elemental analysis and *m/e* 215 (*M* - 15)] and they exhibited neither carbonyl nor hydroxy i.r. absorption bands. Upon acid hydrolysis they yielded a reducing sugar, which was characterised as D-ribulose by paper chromatography, and as the *o*-nitrophenylhydrazone derivative. These findings, the ¹H n.m.r. parameters (Table I), and the ¹³C spectra, indicated that (b) and (d) were anomers of 1,2:3,4-di-*O*-isopropylidene-*erythro*-pentulose (10) and (11). Since both anomers had been produced the anomeric configuration could be assigned. The optical rotation of compound (d) is more positive

C-1 protons in the two isomers, only one is situated close enough to an unshared pair of electrons (*i.e.* on O-3) to deshield it, and this occurred in structure (10) of the β -anomer. This result also permits the previously known ⁸ di-*O*-isopropylidene-D-ribulose derivative to be assigned the β -configuration.

Compound (c) was shown to be the olefin (12) from i.r., m.s., ¹H and ¹³C n.m.r. spectral measurements. Diagnostic signals in the ¹³C spectrum (Table 2) were produced by the vinylic carbons C_Y and C_Z, which resonated at δ 135.5 and at 125.8, the acetal carbon C_a, which appeared at 99.9, and the two Me₂C groupings. One of these, which formed part of a dioxolan ring, gave

TABLE 2

Compound (12)	¹³ C N.m.r. parameters (δ in p.p.m. from SiMe ₄) for compounds (12), (13), and (15)							
	C _a	C _b	C _x	C _y	C _z	CMe ₂		
(12)	99.9 (d)	70.7 (t)	59.0 (t)	135.5 (s)	125.8 (d)	110.9 (s), 115.4 (s)	26.6, 25.3 ^a	27.0
(13)	101.6 (d)	70.7	72.9	199.4 (d)		111.4 (s)	26.3 (q)	26.8 (q)
(15)	102.0 (d)	70.7 (t)	70.5 ^b (t)	62.2 ^b (t)		110.9 (s)	26.4 (q)	26.8 (q)

^a Coincident signals for two methyl groups. ^b These assignments could be interchanged.

resonances at δ 110.9, 26.6, and 27.0 whereas the other, which formed part of a dioxole ring, gave coincidental signals at δ 25.3 for the two methyl groups and a signal at δ 115.4 for the quaternary carbon atom. There were also resonances at δ 70.7 and 59.0 due to C_b and C_x respectively. These assignments and those of the other signals were facilitated by off-resonance spectral measurements and by specific isotopic labelling at C-1.⁹

The ¹H n.m.r. spectrum of (12) was analysed by first-order methods (Table 3). The signals for the methylene protons at C_x were both long-range-coupled (⁴J) by 0.5 Hz to the vinylic proton H_z and signals for the methylene protons at C_b were vicinally coupled to the acetal proton H_a (*J* 2.5 and 4.5 Hz). The isopropylidene group of the dioxole ring gave rise to a six-proton singlet, whereas this group in the dioxolan ring gave two singlets.

Chemical evidence for structure (12) was obtained by catalytic reduction. One mole equivalent of hydrogen was absorbed to give the saturated compound (14) (i.r. spectrum), which was stable. It had a carbon and hydrogen elemental composition which was correct for compound (14) and its ¹H n.m.r. spectrum exhibited four singlets for two isopropylidene groups, a complex multiplet in the range δ 4.5—3.5 for seven protons, and a doublet of doublets for the acetal proton at C_a.

Product (a), which was particularly unstable when isolated from the photolysate, was found to have the structure (13). The aldehydic function was indicated by ν_{max} at 1740 cm⁻¹, the low-field proton triplet at δ 9.80 (*J* 0.7 Hz) and a ¹³C signal at δ 199.4. The ¹³C n.m.r. spectrum (Table 2) further showed signals at δ 111.4, 26.3, and 26.8 due to one isopropylidene residue, at δ 101.6 for the acetal carbon C_a and at δ 70.7 and 72.9 for C_b and C_x respectively. The ¹H n.m.r. spectrum, which was amenable to the first-order analysis recorded in Table 3, showed the presence of a CH₂CHO group

attached through an oxygen atom to a dioxolan ring, as shown in structure (13).

This structure was verified by reducing it with sodium borohydride. The resulting alcohol was formulated as (15) from its elemental analysis, and m.s., ¹H, and ¹³C n.m.r. spectra. The ¹H n.m.r. spectrum (Table 3) gave resolved signals for the C_b methylene protons, H_a, and the isopropylidene methyls, but the signals for the other four hydrogens were unresolved. Esterification of (15) yielded the crystalline *p*-nitrobenzoate (16), the 220-MHz n.m.r. spectrum of which was resolved (Table 3) because the protons of the C_y methylene group were now deshielded.

The photoproducts probably arise from the same decarboxylated diradical (9). Ring-closure affords (10) and (11), whereas intramolecular hydrogen atom abstraction within (9) gives olefins (12), which possess a chiral acetal carbon atom. Since the olefinic fraction was optically active the hydrogen transfer must be stereoselective. However the degree of selectivity is unknown since the amount of racemate formed has not been determined.

From these results it is clear that the photochemistry of the 3-ulose derivative (8) is closer to that of the 2-ulose derivatives [(4) and (5)³] than that of the 4-ulose derivatives [(1) and (2)²], presumably because the carbonyl group in (8) is adjacent to the anomeric centre.

Olefins (12) were unstable, and g.l.c.-purified samples of this fraction were found to undergo chemical change even at 0 °C under nitrogen. The only compound identified in the decomposed residue was aldehyde (13), which was difficult to isolate because it also underwent thermal decomposition. In twenty separate experiments, in which (12) was thermally decomposed under nitrogen in sealed tubes, the yield of (13) never exceeded

TABLE 3

The 100 MHz ¹H n.m.r. parameters for compounds (12) and (13) in CDCl₃^a

Compound	H _a	H _b	H _{b'}	H _x	H _{x'}	H _y	H _z ^b	Me ₂
(12)	5.18 (dd)	3.90 (dd, <i>J</i> _{b,b'} 9.0, <i>J</i> _{b,a} 2.5)	3.80 (dd, <i>J</i> _{b',b} 9.0, <i>J</i> _{b',a} 4.5)	4.20 (dd, <i>J</i> _{x,x'} 13.0, <i>J</i> _{x,z} 0.5)	4.06 (dd, <i>J</i> _{x',x} 13.0, <i>J</i> _{x',z} 0.5)		6.03 (br s)	1.39 (s), 1.46 (s), 1.54 (s) ^c
(13)	5.34 (dd, <i>J</i> _{a,b} 2.8, <i>J</i> _{a,b'} 4.0)	4.08 (dd, <i>J</i> _{b,b'} 9.5, <i>J</i> _{b,a} 2.8)	4.16 (dd, <i>J</i> _{b',b} 9.5, <i>J</i> _{b',a} 4.0)	4.26 (d, <i>J</i> _{x,y} 0.7)	4.22 (d, <i>J</i> _{x',y} 0.7)	9.80 (t, <i>J</i> _{y,x} 0.7, <i>J</i> _{y,x'} 0.7)		1.40 (s), 1.50 (s)
(15) ^d	5.24 (dd, <i>J</i> _{a,b} 2.0, <i>J</i> _{a,b'} 4.0)	3.96 (dd, <i>J</i> _{b,b'} 9.5, <i>J</i> _{b,a} 2.0)	4.08 (dd, <i>J</i> _{b',b} 9.5, <i>J</i> _{b',a} 4.0)	3.6—3.8				1.40 (s), 1.50 (s)
(16) ^e	4.9 (dd, <i>J</i> _{a,b} 2.8, <i>J</i> _{a,b'} 4.5)	3.90 (dd, <i>J</i> _{b,b'} 8.8, <i>J</i> _{b,a} 2.8)	3.76 (dd, <i>J</i> _{b',b} 8.8, <i>J</i> _{b',a} 4.5)	3.80 (dt, <i>J</i> _{x,x'} 11.5, <i>J</i> _{x,y} 4.8, <i>J</i> _{x,y'} 4.8)	3.42 (dt, <i>J</i> _{x',x} 11.5, <i>J</i> _{x',y} 4.8, <i>J</i> _{x',y'} 4.8)	4.26 (t) (<i>J</i> 4.8) (<i>J</i> 4.8)	4.26 (t)	1.35 (s), 1.46 (s)

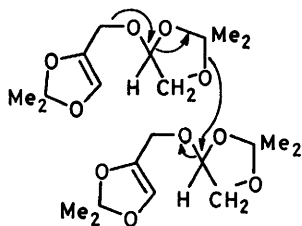
^a Chemical shifts δ /p.p.m., *J* in Hz. ^b H_y in compounds (15) and (16). ^c Intensity 6H. ^d OH signal also present. ^e Nitrophenyl signal also present.

50% (3 experiments) and was sometimes as low as 15% (3 experiments).

It is probable that these thermal transformations are responsible for the variable yields of (12) and (13) produced during the irradiation of ketone (8). A bimolecular mechanism is possible for the transformation of (12) into (13) as shown in the Scheme and this would afford (13) in a 50% yield as a maximum, in accord with our findings. Experiments with a labelled 3-ulose derivative are being conducted to verify this point.

Solvents also affected the photochemical reaction. Total yields of furanosides increased in solvents of low polarity. In methyl cyanide, benzene, and n-hexane the furanose derivatives (10) and (11) were produced in 30, 35, and 45% yields respectively, whereas the amount of olefins (12) formed decreased correspondingly. It is possible that the hydrogen-transfer reaction becomes favoured in solvents of high polarity owing to the transition state possessing some ionic character.¹⁰

Yields of (10) and (11) were unaffected by the temperature at which the solution of (8) was irradiated and by the wavelength of the incident light.



SCHEME

Formation on a preparative scale of an anomeric mixture of 1,2:3,4-di-*O*-isopropylidene-*D*-ribulose (10) and (11) free from compounds (12) and (13) was readily achieved by irradiating (8) in 30-g batches with u.v. light until (8) had undergone complete reaction and (12) and (13) had been decomposed. The crude product obtained after solvent evaporation was distilled to give (10) and (11) in 45% yield from n-hexane solution, and 35% from benzene solution. Although the yield of the ribulose derivatives (10) and (11) was greater in n-hexane, the higher solubility of (8) in benzene makes it the solvent of choice for large-scale reactions. This method of synthesis of *D*-ribulose derivatives compares favourably with the one in current use which is based upon the isomerisation of *D*-arabinose.⁸

EXPERIMENTAL

Unless stated otherwise optical rotations were measured on chloroform solutions with a Bellingham and Stanley Polarimeter; u.v.-absorption spectra were measured with a Perkin-Elmer 402 spectrometer on ethanol solutions; and i.r. spectra were measured on solids dispersed in potassium bromide discs and on gums smeared on sodium chloride plates, with a Perkin-Elmer Infracord model 137. ¹H N.m.r. spectra were measured with Varian Associates EM360 or HA 220 MH instruments, or a JEOL MH100 instrument. ¹³C N.m.r. spectra were measured on chloroform solutions with tetramethylsilane as internal reference

on a JEOL FX60 instrument operating in the Fourier-transform mode.

Column chromatography was carried out on Kieselgel 60 (70–230 mesh) and t.l.c. on Kieselgel G₂₅₄. Varian Aerograph models 2700 with flame-ionisation and t.c. detectors were used for g.l.c. with the following columns: (1) 5 ft × $\frac{1}{8}$ in, 5% OV101; (2) 8 ft × $\frac{1}{8}$ in, 5% Carbowax 20M; (3) 10 ft × $\frac{1}{8}$ in, 10% SE30; (4) 20 ft × $\frac{3}{8}$ in, 15% SE52; and (5) 10 ft × $\frac{3}{8}$ in, 20% SE30. Retention times of a component are expressed as R_t in minutes, or relative to a compound X, when R_X is used.

U.v. irradiation of small volumes of solutions were carried out in either quartz or Pyrex tubes attached to the surface of a quartz, water-cooled, photolysis well at a distance of 25 mm from the centre of a 450-W Hanovia 500 UVS medium-pressure mercury lamp which was situated inside the well. Large volumes of solutions were irradiated in the annular space formed between the quartz well and an outer vessel.

Irradiation of 1,2:4,5-di-O-isopropylidene-β-D-erythro-hexodiulose-2,6-pyranose (8).—In a typical photolysis ketone (8) (5 g) was irradiated in benzene (150 ml) for 1.5 h with unfiltered light or through Pyrex for 2.5 h, when g.l.c. analysis on column 2 at 168 °C showed that <5% of unreacted (8) remained and four compounds with relative retention times of 0.40 (a), 0.59 (b), 0.87 (c), and 1.00 (d) were formed. Peak areas of (a) and (c) were found to vary in otherwise identical experiments. The solvent was evaporated and the residue distilled (0.3 mmHg at 90 °C) to give an oil containing the four products, in which the amount of (a) had increased and (c) had decreased. In some experiments the distillate was stored at 22 °C and during this period the composition of the oil changed. After storage for 24 h the amount of (c) decreased and this was usually accompanied by an increase in (a), while the amounts of (b) and (d) remained unchanged. After a further 3–4 d storage loss of (c) was complete and at this stage the concentration of (a) had usually reached a maximum. The four products were isolated in pure form by preparative g.l.c. on column 2 at 170 °C.

Compound (b) was 1,2:3,4-di-*O*-isopropylidene-β-*D*-erythro-pentulose (10), $[\alpha]_D^{22} -110^\circ$ (*c* 1.0, Me₂CO); *m/e* 215 ($M^+ - 15$); δ_C 111.49, (80.24, 84.85), (69.26, 71.27), 112.59, 112.79, 25.05 (two coincident signals), 26.31, and 26.50; C-2 (C-3, C-4), (C-1, C-5), and 2 × CMe₂; the assignments of the chemical shifts within parentheses are interchangeable. The ¹H n.m.r. parameters are recorded in Table 1 (Found: C, 57.48; H, 7.93. C₁₁H₁₈O₅ requires C, 57.38; H, 7.88%); lit.⁸ $[\alpha]_D^{22} -104^\circ$ (Me₂CO) and n.m.r. signals identical to those reported here.

Acid hydrolysis of a small sample of (b) gave a reducing sugar with an R_F identical to authentic *D*-ribulose on paper chromatography irrigated with butan-1-ol-acetic acid-water (4:1:5 v/v). Treatment of the hydrolysate with *o*-nitrophenylhydrazine gave *D*-ribulose *o*-nitrophenylhydrazone, m.p. 168 °C (lit.⁸ m.p. 168–169 °C).

Compound (d) was 1,2:3,4-di-*O*-isopropylidene-α-*D*-erythro-pentulose (11), m.p. 87–89 °C; $[\alpha]_D^{22} -5.7^\circ$ (*c*, 1.0); *m/e* 215 ($M^+ - 15$); δ_C 108.89, (78.74, 81.08), (69.84, 71.40), 112.01, 115.45, 26.05 (three coincident signals), and 26.76; C-2, (C-3, C-4), (C-1, C-5), and 2 × CMe₂; the assignments of the chemical shifts within parentheses are interchangeable. The ¹H n.m.r. parameters are recorded in Table 1 (Found: C, 57.34; H, 7.80. C₁₁H₁₈O₅ requires C, 57.38; H, 7.88%). Acid hydrolysis of (d), as described for (b),

gave D-ribulose, identified by its R_F and *o*-nitrophenylhydrazine (m.p. 167–169 °C).

Compound (c) was a thermally unstable oil. Consequently it was collected in tubes cooled to –70 °C and protected from the air by a drying agent. It was shown to be 4-(2,2-dimethyl-1,3-dioxolan-4-yloxymethyl)-2,2-dimethyl-2H-dioxole (12); $[\alpha]_D^{22} -26.7^\circ$ (*c* 1.8); ν_{\max} , 1 675 cm^{-1} (C=C); *m/e* 230 (M^+) and 215 ($M^+ - 15$); ^{13}C and ^1H n.m.r. spectral parameters are recorded in Tables 2 and 3, respectively.

Product (12) (74 mg) was reduced in ethanol over Adams catalyst (20 mg) in an atmosphere of hydrogen. After 2 h, g.l.c. analysis on column 3 at 130 °C showed that the olefin (12) (R_t 9.5 min) had completely reacted and that one product (R_t 12.5 min) had been formed. It was isolated by g.l.c. on column 5 at 130 °C and formulated as 4-(2,2-dimethyl-1,3-dioxolan-4-yloxymethyl)-2,2-dimethyl-2H-dioxolan (14); δ (100 MHz) 5.25 (dd, $J_{a,b}$ 2.0, $J_{a,1}$ 4.0 Hz), 3.5–4.5 (m, 7 H), 1.32, 1.36, 1.40, 1.48 (4 s, 4 Me) (Found: C, 56.6; H, 8.85. $\text{C}_{11}\text{H}_{20}\text{O}_5$ requires C, 56.88; H, 8.68%).

Product (a) was also unstable, but it could be isolated in small amounts from g.l.c. under anhydrous conditions at –70 °C. It was characterised as 4-(formylmethoxy)-2,2-dimethyldioxolan (13); ν_{\max} , 1 740 cm^{-1} (CHO); *m/e* 160 (M),⁺ 145 ($M^+ - \text{Me}$), and 101 ($[\text{Me}_2\text{COCH}_2\text{CHO}]^+$); ^{13}C and ^1H n.m.r. spectral parameters are recorded in Tables 2 and 3, respectively. Reduction of the aldehyde (13) (100 mg) with sodium borohydride (60 mg) in ethanol (5 ml) gave, after 2 h, a solution which contained a product (R_t 10.9 min) but no starting material (13) (R_t 6.0 min on column 4 at 174 °C). Work-up gave the alcohol (15) (81 mg); $[\alpha]_D^{22} -13.5$ (*c* 6.8); ν_{\max} , 3 500 cm^{-1} (OH); ^{13}C and ^1H n.m.r. spectral parameters are recorded in Tables 2 and 3, respectively (Found: C, 51.8; H, 8.65. $\text{C}_7\text{H}_{14}\text{O}_4$ requires C, 51.84; H, 8.70%). Alcohol (15) (50 mg) was treated with *p*-nitrobenzoyl chloride (100 mg) in dry pyridine (5 ml). Work-up, followed by product isolation using preparative layer chromatography on silica gel, gave the *p*-nitrobenzoate (16) (47 mg), m.p. 81 °C; ν_{\max} , 1 750 cm^{-1} (C=O); *m/e* 296 ($M^+ - 15$). The ^1H n.m.r. parameters are recorded in Table 3.

Decomposition of the Dioxole (12).—Twenty pure samples (ca. 20 mg) of olefin (12) were placed in sealed tubes under nitrogen. Ten were stored at 22 °C for 5 d and ten for 10 min at 160 °C. G.l.c. analysis, on column 2, of these stored samples showed complete decomposition of (12) and the appearance of a peak with a retention time identical to that of aldehyde (13). The ^1H n.m.r. spectra of these samples exhibited an aldehydic resonance at δ 9.84. These measurements indicated that the efficiency of the conversion of (12) into (13) ranged from 50 to 15%, but the different yields could not be correlated with temperature or any other identifiable reaction variable.

Decomposition of (12) was also induced by prolonged u.v.

irradiation, but this yielded polar products which were not identified.

Irradiations of the Diulose (8) in Benzene, n-Hexane, and Methyl Cyanide.—Solutions of the ketone (8) (0.1 g) as 0.3% solutions in methyl cyanide, benzene, or n-hexane were placed in quartz tubes and irradiated with the full mercury arc at 22 °C until g.l.c. analysis (on column 1 at 135 °C) showed that at least 95% of (8) had undergone reaction and all the olefin (12) had been decomposed. At this stage the furanose derivatives (10) and (11) were present in 30, 35, and 45% yields, respectively, in the three solvents. The best yield of olefin (12) was formed in methyl cyanide. When 40% of (8) had undergone reaction in this solvent, compound (12) accounted for approximately 60% of reacted (8).

Identical results were obtained when the irradiations were carried out with u.v. light filtered through Pyrex, or with light of wavelength 253 nm from a lamp in a Rayonet Irradiator.

Irradiation of the Diulose (8) at 60 °C.—Solutions of compound (8) in benzene (0.3%) were placed in sealed Pyrex tubes, maintained at 60 °C in a water-bath, and irradiated. Analysis of the photolysate by g.l.c. showed that the product spectrum was identical to that obtained in irradiations carried out at 22 °C.

Large-scale Irradiations of the Diulose (8).—Solutions of the diulose derivative (8) (30 g) in n-hexane (7 l) or benzene (3 l) were agitated by the passage of nitrogen gas and irradiated until all the diulose (8), olefin (12), and aldehyde (13) had undergone reaction (ca. 15 h and 10 h in the respective solvents). The solvent was evaporated off and the residual oil distilled under reduced pressure to give a mixture of (10) and (11), in yields of 45 and 35% in the respective solvents. The anomers (10) and (11) could be separated, if required pure, by chromatography on silica gel [CH_2Cl_2 -EtOAc (3 : 1)].

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