

## The Photochemistry of Ketones Derived from Carbohydrates. Part IV.<sup>1</sup> Photochemical Additions of 2,3-Dimethylbut-2-ene to 1,5-Anhydrohex-enuloses

By Peter M. Collins\* and Brian R. Whitton, Chemistry Department, Birkbeck College, University of London, Malet Street, London WC1E 7HX

Irradiation of 1,5-anhydro-4,6-*O*-benzylidene-1,2-dideoxy-D-*threo*-hex-1-en-3-ulose (1) in 2,3-dimethylbut-2-ene with u.v. light afforded three cyclobutane adducts, namely 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-1,2-*C*-tetramethylethylene-D-hex-3-ulose with the (1*S*)-*xylo*- (2), (1*R*)-*xylo*- (3), and (1*R*)-*lyxo*- (4) structures, and a dimer, for which structure (5b) or (5c) has been proposed. Similar treatment of the 1,5-anhydro-*erythro*-enulose derivative (9) also gave adducts, two of which [(10) and (11)] have been isolated and characterised as the (1*S*)-*ribo*- and (1*R*)-*ribo*-1,5-anhydro-D-hexulose derivatives.

PHOTOCHEMICAL dimerisations of  $\alpha\beta$ -unsaturated ketones and addition of olefins to the double bonds of such enones to give cyclobutane derivatives are well documented.<sup>2</sup> However, reactions with cyclic enones possessing an endocyclic oxygen atom have been little studied<sup>3,4</sup> and no report has appeared of work in which carbohydrate substrates have been used. Furthermore, in only a few cases has a study of the stereochemistry of the cyclobutane adducts been made where configurational sites exist in the enone reactant molecule. Therefore it appeared that carbohydrate derivatives would be good models with which to investigate this aspect of these additions. Also recent reports<sup>5</sup> concerning compounds in which pyranoid rings were fused to cyclopropane rings suggested that this photochemical annulation reaction might be used to produce homologues of this class of branched-chain sugars.<sup>6</sup>

Since the preliminary report<sup>7</sup> of this work appeared, Gero and his co-workers<sup>8</sup> have described a cyclobutane

sugar derivative which they prepared by photochemical addition of an olefinic derivative to an unsaturated sugar.

### RESULTS AND DISCUSSION

The first enone studied was 1,5-anhydro-4,6-*O*-benzylidene-1,2-dideoxy-D-*threo*-hex-1-en-3-ulose (1).<sup>9</sup> A preliminary experiment showed that irradiation of this compound in dichloromethane containing cyclopentene rapidly gave a mixture of ketonic products (6). The n.m.r. spectrum of this material indicated that it was an isomeric mixture, but the signals in the high-field region were so complex that another olefin was sought which would afford products with a relatively simple

<sup>5</sup> J. S. Brimacombe, M. E. Evans, E. J. Forbes, A. B. Foster, and J. M. Webber, *Carbohydrate Res.*, 1967, **4**, 239; E. L. Albano, D. Horton and J. H. Lauterbach, *Chem. Comm.* 1968, 357; *Carbohydrate Res.*, 1969, **9**, 149; B. Fraser-Reid and B. Radatus, *Canad. J. Chem.*, 1970, **48**, 2146; W. Meyer zu Reckendorf and U. Kamprath-Scholtz, *Angew. Chem. Internat. Edn.*, 1968, **7**, 143; D. Horton and C. G. Tindall, jun., *Carbohydrate Res.*, 1970, **15**, 215; P. M. Collins, D. Gardiner, S. Kumar, and W. G. Overend, *Chem. Comm.*, 1970, 1433.

<sup>6</sup> H. Grisebach and R. Schmid, *Angew. Chem. Internat. Edn.*, 1972, **11**, 159.

<sup>7</sup> P. M. Collins and B. R. Whitton, *Carbohydrate Res.*, 1972, **21**, 487.

<sup>8</sup> R. Beugelmaus, J. Fourney, S. Gero, M. LeGoff, D. Mercier, V. Ratovelomanana, and M. Janot, *Compt. rend. (C)*, 1972, 882.

<sup>9</sup> P. J. Beynon, P. M. Collins, P. T. Doganges, and W. G. Overend, *J. Chem. Soc. (C)*, 1966, 1131.

<sup>1</sup> Part III, P. M. Collins, P. Gupta, and R. Iyer, *J.C.S. Perkin I*, 1972, 1670.

<sup>2</sup> P. E. Eaton, *Accounts Chem. Res.*, 1968, **1**, 50; P. G. Bauslaugh, *Synthesis*, 1970, 287; P. de Mayo, *Accounts Chem. Res.*, 1971, **4**, 41.

<sup>3</sup> J. W. Hanifin and E. Cohen, *J. Amer. Chem. Soc.*, 1969, **91**, 4494.

<sup>4</sup> P. Yates and D. J. MacGregor, *Tetrahedron Letters*, 1969, 453.

spectrum. For this reason 2,3-dimethylbut-2-ene was selected to examine the scope of the reaction, before using more complex olefins that would have synthetic applications.<sup>10</sup>

decrease in the absorption at 266 nm showed that *ca.* 80% of the enone (1) had reacted. This was substantiated by (t.l.c.) examination of the gum obtained after solvent evaporation. Four products, A—D,

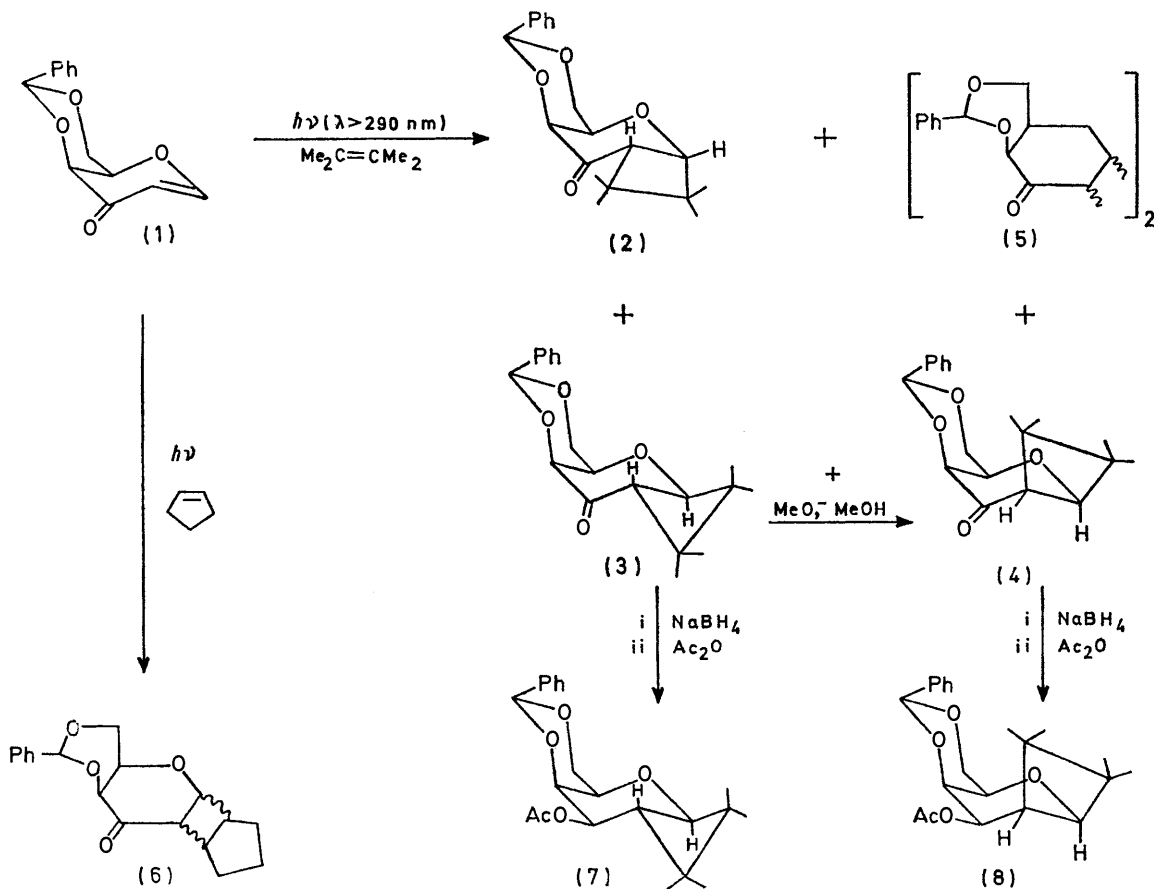
N.m.r. parameters ( $\delta$ ;  $J$  in Hz) for the cyclobutane derivatives measured at 60 or 220 MHz in  $C_6D_6$

Compound	H-1	H-2	H-4	H-5	H-6	H-6'	CMe (singlets)	PhCHO <sub>2</sub>
(2)	4.82(d) $J_{1,2}$ 5.5	2.89(d) $J_{2,1}$ 5.5	3.98(d) $J_{4,5}$ 2.5	3.53(m) $J_{5,6'}$ 2.0	4.12(q) $J_{6,5}$ 2.0	3.45(q) $J_{6',6}$ 13.0	1.27, 0.95, 0.87, 0.77	5.25(s)
(3)	3.64(d) $J_{1,2}$ 9.3	3.41(d) $J_{2,1}$ 9.3	3.93(d) $J_{4,5}$ 1.6	3.04(m) $J_{5,6'}$ 2.0	4.19(q) $J_{6,5}$ 1.0	3.46(q) $J_{6',6}$ 13.0	1.19, 1.07, 0.85, 0.71	5.30(s)
(4)	3.55(d) $J_{1,2}$ 4.5	2.42(d) $J_{2,1}$ 4.5	3.67(d) $J_{4,5}$ 1.5	2.70(m) $J_{5,6'}$ 2.0	4.15(q) $J_{6,5}$ 1.0	3.48(q) $J_{6',6}$ 13.0	1.28, 1.04, 0.94, 0.86	5.32(s)
(5) <sup>a,b</sup>	4.52(d) $J^*$ 6.5	3.60(d) $J^*$ 6.5	4.56(d) $J_{4,5}$ 2.0	4.07(m)	4.16(m)			5.69(s)
(10) <sup>a</sup>	3.40(d) $J_{1,2}$ 5.0	2.60(d) $J_{2,1}$ 5.0	3.88(d) $J_{4,5}$ 9.5	3.32(sex) $J_{5,6'}$ 10.0	3.42(t) $J_{6,5}$ 4.5	4.16(q) $J_{6',6}$ 10.0	1.06, 0.82, 0.82, 0.68	5.26(s)
(11) <sup>a</sup>	4.06(d) $J_{1,2}$ 9.0	2.43(q) $J_{2,1}$ 9.0 $J_{2,4}$ 1.0	3.66(q) $J_{4,5}$ 10.0 $J_{4,2}$ 1.0	3.3—3.5(m)		4.18(m)	1.11, 0.83, 0.81, 0.70	5.31(s)

Aromatic signals (m) appeared in the range 7.15—7.60.

<sup>a</sup> Measured at 220 MHz. <sup>b</sup> Measured in  $(CD_3)_2SO$ .

\* These doublets are simplified splitting patterns for the two parts of an AA'BB' system.



A 1% solution of the enone (1) (2.5 g) in dichloromethane containing 2,3-dimethylbut-2-ene (10 g) was irradiated in the annular space of a conventional photolysis well (diameter 5 cm) with light from a 450 W Hanovia medium-pressure mercury-arc lamp filtered through Pyrex ( $\lambda > 290\text{ nm}$ ) for 1.5 h, after which time a

having  $R_F$  values 0.85, 0.7, 0.5, and 0.15 respectively in system (ii) (see Experimental section) were formed in high yield. Column chromatography gave homogeneous (t.l.c.) samples of A as a syrup (0.28 g),  $[\alpha]_D^{25} +39^\circ$  ( $CHCl_3$ ); B (0.3 g), m.p. 127—128°,  $[\alpha]_D^{25} -28^\circ$ ;

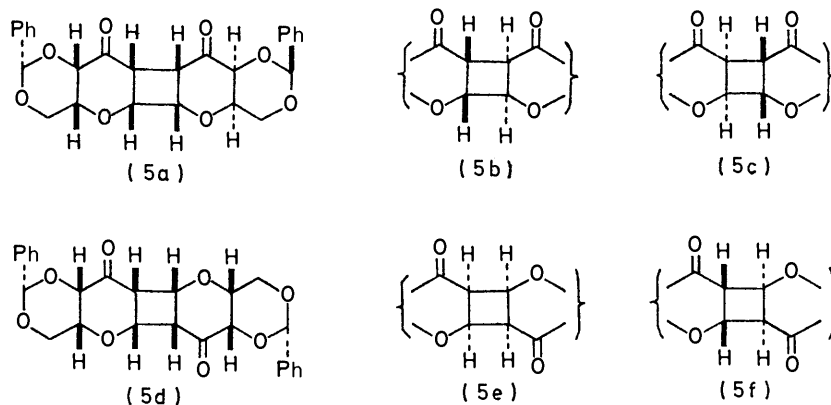
<sup>10</sup> P. G. Sammes, *Quart. Rev.*, 1970, **24**, 37.

and C (0.8 g), m.p. 124–125°,  $[\alpha]_D -136^\circ$ ; and a sample (0.2 g) composed of equal amounts of compounds A and B. Compounds A, B, and C were isomeric saturated ketones (*i.e.* 1,5-anhydro-2-deoxy-1,2-*C*-tetramethylethylenehex-3-ulose derivatives),  $\nu_{\max}$  1720  $\text{cm}^{-1}$  (enone absorptions at 1670 and 1600  $\text{cm}^{-1}$  absent), formed by addition of the 2,3-dimethylbut-2-ene to the carbon-carbon double bond of the 1,5-anhydrohexenulose. The adducts exhibited n.m.r. signals for 4,6-*O*-benzylidene residues, H-1, -2, -4, -5, -6 and -6' (ring protons) and four methyl singlets (Table), and compounds B and C had empirical formulae (elemental analysis and mass spectral molecular weights) expected for cyclobutane adducts.

The component D (0.9 g) also obtained from the column had m.p. 230–235° (decomp.),  $\nu_{\max}$  1725  $\text{cm}^{-1}$  (saturated ketone), and an empirical formula  $\text{C}_{26}\text{H}_{24}\text{O}_8$  [elemental

indicating that it possessed a *trans*-fused ring system. An alternative possibility, that the base had induced isomerisation at C-4, has been excluded by making comparisons with the adducts formed from the *erythro*-enone (9) (see later).

It seems most probable that the *trans*-fused isomer absent from the photolysate was (1*S*)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-1,2-*C*-tetramethylethylene-*D*-*lyxo*-hex-3-ulose. Thus, compound B must have the (1*R*)-*D*-*xylo*-structure (3), a conclusion substantiated by the large coupling between H-1 and H-2 (9.3 Hz), which is satisfactory for a compound existing in a conformation approximating to that depicted in (3). The alcohol formed by sodium borohydride reduction of B was acetylated and found to have the following informative couplings in its n.m.r. spectrum:  $J_{1,2}$  10.4,  $J_{2,3}$  11.6,  $J_{3,4}$  3.4, and  $J_{4,5}$  1.4 Hz. These provide excellent



analysis and molecular weight (Rast)]. It was a dimer of the type (5) which would be expected<sup>2</sup> from the u.v. irradiation of (1); it exhibited n.m.r. absorptions for benzylidene residues and twelve other protons. Further support for the dimeric nature of this compound was obtained when (1) was irradiated in the absence of olefin. Under these conditions the only detectable compound was D. On the other hand irradiation in the presence of a twenty-fold excess of dimethylbutene gave only trace amounts of D and a commensurate increase in yields of A, B, and C.

The detection of three 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-1,2-*C*-tetramethylethylenehex-3-uloses and a dimer, and a product balance better than 95% suggests that only three of the possible four stereoisomers that could be formed by addition of a symmetric olefin to enone (1) were produced in the photolysis. It was shown, by application of the test originally employed by Corey<sup>11</sup> to adducts A, B, and C, that two of these (A and C) were formed by *cis*-fusion between the pyranoid ring and the cyclobutane ring, since they were unaffected by base, and this conclusion is supported by the values found for  $J_{1,2}$  (Table). Compound B, however, was isomerised to C under these conditions,

evidence that the acetate has the (1*R*)-*D*-*galacto*-structure (7) and, consequently the ketone must have the (1*R*)-*D*-*xylo*-structure (3).

Since B [*i.e.* (3)] was transformed into C upon treatment with base, the latter must be the (1*R*)-*D*-*lyxo*-hex-3-ulose derivative (4). This conclusion was supported by the structure of the acetyl derivative (8) of the sodium borohydride reduction product formed from adduct (4). Acetate (8) gave a well resolved n.m.r. spectrum with  $J_{1,2}$  5.3,  $J_{2,3}$  9.0,  $J_{3,4}$  6.1, and  $J_{4,5}$  1.3 Hz, indicating<sup>12</sup> torsion angles of 35, 0, 29, and 83°. These are in reasonable agreement with the angles 30, 10, 27, and 72° measured from a molecular model of an acetate with structure (8). The alcoholic precursor of this acetate would be the one expected<sup>13</sup> to be formed by hydride attack upon the least hindered side of ketone (4). The remaining *cis*-isomer (A) must therefore have the (1*S*)-*D*-*xylo*-hex-3-ulose structure (2).

There are twenty structures possible for dimer D (which include some with the unlikely *trans*-fusion at C-1 and C-2) but, since the dimer was found to be stable in base, the fusion at C-1 and C-2 in both pyranoid rings must be *cis* and this reduced the number of struc-

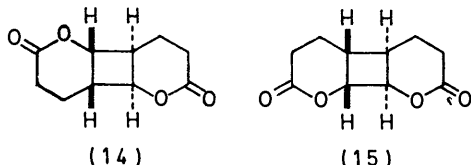
<sup>11</sup> E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, 1964, **86**, 5570.

<sup>12</sup> M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11; *J. Amer. Chem. Soc.*, 1963, **85**, 2870.

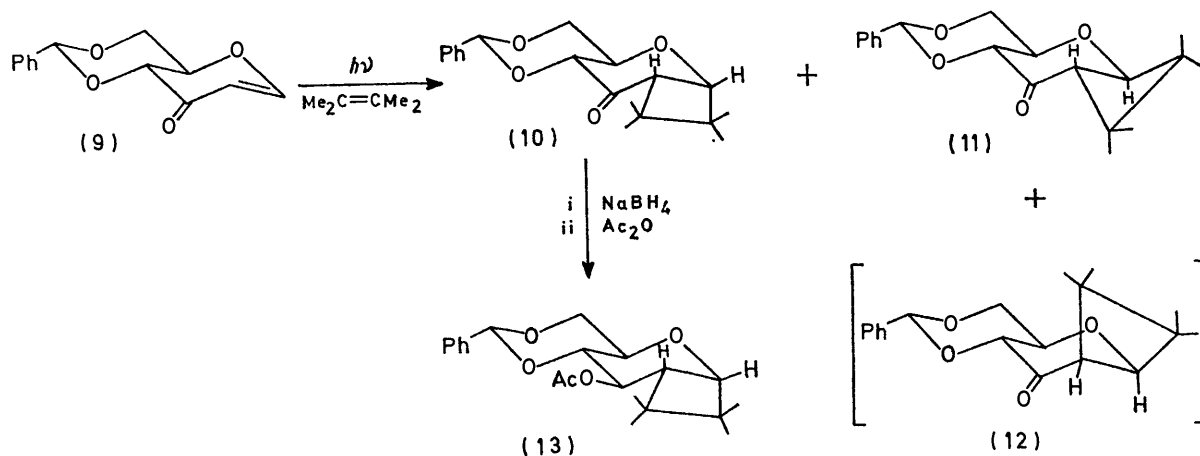
<sup>13</sup> P. M. Collins and W. G. Overend, *J. Chem. Soc.*, 1965, 1912.

tures to those of three head-to-head adducts (5a—c) and three head-to-tail adducts (5d—f). Four of these (5b—e) possess an axis of symmetry, but structures (5a) and (5f) are unsymmetric. Because the n.m.r. spectrum of dimer D is simple (*i.e.* each signal in the spectrum integrates for a pair of chemically equivalent protons, *e.g.* the two benzylidene methine protons appear as one sharp singlet, see Table) it must be one of the symmetric adducts.

It is difficult to distinguish between isomers of the types (5b and c) and (5d and e). A similar problem arose with lactones (14) and (15) formed from isomeric



biscarboxyethylcyclobutanediols, which were studied by Eaton.<sup>14</sup> An obvious difference between the head-to-head and the head-to-tail isomers is in the relationship



of the cyclobutane ring protons with each other. In the head-to-tail isomers [*e.g.* (5d and e) and (14)] each cyclobutane proton is adjacent to a chemically dissimilar proton, whereas in the head-to-head isomers [*e.g.* (5b and c) and (15)] each proton is next to one chemically similar proton and one that is dissimilar. Consequently a difference in n.m.r. spectra might be anticipated, but it is hard to predict this difference, because the four protons form an  $A_2X_2$  spin system.<sup>15</sup> Eaton<sup>14</sup> found that the cyclobutane protons of the head-to-tail lactone (14) formed a pattern of two quartets, whereas the head-to-head lactone (15) gave a pair of broadened doublets.

In the n.m.r. spectrum of compound D the chemically identical protons at the C-2 positions appeared ( $\delta$  3.60) as a slightly broadened doublet, as did those at the C-1

positions ( $\delta$  4.52). This pattern is similar to that which Eaton<sup>14</sup> found for his head-to-head adduct and might indicate that D has structure (5b or c). Unfortunately n.m.r. spectral data are not available for dimers with structures (5d or e). Support for this structural assignment was provided by the report,<sup>4</sup> that 2,3-dihydro-2,6-dimethyl-4-pyrone dimerises to give exclusively head-to-head adducts.

Thus although there are indications that compound D is one of the head-to-head isomers (5b or c) \* the assignment can only be tentative because, as Johnson<sup>16</sup> has shown in his detailed study of a 1,2,3,4-tetra-substituted cyclobutane derivative, there are some stereochemical distinctions that are not readily deduced by the n.m.r. spectroscopic method.

U.v. irradiation of the 1,5-anhydro-D-erythro-enulose (9)<sup>17</sup> with dimethylbutene under similar conditions to those used for (1) gave addition products which appeared as three discrete t.l.c. spots, but with very similar mobilities, *e.g.*  $R_F$  0.6, 0.55, and 0.50 in system (iii). Column chromatography of the crude photolysate afforded a pure sample of adduct Y ( $R_F$  0.55), m.p.

121—122°,  $\nu_{\max}$  1720  $\text{cm}^{-1}$ ,  $[\alpha]_D -8.2^\circ$ . The n.m.r. parameters for this adduct (Table) indicate that it is the (1S)-1,5-anhydro-2-deoxy-1,2-C-tetramethylethylene-D-ribo-hexo-3-ulose derivative (10). In particular the  $J_{1,2}$  value (5 Hz) suggests *cis*-fusion between the four- and six-membered rings, a deduction confirmed by the failure of base to cause this compound to isomerise.

Sodium borohydride reduction of adduct (10) gave an alcohol, which was converted into its acetate (13). This derivative possessed an n.m.r. spectrum which could be readily analysed. The large value for  $J_{3,4}$  (9.0 Hz) indicated the stereochemistry at C-3, which, taken in conjunction with  $J_{3,2}$  (9.0 Hz) and  $J_{1,2}$  (5.0 Hz), permits the (1S)-D-*gluco*-configuration to be assigned

<sup>15</sup> J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1955, pp. 140—142; E. W. Garbisch, *J. Chem. Educ.*, 1968, **45**, 480.

<sup>16</sup> L. F. Johnson, V. Georgian, L. Georgian, and A. V. Robertson, *Tetrahedron*, 1963, **19**, 1219.

<sup>17</sup> P. M. Collins, *Carbohydrate Res.*, 1969, **11**, 125.

\* Molecular models show that (5b) would be preferred on steric grounds.

<sup>14</sup> P. E. Eaton, *J. Amer. Chem. Soc.*, 1962, **84**, 2344.

to acetate (13), confirming that the ketone (10) had the (1*S*)-*D*-*ribo*-structure.

Further purification of the remaining photoadduct mixture was attempted by two applications of preparative layer chromatography (p.l.c.). Extraction of the band with  $R_F$  0.5 gave, after recrystallisation, a material with m.p. 122–125°,  $\nu_{\max}$  1720  $\text{cm}^{-1}$ ,  $[\alpha]_D^{+70}$  which contained adduct Z (55%), still contaminated with adduct Y [*i.e.* (10)] (25%) and a material of unknown structure (20%) as estimated from the relative intensities of their benzylidene methine signals in the n.m.r. spectrum. The n.m.r. signals (Table) show that adduct Z has the (1*R*)-*D*-*ribo*-configuration (11), since the large value for  $J_{1,2}$  (9.0 Hz) strongly suggests a *trans*-diequatorial ring fusion at C-1 and C-2. This deduction was corroborated by treating (11) with sodium methoxide and finding that it was isomerised into a material with  $R_F$  0.6, presumably adduct (12).

Extraction of the band X with  $R_F$  0.6 obtained from p.l.c. of the photolysate gave a syrup,  $\nu_{\max}$  1720  $\text{cm}^{-1}$ ,  $[\alpha]_D^{+100}$ . The n.m.r. spectrum of this syrup showed that it was a mixture which might contain adduct (12).

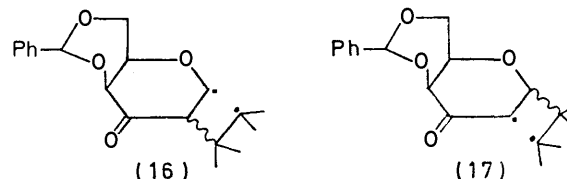
A comparison of the cyclobutyl ketones (2)–(4) with adducts obtained from enone (9) was informative, since isomerisation at C-4 in the former set of ketones could have occurred during their photochemical formation or when they were treated with base. It is important from a structural assignment viewpoint that such a possibility be excluded. Ketone (4), which has  $R_F$  0.5 in system (ii), can be easily distinguished from the adducts formed from enone (9) since these appear in the  $R_F$  range 0.8–0.7 in this solvent system. Furthermore the n.m.r. spectrum of (4) differs from those of the other adducts. Adducts (2) and (3) have similar t.l.c. mobilities to those formed from the enone (9); however their n.m.r. spectra are distinctive. Consequently ketones (2)–(4) were not isomerised at position 4 during their formation, and the base-induced isomerisation of (3) could not have taken place at C-4.

The reluctance of these derivatives to isomerise at C-4 is in keeping with the recent work of Hine *et al.*,<sup>18</sup> who showed that base-induced enolisation with  $\alpha$ -alkoxyketones occurs at the carbon atom not carrying the oxygen substituent.

The products (2)–(4) were obtained in a *ca.* 1 : 1 : 2 ratio. A mixture of *cis*- and *trans*-fused products is usually formed in photoannulations of cyclohex-2-enones with olefins that are not substituted with electron withdrawing groups<sup>2,11,19</sup> (see however ref. 20 for an example where only *trans*-fused products are formed). It is generally accepted that the new bonds are not formed concertedly in these reactions; initial bonding between one carbon atom of the olefin and either the

carbon atom  $\alpha$ <sup>19,21</sup> or  $\beta$ <sup>22</sup> to the carbonyl group in the excited enone is believed to occur, giving a 1,4-diradical intermediate. At present it is not clear which enone carbon atom is involved in this initial step.<sup>2</sup>

The products (2)–(4) could have been formed from the C-2 epimeric diradical intermediates (16*ax*) and (16*eq*), with the provisos that they be formed in equal amounts and that (16*eq*) ring-closed at C-1 to form an equatorial bond and an axial bond to the same extent. The intermediate (16*ax*) would for steric reasons be expected to ring-close exclusively *cis* to give (4). Thus if these conditions were met the isomer ratio would be 1 : 1 : 2, as observed.



Alternatively (2)–(4) could be produced from a pair of C-1 epimeric diradicals (17*ax*) and (17*eq*) formed by initial bonding at the  $\beta$ -carbon atom. In this case the product composition requires the ratio of axial to equatorial diradicals to be 1 : 3 and the closure of the latter isomer to occur in the *cis*-fashion twice as often as in the *trans*.

It is not obvious why the conditions necessary for either route should obtain and thus it is unfortunately not possible to decide between them with the results available. The first route might appear more attractive however because of the balance in the diverging pathways involved and more importantly because of the greater stability of radicals (16) than (17).

#### EXPERIMENTAL

Unless stated otherwise, optical rotations were measured on a Bellingham and Stanley polarimeter for chloroform solutions; i.r. spectra were measured with a Perkin-Elmer Infracord model 137 with solids dispersed in KBr and oils smeared on KBr discs; u.v. spectra were measured with a Perkin-Elmer spectrophotometer model 402 for ethanolic solutions; and n.m.r. spectra were measured with a Varian A-60D, HA100, or HA220 instrument. Measurements at 220 MHz were made by the P.C.M.U. (Harwell). T.l.c. on Silica Gel G was developed with one of the following systems: (i) benzene-ethyl acetate (3 : 1); (ii) benzene-ethyl acetate (5 : 1); (iii) benzene-ethyl acetate (10 : 1); (iv) benzene. Compounds were located with anisaldehyde in ethanol containing sulphuric acid.

*Irradiation of 1,5-Anhydro-4,6-O-benzylidene-1,2-dideoxy-D-threo-hex-1-en-3-ulose* (1).—(a) In 2,3-dimethylbut-2-ene. The enone (1) (2.5 g) was irradiated as a 1% (w/v) solution in dichloromethane containing 2,3-dimethylbut-2-ene (10 g), through Pyrex, in the annular space of a water-cooled photolysis well with a 450 W medium-pressure mercury-

<sup>18</sup> J. Hine, L. G. Mahone, and C. L. Liotte, *J. Amer. Chem. Soc.*, 1967, **89**, 5911.

<sup>19</sup> R. M. Bowman, C. Calvo, J. J. McCullough, P. W. Rasmussen, and F. F. Snyder, *J. Org. Chem.*, 1972, **37**, 2084.

<sup>20</sup> P. J. Nelson, D. Ostrem, J. D. Lassila, and O. L. Chapman, *J. Org. Chem.*, 1969, **34**, 811.

<sup>21</sup> N. J. Turro, 'Molecular Photochemistry,' Benjamin, New York, p. 207; P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, 1968, **5**, 118.

<sup>22</sup> W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *J. Amer. Chem. Soc.*, 1970, **92**, 1399.

arc lamp. The reaction was monitored by u.v. spectroscopy and by t.l.c. [system (i)]. After  $1\frac{1}{2}$  h irradiation, a decrease in the intensity of the enone absorption band at 266 nm indicated that *ca.* 80% of the enone (1) had reacted and t.l.c. analysis showed two new spots, a major one ( $R_F$  0.75–0.90) and a minor one ( $R_F$  0.25) as well as a little unchanged enone (1) ( $R_F$  0.5). After cautious removal of the solvent at 40° ( $15 \times 133 \text{ Nm}^{-2}$ ) a syrup was obtained, which was examined by t.l.c. with a less polar eluant [system (ii)]. This revealed that the original major product spot consisted of three components A ( $R_F$  0.85), B ( $R_F$  0.7), and C ( $R_F$  0.5) in the ratio *ca.* 1 : 1 : 2 whereas the minor product D remained as one spot ( $R_F$  0.15). The crude syrup was fractionated, by column chromatography [system (ii)], into a mixture of A and B (0.8 g); unchanged enone (1) (0.4 g); 1,5-anhydro-3-ulose, C (0.8 g), m.p. 124–125° (from propan-2-ol),  $[\alpha]_D -136^\circ$ ,  $\nu_{\text{max}}$  2800–3000 (C–H) and 1720  $\text{cm}^{-1}$  (C=O), *m/e* 316 ( $M^+$ ) (Found: C, 72.6; H, 7.8.  $\text{C}_{19}\text{H}_{24}\text{O}_4$  requires C, 72.1; H, 7.65%), n.m.r. parameters in the Table; and D (0.9 g), an amorphous solid, m.p. 230–235°,  $\nu_{\text{max}}$  2800–3000 (CH) and 1720  $\text{cm}^{-1}$  (CO), *M* 430 (Rast) ( $\text{C}_{26}\text{H}_{24}\text{O}_8$  requires C, 67.2; H, 5.2%), n.m.r. parameters in the Table.

Further t.l.c. examination [system (iv)] of the fraction containing A and B showed that these compounds had  $R_F$  0.6 and 0.45 respectively in this solvent. Column chromatography with this eluant resolved the mixture into a syrup, the 1,5-anhydro-3-ulose, A (0.28 g),  $[\alpha]_D +39^\circ$ ,  $\nu_{\text{max}}$  2800–3000 (CH) and 1720  $\text{cm}^{-1}$  (CO), n.m.r. parameters in the Table; 1,5-anhydro-3-ulose, B (0.3 g), m.p. 127–128° (from propan-2-ol),  $[\alpha]_D -28^\circ$ ,  $\nu_{\text{max}}$  2800–3000 (CH) and 1720  $\text{cm}^{-1}$  (CO), *m/e* 316 ( $M^+$ ) (Found: C, 72.5; H, 7.8.  $\text{C}_{19}\text{H}_{24}\text{O}_4$  requires C, 72.1; H, 7.65%); and a sample (0.2 g) composed of equal parts of A and B.

(b) *In cyclopentene.* The enone (1) (15 mg) in dichloromethane (0.5 ml) containing cyclopentene (1.5 ml) was irradiated in a Pyrex tube attached to the surface of the water-cooled photolysis well. After 25 min the u.v. absorption indicated that 95% of the enone had reacted and t.l.c. [system (i)] showed the products had  $R_F$  0.8 and the enone  $R_F$  0.5. The solvent was evaporated off and the crude product (6) showed  $\nu_{\text{max}}$  2800–3000 (CH) and 1720  $\text{cm}^{-1}$  (CO),  $\delta$  ( $\text{CCl}_4$ ) 7.1–7.5 (m, Ph), 5.49 (s, 0.25H), 5.45 (s, 0.25H), 5.28 (s, 0.5H), (PhCHO<sub>2</sub> from three components), 3.4–4.5 (m, H-1 to -6' ring protons), and 0.8–1.5 (m, cyclopentane).

(c) *Without olefin.* The enone (1) (5 mg) in dichloromethane (0.5 ml) was irradiated as described in (b) for 2 h; t.l.c. in system (i) then revealed unchanged enone (1),  $R_F$  0.5, and dimer D,  $R_F$  0.25 only.

*Treatment of Adducts A (2), B (3), and C (4) with Sodium Methoxide.*—Adducts A, B, and C (5 mg) were separately dissolved in methanol (0.5 ml) and each sample was treated with sodium methoxide (1 mg) at 65°. The solutions were examined by t.l.c. [system (ii)]. Adducts A and C were unchanged after 2 h, whereas adduct B was transformed into a substance with  $R_F$  0.5, identical with that of adduct C. This transformation was observed after 5 min reaction time.

A t.l.c. examination in system (ii) of this isomerised mixture and the mixture of photoadducts derived from enone (9) (see later) showed that the former had  $R_F$  0.7 and 0.5 whereas the components in the latter appeared as a streak in the region  $R_F$  0.7–0.8.

*Sodium Borohydride Reduction of Adducts.*—(a) *Adduct B (3).* The adduct B (0.15 g) in methanol (8 ml) was treated with sodium borohydride (7 mg) at room temperature for 5 min; t.l.c. analysis then showed reaction was complete. The mixture was neutralised with acetic acid and the product extracted into chloroform. Evaporation afforded an alcohol,  $\nu_{\text{max}}$  3500  $\text{cm}^{-1}$  (OH), which was treated with acetic anhydride (1 ml) in pyridine (1 ml) for 15 h. The usual work-up gave (1R)-3-O-acetyl-1,5-anhydro-4,6-O-benzylidene-2-deoxy-1,2-C-tetramethylethylene-D-galactitol (7) (0.14 g),  $\nu_{\text{max}}$  1750  $\text{cm}^{-1}$  (CO),  $\delta$  ( $\text{CDCl}_3$ ) 7.3–7.7 (m, Ph), 5.53 (s, PhCHO<sub>2</sub>), 3.22 (d,  $J_{1,2}$  10.4 Hz), 2.55 (q,  $J_{2,3}$  11.6), 4.98 (q,  $J_{3,4}$  3.4), 4.32 (q,  $J_{4,5}$  1.4), 3.48 (m,  $J_{5,6}$  1.3), 4.32 (q,  $J_{6,6'}$  12.8), 3.98 (q,  $J_{6',5}$  1.8), 2.02 (s, AcO), 1.19 (s, Me), 1.00 (s, 2Me), and 0.98 (s, Me).

(b) *Adduct C (4).* The adduct C (0.32 g) was treated as in (a). The cyclobutane acetate (8) (0.3 g) obtained had  $\nu_{\text{max}}$  1750  $\text{cm}^{-1}$  (CO),  $\delta$  ( $\text{CDCl}_3$ ) 7.3–7.7 (m, Ph), 5.52 (s, PhCHO<sub>2</sub>), 3.75 (d,  $J_{1,2}$  5.3 Hz), 2.53 (q,  $J_{2,3}$  9.0), 5.12 (q,  $J_{3,4}$  6.1), 4.27 (q,  $J_{4,5}$  1.3), 3.02br (q,  $J_{5,6}$  1.5), 4.33 (q,  $J_{6,6'}$  12.1), 4.03 (q,  $J_{6',5}$  2.0), 2.04 (s, AcO), 1.48, 1.06, 1.00, and 0.94 (4 × s, 4 × Me).

*U.v. Irradiation of 1,5-Anhydro-4,6-O-benzylidene-1,2-di-deoxy-D-erythro-hex-1-en-3-ulose (9) in 2,3-dimethylbut-2-ene.*—The enone (9) (1.8 g) was irradiated as described for (1) [see (a)]. After  $4\frac{1}{2}$  h t.l.c. of the mixture on  $5 \times 20$  cm plates [system (iii)] indicated that *ca.* 80% of the enone (9),  $R_F$  0.35, had been transformed into at least three products,  $R_F$  0.50, 0.55, and 0.60. Column chromatography [system (iii)] of the crude product afforded a fraction (0.85 g) ( $R_F$  0.5–0.6), which was then subjected to p.l.c. [system (iii)] on two plates (1 m × 20 cm) coated with Kieselgel GF<sub>254</sub> (Merck). A broad band, visible under u.v. light, was formed in the range  $R_F$  0.5–0.7. This was divided laterally into three equal strips, the adsorbent of each strip was removed, and the organic material was extracted from the silica gel by stirring twice with acetone-methanol 1 : 1 and once with chloroform. Evaporation of the solution obtained from the middle band gave compound Y (0.15 g), which was t.l.c.-homogeneous, m.p. 120–121° (from propan-2-ol),  $[\alpha]_D -8.2^\circ$ ,  $\nu_{\text{max}}$  1720  $\text{cm}^{-1}$  (CO), n.m.r. parameters in the Table. The material extracted from the least mobile band was a solid (0.16 g) which t.l.c. showed was rich in compound Z and the material from the most mobile band was an oil (0.15 g) which probably contained some of the other expected adduct X. These last two bands were combined and again separated by p.l.c. On this occasion narrower strips of adsorbent, equivalent to approximately the front quarter and rear quarter of the whole band, were removed and extracted separately. The remaining middle band was also extracted and the material so obtained separated again in the same way by p.l.c. Evaporation of the combined extracts from the least mobile band gave a solid which was rich in Z, m.p. 122–125° (from propan-2-ol),  $[\alpha]_D +70^\circ$ ,  $\nu_{\text{max}}$  1720  $\text{cm}^{-1}$  (CO), n.m.r. parameters in the Table. Further signals were present in the spectrum: those at  $\delta$  5.26 (s), 3.88 (d), 2.60 (d), 0.82 (s), and 1.04 (s) arose from the benzylidene methine proton, H-4, H-2, and the cyclobutane methyl groups of the 25% of Y adduct present in the mixture, and those at  $\delta$  5.28 (s), 2.35 (d), 0.73 (s), 0.90 (s), and 1.15 (s) came from the 20% of unknown compound that was present.

Evaporation of the extracts from the most mobile band gave an oil,  $[\alpha]_D +100^\circ$ ,  $\nu_{\text{max}}$  1720  $\text{cm}^{-1}$  (CO). The n.m.r.

spectrum of this fraction was complex, but it showed that it was composed mainly of cyclobutane adducts. At least three components were present (there were three benzyldene methine signals at  $\delta$  5.31, 5.52 and 6.0). One of these components is probably adduct X.

*Treatment of Adducts Y (10) and Z (11) with Sodium Methoxide.*—Adduct Y (3 mg) and crude adduct Z (3 mg) each in methanol (1.5 ml) were treated with sodium methoxide (0.5 mg) at room temperature. After 0.5 h t.l.c. [system (iii)] showed that Z had been partially transformed into a compound with the same  $R_F$  as the band in which X is believed to appear. Adduct Y on the other hand was unaffected, even after 4 h at 60°.

*Sodium Borohydride Reduction of Adduct Y (10).*—Adduct Y (30 mg) was reduced with sodium borohydride

(2 mg) in methanol (0.7 ml) during 5 min at room temperature. The alcohol was isolated in the usual way and acetylated as described for adduct B to give (1S)-3-O-acetyl-1,5-anhydro-4,6-O-benzyldene-2-deoxy-1,2-C-tetramethylethylene-D-glucitol (13),  $\nu_{\text{max}}$  1750  $\text{cm}^{-1}$  (CO),  $\delta$  ( $\text{CDCl}_3$ ) 7.35–7.55 (m, Ph), 5.60 (s,  $\text{PhCHO}_2$ ), 3.84 (d,  $J_{1,2}$  5.0 Hz), 2.92 (q,  $J_{2,3}$  9.0), 5.17 (t,  $J_{3,4}$  9.0), 4.16 (t,  $J_{4,5}$  9.0), 3.35 (sex,  $J_{5,6}$  5.0), 4.36 (q,  $J_{6,6'}$  10), 3.77 (t H-6'), 2.06 (s, AcO), 1.39 (s, Me), 1.04 (s, 2Me), and 0.92 (s, Me).

We thank the S.R.C. for meeting the cost of spectra measured by the P.C.M.U. (Harwell) and we also thank R. Egan for assistance with 100 MHz n.m.r. measurements

[3/082 Received, 15th January, 1973]