Carbohydrate Research, 58 (1977) C4–C6

Preliminary communication

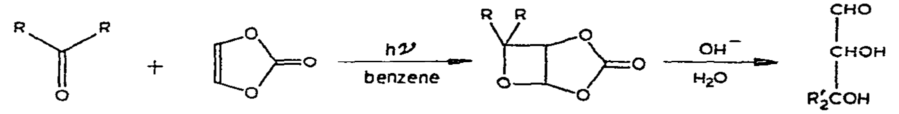
Synthesis of DL-apiose by photochemical cycloaddition of 1,3-dihydroxy-2-propanone diacetate to 1,3-dioxol-2-one

YOUNOSUKE ARAKI, JUN-ICHI NAGASAWA, and YOSHIHARU ISHIDO

Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, O-okayama, Meguro ku, Tokyo 152 (Japan)

(Received April 25th, 1977, accepted for publication, June 20th, 1977)

Oxetane derivatives are formed by photochemical cycloaddition of carbonyl compounds to alkenes and have been used advantageously as synthetic intermediates[1] Our continued investigation on oxetane formation has been focused on carbohydrate chemistry with the synthetic objectives of *C*-glycosyl compounds and branched-chain sugars[2] In this connection, we now report the photochemical cycloaddition of carbonyl compounds, namely 1,3-dihydroxy-2-propanone diacetate (**1a**) and diethyl oxomalonate (**1b**), to 1,3-dioxol-2-one[3] (**2**), which gave the key, intermediate oxetanes **3a** and **3b**, which are derivatives of DL-apiose On account of its enediol structure, compound **2** has been used for the synthesis of sugar[4] and inositol[5] derivatives, and is known to give the corresponding cyclobutane derivatives in photochemical reactions in the presence of carbonyl compounds as the photosensitizer[6,7] Therefore, we set out to develop a new synthetic route to DL-apiose on the assumption that **2** might react with carbonyl compounds (**1**) to give the corresponding oxetane derivatives (**3**), which might be converted into the corresponding oxyaldehydes (**4**), if energy transfer does not occur* from photoexcited **1** to **2**



1
a (R = CH_2OAc)
b (R = CO_2Et)

2

3
a (R = CH_2OAc)
b (R = CO_2Et)

4
a (R′ = CH_2OH)

---

*The energy of the lowest excited triplet-state (E_T) for **2** was deduced to be ~70 kcal/mol[6], close to that for a carbonyl compound, which has an E_T value near or below that of 70 kcal/mol and is thus potentially appropriate for the reaction.

A solution of **1a** (ref 8, 435 mg, 2 5 mmol) and **2** (430 mg, 5 mmol) in benzene[†] (5 ml) was irradiated externally with a high-pressure mercury lamp (450-W, Ushio Electric Inc) for 40 h at room temperature[‡] under nitrogen in a Pyrex-glass tube at the distance of ~5 cm The resulting solution was evaporated *in vacuo* to a syrup, and the latter was chromatographed on a column of silica gel (Wakogel C-300), eluting successively with benzene (500 ml), 99 5 0 5 benzene–acetone (1000 ml), and 99 1 benzene–acetone (1000 ml) to give **1a** (261 mg, 60% recovery) and 7,7-dihydroxymethyl-2,4,6-trioxabicyclo-[3 2 0] heptan-3-one diacetate (4,4′-di-*O*-acetyl-1,2-*O*-carbonyl-DL-apiofuranose, **3a**)[**] as a syrup (150 mg, 23%, 57% yield based on the amount of **1a** consumed), λ_{max}^{NaCl} (determined with a Hitachi 285 instrument) 1830 (cyclic carbonate) and 1745–1755 cm^{-1} (acetate), n m r ($CDCl_3$-Me_4Si) (determined with a Varian T-60 instrument) δ 2 14 (*s*, 3H, OAc), 2 17 (*s*, 3H, OAc), 4 25 (*d*, 1H, methylene, *J* 12 8 Hz), 4 30 (*s*, 2H, methylene), 4 43 (*d*, 1H, methylene), 5 38 (*d*, 1H, methine, *J* 3 8 Hz), and 6 26 (*d*, 1H, methine) Alkaline hydrolysis of **3a** (364 mg) gave syrupy DL-apiose[9] (**4a**) (127 mg, 60%), which was then converted conventionally into its phenylosazone [m p 155 5–157° (from ethanol)] [lit [10] m p 156–157° (from ethanol)].

Similar irradiation of a solution of diethyl oxomalonate[11] (**1b**) (1 742 g, 10 mmol) and **2** (1 721 g, 20 mmol) in benzene (20 ml) for 7 h, followed by evaporation *in vacuo* and chromatography of the resulting syrup, eluting with 1 4 cyclohexane–benzene (1000 ml), benzene (1000 ml), and 99 5 0.5 benzene–acetone (1000 ml), afforded syrupy diethyl 3-oxo-2,4,6-trioxabicyclo[3 2 0]heptane-7,7-dicarboxylate (diethyl 1,2-*O*-carbonyl-DL-apiofuranduronate, **3b**) (590 mg, 23%), λ_{max}^{NaCl} 1840 (cyclic carbonate) and 1745 cm^{-1} (Et ester), n m r δ 1 33 (*t*, 6H, *J* 7 0 Hz, Me), 4 36 (*q*, 2H, methylene), 4 38 (*q*, 2H, methylene), 5 77 (*d*, 1H, methine, *J* 3 6 Hz), and 6 37 (*d*, 1H, methine)][**,††]

[†] A series of organic solvents were used for the reaction, including methanol, tert-butyl alcohol, 1,4-dioxane, tetrahydrofuran, 1,2-dimethoxyethane, acetic acid, acetone, and ethylene carbonate, in place of benzene However, g l.c and t l.c analysis of each product showed only the absence of **3a**, or lower yields of **3a**.

[‡] T l.c of the mixture suggested the potential decomposition of **3a** during the reaction, as the spot round the spotted point on t l.c enlarged with the elapse of time Accordingly, the reaction was discontinued after 40 h, although considerable proportions of **1a** and **2** remained in the mixture

[**] Elementary analyses were consistent with those calculated for the expected structures

[††] The product **3b** decomposed during chromatography on silica gel, probably because of the ethoxycarbonyl functions involved Yields of **3b** after re-chromatography ranged from 55 to 60%

REFERENCES

1 D R. Arnold, *Adv Photochem* , 6 (1968) 301–423
2 K Matsuura, Y Araki, and Y Ishido, *Bull. Chem. Soc Jpn* , 45 (1972) 3496–3498, K Matsuura, Y Araki, Y Ishido, A Murai, and K Kushida, *Carbohydr Res* , 29 (1973) 459–468
3 M S Newman and R. W Addor, *J Am. Chem. Soc* , 77 (1955) 3789–3793
4 T Tamura, T. Kunieda, and T Takizawa, *J Org Chem* , 39 (1974) 38–44
5 C R Kowarski and S Šarel, *J Org Chem* , 38 (1973) 117–119.
6 W Hartmann and R Steinmetz, *Chem. Ber.*, 100 (1967) 217–222
7 W Hartmann, H -G Heine, H -M Fischler, and D Wendisch, *Tetrahedron*, 29 (1973) 2333–2336
8 P H Bentley and W McCrae, *J Org Chem* , 35 (1970) 2082–2083
9 For a recent review, see R R Watson and N S Orenstein, *Adv Carbohydr Chem Biochem* 31 (1975) 135–184
10 E Vongerichten, *Ann* , 321 (1902) 71–83
11 A W Dox, *Org Syn* , *Coll Vol* , 1 (1956) 266–269