

**PHOTOSENSITIZED [2 + 2]-CYCLOADDITION OF
3-ACETYL-2[3H]-OXAZOLONE TO MALEIC ANHYDRIDE,
DIMETHYLMALEIC ANHYDRIDE, AND 1,6-ANHYDRO-4-O-BENZYL-
-2,3-DIDEOXY- β -D-*erythro*-2-HEXENOPYRANOSE**

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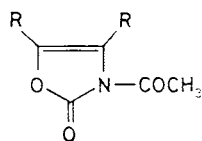
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Acetone-sensitized [2 + 2]-photocycloaddition of 2[3H]-oxazolones (*I–II*) to maleic anhydride and dimethylmaleic anhydride has been used to prepare the corresponding cyclobutane derivatives (*III–VI*) and (*VIII*).

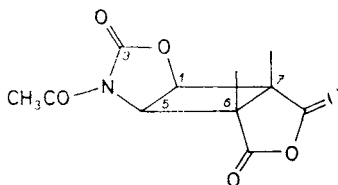
3-Acetyl-2[3H]-oxazolone (*I*) reacts with olefins and acetylene on irradiation in acetone to give the respective [2 + 2]-cycloadducts¹, and, under radical conditions, it gives a homopolymer which can be a potential intermediate in preparation of aminosaccharides². We carried out the acetone-sensitized [2 + 2]-photocycloadditions of 3-acetyl-2[3H]-oxazolone (*I*) and its 4,5-dimethyl derivative (*II*) with maleic anhydride and dimethylmaleic anhydride. The fact that the reaction mixtures contained besides the 1 : 1 cycloadducts also the dimers of both the starting compounds indicates that the excited states of the two components are significant in the reaction. From the reaction of *I* with dimethylmaleic anhydride it was possible to obtain (using the fraction crystallization) the two cycloadducts *III* and *IV* in the overall yield of 56%. Their structures were assigned on the basis of the following consideration. The ¹H NMR spectrum of compound *III* contains signals of methyl groups ($\delta = 1.05$ and 1.20 ppm) at higher field than that of the compound *IV* ($\delta = 1.15$ and 1.25 ppm). From the greater difference in the chemical shifts of the H₁ and H₅ protons ($\Delta\delta_{\text{H}} = 0.54$ ppm) and of the methyl groups ($\Delta\delta_{\text{CH}_3} = 0.15$ ppm) of compound *III* as compared with compound *IV* ($\Delta\delta_{\text{H}} = 0.17$ ppm; $\Delta\delta_{\text{CH}_3} = 0.1$ ppm) it is concluded that, with the presumed deviation of the cyclobutane ring, the effect of different environment will make itself felt to a greater extent in the *anti*-cycloadduct *III* than in the *syn*-cycloadduct *IV*. The reactions of maleic anhydride with *I* and dimethylmaleic anhydride with *II* gave the cycloadducts *V* and *VI*, respectively. Within the attempts at application of the acetone-sensitized photocycloaddition of *I* to preparation of aminosaccharides with cyclobutane ring, we realized a reaction of *I* with 1,6-anhydro-

-4-O-benzyl-2,3-dideoxy- β -D-*erythro*-2-hexenopyranose (VII): compound VIII represented the main product (37%). Besides that we obtained a mixture of other 1 : 1 cycloadducts (11%) and a mixture of dimers of the starting 3-acetyl-2[3H]-oxazolone (6%). The formation of the dimers of compound I in the acetone-sensitized [2 + 2]-photocycloadditions has already been observed earlier^{1,3}, and, in this case, it indicates a reaction course *via* the excited state of compound I. The infrared spectrum of compound VIII exhibits CH-vibrations of phenyl group (3030 cm^{-1}) and vibrations of carbonyl groups of the 3-acetyl-2-oxazolidone part of the molecule at 1785 cm^{-1} (ring) and 1710 cm^{-1} (acetal). In the ^1H NMR spectrum of compound VIII the H(3) proton signal appears as a singlet at 5.59 ppm. It indicates a dihedral angle between H(2) and H(3) close to 90° . By constructing the corresponding Dreiding models we found that this requirement is best fulfilled by the *anti*-cycloadduct VIII. The formation of the *syn*-cycloadduct is sterically hindered by the benzyloxy group. The ^{13}C NMR spectrum of compound VIII exhibits the signals of carbon atoms of carbonyl groups at $\delta = 170.1\text{ ppm}$ (acetyl) and $\delta = 154.3\text{ ppm}$ (ring). It is also

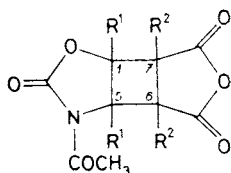


I, R = H

II, R = CH₃

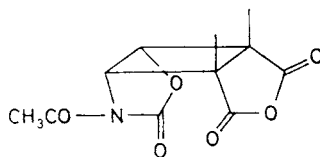


III

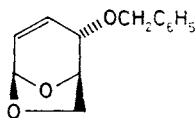


V, R¹ = R² = H

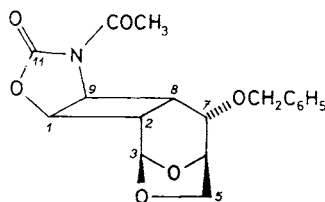
VI, R¹ = R² = CH₃



IV



VII



VIII

possible to carry out unambiguous assignment of the C(3) carbon atom at $\delta = 100.1$ ppm and of the bonding carbon atoms of phenyl and methyl groups at $\delta = 137.1$ and 23.58 ppm, respectively. The other signals were assigned on the basis of published ^{13}C NMR spectra of some 1,6-anhydrosaccharides⁴.

EXPERIMENTAL

The starting compounds were prepared according to literature data: compound *I* (ref.⁵), *II* (ref.⁶), *III* (ref.⁷). The photochemical reactions were carried out in a 150 ml reactor⁸ with Solidex filters ($\lambda < 270$ nm) and Jena Glass filters ($\lambda < 300$ nm). Nitrogen gas was bubbled through the reaction mixture for 15 min before each reaction, whereupon the mixture was irradiated with a 125 W medium-pressure mercury discharge lamp Tesla RVK 125 at temperatures below 20°C. The melting points were determined with a Kofler apparatus and are not corrected. The IR spectra were measured with a UR-20 apparatus (Zeiss Jena), the ^1H and ^{13}C NMR spectra were measured with a JEOL FX-100 apparatus (δ , ppm) in hexadeuteriodimethyl sulphoxide. The chemical shifts are related to tetramethylsilane as the standard. The mass spectra were measured at 40 eV using an MS 902 S apparatus (AEI Manchester).

Anhydrides of *anti*- (*III*) and *syn*-3-Oxo-4-acetyl-6,7-dimethyl-2,4-oxazabicyclo[3,2,0]heptane-6,7-dicarboxylic (*IV*) Acids

A mixture of 0.63 g (5 mmol) compound *I* and 0.63 g (5 mmol) dimethylmaleic anhydride in 100 ml acetone was irradiated through the Solidex filter 50 h. The solvent was evaporated, the residue was washed with 50 ml diethyl ether, and the mixture obtained (0.9 g) was recrystallized from acetonitrile to give 0.5 g (40%) compound *III*, m.p. 268–270°C (crystallization from acetonitrile and subsequent sublimation at 210°C and 13 Pa). IR spectrum (KBr): 1 855, 1 793, 1 703, 1 445, 1 389, 1 300, 1 340, 1 200, 990, 985, 920 cm^{-1} . ^1H NMR spectrum: 1.05 (s, 3 H, CH_3 on C(6)), 1.20 (s, 3 H, CH_3 on C(7)), 2.43 (s, 3 H, CH_3CO), 4.71 (d, 1 H, H(5)), 5.25 (d, 1 H, H(1)), $J_{1,5} = 7.5$ Hz. For $\text{C}_{11}\text{H}_{11}\text{NO}_6$ (253.2) calculated: 52.17% C, 4.38% H, 5.53% N; found: 52.35% C, 4.58% H, 5.20% N. Evaporation of the mother liquors and recrystallization gave 0.2 g (16%) compound *IV*, m.p. 188–190°C (ethyl acetate). IR spectrum (KBr): 1 855, 1 785, 1 710, 1 370, 1 300, 1 205 cm^{-1} . ^1H NMR spectrum: 1.15 (s, 3 H, CH_3 on C(6)), 1.25 (s, 3 H, CH_3 on C(6)), 2.43 (s, 3 H, CH_3CO), 5.00 (d, 1 H, H(1)), $J_{1,5} = 7$ Hz.

Anhydride of 3-Oxo-4-acetyl-2,4-oxazabicyclo[3,2,0]heptane-6,7-dicarboxylic Acid (*V*)

A mixture of 0.63 g (5 mmol) compound *I* and 0.5 g (5 mmol) maleic anhydride in 100 ml acetone was irradiated through the Jena Glass filter 40 h. The solvent was evaporated and the evaporation residue was recrystallized to give 0.5 g (43%) compound *V*, m.p. 235–240°C (acetonitrile–diethyl ether). The residue represented a mixture of dimers and polymers of the starting compounds. IR spectrum (KBr): 1 855, 1 800, 1 705, 1 370 cm^{-1} . ^1H NMR spectrum: 2.41 (s, 3 H, CH_3CO), 3.43 (dd, 1 H, H(6)), 3.95 (dd, 1 H, H(7)), 4.62 (dd, 1 H, H(5)), 5.10–5.35 (m, 1 H, H(1)), $J_{1,5} = 7$ Hz, $J_{1,7} = 5$ Hz, $J_{5,6} = 2$ Hz, $J_{6,7} = 11$ Hz. Mass spectrum m/z (rel. int.): 250 (0.1), 183 (1), 170 (2), 128 (4), 127 (7), 85 (13), 43 (100), 28 (9). For $\text{C}_9\text{H}_7\text{NO}_6$ (225.1) calculated: 48.01% C, 3.13% H, 6.22% N; found: 47.69% C, 3.18% H, 5.98% N.

Anhydride of 3-Oxo-4-acetyl-1,5,6,7-tetramethyl-2,4-oxazabicyclo[3,2,0]heptane-6,7-dicarboxylic Acid (*VI*)

A mixture of 0.77 g (5 mmol) compound *II* and 0.63 g (5 mmol) dimethylmaleic anhydride in

100 ml acetone was irradiated through the Solidex filter 50 h. The solvent was evaporated, and the residue was recrystallized from acetonitrile to give 0.6 g (43%) compound *VI*, m.p. 236–237°C (recrystallization from acetonitrile–diethyl ether and subsequent sublimation at 190°C and 13 Pa). IR spectrum (KBr): 1 843, 1 788, 1 708, 1 370, 1 315 cm^{-1} . ^1H NMR spectrum: 1.23 (s, 3 H, CH_3 on C(6)), 1.28 (s, 3 H, CH_3 on C(7)), 1.41 (s, 3 H, CH_3 on C(5)), 1.58 (s, 3 H, CH_3 on C(1)), 2.48 (s, 3 H, CH_3CO). Mass spectrum m/z (rel. int.): 239 (0.1), 195 (0.2), 155 (7), 127 (2), 114 (7), 113 (100), 54 (4), 44 (6), 43 (58), 42 (17), 28 (13). For $\text{C}_{13}\text{H}_{15}\text{NO}_6$ (281.3) calculated: 55.51% C, 5.38% H, 4.98% N; found: 55.66% C, 5.44% H, 4.89% N.

10-Acetyl-7-benzyloxy-4,12,13-trioxa-10-azatetracyclo-[7,3,1^{3,6,0,2,8}]tridecan-11-one (*VIII*)

A mixture of 1.27 g (10 mmol) compound *I* and 2.2 g (10 mmol) compound *VII* in 100 ml acetone was irradiated through the Solidex filter 64 h. After concentration to a volume of 10 ml and addition of 15 ml diethyl ether the mixture deposited dimers of compound *I* (0.2 g, i.e. 6%), m.p. 280°C (acetonitrile) in a sealed capillary. Ref.³ gives m.p. 290 and 278°C for the *anti*- and *syn*-dimer, respectively. The residue was submitted to column chromatography (silica gel, benzene–acetone 15 : 1) to give 1.3 g (37%) compound *VIII* as an oil. IR spectrum (CHCl_3): 3 030, 2 940, 2 890, 1 785, 1 710, 1 445, 1 370, 1 350 cm^{-1} . ^1H NMR spectrum ($^2\text{HCCl}_3$): 2.46 (m, 1 H, H(8)), 2.54 (s, 3 H, CH_3CO), 3.07 (m, 1 H, H(2)), 3.54–3.82 (m, 3 H, H(6), H(5)_{exo,endo}), 4.37 to 4.67 (m, 4 H, H(7), H(9), OCH_2), 5.26 (dd, 1 H, H(1)), 5.56 (s, 1 H, H(3)), 7.34 (s, 5 H, C_6H_5), $J_{1,2} = 4.2 = 4.2$ Hz, $J_{1,9} = 7.1$ Hz. ^{13}C NMR spectrum ($^2\text{HCCl}_3$): 23.58 (q, CH_3 , $J_{\text{CH}} = 130.4$ Hz), 38.55 (d, C(8), $J_{\text{CH}} = 142.1$ Hz), 40.66 (d, C(2), $J_{\text{CH}} = 149.4$ Hz), 53.82 (d, C(9), $J_{\text{CH}} = 159.7$), 67.98 (t, C(5); $J_{\text{CH}} = 143.0$ Hz), 70.62 (t, OCH_2 , $J_{\text{CH}} = 150.7$ Hz), 71.84 (d, C(7)), 74.94 (d, C(6), $J_{\text{CH}} = 146.5$ Hz), 76.06 (d, C(1), $J_{\text{CH}} = 154.8$ Hz), 100.10 (d, C(3), $J_{\text{CH}} = 173.0$ Hz), 127.83–128.59 (m, 5 C, C_6H_5), 137.08 (s, C(1), phenyl group), 154.30 (s, C(11)), 170.13 (s, C=O of acetyl group).

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