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CHEMO- AND STEREOSELECTIVE FUNCTIONALIZATION OF 7-OXABICYCLO[2.2.1]HEPT-5-EN-2-ONE WITH DICHLOROKETENE

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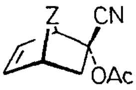
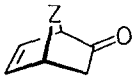
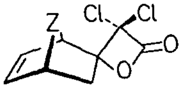
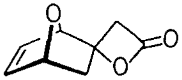
Summary. Dichloroketene adds onto the exo face of the carbonyl group of 7-oxabicyclo[2.2.1]-hept-5-en-2-one giving a dichloro-β-lactone which was transformed into the corresponding 1,3-diol.

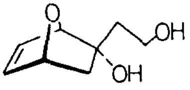
The regioselectivity of electrophilic additions of the C(5)-C(6) double bonds in norbornenes depends on the nature of the substituents at C(2).[1] While the CN and AcO groups in 1 and 3 act as electron-withdrawing groups, the carbonyl group in 2 and 4 behaves as an electron-donating substituent.[1] Since the 7-oxanorbornenes 1 and 2 can be obtained readily optically pure,[2] they are expected to become useful synthetic intermediates ("naked sugars"[3]). During the course of our studies on the functionalization of C(5) and C(6) of 1 and 2 via cycloadditions,[4] we explored the reaction of 2 with dichloroketene. We report here the unexpected outcome of this reaction.







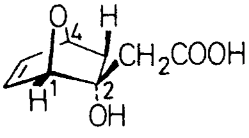




Z = O : 1 2 5 7 8
Z = CH_2 : 3 4 6

When 2 was treated with an excess of Cl_3CCOCl and Zn/Cu couple in refluxing Et_2O[5] (12 h), the spiro β-lactone 5 was obtained in 87% isolated yield. Even in the presence of a 4-fold excess of the ketene precursor and $POCl_3$, no trace of the expected cyclobutane derivatives resulting from the [2+2] cycloaddition of the C(5)-C(6) double bond of 2 could be detected. This contrasts with the reaction of 4 which yielded, under the same conditions, 60% of a mixture of cyclobutane derivatives[6] and only 10% of lactone 6.[7] The lack of reactivity of the C(5)-C(6) double bond in 2 is attributed tentatively to the inductive effect of the O(7) bridge. The high exo-face selectivity of the reaction 2 → 5 is noteworthy.

The structure of 5 was given by its spectral data[8] and by its reduction with Al(Hg)/THF-H_2O[9] (20°C, 2 h) to the β-lactone 7 (78%)[10] which corresponds to the Diels-Alder adduct of furan to the ketene dimer.



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On treatment with $LiAlH_4$ (THF, 0°C, 15 min), 7 was reduced to the diol 8[11] (75%). The relative configuration at C(2) in 5, 7 and 8 was confirmed by NOE measurements in the 360 ^{1}H-NMR spectrum of the hydroxy-acid 9[12] obtained by hydrolysis of 7. For instance, irradiation of the CH_2-COOH signal at δ_H = 2.86 ppm led to significant NOE's at δ_H = 1.94 ppm (H-C(3-exo)) and δ_H = 4.63 ppm (H-C(1)).

The reaction of dichloroketene with 7-oxanorbornenone 2 proceeds chemo- and stereoselectively on its carbonyl function. This allows one to graft a functionalized two-carbon unit at C(2) in a stereoselective fashion. The synthetic potential of compounds 5, 7 and 8 are currently being explored in our laboratories.[13]

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4. See e.g.: J. Plumet, G. Escobar, C. Manzano, O. Arjona, P.-A. Carrupt, P. Vogel, Heterocycles 24 (1986) 1535.
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6. See e.g.: L.R. Krepski, A. Hassner, J. Org. Chem. 43 (1978) 2879; R. Huisgen, L.A. Feiler, Chem. Ber. 102 (1969) 3391.
7. For an example of [2+2] cycloaddition of dichloroketene to a strained ketone competitive with the cycloaddition of a norbornene double bond, see: W. Ried, O. Bellinger, Liebigs Ann. Chem. 1984, 1778.
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9. E.J. Corey, M. Chaykovsky, J. Am. Chem. Soc. 86 (1964) 1639.
10. Data of 7: IR(film): 710, 800, 885, 1005, 1120, 1325, 1415, 1830, 2880-3100 cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 1.78 (d, 14, H-C(3-endo)); 2.32 (dd, 14, 4.5, H-(3-exo)); 3.62 (br.s, 2H); 4.8 (br.s, H-C(1)); 5.07 (dd, 4.5, 1.8, H-C(4)); 6.42 (dd, 6.0, 1.8, H-C(5)); 6.60 (dd, 6.0, 1.5, H-C(6)). ^{13}C-NMR($CDCl_3$): δ 38.0; 47.5; 78.6; 79.8; 81.8; 132.4; 137.9; 166.8.
11. Data of 8: IR(film): 710, 900, 1085, 1320, 140, 2800, 3050-3650 cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 1.27 (d, 12); 1.97 (dd, 12, 4.5); 2.02 (t, 6, CH_2-C(2)); 3.35-3.8 (m, 2H); 3.92 (t, 6, CH_2-OH); 4.55 (d, 1.8); 4.9 (dd, 4.5, 1.5, H-C(4)); 6.4 (dd, 6, 1.8); 6.57 (dd, 6.0, 1.5). ^{13}C-NMR($CDCl_3$): δ 40.7; 41.0; 59.8; 78.7; 79.4; 82.8; 133.0; 137.2.
12. Data of 9: IR($CHCl_3$): 1020, 1080, 1180, 1210, 1320, 1345, 1440, 1720, 2980, 3020,3520. ^{1}H-NMR ($CDCl_3$): δ 1.36 (d, 12, H-C(3-endo)); 1.94 (dd, 12, 5, H-C(3-exo)); 2.86 (m, CH_2-C(2)); 4.63 (d, 2, H-C(1)); 4.94 (dd, 5, 2, H-C(4)); 6.47 & 6.57 (2 dd, 6, 2, H-C(5),H-C(6)).
13. For recent examples of β-lactones in synthesis, see: a) L.D. Arnold, T.H. Kelantar, J.C. Vederas, J. Am. Chem. Soc. 107 (1985) 7105; M. Shinada, K. Iseki, T. Oguri, Y. Hayasi, S. Yamada, M. Shibasaki, Tetrahedron Lett. 27 (1986) 87.

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