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# CHEMO- AND STEREOSELECTIVE FUNCTIONALIZATION OF 7-OXABICYCLO[2.2.1]HEPT-5-EN-2-ONE DERIVATIVES WITH THE SYSTEM TRICHLOROACETYL CHLORIDE/Zn(Cu) [1].

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Abstract- Dichloroketene adds onto the *exo* face of the carbonyl group of 7-oxabicyclo[2.2.1]hept-5-en-2-one to yield a dichloro- β-lactone with complete chemo- and stereoselectivity. This dichlorolactonization has been extended to other oxanorbornenic systems and the resulting β-lactones were transformed into the corresponding 1,3-diols.

The regioselectivity of electrophilic additions to the endocyclic double bond of 7-oxanorbornenic systems is controlled by the remote substituents at C-2 [2]. For example, while a cyanoacetoxy functionality acts as an electron withdrawing group, a carbonyl at C-2 behaves as an electron donating substituent. The synthetic potential of such substrates has been greatly increased by the fact that they can now be obtained readily optically pure [3]; an example of this is the short synthesis of L-Daunosamine recently reported by Warm and Vogel [4]. During the course of our studies on the functionalization of C-5 and C-6 of 7-oxanorbornenic systems via cycloadditions [5], we explored the reaction of 7-oxabicyclo[2.2.1]hept-5-en-2-one with dichloroketene [1]; the unexpected outcome of that reaction has been reported in a preliminary form [1]. The purpose of the present paper is to study the unusual reactivity of 7-oxanorbornen-2-one with dichloroketene and to extend this methodology to other oxanorbornenic systems.

Dichloroketene, generated *in situ* by dehalogenation of trichloroacetyl chloride with activated Zn, adds to the endocyclic double bond of bicyclo[2.2.1]hept-2-ene, 1, to yield the corresponding cyclobutanone 2 [6,7]. In the case of systems such as 5-methylene-bicyclo[2.2.1]hept-2-ene, 3, in which two carbon-carbon double bonds compete for the cycloaddition process, the reaction takes place preferentially at the exocyclic double bond to afford the corresponding spiro cyclobutanone 4. On the other hand, dichloroketene adds to the carbonyl double bond of

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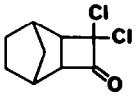


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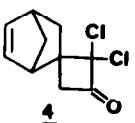


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saturated ketones to afford β-lactones. Apparently, the zinc halide activates the carbonyl group, thus increasing the reactivity of simple ketones towards dichloroketene[8]. Therefore, bicyclic systems such as bicyclo[2.2.1]hept-5-en-2-one, 5, and 7-oxabicyclo[2.2.1]hept-5-en-2-one, 6, contain two potentially competitive reactive centers for the cycloaddition with dichloroketene. The only example found in the literature of a related [2+2] cycloaddition of dichloroketene to a strained ketone in the presence of a norbornenic double bond was reported by Reid and Bellinger[9]. These authors found that the reaction of tricyclic compound 7 with the system $Cl_3CCOCl/Zn$ yielded β-lactone 8 in poor yields (16-25%).

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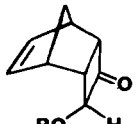


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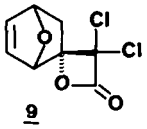
The reaction of 6 with an excess of trichloroacetyl chloride and zinc/copper couple in refluxing ether, (the conditions described by Brady[3]), afforded a good yield of spiro β-lactone 9. Even in the presence of four equivalents of the ketene precursor and phosphorus oxychloride[6], none of the expected cyclobutane derivative arising from [2+2] cycloaddition to the endocyclic double bond could be detected. We encountered analogous results, relative to the carbon-carbon double bond, for norbornenic ketone 5, wich yielded only 11% of spiro dichlorolactone 10, along with recovered starting material, when the reaction was effected in an identical manner. This shows that although the carbon-carbon double bonds of 5 and 6 are "similarly" unreactive towards dichloroketene[10], there is a significant difference in the reactivity of their carbonyl functionalities.

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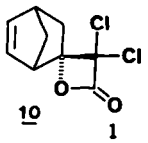


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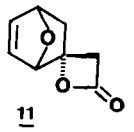


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The stereochemistry of 9 was determined from its H-NMR data. A remarkable downfield shift for H-1 (0.80 ppm) and H-3 exo (0.72 ppm) was observed upon dichlorolactonization of 6. Furthermore, dechlorination to yield β-lactone 11 (see below) resulted in large upfield shifts for H-1 (0.52 ppm) and H-3 exo (0.55 ppm). These changes in the chemical shifts are consistent with a cis arrangement of H-1, H-3 exo and the dichloromethylene moiety with respect to the tetrahydrofuran subunit (Figure 1).

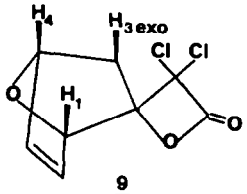


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Figure 1

The reaction considered here presents three noteworthy features : a) the high chemoselectivity observed in the formation of 9 from 5; b) the important role of the oxygen

bridge, which is apparent upon comparison of the results of the dichlorolactonizations of 5 and 6 and c) the complete exo selectivity encountered for the process. The high chemoselectivity found in the dichlorolactonization of 5 may be accounted for by a differential activation of the carbonyl group by the zinc halide[8,11] which cannot take place for the carbon-carbon double bond. As for the precise role of the oxygen brigde[12] and the complete exo selectivity of the reaction[13], the results obtained in the present study are insufficient to establish a mechanistic rationale.

From a synthetic point of view, this dichlorolactonization reaction has been extended to oxanorbornenic derivatives 12 and 13, to afford spiro β-dichlorolactones 14 and 15 with complete exo selectivity and in good yields. Dichlorolactones 9, 14 and 15 were readily dehalogenated to the corresponding spiro β-lactones (11, 16 and 17) with an aluminum amalgam,

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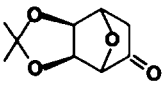

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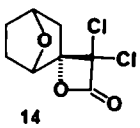

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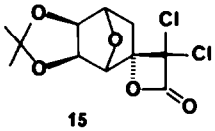

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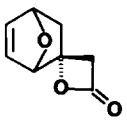
in aqueous tetrahydrofuran[14]. Reductive cleavage of oxetanones 11, 16 and 17 with lithium aluminum hydride in tetrahydrofuran afforded good yields of bicyclic diols 18-20.



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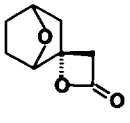

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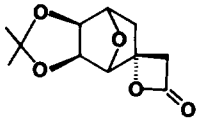

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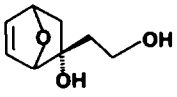

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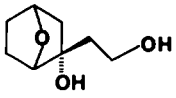

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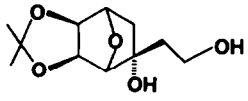

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The reaction of dichloroketene with 7-oxanorbornenone, 6, proceeds chemo- and stereoselectively on its carbonyl function. This dichlorolactonization appears to be quite general for oxanorbornenic substrates, allowing for the straightforward stereoselective introduction at C-2 of a β-functionalized two carbon unit. The resulting oxanorbornenic diols and β-lactones are systems of high potential in synthesis[15].

## EXPERIMENTAL

### General.

All reactions were conducted under a positive pressure of dry nitrogen using freshly distilled solvents under anhydrous conditions unless otherwise stated. Diethyl ether and tetrahydrofuran were distilled from lithium aluminum hydride; hexane and ethyl acetate from phosphorus pentoxide and methylene chloride from calcium hydride. All other commercially available reagents were used without further purification unless otherwise noted.

Analytical TLC was carried out on 0.20 mm E. Merck precoated silica gel plates (60 F-254), using iodine, 2,4-dinitrophenylhydrazine or acidic vanillin solution as visualizing agents. Column chromatography was performed using E. Merck 230-400 mesh or 70-230 mesh silica gel. Sensitive compounds were purified using deactivated silica gel (washed with a 5% solution of $NaHCO_3$ in methanol).

Infrared spectra were recorded on either a Perkin-Elmer 781 or 257 grating

spectrophotomethers; band positions are indicated in wavenumbers.

$^1$H-NMR spectra were recorded on a Varian T-60 A or on a Brüker WH-360 FT spectrometer, using $CDCl_3$ as solvent. $^{13}$C-NMR spectra were measured on a Varian FT-80A in $CDCl_3$ solution. In both, $^1$H-NMR and $^{13}$C-NMR, chemical shifts are reported in units downfield from tetramethylsilane. The following abbreviations are used to describe peak patterns when appropriate: br= broad, s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet.

Melting points were recorded on a Büchi 512 apparatus and are uncorrected.

Elemental analyses were performed by the Consejo Superior de Investigaciones Científicas, Madrid.

## General Procedure for the Dichlorolactonization of 7-Oxanorbornenic Ketones

A flame-dried round-bottomed flask fitted with a magnetic stirring bar, a reflux condenser and a pressure-equalizing addition funnel was charged with 8.0 equivalents of zinc-copper couple, 1 equivalent of ketone and dry ether (20 ml/mmol of ketone). The above suspension was heated at reflux and a solution of 4 equivalents of trichloroacetyl chloride in 10 ml of dry ether/mmol of ketone was added dropwise from the addition funnel. After the addition was complete (ca 1h), the reaction mixture was stirred under reflux for an additional 12 h. The excess zinc was removed by filtration and the resulting yellow solution was poured into cold, saturated sodium bicarbonate (30 ml/mmol of ketone). This mixture was stirred vigorously for 30 min and then the layers were separated. The aqueous portion was extracted once with 50 ml of ether/mmol of ketone and the combined ether fractions were dried over magnesium sulfate. The ether was removed in vacuo leaving the crude lactone as a brown oil. Purification was effected by chromatography on deactivated silica gel.

### (1R*,2R*,4R*)-3',3'-Dichloro-4'-oxa-2,2'-spiro-oxetan-7-oxabicyclo[2.2.1]hept-5-ene, (9)

From 550 mg (5mmol) of 6 was obtained 961 mg of 9 (87%) as a pale yellow oil after chromatography (hexane:ethyl acetate, 5:1, $R_f$= 0.38). $^1$H-NMR $\delta$ 1.83(1H, d, J= 14.0 Hz, H-3 endo), 2.87 (1H, dd, J= 14.0, 5.0 Hz, H-3 exo), 5.17 (1H, dd, J= 5.0, 1.8 Hz, H-4), 5.32 (1H, d, J= 1.8 Hz, H-1), 6.43 (1H, dd, J= 6.0, 1.8 Hz), 6.77 (1H, dd, J= 6.0, 1.8 Hz). $^{13}$C-NMR $\delta$ 38.2, 79.5, 80.2, 84.5, 94.1, 131.9, 140.8, 160.8. IR(film) 675, 830, 855, 1035, 1135, 1205, 1325, 1860, 2880-3050.

### (1R*,2R*,4R*)-3',3'-Dichloro-4'-oxa-2,2'-spiro-oxetan-bicyclo[2.2.1]hept- 5-ene, (10)

The reaction of 5 (270 mg, 2.5 mmol) with trichloroacetyl chloride and 4 equivalents of phosphorus oxychloride (mixed with the acid chloride) according to the general procedure, afforded 60 mg of 10 (11%) after chromatography (hexane:chloroform, 1:1, $R_f$= 0.43). $^1$H-NMR 1.16-2.06 (3H, m), 2.70 (1H, dd, J= 13.0, 4.0 Hz), 3.03 (1H, m) 3.40 (1H, m), 6.13 (1H, dd, J= 6.0, 3.0 Hz), 6.53 (1H, dd, J= 6.0, 3.0 Hz). IR (film) 670, 720, 815, 1030, 1130, 1200, 1330, 1855, 2880-3080.

### (1R*,2R*,4S*)-3',3'-Dichloro-4'-oxa-2,2'-spiro-oxetan-7-oxabicyclo[2.2.1]heptane, (14)

From 448 mg (4 mmol) of 12 was obtained 713 mg of 14 (80%) as a pale yellow oil after chromatography (hexane:ethyl acetate, 5:1, $R_f$= 0.47). $^1$H-NMR $\delta$ 1.60-2.26 (5H, m), 2.74 (1H, dd, J= 14.0, 5.0 Hz, H-3 exo), 4.53-4.80 (1H, m, H-4), 4.91 (1H, d, J= 4.0 Hz, H-1). $^{13}$C-NMR $\delta$ 22.3, 28.3, 39.0, 76.7, 78.7, 83.7, 93.1, 160.1. IR (film) 670, 830, 915, 1020, 1140, 1200, 1280, 1430, 1475, 1855, 2890-3100.

### (1R*,2R*,4R* )-3',3'-Dichloro-4'-oxa-2,2'-spiro-oxetan-5-exo, 6-exo-isopropylidenedioxy-7-oxabicyclo[2.2.1]heptane, (15)

From 644 mg (3.5 mmol) of 13 was obtained 877 mg of 15 (85%) as a white solid (mp= 124-125 °C) after chromatography (hexane:ethyl acetate, 3:1, $R_f$= 0.31). $^1$H-NMR $\delta$ 1.33 (3H, s), 1.50 (3H, s), 1.71 (1H, d, J= 15.0 Hz, H-3 endo), 2.86 (1H, dd, J= 15.0, 6.0 Hz, H-3 exo), 4.46 (1H, d, J= 6.0 Hz, H-5), 4.60 (1H, d, J= 6.0 Hz, H-4), 4.75 (1H, d, J= 6.0 Hz, H-6), 4.85 (1H, s, H-1). $^{13}$C-NMR $\delta$ 24.9, 25.6, 34.6, 77.5, 79.9, 80.8, 80.9, 85.0, 92.2, 112.3, 160.1. IR (KBr): 665, 875, 1035, 1140, 1385, 1885, 2900-3050. Anal. Calcd for $C_{11}H_{12}O_5Cl_2$: C, 44.75; H, 4,07; Cl, 24.07. Found: C, 44.71; H, 4.09; Cl, 24.02.

## General Procedure for Dehalogenation of Dichloro-$\beta$-lactones

To a solution of 1 equivalent of dichlorolactone in tetrahydrofuran/water, 9:1, (30 ml/mmol of lactone), was added 10 equivalent of aluminum amalgam generated from aluminum foil by the procedure of Corey[14]. The mixture was stirred for 3h at room temperature after which time it was filtered through a Celite pad, and the filter cake was rinsed with ether. The combined organic extracts were washed with a saturated sodium chloride solution and dried over magnesium sulfate. The solvent was removed in vacuo, and the crude product was purified by chromatography on silica gel.

(1R*,2S*,4R*)-4'-Oxa-2,2'-spiro-oxetan-7-oxabicyclo[2.2.1]hept-5-en, (11)

From 450 mg (2.04 mmol) of 9 was obtained 242 mg of 11 (78%) as a transparent oil after chromatography (hexane:ethyl acetate, 5:1, $R_f$= 0.21). $^1$H-NMR δ 1.78 (1H, d, J= 14.0 Hz, H-3 endo), 2.32 (dd, J= 14.0, 4.5 Hz, H-3 exo), 3.62 (2H, br s, -$CH_2$-), 4.80 (1H, br s, H-1), 5.07 (1H, dd, J= 4.5, 1.8, H-4), 6.42 (1H, dd, J= 6.0, 1.8 Hz, H-5), 6.60 (1H, dd, J= 6.0, 1.5 Hz, H-6). $^{13}$C-NMR δ 38.0, 47.5, 78.6, 79.8, 81.8, 132.4, 137.9, 166.8. IR (film) 710, 800, 885, 1005, 1120, 1325, 1415, 1830, 2880-3100. Anal. Calcd for $C_8H_8O_3$: C, 63.16; H, 5.26. Found: C, 63.20; H, 5.23.

(1R*,2S*,4S*)-4'-Oxa-2,2'-spiro-oxetan-7-oxabicyclo[2.2.1]heptane, (16).

From 510 mg (2.28 mmol) of 14 was obtained 288 mg of 16 (82%) as a transparent oil after chromatography (methylene chloride, $R_f$= 0.28). $^1$H-NMR δ 1.60-2.24 (5H, m), 2.26 (1H, dd, J= 13.0, 5.0 Hz, H-3 exo), 3.28 (1H, d, J= 17.0 Hz, -$CH_2$-), 3.55 (1H, d, J= 17.0 Hz, -$CH_2$-), 4.48 (1H, d, J= 4.0 Hz, H-1), 4.63 (1H, m, H-4). $^{13}$C-NMR δ 22.9, 28.2, 41.3, 48.4, 77.5, 80.2, 80.6, 167.8. IR (film) 810, 1020, 1255, 1410, 1820, 2900-3020. Anal. Calcd for $C_8H_{10}O_3$: C, 62.31; H, 6.54. Found: C, 62.25; H, 6.51.

(1R*,2S*,4R*)-4'-Oxa-2,2'-spiro-oxetan-5-exo, 6-exo-isopropylidenedioxy-7-oxabicyclo-[2.2.1]heptane, (17)

From 790 mg (2.67 mmol) of 15 was obtained 452 mg of 17 (75%) as a white solid (mp= 134-135 °C) after chromatography (chloroform:hexane, 1:1, $R_f$= 0.28). $^1$H-NMR δ 1.35 (3H, s), 1.50 (3H, s), 1.80 (1H, d, J= 14.0 Hz, H-3 endo), 2.28 (1H, dd, J= 14.0, 6.0 Hz, H-3 exo), 3.40 (1H, d, J= 17.0, -$CH_2$-), 3.64 (1H, d, J= 17.0 Hz, -$CH_2$), 4.33 (1H, br s, H-1), 4.42 (1H, d, J= 5.0 Hz, H-5), 4.46 (1H, d, J= 6.0 Hz, H-4), 4.75 (1H, d, J= 5.0 Hz, H-6). $^{13}$C-NMR δ 24.7, 25.5, 36.2, 49.6, 77.9, 78.5, 80.3, 81.0, 82.9, 111.7, 165.7. IR (KBr) 665, 820, 1075, 1125, 1370, 1830, 2930-3040. Anal. Calcd for $C_{11}H_{14}O_5$: C, 58.41; H, 6.19. Found: C, 58.45; H, 6.16.

General Procedure for Reductive Cleavage of β-Lactones

To a cold (0 °C) solution of 1 equivalent of β-lactone in anhydrous tetrahydrofuran (10 ml/mmol of lactone) was added 8 equivalents of lithium aluminum hydride and the resulting mixture was stirred for 5 min after which time the reaction was quenched with a saturated solution of ammonium chloride. The solid residue was removed by filtration and the filter cake was washed with ethyl acetate. The combined organic extracs were washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the crude diol was purified by chromatography on silica gel.

2-endo-Hydroxy-2-exo-2'-hydroxyethyl-7-oxabicyclo[2.2.1]hept-5-ene, (18)

From 320 mg (2.10 mmol) of 11 was obtained 245 mg (75%) of 18 as a pale yellow oil after chromatography (hexane:ethyl acetate, 1:1, $R_f$= 0.25). $^1$H-NMR δ 1.27 (1H, d, J= 12.0 Hz, H-3 endo), 1.97 (1H, dd, J= 12.0 Hz, 4.5 Hz), 2.02 (2H, t, J= 6.0 Hz, -$CH_2$-C), 3.63 (2H, br s, 2 -OH), 3.92 (2H, t, J= 6.0 Hz, -$CH_2$-OH), 4.55 (1H, d, J= 1.8 Hz, H-1), 4.90 (1H, dd, J= 4.5, 1.5 Hz, H-4), 6.40 (1H, dd, J= 6.0, 1.8 Hz, H-5), 6.57 (1H, dd, J=6.0, 1.5 Hz, H-6). $^{13}$C-NMR δ 40.7, 41.0, 59.8, 78.7, 79.4, 82.8, 133.0, 137.2. IR (film) 710, 900, 1085, 1320, 1440, 2800-3050, 3050-3650. Anal. Calcd for $C_8H_{12}O_3$: C, 61.54; H, 7.69. Found: C, 61.50; H, 7.65.

2-endo-Hydroxy-2-exo-2'-hydroxyethyl-7-oxabicyclo[2.2.1]heptane, (19)

From 150 mg (0.97 mmol) of 16 was obtained 135 mg (88%) of 19 as a pale yellow oil after chromatography (ethyl acetate, $R_f$= 0.37). $^1$H-NMR δ 1.40 (1H, d, J= 12.0 Hz, H-3 endo), 1.56-2.50 (7H, m), 3.66 (2H, br s, 2 -OH), 3.90 (2H, t, J= 6.0 Hz, -$CH_2$-OH), 4.23 (1H, d, J= 6.0 Hz, H-1), 4.50 (1H, m, H-4). $^{13}$C-NMR δ 22.5, 29.8, 41.0, 45.0, 59.3, 78.0, 80.6, 82.0. IR (film) 770, 890, 985, 1230, 1440, 2800-3050, 3350. Anal. Calcd for $C_8H_{14}O_3$: C, 60.76; H, 8.86. Found: C, 60.81; H, 8.81.

2-endo-Hydroxy-2-exo-2'-hydroxyethyl-5-exo,6-exo-isopropylidenedioxy-7-oxabicyclo[2.2.1]heptane, (20)

From 190 mg (0.84 mmol) of 17 was obtained 185 mg (96%) of 20 as a white solid (mp= 74-76 °C) after chromatography (ethyl acetate, $R_f$= 0.30). $^1$H-NMR δ 1.30 (1H, d, J= 13.0 Hz, H-3 endo), 1.33 (3H, s), 1.50 (3H, s), 1.66-2.13 (3H, m, H-3 exo and -$CH_2$-C), 3.53 (2H, br s, 2 -OH), 3.96 (2H, t, J= 6.0 Hz, -$CH_2$-OH), 4.10 (1H, s, H-1), 4.33 (1H, d, J= 6.0 Hz, H-4), 4.40 (1H, d, J=6.0 Hz, H-5), 5.03 (1H, d, J= 6.0 Hz, H-6). $^{13}$C-NMR δ 34.2, 35.2, 49.0, 49.8, 69.0, 77.8, 78.0, 79.8, 81.2, 83.2, 110.2. IR(KBr) 790, 870, 1100, 1210, 1375, 2800-3040, 3400. Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.39; H, 7.83. Found: C, 57.34; H, 7.79.

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