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Dichlorocyclopropanation of sugar dichloroolefins: a new route to spirocyclopropanes at the anomeric position†

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Summary — Some sugar dichloroolefins, readily available from sugar lactones, react with dichlorocarbene, generated under phase transfer catalysis, to provide tetrachloro-*C*-1-spirocyclopropanes in good yields. These new compounds have been reduced to spirocyclopropanes anchored at the anomeric position.

lactone / dichloroolefin / anomeric spirocyclopropane / reduction

Résumé — Dichlorocyclopropanation de dichlorooléfines dérivées de sucres: une nouvelle voie d'accès à des spirocyclopropanes en position anomérique. *Quelques dichlorooléfines, préparées à partir de lactones de sucres réagissent avec le dichlorocarbène pour fournir des tétrachlorospirocyclopropanes dont la réduction par l'hydrure de lithium et d'aluminium fournit de nouveaux spirocyclopropanes en position anomère*

lactone / dichlorooléfine / spirocyclopropane anomère / réduction

Introduction

Glycosidases as well as glycosyl transferases inhibitors have received much attention in the last few years because they could interfere with glycosylating processes and thus play a role in the control of several biological events [1]. *C*-1-Spirocyclopropanes constitute a new class of compounds which could have interesting potential as enzyme inhibitors because of the possible formation of covalent bonds between the strained cyclopropanes and reactive functional groups of enzymes [2, 3]. These spirocyclopropanes may also be regarded as intermediates for the synthesis of complex *C*-glycosidic compounds with two branched carbon chains at the anomeric position. Some carbohydrates having a spirocyclopropane branch have been described [3, 4], but only a few representatives of 'spiroanomeric' cyclopropanes, obtained by reaction of anomeric carbenes with olefins, have been recently described [5]. To the best of our knowledge, the reversal procedure, eg, the reaction of glycosylidene olefins with carbenes, has not been investigated. The dihalocyclopropanation of 5,6-unsaturated methyl glycosides has been reported by Gross and coworkers [6] and later by Vasella and coworkers [7]. In connection with our ongoing programme of synthesis of new *C*-glycosidic bonds as mimics of *O*-glycosidic bonds, we have investigated the cyclopropanation of anomeric double bonds. Dichloroolefins have been recently introduced by our group, and are now easily available from the reaction of sugar lactones with triphenylphosphine-tetrachloromethane [8]. We report here our results on the dichlorocyclopropanation [9] of some representative dichloroolefins and their subsequent transformations into *C*-1 spirocyclopropanes.

Results

Dichloroolefins **1–4**, prepared according to our recently published procedure [8], were treated with dichlorocarbene generated under phase transfer catalysis conditions using 50% aqueous solution of sodium hydroxide and chloroform, and benzyltriethylammonium chloride as a catalyst [10]. The reaction proceeded well within several hours, giving only one compound in good yield in each case. The results of this study are summarized in table I. The structures of dichlorocyclopropanes **5–8a** were confirmed by examination of their ^{13}C NMR spectra in which the signal of the olefinic carbons of the starting dichloroolefins were no longer present. Two signals around 65–68 ppm corresponding to

† Warmly dedicated to Pr Bernard Gross on the occasion of his retirement.

* Correspondence and reprints

quaternary carbons were attributed to the chlorine-substituted carbons of the cyclopropane ring. Furthermore, mass spectra showed the characteristic isotopic pattern for compounds containing four chlorine atoms. Proton NMR spectroscopy showed only small shifts for the H-2 sugar proton. As seen from table I, the cyclopropanation proceeded well with different olefins derived from D-gulono-, D-mannono-, D-ribono- and D-erythrono-1,4-lactones. The reaction tolerates the presence of acid-sensitive groups such as isopropylidene and methoxymethyl acetals, but due to the strong basic conditions no reaction was possible using ester-protecting groups. All attempts to extend the cyclopropanation procedure to *O*-benzyl protected dichloroolefins derived from D-arabino-1,4-lactone failed. The six-membered dichloroolefin derived from 2,3,4,6-tetra-*O*-benzyl-D-glucono-1,5-lactone also failed to react with dichlorocarbene. These failures can be explained by the presence of benzyl protecting groups which can react with dichlorocarbene by insertion into the benzylic C–H bond [11].

Table I. Dichlorocyclopropanation of dichloroolefins.

Entry	*Starting compound*	*Product*	*Time (h)*	*Yield (%)*[a]
1	1	**5a**	2	79
2	2	**6a**	2	70
3	3	**7a**	2	92
4	4	**8a**	2.5	100

[a] Yields refer to pure isolated compounds.

In an effort to prepare unsymmetrical spirocyclopropane derivatives, we tried to use dibromocarbene instead of dichlorocarbene. Instead of the expected unsymmetrical derivatives, variable yields of the tetrachlorocyclopropanes were obtained. Chlorobromocarbene, generated according to Jonczyk and Balcerzak [12], also gave the tetrachlorocyclopropanes. The absence of mixed chlorobromocyclopropanes in both reactions was probably the result of a halogen exchange from bromide to chloride under the reaction conditions. This type of halogen exchange has been reported previously [13].

Tetrachlorocyclopropanes are rather unreactive and their transformation into more reactive cyclopropanes by reduction of the carbon–chlorine bonds was attempted. Tributyltin hydride has been successfully used for the reduction of dibromocyclopropanes [6b], but with our substrates this method was uneffective and gave complex mixtures of products resulting probably from partial reduction as shown by mass spectrometry. Lithium aluminium hydride is known to reduce cyclopropyl halides [14]. Thus, the reaction of compounds **5a–8a** with lithium aluminium hydride in dry tetrahydrofuran at room temperature was explored. The reduction was slow but provided the expected cyclopropanes **5b–8b** in good yields. These results are summarized in table II. Here again the presence of the cyclopropane was confirmed by the presence of high-field signals below 1 ppm in ^{1}H- and below 20 ppm in ^{13}C-NMR spectra.

In conclusion the combination of dichloromethylenation of sugar lactones and cyclopropanation using

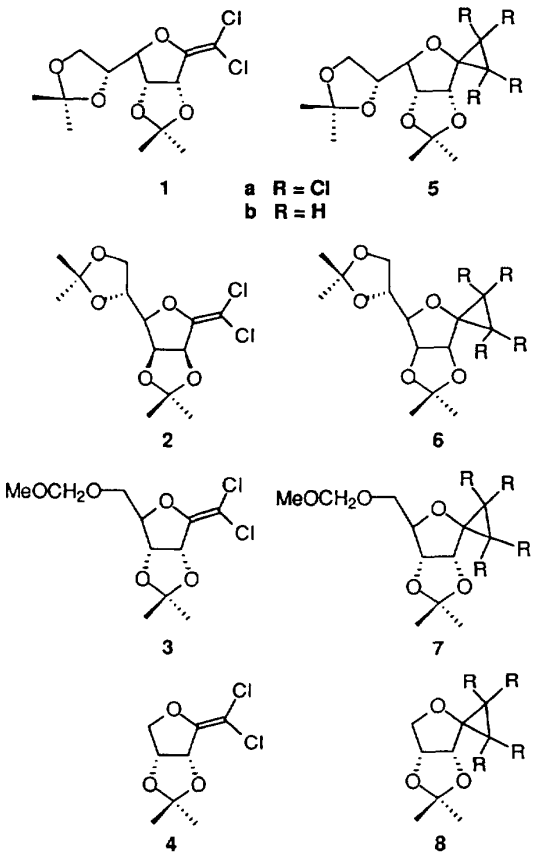

Fig 1

Table II. Reduction of tetrachlorocyclopropanes.

Entry	*Starting compound*	*Product*	*Time (h)*	*Yield (%)*[a]
1	**5a**	**5b**	66	74
2	**6a**	**6b**	64	62
3	**7a**	**7b**	75	59
4	**8a**	**8b**	48	62

[a] Yields refer to pure isolated compounds.

dichlorocarbene opens the way to the synthesis of a new type of C-1 spirocyclopropane. Until now this reaction is limited to acetal-protected dichloroolefins, since benzyl ethers cause side reactions. The reduction of the tetrachlorocyclopropanes to cyclopropane proceeds well and this new class of compounds may find some applications in the field of carbohydrate-mimics chemistry and biochemistry. Other synthetically-useful transformations of compounds **5a–8a** and **5b–8b** are currently being investigated.

Experimental section

^{1}H-NMR spectra were recorded with a Bruker Aspect 3000 spectrometer operating at 400 MHz and an AC 250 operating at 250 MHz, using deuteriochloroform as solvent. Assignments were confirmed by double irradiation or two-

dimensional spectroscopy. Chemical shifts are reported relative to internal $SiMe_4$. TLC was performed on silica-gel plates (Merck $60F_{254}$). Column chromatography used silica gel (Merck 60 70-23 mesh). Mixtures of ethyl acetate (A) and hexane (H) were used as eluents. Optical rotations were measured on a Perkin-Elmer 141 polarimeter at 20 °C. Melting points were measured in capillary tubes and are uncorrected. The elementary analyses were performed by the Service central de microanalyses du CNRS at Vernaison, France. Mass spectra were obtained on a Nermag R10-10C in the EI mode. Tetrahydrofuran was distilled prior to use from sodium benzophenone. All reactions were performed under nitrogen atmosphere. The IUPAC nomenclature has been used to name the compounds **5**, **6**, **7** and **8**, but for sake of convenience carbon atoms 4 and 5 of the 1,3-dioxolan-4-yl appendage of compounds **5** and **6** have been numbered 7 and 8 respectively in the NMR description.

General procedure for dichlorocyclopropanation

To a solution of the dichloroolefin (1 mmol) and benzyltriethylammonium chloride (0.1 mmol) in chloroform (10 mL) was added dropwise at 0 °C a 50% aqueous solution of sodium hydroxide (5 mL). The mixture was stirred at 0 °C for 30 min and allowed to warm to room temperature and stirred for the time indicated in table I. At the end of the reaction, 10 mL water was cautiously added and the mixture extracted with methylene chloride (3 × 50 mL). The organic layer was washed with water until neutral and dried over magnesium sulfate. After removal of the solvent under vacuum, the residue was chromatographed on a silica-gel column using hexane and ethyl acetate mixtures.

• *(3′aR)-2,2,3,3-Tetrachloro-6′c-((4R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2′,2′-dimethyl-(3′ar,6′ac)-tetrahydrospiro[cyclopropane-1,4′-furo[3,4-d][1,3]dioxolane]* **5a**

Yield: 320 mg, 79%. R_f = 0.56 (H/A: 3/1); mp 124 °C (CH_2Cl_2/hexane); $[\alpha]_D = -96°$ (*c*, 0.6, $CHCl_3$).

^{1}H NMR: δ 1.20 (s, 6H, $2CH_3$); 1.25 (s, 3H, CH_3); 1.35 (s, 3H, CH_3); 3.79 (dd, 1H, H-6′, J = 8 Hz); 3.81 (dd, 1H, H-8′, J = 6, 9 Hz); 4.22 (dd, 1H, H-8); 4.49 (ddd, 1H, H-7, J = 6.5, 6 Hz); 4.83 (dd, 1H, H-6′a, J = 3.5 Hz); 5.05 (d, 1H, H-3′a, J = 6 Hz).

^{13}C NMR: δ 25.4, CH_3; 25.7, CH_3; 26.0, CH_3; 26.0, CH_3; 65.8, C-2, 65.8, C-8; 67.9, C-1; 73.7, C-4′; 74.9, 81.2, 81.6, 84.6, (C-3′a, C-6′a, C-6′, C-7); 110.26, (C acetal); 114.4, (C acetal).

MS (EI, 70 eV): *m/z* 395, 393, 391 $(M-15)^+$, 375, 373, 371 $(M-Cl)^+$, 337, 335, 333, 317, 315, 313, 101, and 43.

Anal calc for $C_{14}H_{18}Cl_4O_5$ C, 41.38; H, 4.47; Cl, 34.45. Found: C, 41.45; H, 4.42; Cl, 34.61.

• *(3′aS)-2,2,3,3-Tetrachloro-6′c-((7R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2′,2′-dimethyl-(3′ar,6′ac)-tetrahydrospiro[cyclopropane-1,4′-furo[3,4-d][1,3]dioxolane]* **6a**

Yield: 284 mg, 70%; R_f = 0.66 (H/A: 3/1); mp 93 °C (CH_2Cl_2/hexane); $[\alpha]_D = +75°$ (*c*, 0.3, $CHCl_3$).

^{1}H NMR: δ 1.39 (s, 3H, CH_3); 1.41 (s, 3H, CH_3); 1.43 (s, 3H, CH_3); 1.57 (s, 3H, CH_3); 3.67 (dd, 1H, H-6′, J = 8 Hz); 4.05 (dd, 1H, H-8′, J = 4 Hz); 4.15 (dd, 1H, H-8, J = 6, 9 Hz); 4.48 (m, 1H, H-7); 4.96 (dd, 1H, H-6′a, J = 3.5 Hz); 5.06 (d, 1H, H-3′a, J = 6 Hz).

^{13}C NMR: δ 25.0, CH_3; 25.6, CH_3; 26.1, CH_3; 26.8, CH_3; 65.7, C-1; 66.9, C-8; 67.9, C-2; 72.2, C-4′; 73.6, 81.0, 81.6, 82.7 (C-3′a, C-6′a, C-6′, C-7); 109.7 (C acetal); 114.4 (C acetal).

MS (EI, 70 eV): *m/z* 395, 393, 391 $(M-15)^+$, 375, 373, 371 $(M-Cl)^+$, 337, 335, 333, 317, 315, 313, 157, 101, and 43.

Anal calc for $C_{14}H_{18}Cl_4O_5$: C, 41.38; H, 4.47; Cl, 34.45. Found: C, 41.25; H, 4.52; Cl, 34.51.

• *(3′aR)-2,2,3,3-Tetrachloro-6′t-((methoxymethyloxy)methyl)-2′,2′-dimethyl (3′ar,6′ac)-tetrahydrospiro[cyclopropane-1,4′-furo[3,4-d][1,3]dioxolane]* **7a**

Yield: 350 mg, 92%; R_f = 0.33 (H/A: 4/1); mp 73 °C (CH_2Cl_2/hexane); $[\alpha]_D = -77.6°$ (*c*, 0.1, $CHCl_3$).

^{1}H NMR: δ 1.42 (s, 3H, CH_3); 1.60 (s, 3H, CH_3); 3.39 (s, 3H, OCH_3); 3.61 (dd, 1H, H-7′, J = 11, 2.5 Hz); 3.83 (dd, 1H, H-7, J = 3 Hz); 4.59 (m, 1H, H-6′); 4.64 (t, 2H, OCH_2); 4.95 (d, 1H, H-6′a, J = 6 Hz); 5.13 (d, 1H, H-3′a).

^{13}C NMR: δ 26.5, CH_3; 26.6, CH_3; 55.7, OCH_3; 66.9, C-1; 68.7, C-7; 69.9, C-2, 75.3, C-4′; 83.6, 83.9, 85.1 (C-3′a, C-6′, C-6′a); 97.2, OCH_2; 113.3 (C acetal).

MS (EI, 70 eV): *m/z*: 369, 367, 365 $(M-15)^+$, 349, 347, 345, 289, 287, 285, 229, 227, 225.217, 215, 213, 199, 157, 103, 87, 69, and 45.

Anal calc for $C_{12}H_{16}Cl_4O_5$: C, 37.90; H, 4.24; Cl, 36.81. Found: C, 38.21; H, 4.29; Cl, 35.21.

• *(3′aR)-2,2,3,3-Tetrachloro-2′,2′-dimethyl-(3′ar,6′ac)-tetrahydro-spiro[cyclopropane-1,4′-furo-[3,4-d][1,3]dioxolane]* **8a**

Yield: 306 mg, 100%; R_f = 0.53 (H/A: 3/1); mp 84 °C (CH_2Cl_2/hexane); $[\alpha]_D = -13.3°$ (*c*, 0.5, $CHCl_3$).

^{1}H NMR: δ 1.40 (s, 3H, CH_3); 1.60 (s, 3H, CH_3); 3.60 (d, 1H, H-6′, J = 9.5 Hz); 4.70 (dd, 1H, H-6′, J = 3 Hz); 4.76 (dd, 1H, H-6′a, J = 7 Hz); 5.00 (d, 1H, H-3′a).

^{13}C NMR: δ 25.7, CH_3; 26.3, CH_3; 65.8, C-1; 68.0, C-2; 74.0, C-6′; 74.6, C-2; 81.1, 81.3, (C-3′a, C-6′a); 114.0 (C acetal).

MS (EI, 70 eV): *m/z*: 311, 309, 307 $(M + H)^+$, 295, 293, 291 $(M-Cl)^+$, 275, 273, 271, 161, 159, 157, and 43.

Anal calc for $C_9H_{10}Cl_4O_3$: C, 35.30; H, 3.29; Cl, 45.72. Found: C, 35.43; H, 3.18; Cl, 46.36.

General procedure for reduction of tetrachlorocyclopropanes

Lithium aluminium hydride (190 mg, 5 mmol) was suspended in dry tetrahydrofuran (6 mL) and stirred for 30 min. The tetrachlorocyclopropane derivative (1 mmol) was added and the reaction was stirred at room temperature for the time indicated in table II. At the end of the reaction, the excess reagent was destroyed by careful introduction of water (0.2 mL), 30% aqueous sodium hydroxide (0.2 mL), and water (0.6 mL). After filtration of the solid and evaporation of the solvent the residue was chromatographed on a silica-gel column to give the pure spirocyclopropanes.

• *(3′aR)-6′c-((4R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2′,2′-dimethyl-(3′ar,6′ac)-tetrahydrospiro[cyclopropane-1,4′-furo[3,4-d][1,3]dioxolane]* **5b**

Yield: 200 mg, 74%; R_f = 0.43 (H/A: 3/1); mp 98 °C (CH_2Cl_2/hexane); $[\alpha]_D = -42.9°$ (*c*, 0.1, $CHCl_3$).

^{1}H NMR: δ 0.50 (ddd, 1H, H-1, J = 10, 7, 4.5 Hz); 0.85 (ddd, 1H, H-2, J = 11 Hz); 0.95 (ddd, 1H, H-1, J = 5.5, 7 Hz); 1.15 (ddd, 1H, H-2); 1.31 (s, 3H, CH_3); 138 (s, 3H, CH_3); 1.44 (s, 3H, CH_3); 1.53 (s, 3H, CH_3); 3.70 (m, 2H, H-6′ and H-8); 4.24 (dd, 1H, H-8, J = 8, 7Hz); 4.40 (m, 2H, H-3′a and H-7); 4.74 (dd, 1H, H-6′a, J = 6, 4 Hz).

^{13}C NMR: δ 5.6, C-1; 11.8, C-2; 25.3, CH_3; 25.4, CH_3; 26.0, CH_3; 26.7, CH_3; 66.0, C-8; 66.8, C-4′; 75.7, 81.6, 83.5,

85.4 (C-3'a, C-6'a, C-6', C-7); 109.7 (C acetal); 112.7 (C acetal).

Anal calc for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 61.92; H, 7.94.

• *(3'aS)-6'c-((4R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2',2'-dimethyl (3'ar,6'ac)-tetrahydrospiro[cyclopropane-1,4'-furo[3,4-d][1,3]dioxolane]* **6b**

Yield 166 mg, 62% (oil); $R_f = 0.47$ (H/A: 3/1); $[\alpha]_D = +24°$ (*c*, 0.17, $CHCl_3$).

^{1}H NMR: δ 0.54 (ddd, 1H, H-1, $J = 8, 4, 5.5$ Hz); 0.70 (ddd, 1H, H-2, $J = 5.5, 4$ Hz); 0.95 (ddd, 1H, H-1, $J = 8$ Hz); 1.10 (ddd, 1H, H-2); 1.35 (s, 3H, CH_3); 1.36 (s, 3H, CH_3); 1.45 (s, 3H, CH_3); 1.55 (s, 3H, CH_3); 3.60 (dd, 1H, H-6', $J = 3, 4.5$ Hz); 3.97 (dd, 1H, H-8, $J = 3.5, 7$ Hz); 4.07 (dd, 1H, H-8, $J = 5$ Hz); 4.36 (d, 1H, H-3'a, $J = 4.5$ Hz); 4.42 (ddd, 1H, H-7); 4.87 (dd, 1H, H-6'a).

^{13}C NMR: δ 5.5, C-1; 11.9, C-2; 24.9, CH_3; 25.2, CH_3; 25.9, CH_3; 26.9, CH_3; 66.7, C-8; 66.9, C-4'; 73.0, 81.3, 81.8, 85.2 (C-3'a, C-6'a, C-6', C-7); 109.1 (C acetal); 112.45 (C acetal).

Anal calc for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 61.88; H, 7.95.

• *(3'aR),6't-((Methoxymethyloxy)methyl)-2',2'-dimethyl (3'ar,6'ac)-tetrahydrospiro[cyclopropane-1,4'-furo[3,4-d][1,3]dioxolane]* **7b**

Yield: 142 mg, 59% (oil); $R_f = 0.39$ (H/A: 2/1); $[\alpha]_D = -23.7°$ (*c*, 0.4, $CHCl_3$).

^{1}H NMR: δ 0.65 (ddd, 1H, H-1, $J = 11$, $J = 5$, $J = 7.5$ Hz); 0.80 (ddd, 1H, H-1, $J = 7.5$, $J = 5$ Hz); 0.92 (ddd, 1H, H-2, $J = 11$ Hz); 1.00 (ddd, 1H, H-2); 1.35 (s, 3H, CH_3); 1.55 (s, 3H, CH_3); 3.35 (s, 3H, OCH_3); 3.60 (m, 3H, H-6'a, H-7 and H-7'); 4.20 (m, 1H, H-6'); 4.65 (s, 2H, OCH_2); 4.75 (d, 1H, H-3'a, $J = 6$ Hz).

^{13}C NMR: δ 5.7, C-1, 13.0, C-2; 25.5, CH_3; 25.6, CH_3; 55.4, OCH_3; 67.0, C-7; 67.1, C-4'; 82.7, 83.3, 84.6 (C-6', C-3'a, C-6'a); 96.7, OCH_2; 112.8 (C acetal).

Anal calc for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 61.20; H, 8.42.

• *(3'aR)-2,2-Dimethyl-(3'ar,6'ac)-tetrahydrospiro-[cyclopropane-1,4'-furo[3,4-d][1,3]dioxolane]* **8b**

Yield: 104 mg, 62% (oil); $R_f = 0.25$ (H/A: 2/1); $[\alpha]_D = -65°$ (*c*, 0.17, $CHCl_3$).

^{1}H NMR: δ 0.45 (ddd, 1H, H-1, $J = 7.5, 4.5$ Hz); 0.55 (ddd, 1H, H-1, $J = 4.5, 4$ Hz); 0.95 (ddd, 1H, H-2, $J = 8$ Hz); 1.10 (ddd, 1H, H-2); 1.40 (s, 3H, CH_3); 1.50 (s, 3H, CH_3); 4.00 (dd, 1H, H-6', $J = 4, 11$ Hz); 4.25 (d, 1H, H-6'); 4.50 (d, 1H, H-3'a, $J = 6$ Hz); 4.90 (dd, 1H, H-6'a).

^{13}C NMR: δ 5.6, C-1; 11.2, C-2; 25.3, CH_3; 26.2, CH_3; 67.2, C-4'; 69.1, 75.2, 79.1, (C-6', C-3'a, C-6'a); 110.1 (C acetal).

Anal calc for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.80; H, 8.25.

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