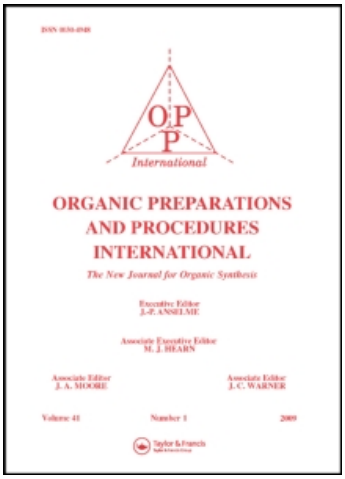

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PREPARATION AND REACTIVITY OF CERTAIN OXAPOLYCYCLIC SYSTEMS

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PREPARATION AND REACTIVITY OF CERTAIN OXAPOLYCYCLIC SYSTEMS

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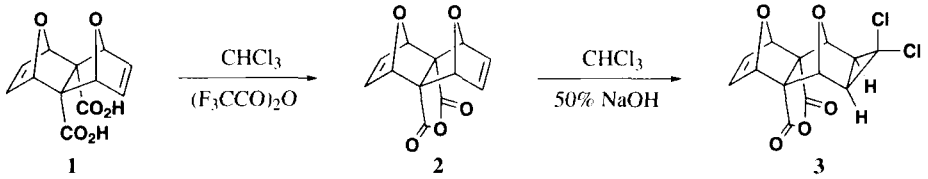
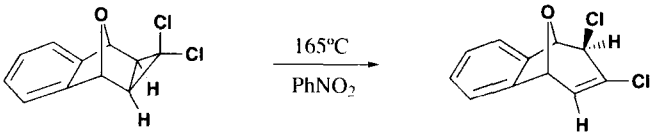
In the course of our studies on the preparation of polyfunctional *cis* substituted decalins,[1] we became interested in a group of compounds derived from the dicarboxylic acid **1**. This oxapolycyclic system, first described by Diels and Alder,[2] is obtained from the twofold [4+2] cycloaddition of two equivalents of furan to acetylene dicarboxylic acid.[2,3] As the dimethyl ester corresponding to the diacid **1** is prone to retro Diels-Alder reaction, the much more stable anhydride **2** was selected for further investigations. Conversion of **1** to **2** was achieved by treatment of a suspension of **1** in chloroform with trifluoroacetic acid anhydride (*Scheme 1*).[4] This method is superior to the literature procedure ($SOCl_2$) described by Warrener,[5] because now the polymerisation of the sensitive compound is reduced to a minimum.



1 **2** **3**

Scheme 1

Our original synthetic plan called for a two-fold dichlorocyclopropanation of anhydride **2**, because a two-fold ring enlargement of type **4** to **5** (*Scheme 2*)[6] would lead to a useful building block. Unfortunately, several methods of dichlorocarbene generation and addition failed. Under phase transfer conditions (50% NaOH, $CHCl_3$, CH_2Cl_2, TEBA), we were only able to get the mono addition product **3** when using a very large excess of the reagents (*Scheme 1*). It was not possible to force the



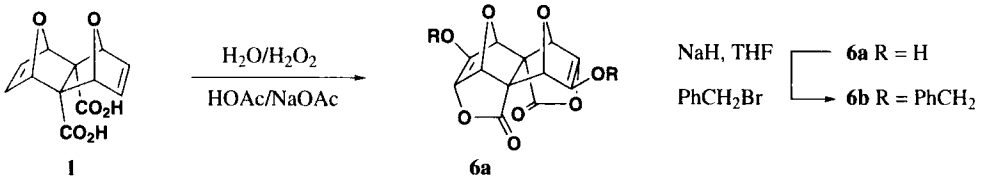
4 **5**

Scheme 2

addition of a second equivalent of CCl_2, neither by use of an even larger excess of $NaOH/CHCl_3$, nor by treating isolated **3** again under similar conditions. Apparently the double bond of **3** is electronically deactivated. In addition, the bisadduct would be strained excessively. It should be noted that we were able to prepare the formal bisadduct of CH_2 to a related compound (carrying ester groups at the double

bonds) *via* a detour.[1] This product lacks the endo positioned chlorine atoms which would be responsible for excessive strain. Interestingly, **3** is stable towards attempted rearrangements. It is only polymerized presumably *via* retro Diels-Alder reaction at higher temperatures or long reaction times.

Apart from the just mentioned reactions of the diacid **1**, we were also interested in a further functionalisation of the polycyclic carbon framework of these compounds. Here, especially a selective oxidation of the two double bonds should lead to an interesting substitution pattern. Deslongchamps described a dibromo bislactone which is formed on treatment of a slightly basic aqueous solution of diacid **1** with bromine.[3] We were able to develop a very simple method for the bishydroxylation of **1** using a similar approach.[7] We found that by stirring a solution of the disodium salt of the diacid **1** in a mixture of dilute acetic acid and hydrogen peroxide at 70° for 24h, the dihydroxy bislactone **6a** crystallized directly from the reaction mixture on cooling (*Scheme 3*). This lactone proved to be extraordinary stable: Attempted lactone opening reactions failed to give diesters from compound **6a** or from the mentioned dibromo bislactone under acidic as well as under basic conditions. Likewise, it was impossible to form the corresponding imides by heating with primary amines.



1 6a

Scheme 3

As compound **6a** is quite insoluble in common organic solvents, we also prepared the corresponding bisbenzyl ether **6b** for a more detailed characterization.

EXPERIMENTAL SECTION

Melting points were determined using a Büchi 510 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Mattson Model Genesis FT-IR. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AC 250-P spectrometer operating at 250 MHz for ^{1}H and at 62 MHz for ^{13}C. Chemical shifts are in ppm relative to TMS as internal standard. Mass spectra were recorded on a Fisons Instruments VG AutoSpec with methane as ionization gas. Elemental analyses were performed on a Leco Model CHNS-932.

***exo,exo*-11,12-Dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene 2,7-dicarboxylic Acid Anhydride (2).**- A suspension of 32.6 g (130 mmol) of diacid **1** in 250 mL of dry chloroform was cooled to 0° and treated within 1 hour with 40 mL (288 mmol) of trifluoroacetic acid anhydride. After 15 hours stirring at rt all volatile compounds were removed *in vacuo* and the solid residue was again taken up in 400 mL of chloroform. Then 20 g of SiO_2 and 1 g of active carbon were added and after another 15 minutes the slurry was filtered. The red solution was concentrated *in vacuo* (150 mL) and on cooling to 0° crystallization of the anhydride occurred to give 28.3 g (94%) of **2**, mp 190°. IR (KBr): 3019,

1851, 1778, 1315, 1226, 1176, 971, 917 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.30 (s, 4H), 6.78 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$): δ 72.67, 81.55, 139.89, 167.24 ppm. MS (CI) m/z (%): 233 (9), 215 (18), 204 (32), 187 (44), 171 (60), 165 (92), 137 (61), 121 (100).

Anal. Calcd for $C_{12}H_8O_5$: C, 62.07; H, 3.47. Found C, 62.03; H, 3.36

10,10-Dichloro *exo,exo*-12,13-dioxapentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]trideca-4-ene 2,7-dicarboxylic Acid Anhydride (3).- Anhydride **2** (2.32 g, 10 mmol) was dissolved in a mixture of 80 mL of chloroform and 20 mL of dichloromethane. Then 2 mL ethanol, 100 mg benzyltriethyl-ammonium chloride (TEBA), and 0.8 mol of a cold, freshly prepared 50% aqueous NaOH (32 g NaOH and 32 g water) were added. The reaction mixture was stirred violently for 3 days at 45°. After this time the brown slurry was diluted with 400 mL of water and extracted several times with CH_2Cl_2. The combined organic layers were washed with water (3x), dried (Na_2SO_4) and concentrated *in vacuo*. The solid residue was purified by column chromatography on silica gel using dichloromethane and ethyl acetate (8:1) as eluent to give 1.92 g (61%) of **3**, mp 215°. IR (KBr): 3085, 1851, 1778, 1353, 1303, 1226, 1180, 1049, 971 cm^{-1}. ^1H NMR (DMSO-d_6): δ 2.47 (s, 2H), 5.39 (s, 2H), 5.52 (s, 2H), 6.84 (s, 2H) ppm. ^{13}C NMR (DMSO-d_6): δ 33.93, 62.19, 72.84, 77.90, 81.39, 138.48, 166.41 ppm. MS (CI) m/z (%): 315 (17), 247 (83), 219 (26), 205 (22), 183 (55), 151 (33), 139 (22).

Anal. Calcd for $C_{13}H_8Cl_2O_5$: C, 49.55; H, 2.56. Found C, 49.28; H, 2.31

***exo,exo*-4,9-*endo,endo*-5,10-Tetrahydroxy *exo,exo*-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]-dode-cane 2,7-dicarboxylic Acid 5,10-Dilactone (6a)**.- To a suspension of 12.5 g (50 mmol) of diacid **1** in 100 mL of a commercial 30% H_2O_2 solution, 12.6 g (150 mmol) of $NaHCO_3$ was added in small portions to dissolve the solid. Then the reaction mixture was treated with 50 mL of acetic acid and stirred at rt for 1 hour, then for 24 hours at 70°. Upon cooling (*without stirring!*) the dihydroxy bislactone **6a** crystallized in tiny white needles. The product was collected and washed with ice water and dried *in vacuo* to give 10.7 g (76%) of **6a**, mp (dec.) 250°. IR (KBr): 3486, 3382, 3162, 2888, 1762, 1334, 1261, 1095, 1025, 948 cm^{-1}. ^1H NMR (DMSO-d_6): δ 4.48 (dd, J = 5.15 Hz, J = 5.15 Hz, 2H), 4.58 (d, J = 5.11 Hz, 2H), 4.75 (s, 2H), 5.42 (d, J = 5.17 Hz, 2H), 5.60 (d, J = 5.12 Hz, 2H) ppm. ^{13}C NMR (DMSO-d_6): δ 59.83, 72.22, 83.85, 84.52, 85.09, 172.10 ppm. MS (CI) m/z (%): 283 (100), 152 (10).

Anal. Calcd for $C_{12}H_{10}O_8$: C, 51.07; H, 3.57. Found C, 51.05; H, 3.44

***exo,exo*-4,9-Dibenzyloxy-*endo,endo*-5,10-dihydroxy *exo,exo*-11,12-dioxatetracyclo-[6.2.1.1^{3,6}.0^{2,7}]dodecane 2,7-dicarboxylic Acid 5,10-Dilactone (6b)**.- Dihydroxy bislactone **6a** (11.3 g, 40 mmol) and 100 mg of tetra-*n*-butylammonium iodide were added in small portions to a suspension of 5.76 g (240 mmol) of oil-free NaH in 100 mL of dry THF. Then, 9.6 mL (80 mmol) of benzyl bromide were added carefully under stirring, and the reaction mixture was heated to reflux for 80 hours. After about 40 hours another 4.8 mL (40 mmol) of benzyl bromide were added. For workup, the resulting slurry was treated cautiously with 100 mL of water and then acidified with conc. HCl to pH 1-2. The solution was extracted with dichloromethane (4 x 100 mL) and the combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The solid residue was recrystallized from CH_2Cl_2 and ethyl acetate (1:2) to give, after separation and drying, colorless crystals (10.3 g, 56%) of

6b, mp 222°. IR (KBr): 3035, 3008, 2877, 1774, 1454, 1365, 1334, 1268, 1168, 1122 cm^{-1}. ^1H NMR (DMSO-d_6): δ 4.54 (s, 4H), 4.57 (m, 2H), 4.83 (m, 2H), 5.09 (s, 2H), 5.50 (m, 2H), 7.30-7.38 (m, 10H) ppm. ^{13}C NMR (DMSO-d_6): δ 60.05, 69.95, 79.51, 81.04, 82.25, 85.22, 127.66, 127.83, 128.21, 137.25, 171.82 ppm.

Anal. Calcd for $C_{26}H_{22}O_8$: C, 67.53; H, 4.79. Found C, 67.24; H, 4.91

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AN EFFICIENT OXIDATION OF LONG CHAIN ALKYL METHYL SULFIDES TO SULFOXIDES

Submitted by (12/16/99)

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The oxidation of sulfides with sodium periodate in water[1] or in aqueous methanol[2] affords sulfoxides selectively and in high yields. On the other hand, the oxidation of sulfides which are poorly soluble or insoluble in these solvent systems does not lead to good results. We now report that long chain alkyl methyl sulfoxides (LCAMSO), which exhibit molecular alignment similar to those of