(20 × 20 cm, 2-mm thick, Merck). Yields of the major products are based on the weights of their isolated samples. Those for minor products were determined by ^1H NMR integration of their characteristic signals relative to that of $CHCl_2CHCl_2$ added to the reaction mixture as an internal standard.

All the spectroscopic data and/or melting points of the compounds obtained showed satisfactory agreement with the literature values.[5,8] The previously unreported 1-(1-triptycyl)ethanol (3) gave satisfactory analytical and spectral data: mp 152–153 °C (from hexane); ^1H NMR ($CDCl_3$) δ 2.19 (d, J = 6.3 Hz, 3 H), 2.41 (d, J = 3.4 Hz, 1 H), 5.36 (s, 1 H), 5.69 (dq, J = 6.3, 3.4 Hz, 1 H), 6.96–7.13 (m, 6 H), 7.26–7.60 (m, 4 H), 7.69–7.80 (dd, 1 H), 7.96–8.12 (dd, 1 H). Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.52; H, 5.96.

Registry No. 1, 59239-90-6; 2, 4423-49-8; 3, 77924-80-2; triptycene, 477-75-8.

β-Lactones as Convenient Precursors to Sterically Congested Olefins

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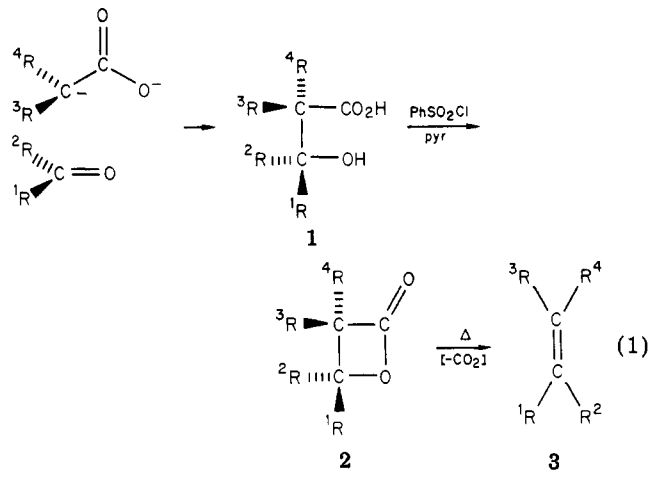
Of the numerous methods for the preparation of alkenes,[3] the McMurray coupling[4] and the Barton extrusion[5] reactions are among the most impressive for the synthesis of sterically congested olefins.[6,7] Some time ago[8] we showed that the β-lactone route (eq 1) is a convenient, stereospecific method for the preparation of alkenes. However, this method was limited to tri- and tetrasubstituted alkenes because otherwise the β-hydroxy acids 1 could not be cyclized into the β-lactones 2 with the benzenesulfonyl chloride–pyridine reagent.



1 2 3 (1)

Inspection of space-filling models of α,β-disubstituted β-hydroxy acids 1 shows that if large alkyl groups are present in the threo configuration, e.g., *tert*-butyl (*t*-Bu) or 1-adamantyl (1-Ad) as in **1a–c** in which $R_1 = R_4$ = *t*-Bu or 1-Ad and $R_2 = R_3$ = H, then through steric repulsion of the large substituents the carboxy and hydroxy groups are optimally juxtaposed to effect dehydrative cyclization. Furthermore, through lithium cation coordination of the carboxylate center with the oxygen of the carbonyl electrophile, it is expected that the condensation of the α-lithiocarboxylate with the carbonyl substrate should afford predominantly the desired *threo*-β-hydroxy acid 1.[9] Indeed, via the sequence in eq 1 a number of sterically hindered olefins 3 could be prepared stereospecifically. GLC analysis showed that only one product, namely, the trans olefin, was formed in the thermal decarboxylation of the β-lactones 2. The results are summarized in Tables I–III. In view of its convenience, this synthetic method is an attractive alternative route to sterically congested olefins.

Experimental Section

Melting points, which were determined on a Thomas-Hoover melting point apparatus, and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 283 infrared spectrophotometer and ^1H NMR spectra on a Hitachi Perkin-Elmer Model R-24B spectrometer. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA. Starting materials were either purchased from standard suppliers or prepared according to literature methods and purified to match the reported physical constants and spectral data. Solvents were purified according to standard literature procedures. Room temperature was normally ca. 30 °C, unless otherwise stated. Rotary evaporations of solvents were usually performed at room temperature and 15–20 torr, unless otherwise stated.

General Procedure for Generation of the Lithium α-Lithiocarboxylate Synthons. A 250-mL, 2-necked, round-bottomed flask, provided with magnetic spinbar, rubber septum, and three-way stopcock, was connected to a nitrogen manifold and flame-dried under vacuum (ca. 1 torr) while flushing with dry nitrogen for at least 5 min. Into the reaction vessel was syringed 12.1 g (110 mmol) of diisoropylamine (freshly distilled from calcium hydride) and 60 mL of anhydrous THF (freshly distilled from benzophenone ketyl). By means of a dry ice–methanol bath the reaction flask was cooled to −78 °C and while the mixture was stirred vigorously, 44 mL of a 2.5 N (100 mmol) solution of *n*-butyllithium in *n*-hexane (standardized acidimetrically) was added with the help of a syringe. After complete addition (ca. 10 min), the cooling bath was removed and the reaction mixture allowed to reach room temperature and stirred at room temperature for 1 h. The reaction mixture was cooled again to −78 °C by means of a dry ice–methanol bath and 50 mmol of the carboxylic acid was added dropwise with the help of a syringe. Subsequently, the reaction mixture was allowed to warm up to room temperature and stirred at room temperature for 1 h. Deuteration of an aliquot of the straw-yellow-colored solution with deuterium oxide confirmed that the extent of α-lithiation was at least 98% by ^1H NMR.

General Procedure for Preparation of the β-Hydroxy Acids 1. The α-lithiocarboxylate solution as prepared above was cooled to 0 °C and while the mixture was stirred 55 mmol of the aldehyde or ketone was syringed into the reaction mixture and allowed to stir at room temperature under nitrogen overnight. The solvent was removed by rotary evaporation and the solid residue dissolved in the minimum amount (ca. 30 mL) of distilled

(1) NIH Career Development Awardee (1975–80); direct correspondence to the Würzburg address.
(2) Undergraduate Research Participants in the Support for University Biomedical Education (SUBE) Program sponsored by NIH-MBS.
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Table I. Yields, Physical Constants, and Spectral Data of β-Hydroxy Acids 1

	R_1	R_2	R_3	R_4	% yield[a]	mp,[b] °C	^{1}H NMR solvent	^{1}H NMR δ (no.,[c] pattern)	IR (KBr), cm^{-1}
1a	*t*-Bu	H	H	*t*-Bu	79	225-226[d] (MeOH-acetone-*n*-hexane)	CCl_4	0.90 (9, s), 1.07 (9, s), 2.43 (1, s), 3.54 (1, s), 10.50 (2, s)	3500-3000, 1675, 1360, 1340
1b	*t*-Bu	H	H	1-Ad	64	279-281 (EtOH)	Me_2SO	0.85 (9, s), 1.65 (15, br s), 2.50 (1, br s), 3.45 (1, br s)	3300-3000, 1670, 1365-1340
1c	1-Ad	H	H	1-Ad	22	>280 (sublimed)	Me_2SO	1.32-2.03 (30, br s), 2.40 (1, br s), 3.32 (1, br s)	3500-3000, 1670
1d	Ad[e]		H	*t*-Bu	23	190-191 (EtOH)	pyridine	1.26 (9, s), 1.45-2.75 (14, br s), 3.30 (1, s)	3500-3000, 1690, 1370, 1355
1e	Ad[e]		H	1-Ad	30	243-245 (EtOH)	pyridine	1.4-2.15 (29, br s), 2.90 (1, s)	3500-3000, 1685

[a] No efforts were made to improve these yields. [b] Satisfactory elemental composition by combustion analysis (within ±0.30% for C and H). [c] Integration was difficult due to the low solubility of the hydroxy acids. [d] Lit.[9b] mp 225-226 °C. [e] Adamantylidene.

Table II. Yields, Physical Constants, and Spectral Data of β-Lactones 2

	R_1	R_2	R_3	R_4	% yield[a]	mp,[b] °C	^{1}H NMR (CCl_4), δ (no., pattern)	IR (CCl_4), cm^{-1}
2a	*t*-Bu	H	H	*t*-Bu	82	70 (hexane)	0.95 (9, s), 1.00 (9, s), 3.00 (1, s), 3.92 (1, s)	1800, 1360, 1350
2b	*t*-Bu	H	H	1-Ad	85	164-165[c] (hexane)	0.98 (9, s), 1.4-2.2 (15, br s), 2.80 (1, d, J = 3 Hz), 3.90 (1, d, J = 3 Hz)	1825, 1400, 1380, 1115
2c	1-Ad	H	H	1-Ad	43	>260	1.3-2.2 (30, br s), 2.9 (1, d, J = 4 Hz), 3.72 (1, d, J = 4 Hz)	1825, 1450, 1115
2d	Ad[d]		H	*t*-Bu	31	56-57 (pentane)	1.17 (9, s), 1.6-2.6 (14, br s), 2.80 (1, s)	1840, 1455, 1372
2e	Ad[d]		H	1-Ad	40	124 dec (pentane)	1.5-2.4 (br s), 2.51 (1, s)	1820, 1458, 1380, 1360, 1182

[a] No efforts were made to improve these yields. [b] Satisfactory elemental composition by combustion analysis (within ±0.30% for C and H). [c] Lit.[9b] mp 155-156 °C. [d] Adamantylidene.

Table III. Yields, Physical Constants, and Spectral Data of Alkenes 3

	R_1	R_2	R_3	R_4	% yield	bp (torr)[a] or mp, °C	^{1}H NMR (CCl_4), δ (no., pattern)	IR (CCl_4), cm^{-1}
3a	*t*-Bu	H	H	*t*-Bu	95	125 (760)	0.95 (18, s), 5.15 (2, s)	3010, 1370, 1345, 975
3b	*t*-Bu	H	H	1-Ad	100	76-78 (0.9)	0.94 (9, s), 1.4-2.1 (15, br s), 5.11 (2, s)	3010, 1365, 1345, 975
3c	1-Ad	H	H	1-Ad	82	>260 (sublimed)	1.3-2.2 (30, br s), 5.00 (2, s)	3010, 1360, 1340, 950
3d	Ad[b]		H	*t*-Bu	90	90-95 (0.1)	1.04 (9, s), 1.80 (14, br s), 4.97 (1, s)	1650, 1450, 1370, 1345
3e	Ad[b]		H	1-Ad	88	149-150 (sublimed)	1.45-2.20 (29, s), 4.56 (1, s)	1450, 1200

[a] Satisfactory elemental composition by combustion analysis (within ±0.30% for C and H). [b] Adamantylidene.

water. After the aqueous mixture was washed with diethyl ether (3 × 25 mL), it was acidified with 12 N HCl to ca. pH 1. The white β-hydroxy acid 1 precipitate was collected on a Büchner funnel, dried under vacuum over P_2O_5, and recrystallized from the appropriate solvent. The results are summarized in Table I.

General Procedure for Preparation of the β-Lactones 2. A 500-mL, two-necked, round-bottomed flask, provided with magnetic spinbar, rubber septum, and reflux condenser was connected to a nitrogen manifold, flame-dried under vacuum (ca. 3 torr), and subsequently kept under dry nitrogen. A solution of 4.81 g (24 mmol) of β-hydroxy acid 1 in 75 g of dry pyridine (freshly distilled from calcium hydride) was syringed into the reaction vessel and while the mixture was stirred 17.7 g (100 mmol) of benzenesulfonyl chloride (freshly distilled) was added dropwise by means of a syringe. The reaction mixture was allowed to reflux under nitrogen overnight. After cooling to room temperature, the reaction mixture was poured into 150 mL of an ice–water mixture and the insoluble β-lactone 2 collected on a Büchner funnel. The crude β-lactone 2 was dried over P_2O_5 under vacuum (ca. 5 mm) and recrystallized from the appropriate solvent. The results are summarized in Table II.

General Procedure for Preparation of Alkenes 3. Into a thick-walled (ca. 3 mm) Pyrex ampule (10 × 1 cm o.d.) was placed 2.5 mmol of the solid β-lactone **2**. The constricted ampule was sealed under vacuum [ca. −78 °C (0.1 torr)] and subsequently heated in a metal furnance at 180 °C for 6 h. The ampule was cooled to dry ice temperature and opened, and the olefin product was bulb-to-bulb distilled or sublimed and recrystallized. The results are summarized in Table III.

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Registry No. 1a, 70982-82-0; **1b**, 75245-30-6; **1c**, 77984-31-7; **1d**, 77984-32-8; **1e**, 78003-77-7; **2a**, 70982-93-3; **2b**, 75245-54-4; **2c**, 77984-33-9; **2d**, 77984-34-0; **2e**, 77984-35-1; **3a**, 692-48-8; **3b**, 77984-36-2; **3c**, 77984-37-3; **3d**, 77984-38-4; **3e**, 77984-39-5; 3,3-dimethylbutanoic acid, 1070-83-3; tricyclo[3.3.1.1^{3,7}]decane-1-acetic acid, 4942-47-6; 2,2-dimethylpropanol, 630-19-3; tricyclo[3.3.1.1^{3,7}]decane-1-carboxaldehyde, 2094-74-8; tricyclo[3.3.1.1^{3,7}]decylidenemethanone, 54781-13-4.

Triphenylphosphine–Tetrachloromethane Promoted Chlorination and Cyclodehydration of Simple Diols

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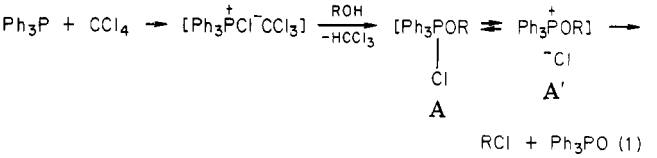
Introduction

The reactions of a variety of alcohols with triphenylphosphine (TPP) and tetrachloromethane (CCl_4) are well documented.[1] As a contribution to the storehouse of useful synthetic methodology, these "three-component"[1] reactions are characterized as (i) mild[2] and (ii) highly stereoselective, occurring with predominant inversion of stereochemistry at the carbinyl carbon.[3] But while new applications of this and analogous chlorination procedures are rapidly accruing, interest has recently focused on the intimate, mechanistic details of the substitution process, with particular emphasis on the modes of decomposition of chloroalkoxytriphenylphosphorane (A)[3c,d,4] and alkoxytriphenylphosphonium chloride (A′)[3c,d,4] to alkyl chlorides as shown in the *simplified*[1] reaction scheme of eq 1.

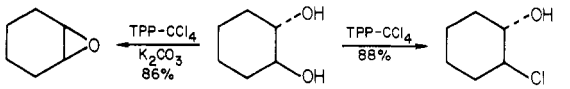


RCl + Ph_3PO (1)

On the basis of previous experience with reactions of diethoxytriphenylphosphorane [$Ph_3P(OEt)_2$] with diols affording cyclic ethers,[7] we became interested in developing other mild, effective, cyclodehydrating media for diols and triols. To our knowledge, general applications of the TPP–CCl_4 reagent to the synthesis of cyclic ethers from diols have not been previously made, and in this report, we describe our findings from the reactions of TPP–CCl_4 with simple diols.

Results and Discussion

When *trans*-1,2-cyclohexanol (**1**) is treated with equimolar TPP in excess CCl_4, a 88% yield of *trans*-2-chlorocyclohexanol (**2**), along with starting diol **1**, can be realized by ^1H and ^{13}C NMR and GLC analyses of the reaction mixture. We obtained no evidence for formation of either *cis*-2-chlorocyclohexanol (**3**) or *trans*-1,2-dichlorocyclohexane which would be expected from a single or sequential chloride ion displacement (respectively) of triphenylphosphine oxide (TPPO) from **1**. Formation of **2** by Cl^- displacement of TPPO from **1** with retention of stereochemistry is unlikely,[3,4] and we, therefore, suspected the intermediacy of cyclohexene oxide (**4**). In fact, reaction of **4** with hydrochloric acid (HCl) generated in solution was easily proven by repeating the reaction in the presence of finely ground potassium carbonate (K_2CO_3) and realizing an 86% yield of **4**.[8] It is doubtful that **4** comes from intramolecular alkoxide displacement of chloride ion from **2** since **2** appears to be relatively stable in the presence of solid K_2CO_3 in CCl_4 solvent. Thus, it seems certain that cyclohexane oxide must arise from TPP–CCl_4-mediated cyclodehydration of diol **1**.



4 **1** **2**

The results with **1** and TPP–CCl_4 may not be too surprising in light of the results from analogous reactions using tris(dimethyamino)phosphine (TDAP). For example, Anselmi et al.[9] have demonstrated that oxytris(dimethylamino)phosphonium α-trifluoroacetate salts form epoxides in 2 N NaOH while Boigegrain and Castro[10] have shown the *meso*-dihydrobenzoin and *o,o′*-dimethoxy *meso*-hydrobenzoin with 2 equiv of TDAP in CCl_4 afford epoxides in 66% and 97% yields, respectively. However, the fact that we observe no *cis*- or *trans*-1,2-dichloro-

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(4) Until recently,[3d] there were two views of the TPP–CCl_4-mediated *inversion* of stereochemistry by chloride ion at the carbinyl carbon of alcohols. Jones et al.[3c] and Weiss and Snyder[5] have suggested that the decomposition of the chloroalkoxytriphenylphosphorane intermediate occurs by cleavage of the P–Cl bond first, followed by cleavage of the C–O bond. Alternatively, Aneja and Davies[6] argue that fragmentation of the phosphorane intermediate is consistent with a symmetry allowed [$_\sigma 2_s + {}_\sigma 2_a$] thermal pericyclic process. However, Franzus et al.[3d] have presented recent evidence favoring *clustered* ion pairs in the chlorination reaction.

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