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Synthesis of 3,6-dihydro-2*H*-pyran-2-ones via cationic palladium(II) complex-catalyzed tandem [2+2] cycloaddition-allylic rearrangement of ketene with α,β-unsaturated aldehydes and ketones

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Abstract—Treatment of ketene with α,β-unsaturated aldehydes and ketones in the presence of $[Pd(dppb)(PhCN)_2](BF_4)_2$ leads to the formation of 4-vinyloxetan-2-ones, which rearrange under the conditions to give 3,6-dihydro-2*H*-pyran-2-ones in a variety of yields, depending on the substituents. Asymmetric induction with up to 57% de has been achieved by using α,β-unsaturated aldehydes bearing an asymmetric carbon center at the β-position. A zwitterion generated by heterolytic cleavage of the C(4)–O bond of the 4-vinyloxetan-2-one is considered to be an intermediate in the allylic rearrangement. Ethanolysis of 3,6-dihydro-6-methyl-2*H*-pyran-2-one under acid conditions, followed by saponification of the resulting ethyl 2,4-hexadienoate (ethyl sorbate), gives sorbic acid in 90% yield.

1. Introduction

Oxetan-2-ones (β-lactones) undergo a variety of transformations triggered by heterolytic cleavage of the C(4)–O bond, as well as the O–CO bond, to release ring strain of the four-membered cycle, which makes this class of compounds versatile synthetic intermediates in the preparation of alkenes, acids, butan-4-olides (γ-lactones), polyesters, and so on.[1,2] In this respect, 4-vinyl-substituted oxetan-2-ones are of particular interest because they should show enhanced reactivity toward the C(4)–O bond cleavage due to the stability of the resulting allyl cation species. For example, it is known that the [2+2] cycloaddition of trimethylsilylketene with α,β-unsaturated aldehydes and ketones in the presence of a Lewis acid affords the corresponding 3-trimethylsilyl-4-vinyloxetan-2-ones, which rearrange spontaneously to trimethylsilyl 2,4-dienoic esters.[3] A palladium(0)-catalyzed rearrangement of 4-vinyloxetan-2-ones with no silyl moiety at the 3-position to 2,4-dienoic acids was also reported.[4] Enhanced tendency of 4-vinyloxetan-2-ones for decarboxylation to dienes has often been noted in the literature and was applied to the construction of conjugated π-systems.[3a,5] It was also reported that reaction of ketene with but-2-enal (crotonaldehyde, **1a**) in the presence of $BF_3{\cdot}Et_2O$ gave not 4-propenyloxetan-2-one (**2a**) but its ring-opening polyester.[6] We have found another reaction of 4-vinyloxetan-2-ones, that is, isomerization to 3,6-dihydro-2*H*-pyran-2-ones.[7] Thus, cationic palladium(II) complexes, which have been recognized as a class of transition metal-based Lewis acids,[8] were used as a catalyst for the [2+2] cycloaddition of ketene with aldehydes to give the corresponding oxetan-2-ones, among which 4-vinyl-substituted ones were further isomerized under the conditions to give 3,6-dihydro-2*H*-pyran-2-ones (e.g. **3a**). The tandem reaction will attract much interest because such unsaturated δ-lactones are important intermediates for the synthesis of biologically active natural products.[9,10] Close scrutiny of the literature revealed that Young reported the formation of similar δ-lactones in the cycloaddition of ketene with a couple of ketones in as early as 1949.[11] In spite of the potential importance of the reaction, it has not appeared in the literature thereafter. Here, we wish to report scope and limitations of the tandem reaction in detail.

2. Results and discussion

2.1. Synthesis of 3,6-dihydro-2*H*-pyran-2-ones (3)

First, the reaction of ketene with crotonaldehyde (**1a**) was examined. As for the catalyst, $[Pd(dppb)(PhCN)_2](BF_4)_2$ [dppb=1,4-bis(diphenylphosphino)butane] was employed

Keywords: cycloaddition; allylic rearrangement; lactones; Lewis acid catalysts.

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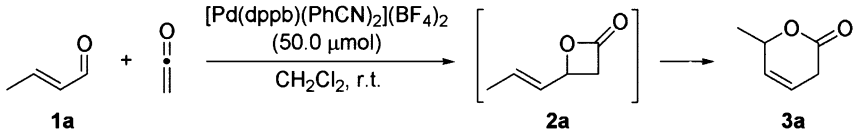
Table 1. Reaction of ketene with aldehyde **1a** conducted by various methods



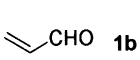
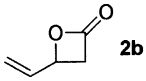
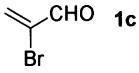
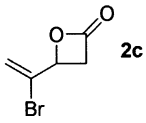
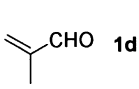
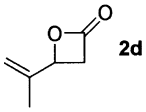
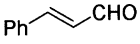
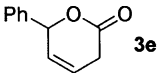
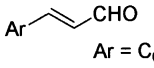
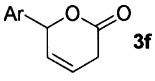
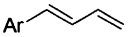
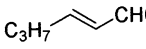
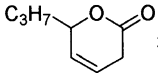
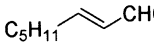
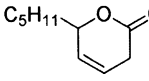
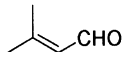
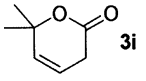
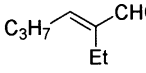
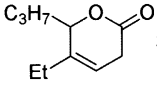
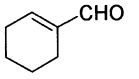
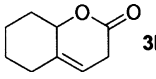
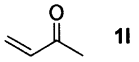
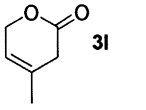
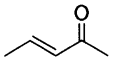
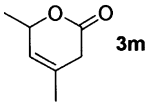
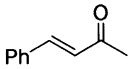
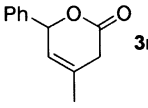
Entry	Method	Yield (%)
1	A: catalyst solution (20 cm^3) → **1a** (1.00 mmol) → ketene (2.5 mmol / 5 min) → stirred for 1 h	13
2	B: catalyst solution (200 cm^3) → **1a** (1.00 mmol) → ketene (2.5 mmol / 5 min) → stirred for 1 h	55
3	C: catalyst solution (200 cm^3) → [**1a** (200 μmol) → ketene (250 μmol / 1 min) → stirred for 5 min] × 5 → ketene (1.0 mmol / 2 min) → stirred for 1 h	70
4	D: catalyst solution (500 cm^3) → [**1a** (200 μmol) → ketene (250 μmol / 1 min) → stirred for 5 min] × 5 → ketene (1.0 mmol / 2 min) → stirred for 1 h	80
5	E: catalyst solution (200 cm^3) → [**1a** (200 μmol) → ketene (250 μmol / 1 min) → stirred for 5 min] × 10 → ketene (1.0 mmol / 2 min) → stirred for 1 h	65

because it catalyzed the [2+2] cycloaddition of ketene with aldehydes most efficiently among the palladium-based Lewis acids previously examined.[7] In the presence of the complex (50.0 μmol), aldehyde **1a** (1.00 mmol) was allowed to react with ketene in dichloromethane (20 cm^3) at room temperature by bubbling ketene (ca. 2.5 mmol) into the aldehyde solution over a period of 5 min and stirring the solution for a further 1 h (Table 1, entry 1). The procedure gave 3,6-dihydro-6-methyl-2*H*-pyran-2-one (isoparasorbic acid, **3a**) only in an unsatisfactory yield, along with an unidentifiable polymer (see Section 2.4). Lowering the reaction temperature and changing the molar ratios of ketene and the catalyst to the aldehyde did not improve the product yield, while dilution of the reaction solution was found to be highly effective (entry 2). Eventually, lactone **3a** was obtained in a good yield by adding aldehyde **1a** and ketene portionwise to a dilute solution of the catalyst (entries 3 and 4). Thus, the manipulations (entry 3) were adopted as a standard procedure thereafter. Under the diluted conditions, 2.5 mol% of the catalyst was sufficient to complete the reaction (compare entry 5 (**1a**/cat.=2000/50 μmol/μmol) with entry 3 (**1a**/cat.=1000/50 μmol/μmol)).

Table 2 lists the results of the reaction of ketene with other unsaturated aldehydes and ketones under the standard conditions. Similar δ-lactones **3e–i** were obtained from the reaction of aldehydes **1e–i**, which have at least an alkyl or aryl substituent at the 3-position (entries 4–8), while aldehydes **1b–d** gave β-lactones **2b–d** (entries 1–3). Methyl vinyl ketones **1l–n** also afforded δ-lactones **3l–n**, though in poor yields, along with unchanged ketones (entries 11–13). These observations may indicate that the initially formed β-lactone undergoes ring cleavage at the C(4)–O bond if the resulting allyl cation species **5** (see Section 2.3) is stabilized by a substituent at the allylic terminus, R^1 or R^4 (Scheme 1). Interestingly, the 2-alkyl substituent (R^3) of aldehyde **1j** improved the δ-lactone yield (compare entry 9 with entry 6), although such an alkyl substituent R^3 did not induce the ring cleavage of β-lactone **2d** (entry 3). The allylic intermediate should be in an equilibrium state between conformations **5** and **6**, and needs to adopt the less stable conformation **6** in the ring-closure step (Scheme 1). The R^3 substituent of aldehyde **1j** seems to stabilize the conformation **6**, being *trans* to the methylene moiety adjacent to the carboxylate group, which may improve the δ-lactone yield. Bicyclic lactone **3k** was obtained in a good yield with the aid of such a substituent effect (entry 10).

Next, reaction of substituted ketenes was shortly examined. As mentioned above, it was reported that treatment of trimethylsilylketene with α,β-unsaturated aldehydes and ketones in the presence of an aluminum- or boron-based Lewis acid gave the corresponding trimethylsilyl

Table 2. Reaction of ketene with α,β-unsaturated aldehydes and ketones

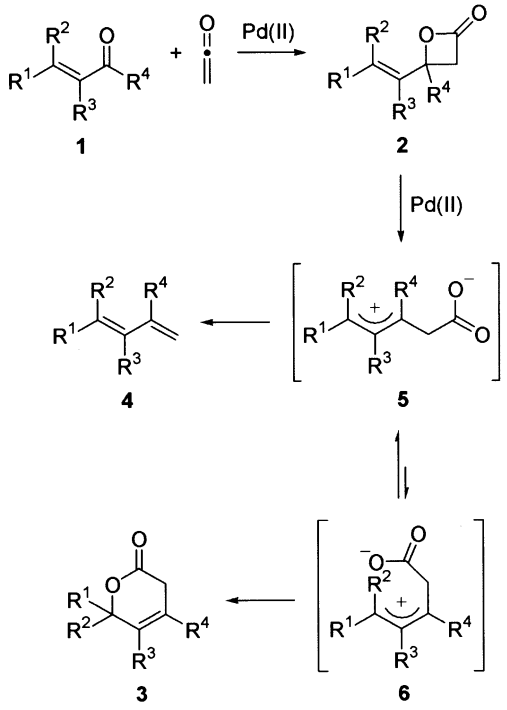
Entry	Substrate	Product	Yield (%)
1	 **1b**	 **2b**	96[a]
2	 **1c**	 **2c**	93
3	 **1d**	 **2d**	96[a]
4	 **1e**	 **3e**	77
5	 **1f** Ar = C_6H_4-*p*-NO_2	 **3f**  **4f**	36/28
6	 **1g**	 **3g**	58
7	 **1h**	 **3h**	58
8	 **1i**	 **3i**	31
9	 **1j**	 **3j**	66
10	 **1k**	 **3k**	52
11	 **1l**	 **3l**	7
12	 **1m**	 **3m**	19
13	 **1n**	 **3n**	18

[a] Determined by GC analysis.

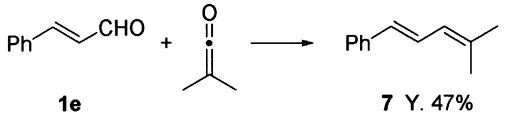
2,4-dienoic esters.[3] However, the palladium-based Lewis acid did not catalyze the cycloaddition of trimethylsilylketene with 3-phenylpropenal (cinnamaldehyde, **1e**) under the standard conditions, recovering the aldehyde almost unchanged. On the other hand, dimethylketene, on treatment with aldehyde **1e**, gave diene **7**, formation of which is rationalized by decarboxylation of the initially formed β-lactone (Scheme 2). It should be noted that a considerable amount of diene **4f** was obtained in the reaction of ketene with aldehyde **1f** (Table 2, entry 5). The decarboxylation apparently competes with the allylic rearrangement for the allylic intermediate **5**, the nature of which seems to determine the dichotomy between the reaction paths (Scheme 1). In the former case (Scheme 2), the two methyl groups introduced by the ketene to the intermediate seem to have accelerated the formation of the diene by stabilizing the transition state, while in the latter case (Table 2, entry 5), the electron-withdrawing effect of the nitro group on the phenyl ring might prevent recombination of the allylic intermediate **6**.

2.2. Asymmetric induction by using chiral aldehydes 1o–s

The diastereoselective tandem [2+2] cycloaddition-allylic



Scheme 1.



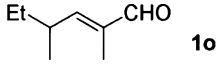
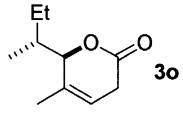
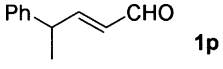
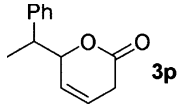
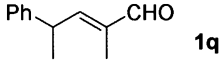
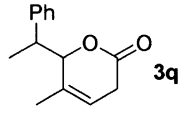
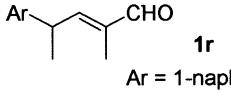
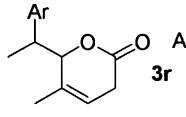
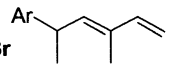
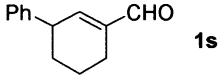
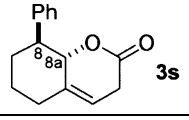
Scheme 2.

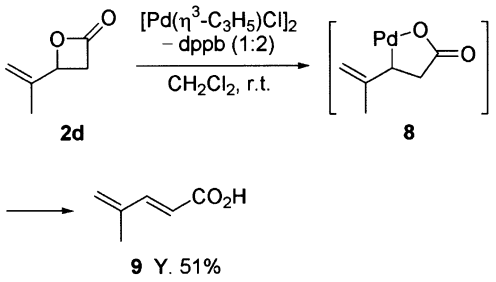
rearrangement was examined by using racemic α,β-unsaturated aldehydes bearing an asymmetric carbon center at the β-position (Table 3). The reaction of aldehyde **1o** with ketene under the standard conditions gave lactone **3o** in a good yield but with poor diastereoselectivity (entry 1). However, upon replacing the ethyl group of **1o** with a bulkier substituent, a higher diastereoselectivity was obtained in the reaction (entries 3 and 4). The reaction of aldehyde **1r** bearing a 1-naphthyl group accompanied the formation of an appreciable amount of diene **4r** at the expense of the desired lactone **3r** (entry 4). This may be attributed to the steric hindrance imposed by the naphthyl group on approach of the carboxylate anion to the allylic terminus in the ring-closure step (**6**) (Scheme 1). The 2-alkyl substituent of aldehyde **1** improved not only the yield of lactone **3** (vide supra) but also its diastereomeric excess (compare entry 3 with entry 2), and cyclic aldehyde **1s** gave bicyclic lactone **3s** in a good yield with the best diastereoselectivity (57% de) (entry 5). The two diastereomers of lactone **3s** were readily separated by HPLC on a silica gel column. The ^{1}H NMR spectrum of the major diastereomer showed a large coupling constant (10.9 Hz) between the two protones at the C(8) and C(8a), corresponding to their *trans*-diaxial arrangement, which assigned the relative configuration of the major diastereomer of **3s** to be *trans*.

2.3. Mechanistic consideration

The initial formation of β-lactone **2** in the present tandem reaction can be rationalized by the Lewis acid-catalyzed [2+2] cycloaddition,[1] where the palladium complex acts as a Lewis acid.[8] On the other hand, there may be two plausible mechanisms for the rearrangement of **2** to δ-lactone **3**. It is known that 1,3-rearrangement of allylic esters is promoted by palladium(0) and (II) complexes. The palladium(II)-catalyzed reaction is, however, reportedly a [3,3]-sigmatropic rearrangement of allyl

Table 3. Reaction of ketene with chiral α,β-unsaturated aldehydes

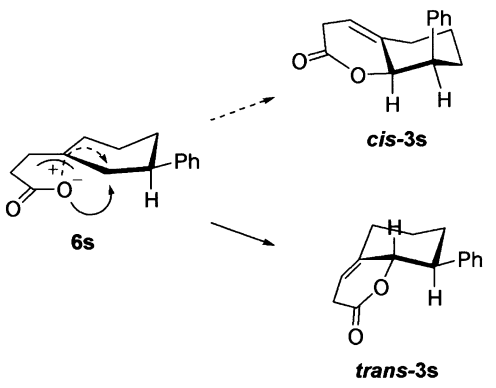
Entry	Aldehyde	Product	Yield (%)	de (%)	Configuration
1	 **1o**	 **3o**	66	4	6*RS*, (*RS*)
2	 **1p**	 **3p**	47	6	–
3	 **1q**	 **3q**	70	36	–
4	 **1r** Ar = 1-naphthyl	 **3r**  **4r**	50/29	51/–	–/–
5	 **1s**	 **3s**	60	57	*trans*



Scheme 3.

esters,[12] which is impossible for the present lactone **2** because of the steric reasons. On the other hand, the palladium(0)-catalyzed rearrangement is believed to involve a π-allylpalladium(II) intermediate.[13] In this respect, it should be noted that palladium(II) salts were reported to promote the ring opening of 4-vinyl- and 4-isopropenyl-oxetan-2-one **2b**,**d** to afford the corresponding penta-2,4-dienoic acids.[4] A metallacyclic σ-allylpalladium intermediate (e.g. **8**) generated by oxidative addition of the C(4)–O bond of the β-lactones to a palladium(0) species was proposed for the reaction. We also found that lactone **2d**, on treatment with a palladium complex generated in situ by treatment of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with dppb, gave dienoic acid **9** in a good yield (Scheme 3). These observations may indicate that if a palladium(0) species had been generated in the present system, it would have cleaved not only β-lactones bearing an alkyl or aryl substituent as the R^1 or R^4 substituent but also **2b**,**d**, and moreover, the resulting allylpalladium species would have afforded the corresponding dienoic acid rather than δ-lactone by a β-hydride elimination. In addition, we found that $BF_3{\cdot}Et_2O$, which cannot form such an allylmetal species, also afforded δ-lactone **3a**, though only in 13% yield, when aldehyde **1a** was treated with ketene under the standard conditions in the presence of 1.5 equiv. of the Lewis acid. This may suggest an alternative mechanism, that is, coordination of the carbonyl oxygen of **2** to the palladium Lewis acid promotes the heterolytic cleavage of the C(4)–O bond to form a zwitterion, recombination of which at the other allylic terminus affords lactone **3** (Scheme 1).

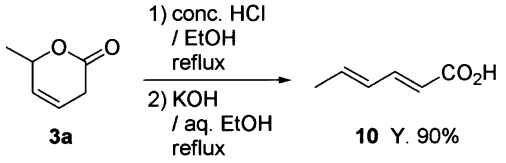
The stereochemical course of the formation of *trans*-**3s** can be rationalized based on the zwitterion-mediated mechanism (Scheme 4). Thus, zwitterion **6s** will adopt a half-chair conformation bearing the phenyl group at an equatorial position. Accordingly, the ring closure will take place from the opposite side of the phenyl group to avoid steric repulsion, leading to the preferential formation of *trans*-**3s**.



Scheme 4.

2.4. Conversion of 3,6-dihydro-6-methyl-2*H*-pyran-2-one (3a) to hexa-2,4-dienoic acid (10)

2,4-Hexadienoic acid (sorbic acid, **10**) is important as a mould and yeast inhibitor, the first step of an industrial synthesis of which relies on the reaction of ketene with crotonaldehyde (**1a**) catalyzed by a zinc carboxylate.[14] However, the product obtained from the reaction is not the β-lactone **2a** but its ring-opening polymer, poly(3-hydroxyhex-4-enoic acid),[6] viscosity of which causes a great deal of trouble to the subsequent destructive distillation of the polyester to acid **10**. We have found that treatment of lactone **3a** with ethanol in the presence of hydrochloric acid, followed by saponification of the resulting ethyl sorbate gave the acid in 90% yield (Scheme 5). Therefore, the present method provides an easy access to sorbic acid. Furthermore, the method will be applicable to the synthesis of other biological active dienoic acids.[15]



Scheme 5.

In conclusion, we have shown here that 4-vinyloxetan-2-one **2**, generated in situ by treatment of α,β-unsaturated carbonyl compound **1** with ketene with the aid of a cationic palladium(II) Lewis acid, isomerizes to 3,6-dihydro-2*H*-pyran-2-one **3**, if the β-lactone has an alkyl or aryl moiety as the R^1 or R^4 substituent. The reaction competes with decarboxylation to diene **4**. Zwitterion **5** is considered to be their common intermediate, the electronic and/or steric nature of which determines the dichotomy between the reaction paths.

3. Experimental

3.1. General

IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-250T, DPX-400 or DRX-500 spectrometer using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent. Microanalyses were carried out in the Microanalytical Laboratory of Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. A Quadrex MPS-10 column (0.32 mm i.d.×25 m) was used for GC analysis. Merck silica gel $60GF_{254}$ was used for analytical and preparative TLC (PLC). Silica gel columns were prepared by use of Merck silica gel 60 (70–230 mesh). Water- and air-sensitive reactions were routinely carried out under nitrogen. Dichloromethane was distilled from CaH_2.

2-Bromopropenal (**1c**),[16] 2,4-dimethylhex-2-enal (**1o**),[17] 2-methyl-4-phenylpent-2-enal (**1q**)[18] and 3-phenylcyclohex-1-enecarboxaldehyde (**1s**)[19] were prepared according to the literature procedures. 4-Phenylpent-2-enal (**1p**) was prepared by the same procedure as used for the preparation of aldehyde **1o**. **1p**: ^{1}H NMR (400 MHz) δ 9.53 (1H, d, J=7.8 Hz, CHO), 7.36–7.19 (5H, m, ArH), 6.97 (1H, dd, J=15.7 and 6.4 Hz, CH=), 6.12 (1H, ddd, J=15.7, 7.8 and 1.5 Hz, CH=), 3.78–3.71 (1H, m, PhC*H*), 1.48 (3H, d, J=7.0 Hz, Me); ^{13}C NMR (100 MHz) δ 194.1, 161.8, 142.7, 131.3, 128.9, 127.4, 127.1, 42.6 and 20.0. Found: C, 82.15; H, 7.56%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%. 2-Methyl-4-(1-naphthyl)pent-2-enal (**1r**) was prepared by the same procedure as used for the preparation of aldehyde **1q**. **1r**: ^{1}H NMR (400 MHz) δ 9.40 (1H, s, CHO), 7.98–7.96 (1H, m, ArH), 7.89–7.87 (1H, m, ArH), 7.78–7.76 (1H, m, ArH), 7.54–7.45 (4H, m, ArH), 6.66 (1H, dq, J=9.1 and 1.3 Hz, CH=), 4.72 (1H, dq, J=9.1 and 7.0 Hz, ArC*H*), 1.89 (3H, d, J=1.3 Hz, Me) and 1.61 (3H, d, J=7.0 Hz, ArCH*Me*); ^{13}C NMR (100 MHz) δ 195.4, 158.7, 140.0, 138.2, 134.0, 131.4, 129.2, 127.6, 126.3, 125.8, 125.7, 123.3, 122.9, 34.6, 20.6 and 9.6. Found: C, 85.55; H, 7.33%. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19%. Other aldehydes and ketones were used as purchased. $[Pd(dppb)(PhCN)_2](BF_4)_2$ was prepared according to the literature procedure.[8c,20] Ketene was generated by pyrolysis of acetone according to the literature procedure.[21]

3.2. General procedure for the reaction of ketene with aldehydes and ketones (method C in Table 1)

To a solution of $[Pd(dppb)(PhCN)_2](BF_4)_2$ (45.6 mg, 50.0 μmol) in dichlorometane (200 cm^3) was added an aldehyde or ketone **1** (200 μmol). Ketene (ca. 250 μmol) was bubbled into the mixture over a period of 1 min and the mixture was stirred for 5 min. This series of operations was repeated until added **1** reached to the total amount of 1.00 mmol. To the mixture was added an additional amount of ketene (ca. 1.0 mmol) over a period of 2 min and the resulting mixture was stirred for 1 h. The reaction was quenched with 2 M HCl and the two layers were separated. The aqueous layer was extracted with dichlorometane and the combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by column chromatography on silica gel, unless otherwise noted. The diastereomeric compositions of lactones **3o–s** were determined by GC analyses. See Tables 1–3 for the yield and diastereomeric excess of the product obtained in each reaction. The eluent for the chromatographic purification and the spectral characteristics of the product are given below.

3.2.1. 3,6-Dihydro-6-methyl-2*H*-pyran-2-one (3a).[9c] Hexane–ethyl acetate (1:1) as the eluent; ^{1}H NMR (400 MHz) δ 5.87–5.84 (2H, m, CH=×2), 5.11–5.06 (1H, m, OCH), 3.12–3.04 (2H, m, CH_2) and 1.46 (3H, d, J=6.8 Hz, Me); ^{13}C NMR (100 MHz) δ 169.3, 127.8, 121.2, 76.1, 29.7 and 21.7; IR (neat) 1738 cm^{-1}.

3.2.2. 4-Vinyloxetan-2-one (2b).[6] The yield was determined by GC analysis using phenyl acetate as an internal standard. The crude product was distilled under reduced pressure by use of a Kugelrohr (50°C/500 Pa) to give spectrometrically pure **2b**; ^{1}H NMR (400 MHz) δ 6.03 (1H, ddd, J=17.0, 10.5 and 6.0 Hz, CH=), 5.51 (1H, dt, J=17.0 and 1.0 Hz, CH_2=), 5.41 (1H, dt, J=10.5 and 1.0 Hz, CH_2=), 4.94–4.92 (1H, m, OCH), 3.66 (1H, dd, J=17.0 and 6.0 Hz, CH_2), 3.23 (1H, dd, J=17.0 and 4.4 Hz, CH_2); ^{13}C NMR (100 MHz) δ 167.7, 134.1, 120.3, 70.5 and 44.1; IR (neat) 1828 cm^{-1}.

3.2.3. 4-(1-Bromovinyl)oxetan-2-one (2c). Hexane–ethyl acetate (1:1) as the eluent; ^{1}H NMR (250 MHz) δ 6.16–6.15 (1H, dd, J=2.4 and 1.0 Hz, CH_2=), 5.81 (1H, d, J=2.4 Hz, CH_2=), 4.98–4.94 (1H, m, OCH), 3.72 (1H, dd, J=17.0 and 6.2 Hz, CH_2), 3.45 (1H, dd, J=17.0 and 4.3 Hz, CH_2); ^{13}C NMR (100 MHz) δ 166.2, 128.1, 120.5, 70.9 and 44.9; IR (neat) 1836 cm^{-1}. Found: C, 33.69; H, 3.12%. Calcd for $C_5H_5BrO_2$: C, 33.93; H, 2.85%.

3.2.4. 4-Isopropenyloxetan-2-one (2d).[4] The yield was determined by GC analysis using methyl benzoate as an internal standard. The crude product was purified by column chromatography on silica gel with hexane–ethyl acetate (2:1) as the eluent to give spectrometrically pure **2d** in 37% yield; ^{1}H NMR (500 MHz) δ 5.18 (1H, br, CH_2=), 5.09 (1H, br, CH_2=), 4.91–4.89 (1H, m, OCH), 3.62 (1H, dd, J=16.3 and 6.2 Hz, CH_2), 3.26 (1H, dd, J=16.3 and 4.5 Hz, CH_2) and 1.81 (3H, s, Me); ^{13}C NMR (125 MHz) δ 167.9, 140.6, 114.8, 72.2, 42.7 and 16.7; IR (neat) 1832 cm^{-1}.

3.2.5. 3,6-Dihydro-6-phenyl-2*H*-pyran-2-one (3e). Hexane–ethyl acetate (1:1) as the eluent; ^{1}H NMR (500 MHz) δ 7.39–7.33 (5H, m, ArH), 6.03–5.98 (3H, m, CH=×2 and OCH) and 3.18–3.15 (2H, m, CH_2); ^{13}C NMR (125 MHz) δ 164.1, 144.9, 138.5, 128.7, 128.7, 126.1, 121.7, 79.3 and 31.7; IR (neat) 1736 cm^{-1}. Found: C, 75.62; H, 5.79%. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79%.

3.2.6. 3,6-Dihydro-6-(4-nitorophenyl)-2*H*-pyran-2-one (3f). Hexane–ethyl acetate (1:1) as the eluent; ^{1}H NMR (500 MHz) δ 8.25 (2H, d, J=8.8 Hz, ArH), 7.55 (2H, d, J=8.8 Hz, ArH), 6.12–6.02 (3H, m, CH=×2 and OCH) and 3.23–3.21 (2H, m, CH_2); ^{13}C NMR (125 MHz) δ 167.4, 148.0, 145.3, 127.5, 125.0, 124.2, 123.1, 79.9 and 29.8; IR (neat) 1744 cm^{-1}. Found: C, 60.00; H, 4.31; N, 6.25%. Calcd for $C_{11}H_9NO_4$: C, 60.27; H, 4.14; N, 6.39%.

3.2.7. 1-(Buta-1,3-dienyl)-4-nitrobenzene (4f).[22] Hexane–ethyl acetate (1:1) as the eluent; ^{1}H NMR (500 MHz) δ 8.18 (2H, d, J=8.8 Hz, ArH), 7.52 (2H, d, J=8.8 Hz, ArH), 6.93 (1H, dd, J=15.7 and 10.6 Hz, ArCH=C*H*), 6.60 (1H, d, J=15.7 Hz, ArC*H*), 6.54 (1H, ddd, J=17.0, 10.6 and 9.7 Hz, CH_2=C*H*), 5.48 (1H, d, J=17.0 Hz, CH_2=) and 5.34 (1H, d, J=9.7 Hz, CH_2=); ^{13}C NMR (125 MHz) δ 146.8, 143.7, 136.4, 134.0, 130.4, 126.8, 124.1 and 121.0; IR (KBr) 1589, 1514, 1355 and 1003 cm^{-1}.

3.2.8. 3,6-Dihydro-6-propyl-2*H*-pyran-2-one (3g). Hexane–ethyl acetate (2:1) as the eluent; ^{1}H NMR (400 MHz) δ 5.85–5.84 (2H, m, CH=×2), 5.00–4.97 (1H, m, OCH), 3.06–3.05 (2H, m, CH_2C=O), 1.74–1.69 (2H, m, EtCH_2), 1.53–1.43 (2H, m, MeCH_2) and 0.96 (3H, t, J=7.4 Hz, Me); ^{13}C NMR (100 MHz) δ 169.2, 126.7, 121.5,

79.5, 37.8, 30.0, 17.7 and 13.7; IR (neat) 1740 cm^{-1}. Found: C, 68.17; H, 8.74%. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63%.

3.2.9. 3,6-Dihydro-6-pentyl-2*H*-pyran-2-one (3h).[23] Hexane–ethyl acetate (1:1) as the eluent; ^1H NMR (400 MHz) δ 5.88–5.81 (2H, m, CH=×2), 5.00–4.95 (1H, m, OCH), 3.11–3.04 (2H, m, CH_2C=O), 1.78–1.72 (2H, m, BuCH_2), 1.33–1.30 (6H, m, CH_2×3) and 0.91–0.88 (3H, m, Me); ^{13}C NMR (100 MHz) δ 169.2, 126.7, 121.5, 79.8, 33.7, 31.5, 30.0, 24.0, 22.5 and 14.0; IR (neat) 1740 cm^{-1}.

3.2.10. 3,6-Dihydro-6,6-dimethyl-2*H*-pyran-2-one (3i).[24] Hexane–ethyl acetate (2:1) as the eluent; ^1H NMR (500 MHz) δ 5.84 (1H, dt, J=10.0 and 1.9 Hz, CH=), 5.74 (1H, dt, J=10.0 and 3.5 Hz, CH=), 3.04 (2H, dd, J=3.5 and 1.9 Hz, CH_2) and 1.48 (6H, s, Me×2); ^{13}C NMR (125 MHz) δ 169.1, 131.9, 119.2, 82.9, 29.0 and 28.9; IR (neat) 1736 cm^{-1}.

3.2.11. 5-Ethyl-3,6-dihydro-6-propyl-2*H*-pyran-2-one (3j). Hexane–ethyl acetate (3:1) as the eluent; ^1H NMR (400 MHz) δ 5.43–5.41 (1H, m, CH=), 4.74–4.71 (1H, m, OCH), 2.98–2.96 (2H, m, CH_2C=O), 2.00–1.94 (2H, m, CH_2), 1.71–1.65 (2H, m, CH_2), 1.57–1.35 (2H, m, CH_2), 1.46 (3H, t, J=7.4 Hz, Me) and 1.01 (3H, t, J=7.3 Hz, Me); ^{13}C NMR (100 MHz) δ 170.0, 139.5, 114.1, 82.3, 36.5, 30.0, 25.1, 17.7, 13.7 and 11.7; IR (neat) 1736 cm^{-1}. Found: C, 71.12; H, 9.49%. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%.

3.2.12. 3,5,6,7,8,8a-Hexahydrochromen-2-one (3k). Hexane–ethyl acetate (1:1) as the eluent; ^1H NMR (500 MHz) δ 5.38–5.37 (1H, m, CH=), 4.82 (1H, m, OCH), 3.06 (2H, m, CH_2C=O), 2.41 (1H, m, CH_2), 2.32–2.30 (1H, m, CH_2), 2.05–1.99 (1H, m, CH_2), 1.90–1.86 (1H, m, CH_2), 1.81–1.78 (1H, m, CH_2), 1.51–1.39 (2H, m, CH_2) and 1.30–1.22 (1H, m, CH_2); ^{13}C NMR (100 MHz) δ 168.4, 135.7, 111.9, 81.0, 35.4, 32.7, 29.3, 26.6 and 24.0; IR (neat) 1740 cm^{-1}. Found: C, 70.72; H, 7.95%. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95%.

3.2.13. 3,6-Dihydro-4-methyl-2*H*-pyran-2-one (3l).[25] Hexane–ethyl acetate (1:1) as the eluent; ^1H NMR (250 MHz) δ 5.61–5.60 (1H, m, CH=), 4.86–4.84 (2H, m, OCH_2), 2.99 (2H, s, CH_2C=O) and 1.80 (3H, s, Me); ^{13}C NMR (62.5 MHz) 169.5, 130.4, 115.9, 68.4, 34.6 and 21.1; IR (neat) 1738 cm^{-1}.

3.2.14. 3,6-Dihydro-4,6-dimethyl-2*H*-pyran-2-one (3m).[26] Hexane–ethyl acetate (3:1) as the eluent; ^1H NMR (500 MHz) δ 5.53 (1H, br, CH=), 5.03–5.01 (1H, m, OCH), 2.95 (2H, s, CH_2), 1.78 (3H, s, MeC=) and 1.42 (3H, d, J=6.7 Hz, *Me*CH); ^{13}C NMR (100 MHz) δ 169.8, 130.0, 121.9, 75.8, 34.5, 22.0 and 21.5; IR (neat) 1740 cm^{-1}.

3.2.15. 3,6-Dihydro-4-methyl-6-phenyl-2*H*-pyran-2-one (3n).[27] Hexane–ethyl acetate (3:1) as the eluent; ^1H NMR (500 MHz) δ 7.38–7.30 (5H, m, ArH), 5.91 (1H, br, CH=), 5.73–5.71 (1H, m, OCH), 3.06 (2H, s, CH_2), 1.85 (3H, s, Me); ^{13}C NMR (100 MHz) δ 169.1, 138.9, 130.6, 128.8, 128.7, 126.8, 120.3, 81.1, 34.7 and 21.6; IR (neat) 1740 cm^{-1}.

3.2.16. 6-*sec*-Butyl-3,6-dihydro-5-methyl-2*H*-pyran-2-one (3o). Hexane–ethyl acetate (1:1) as the eluent; ^1H NMR (500 MHz) δ 5.54–5.53 (1H, m, CH=), 4.83, 4.71 (1H: d, J=2.0 Hz, OCH (minor); d, J=2.7 Hz, OCH (major)), 3.02–2.99 (2H, m, CH_2C=O), 1.83–1.75 (1H, m, Et*CH*), 1.74, 1.72 (3H: d, J=1.9 Hz, CH_3C= (major); d, J=1.8 Hz, CH_3C= (minor)), 1.65–1.48, 1.41–1.04 (2H: m, MeCH_2 (minor); m, MeCH_2 (major)); 1.11, 0.82 (3H: d, J=6.9 Hz, *Me*CH (major); d, J=6.9 Hz, *Me*CH (minor)) and 0.97, 0.91 (3H: t, J=7.4 Hz, *Me*CH_2 (minor); t, J=7.4 Hz, *Me*CH_2 (major)); ^{13}C NMR (100 MHz) δ 169.6, 131.9 (minor), 131.8 (major), 117.3 (minor), 117.0 (major), 88.1 (minor), 85.8 (major), 38.6 (minor), 38.4 (major), 30.1 (minor), 29.9 (major), 26.1 (minor), 21.9 (major), 19.4 (major), 19.0 (minor), 15.9 (major), 12.1 (minor) and 12.0; IR (neat) 1740 cm^{-1}. Found: C, 71.01; H, 9.57%. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%.

The ^1H NMR signals of the minor diastereomer agreed well with those of the [6*R*,(*S*)]-isomer reported in the literature.[9e] Thus, the relative configuration of the major diastereomer was determined to be 6*RS*,(*RS*).

3.2.17. 3,6-Dihydro-6-(1-phenylethyl)-2*H*-pyran-2-one (3p). Hexane–ethyl acetate (2:1) as the eluent; ^1H NMR (500 MHz) δ 7.30–7.20 (5H: m, ArH), 5.77–5.76, 5.72–5.71 (2H: m, CH= (major); m, CH= (minor)), 5.13–5.11, 5.08–5.05 (1H: m, OCH (minor); m, OCH (major)), 3.18, 3.16 (1H: q, J=7.1 Hz, PhC*H* (minor); q, J=7.2 Hz, PhC*H* (major)), 2.88–2.82, 2.85–2.79 (1H: m, CH_2 (major); m, CH_2 (minor)), 2.48–2.42, 2.39–2.33 (1H: m, CH_2 (major); m, CH_2 (minor)) and 1.44, 1.39 (3H: d, J=7.1 Hz, Me (minor); d, J=7.2 Hz, Me (major)); ^{13}C NMR (125 MHz) δ 169.0, 140.8 (major), 139.8 (minor), 128.6, 128.4, 127.2, 124.3 (major), 124.1 (minor), 122.9 (major), 122.5 (minor), 83.9 (minor), 83.6 (major), 45.3 (major), 44.4 (minor), 29.9 (major), 29.7 (minor), 16.1 (major) and 15.5 (minor); IR (neat) 1740 cm^{-1}. Found: C, 76.88; H, 7.01%. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.

3.2.18. 3,6-Dihydro-5-methyl-6-(1-phenylethyl)-2*H*-pyran-2-one (3q). Hexane–ethyl acetate (2:1) as the eluent; ^1H NMR (500 MHz) δ 7.33–7.15 (5H, m, ArH), 5.56–5.54, 5.26–5.25 (1H: m, CH= (major); m, CH= (minor)), 4.85–4.84, 4.82 (1H: m, OCH (major); d, J=2.0 Hz, OCH (minor)), 3.18, 3.17 (1H: qd, J=7.3 and 2.0 Hz, PhC*H* (minor); qd, J=7.2 and 4.2 Hz, PhC*H* (major)), 2.98–2.91, 2.52–2.46 (1H: m, CH_2 (major); m, CH_2 (minor)), 2.79–2.72, 1.46–1.40 (1H: m, CH_2 (major); m, CH_2 (minor)), 1.84–1.83, 1.66 (3H: m, *Me*C= (minor); m, *Me*C= (major)) and 1.57, 1.32 (3H: d, J=7.3 Hz, *Me*CH (minor); d, J=7.2 Hz, *Me*CH (major)); ^{13}C NMR (125 MHz) δ 169.8 (minor), 169.6 (major), 142.0 (major), 138.9 (minor), 132.3 (major), 130.9 (minor), 129.1 (minor), 128.5 (major), 128.2 (major), 128.1 (minor), 127.3 (minor), 127.1 (major), 118.3 (major), 118.2 (minor), 87.4 (major), 87.2 (minor), 43.9 (major), 42.4 (minor), 30.1 (major), 29.4 (minor), 19.9 (major), 19.3 (minor), 17.5 (minor) and 14.7 (major); IR (neat) 1740 cm^{-1}. Found: C, 77.45; H, 7.46%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

3.2.19. 3,6-Dihydro-5-methyl-6-[1-(naphthalen-1-yl)ethyl]-2*H*-pyran-2-one (3r). Hexane–ethyl acetate (2:1) as the

eluent; ^{1}H NMR (500 MHz) δ 8.00–7.40 (7H, m, ArH), 5.55–5.00 (2H, m, CH═ and OCH), 4.19, 3.02 (1H: q, J=7.1 Hz, ArC*H* (minor); q, J=6.9 Hz, ArC*H* (major)), 3.01, 2.46, 1.48–1.43 (2H: br, CH_2 (major); dd, J=21.7 and 4.3 Hz, CH_2 (minor); m, CH_2 (minor)), 1.78, 1.69 (3H: s, *Me*C═ (major); s, *Me*C═ (minor)), and 1.64, 1.40 (3H: d, J=7.1 Hz, *Me*CH (minor); d, J=6.9 Hz, *Me*CH (major)); ^{13}C NMR (125 MHz) δ 170.2 (minor), 169.3 (major), 137.8 (major), 136.2 (minor), 134.1 (major), 133.6 (minor), 132.4 (minor), 132.1 (major), 131.2 (major), 131.1 (minor), 129.4 (major), 129.0 (minor), 127.8 (minor), 127.6 (major), 126.4 (minor), 126.2 (major), 125.8 (minor), 125.7 (major), 125.6 (minor), 125.5 (major), 125.4, 122.9 (minor), 122.1 (major), 118.4 (minor), 118.2 (major), 86.8 (minor), 86.3 (major), 37.0 (major), 36.7 (minor), 30.2 (major), 30.0 (minor), 19.9 (minor), 19.6 (major), 18.2 (minor) and 13.8 (major); IR (neat) 1736 cm^{-1}. Found: C, 80.77; H, 6.96%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

3.2.20. (*E*)-1-(1,3-Dimethylpenta-2,4-dienyl)naphthalene (4r). Hexane–ethyl acetate (2:1) as the eluent; ^{1}H NMR (500 MHz) δ 8.07 (1H, d, J=8.5 Hz, ArH), 7.84 (1H, d, J=7.5 Hz, ArH), 7.69 (1H, d, J=4.7 Hz, ArH), 7.51–7.41 (4H, m, ArH), 6.37 (1H, dd, J=10.7 and 17.4 Hz, C*H*═CH_2), 5.73 (1H, d, J=8.8 Hz, ArCHC*H*═), 5.13 (1H, d, J=17.4 Hz, CH_2═), 4.96 (1H, d, J=10.7 Hz, CH_2═), 4.54 (1H, dq, J=8.8 and 7.0 Hz, ArC*H*), 1.84 (3H, s, MeC═) and 1.49 (3H, d, J=7.0 Hz, *Me*CH); ^{13}C NMR (125 MHz) δ 142.6, 141.5, 138.3, 134.0, 133.4, 131.5, 129.0, 126.8, 125.9, 125.8, 125.4, 123.5, 123.3, 111.4, 33.9, 22.0 and 12.2; IR (neat) 1605, 1508, 1450 and 993.3 cm^{-1}. Found: C, 91.65; H, 8.32%. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16%.

3.2.21. 3,5,6,7,8,8a-Hexahydro-8-phenylchromen-2-one (3s). The crude product was purified by column chromatography on silica gel with hexane–ethyl acetate (1:1) as the eluent to give a diastereomeric mixture of lactone **3s** in 60% yield; Found: C, 78.58; H, 7.09%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%. By preparative HPLC on a YMC silica gel column (S-5 120A SIL; 20 mm i.d.×25 cm) with hexane–ethyl acetate (4:1) as the eluent, the mixture was separated into each diastereomer.

trans-**3s**: ^{1}H NMR (400 MHz) δ 7.35–7.30 (2H, m, ArH), 7.25–7.21 (3H, m, ArH), 5.50–5.48 (1H, m, CH═), 5.00 (1H, br, OCH), 3.15–2.99 (2H, m, CH_2C═O), 2.75 (1H, ddd, J=12.5, 10.9 and 3.8 Hz, PhC*H*), 2.54–2.48 (1H, m, C(5)H_2), 2.22–2.14 (1H, m, C(5)H_2), 2.02–1.96 (1H, m, C(7)H_2), 1.93–1.86 (1H, m, C(6)H_2), 1.72 (1H, m, C(7)H_2) and 1.45 (1H, m, C(6)H_2); ^{13}C NMR (100 MHz) δ 168.0, 141.9, 135.2, 128.6, 127.5, 126.9, 113.3, 83.9, 52.7, 33.5, 33.2, 29.5 and 26.5; IR (neat) 1736 cm^{-1}.

cis-**3s**: ^{1}H NMR (400 MHz) δ 7.35–7.32 (2H, m, ArH), 7.27–7.19 (3H, m, ArH), 5.53–5.50 (1H, m, CH═C), 5.25–5.21 (1H, m, OCH), 3.60 (1H, dt, J=6.4 and 3.8 Hz, PhC*H*), 2.99–2.90 (1H, m, O═CCH_2), 2.78–2.70 (1H, m, O═CCH_2), 2.61–2.56 (1H, m, C(5)H_2), 2.27–2.17 (1H, m, C(5)H_2), 2.02–1.98 (2H, m, C(7)H_2), 1.86–1.73 (1H, m, C(6)H_2) and 1.71–1.63 (1H, m, C(6)H_2); ^{13}C NMR (100 MHz) δ 168.0, 140.4, 129.4, 128.2, 126.7, 119.6, 113.9, 82.5, 46.3, 32.5, 30.5, 29.4 and 21.3; IR (neat) 1736 cm^{-1}.

3.3. Reaction of cinnamaldehyde (1e) with dimethylketene

Gaseous dimethylketene, which was generated by pyrolysis of tetramethylcyclobutane-1,3-dione (3.04 g, 21.7 mmol),[28] was bubbled into a solution of [Pd(dppb)(PhCN)$_2$](BF$_4$)$_2$ (47.1 mg, 51.6 μmol) and cinnamaldehyde (**1e**) (129 mg, 976 μmol) in dichloromethane (200 cm^3). The mixture was stirred for 1 h and worked up as above. The crude product was purified by column chromatography on silica gel with hexane–ethyl acetate (4:1) as the eluent to give (4-methylpenta-1,3-dienyl)benzene (**7**)[29] (72.8 mg, 47%); ^{1}H NMR (500 MHz) δ 7.40–7.38 (2H, m, ArH), 7.31–7.28 (2H, m, ArH), 7.20–7.16 (1H, m, ArH), 6.99 (1H, dd, J=15.5 and 11.0 Hz, PhCH═C*H*), 6.42 (1H, d, J=15.5 Hz, PhC*H*), 6.00 (1H, d, J=11.0 Hz, C*H*═CMe_2), 1.86 (3H, s, Me) and 1.85 (3H, s, Me); ^{13}C NMR (125 MHz) δ 138.2, 136.6, 129.6, 128.6, 126.9, 126.1, 125.8, 125.5, 26.3 and 18.6; IR (KBr) 1595, 1497, 1448 and 954.7 cm^{-1}.

3.4. Rearrangement of 4-isopropenyloxetan-2-one (2d) to 4-methylpenta-2,4-dienoic acid (9)

A solution of lactone **2d** (35.0 mg, 312 μmol), [Pd(η^3-C_3H_5)Cl]$_2$ (2.8 mg, 7.6 μmol) and dppb (6.6 mg, 15.5 μmol) in dichloromethane (5.0 cm^3) was stirred for 1 h at room temperature. The reaction was quenched with water and the mixture was extracted with 1 M NaOH. The aqueous layer was acidified by addition of conc. HCl to liberate the free acid, which was extracted with diethyl ether. The extract was dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by PLC with hexane–ethyl acetate (1:1) as the eluent to give acid **9**[30] (17.8 mg, 51%); ^{1}H NMR (400 MHz) δ 7.46 (1H, d, J=15.7 Hz, CH═), 5.88 (1H, d, J=15.7 Hz, CH═), 5.41 (2H, m, CH_2═) and 1.91 (3H, s, Me); ^{13}C NMR (100 MHz) δ 172.5, 149.5, 140.5, 125.6, 117.9 and 18.0.

3.5. Conversion of lactone 3a to sorbic acid (10)

Lactone **3a** (103 mg, 919 μmol) was boiled with conc. HCl (1.0 cm^3) in ethanol (5.0 cm^3) for 24 h. To the cooled mixture was added water and the resulting mixture was extracted with diethyl ether. The extract was washed with brine, dried over $MgSO_4$ and evaporated to give ethyl sorbate, which was boiled with KOH (500 mg) in a mixture of ethanol (4.0 cm^3) and water (1.0 cm^3) for 6 h. The cooled mixture was diluted with water and acidified by addition of conc. HCl to liberate the free acid, which was extracted with diethyl ether. The extract was washed with brine, dried over $MgSO_4$ and evaporated. The residue was purified by PLC with hexane–ethyl acetate (1:1) as the developer to give sorbic acid (**10**) (92.4 mg, 90%), the spectral data of which were identical with those of the commercial sample.

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