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REARRANGEMENTS OF OPTICALLY ACTIVE CYCLOPROPYL ALLYL ESTERS BY LEWIS ACIDS AND PALLADIUM (0) CATALYSIS

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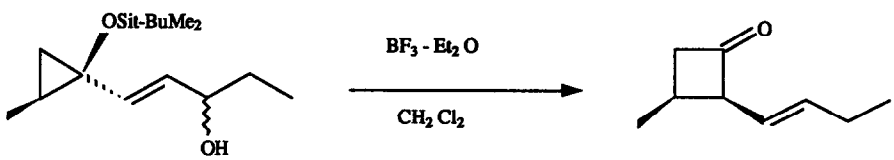
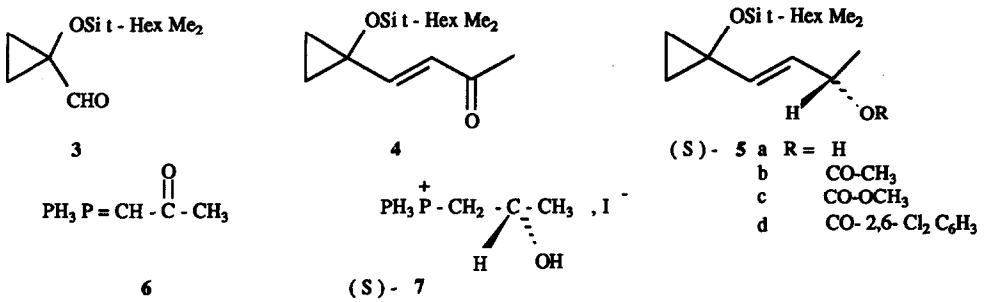
Abstract : While optically active (1-siloxycyclopropyl) allyl esters underwent ready Lewis acids induced rearrangement into 2-vinylcyclobutanone with chirality transfer up to 71.5%, Pd (0) failed for stereoelectronic reason to catalyse the expected $C_3 \rightarrow C_4$ ring expansion.

We have mentioned recently the synthetic potential of 2-vinylcyclobutanones;they can undergo either acid, base, thermally and photolytically induced ring expansions and lead to five-, six- and eight membered-rings selectively or are opened to give functionalized acyclic fragments [1].Currently accessible from the cycloaddition of vinylketenes to olefins [2], these attractive synthons have been recently obtained optically active by BF_3-Et_2O induced regio- and stereospecific ring expansion of chiral (1-siloxycyclopropyl)allyl alcohols [3]. Thus, the E allylic alcohol (1R,2S)-**1** underwent catalytic BF_3-Et_2O induced diastereoselective $C_3 \rightarrow C_4$ ring enlargement into the E cyclobutanone (2R,3S)-**2** (ds > 95%), which allowed the first synthesis of the optically active cis *Quercus* lactone (> 90% ee) [3].

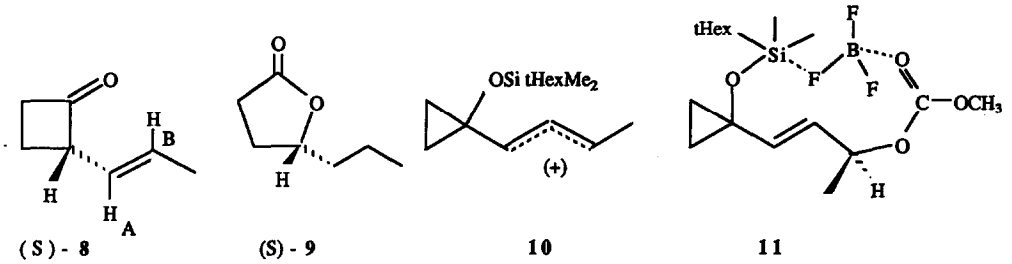


(1R,2S) - (+) - **1** (2R , 3S) - (-) - **2** (ds >95%)

Ring formation by intramolecular displacement of an allylic leaving group (ScN') is well known to occur stereoselectively when the entering group is a carbanion [4,5] or when the reaction is promoted by Pd (0) catalysis [6], so we have prepared the optically active cyclopropylallyl alcohol and esters (R) and (S)-**5a-d** in order to test their ability to undergo $C_3 \rightarrow C_4$ ring expansion with expected chirality transfer under Lewis acids and Pd (0) catalysis, taking into account the homoenolate behaviour of the cyclopropanolate anion [7]. A recent report on the palladium catalyzed reaction of siloxycyclopropanes providing 1,4-dicarbonyl compounds [8] prompts us to disclose our results in this field.



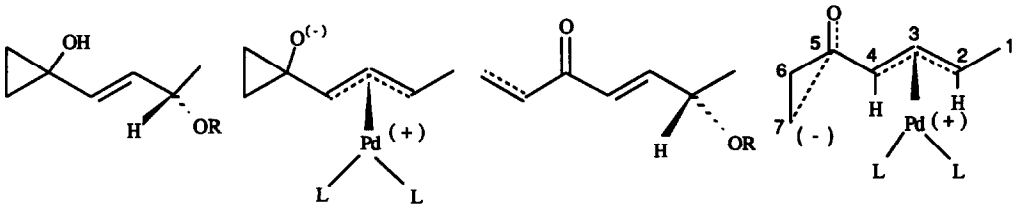
Wittig reaction of the readily available 1-siloxycyclopropanecarboxaldehyde **3** [9,10] with commercial 1-triphenylphosphoranylidene-2-propanone **6** in CH_2Cl_2 gave the E enone **4** (83% y.). Reduction of the carbonyl of **4** with chiral (R)-(+) or (S)-(-) binaphthol modified $LiAlH_4$ (Binal-H) [11] provided in 85% yield the 4-(1-siloxycylopropyl) but-3-en-2-ol (R)-(+) or (S)-(-) **5a**, (88% ee). Alternatively,addition of the aldehyde **3** to the ylide obtained upon treatement of phosphonium iodide (S)-(-)-**7** (prepared from (S)-(-) ethyl lactate) with methyllithium in THF at -78°C provided also (S)-(-)-**5a** (98% ee) [12]. Esterification with acetic anhydride (DMAP, CH_2Cl_2,0°C), methyl chloroformate (pyridine, CH_2Cl_2,0°C) and with 2,6-dichlorobenzoyl chloride (pyridine, CH_2Cl_2,0°C) gave the acetate **5b** , carbonate **5c** and 2,6- dichlorobenzoate **5d** in 83-90% yields. The optical purities of (R)-(+) and (S)-(-)-**5a-d** have been determined by ^1H n.m.r. (250 MHz) analysis of the splitting of the methyl protons of the butenol moiety which occurred in the presence of a chemical shift reagent ($Eu(hfc)_3$), comparatively to the racemic compounds.



Upon treatment with a catalytic amount of BF_3-Et_2O in CH_2Cl_2, the allyl alcohol (S)-**5a** underwent total $C_3 \rightarrow C_4$ ring expansion into the E 2-(1-propenyl) cyclobutanone **8** [13](J_{AB} = 15.25 Hz) within 15 mn at r.t., as shown by t.l.c. Irradiation of the methyl of **8** at δ 1.70 ppm (dd) simplified the ^1H n.m.r. vinylic protons multiplet signal into a doublet of doublet centered at δ 5.46 ppm (J = 15.9 and 6.5 Hz) for H_A and into a doublet centered at δ 5.60 ppm (J = 15.9 Hz) for H_B, which are splitted in the presence of 0.25 equiv. of $Eu(hfc)_3$, allowing to determine the enantiomeric purity of **8**.While allylic alcohol **5a** and acetate **5b** underwent BF_3-Et_2O induced ring expansion into quasi-racemic 2-vinyl cyclobutanone **8**, involving the intermediary of (1-siloxycyclopropyl) allyl cation **10** on the other hand, upon treatment with BF_3-Et_2O at 0°C, the allyl carbonate **5c** was rearranged into (S)-(-)-**8** ($[\alpha]_D$ = -8 °, c 1, CH_2Cl_2) with 43% enantiomeric excess, resulting of a partial (71.5%) chirality transfer. Rearrangement performed at -78, -30 and 20°C led quantatively to **8** with 20, 23 and 34 e.e., respectively ; use of $ZnCl_2$ or $Eu(fod)_3$ gave **8** with 31 and 21 enantiomeric purities.

The (S)-configuration of **8** determined by its transformation into the 4-propyl-γ-lactone (S)-**9** [14] by successive reduction (H_2, Pd/C) and Bayer-Villiger oxidation (MCPBA) following a reported procedure [3], implies likely also and *anti* relationship [4] between the leaving group (*i.e.*, CH_3OCOO-) and the migrating cyclopropane bond. A concerted rearrangement through a BF_3-complex such as **11** (involving one or two mol. of BF_3), is likely responsible for the enantioselectivity observed in this ring enlargement.

Pd(0) is well known to accelerate and induce stereoselectivity in the cyclization of allylic esters [6]. So, it appeared then worthwhile to investigate the rearrangement of optically active (1-hydroxycyclopropyl) allylic esters (R) or (S)-**12**b-d under Pd(0) catalysis ; formation of a cyclopropyl allyl palladium complex such as **13** followed by stereoselective C-3 → C-4 ring expansion with chirality transfer was expected.



(S) - 12 a-d (98% ee) 13 14 (50% ee) 15

Desilylation of **5**b-d with Bu_4N^+,F^- in THF gave the corresponding 1-vinylcyclopropanols **12**b-d in 95% yield. Addition of the Palladium catalyst [15] (5%) to the allyl acetate (S)-**12**b or benzoate (S)-**12**d in the presence of NaH (1 equiv.) and to the allyl carbonate (S)-**12**c (known to produce methylate anion used to form carbanion *in situ* [16]),or directly to the silylated allylic esters **5**b-d in the presence of Bu_4N^+,F^-(1 equiv.),under various conditions led exclusively to a 1:1 mixture of conjugated enones and dienones (S)-**14** [17] in 15-30% yields,besides polymers. Although probably formed, as shown by the partial racemisation of **12**c(98% ee) → **14** (50% ee) consistent with a reversible palladium-coordination [18] and by the ready Pd (0) catalyzed nucleophilic alkylation of allylic esters (S) **5**b-d with dimethyl malonate anion [19], the π-allylpalladium complex **13** did not undergo the C-3 → C-4 ring expansion expected comparatively to the BF_3-Et_2O induced (S)-**5**a-c → (S)-**8** rearrangement.

In summary, while the (1-siloxycyclopropyl) allyl alcohol and esters **5**a-d underwent readily BF_3-Et_2O induced ring expansion either via the cyclopropylcarbinyl cation complex **10** or via a BF_3-complex such as **11** allowing concerted rearrangement with partial chirality transfer, on the other hand the π–allylpalladium complex **13** formed under Pd(0) catalysis , did not followed the geometrically favored 4- *exo-trig* process expected to produce a four - membered ring but , even under neutral condition, underwent ring opening into a zwitterionic complex such as **15** ; then occurrence of a sp^2 carbon at C_5 (*i.e.*, carbocation or carbonyl) precluded to attain the transition state required for ring closure, analagously to the disfavored 5-*endo trig* process [20] which forbade the palladium catalyzed vinylcyclopropane - cyclopentene rearrangement [21].

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12) $[\alpha]_D$ = -3.7 °, c 1.05, CH_2Cl_2; ^1H NMR ($CDCl_3$, 250 MHz).0.15 (s, 6H), 0.70 (m, 2H), 0.8 (s, 6H), 0.86 (d, 6H, J = 6.8 Hz), 1.0 (m, 2H), 1.28 (d, 3H, J = 6.35 Hz), 1.5 (m, 1H), 1.62 (sept., 1H, J = 6.8 Hz), 4.32 (m, 1H, J = 6.35 Hz), 5.5 (d, J = 15.3 Hz), 5.7 (dd, 1H, J = 15.3 and 6.3 Hz) ; IR ($CHCl_3$) 3350 (γ_{OH}), 3100 (γ_{C-H} cyclopropane) and 1670 cm^{-1}($\gamma_{C=C}$) ; Anal. calcd for $C_{15}H_{30}O_2Si$: C 66.66 ; H 11.11. Found : C 66.68 ; 11.20.

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15) Pd(0) was prepared *in situ* either from $Pd(OAc)_2$ and 1 equiv. of 1,2-bis(diphenylphosphino)-ethane (dppe) in CH_3CN at reflux[16] or from bis(dibenzylideneacetone) palladium [$Pd(dba)_2$] and 1 equiv. of dppe in THF at r.t. Fiaud, J.C.;Malleron,J.L.*Tetrahedron Lett.*, 1980, *21*, 4437.

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17) Dienone **14** (R = $COCH_3$) : ^1H NMR ($CDCl_3$, 250 MHz), 1.38 (3H, d, J = 5 Hz), 2.12 (3H, s), 5.52 (1H, m), 5.86 (1H, dd, J = 10.6 and 1.5 Hz), 6.29 (1H, dd, J = 17.4 and 1.5 Hz), 6.47 (1H, dd, J = 15.9 and 1.4 Hz), 6.57 (1H, dd, J = 17.4 and 10.6 Hz), 6.8 (1H, dd, J = 15.9 and 5 Hz) ; IR ($CHCl_3$) 1745 and 1640 ($\gamma_{C=O}$) , 1615 cm^{-1}($\gamma_{C=C}$) ; MS m/e (rel. int.) 126 (M+, 6.70), 109 (67), 99 (16), 83 (37), 71 (33), 58 (33), 48 (100).
Enone **14** (R = $COCH_3$) : ^1H NMR ($CDCl_3$, 250 MHz), 1.11 (3H, t, J = 7 Hz), 1.40 (3H, d, J = 5 Hz), 2.13 (3H, s), 2.6 (2H, q, J = 5 Hz), 5.52 (1H, m), 6.19 (1H, dd, J = 16 and 1.5 Hz), 6.7 (1H, dd, J = 16 and 5 Hz). IR ($CHCl_3$) 1745 and 1673 ($\gamma_{C=O}$) , 1615 cm^{-1}($\gamma_{C=C}$) ; MS m/e (rel. int.) 128 (M+, 7.6), 111 (34), 99 (100), 85 (13), 71 (20), 59 (11), 48 (77).

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