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Tandem Carbonyl Coupling-Rearrangements Promoted by the Niobium(III) Reagent. Dual Reductive and Lewis Acid Properties of $NbCl_3$(DME)

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Abstract *: Benzaldehyde (**1a**) and acetophenone (**6**) are shown to undergo highly stereoselective reductive couplings by $NbCl_3$(DME). When the reaction is performed at - 10°C, the threo diols can be isolated. The intermediate niobiopinacols reveal the ability of subsequent transformations, due to the Lewis acid properties of the reagent used. Starting from **1a** stereospecific acetalization leads to threo-2,4,5-triphenyl-1,3-dioxolane (**3a**), whereas 3,3-diphenyl-2-butanone (**7**) is obtained from **6** in a pinacol-pinacolone type rearrangement. Alkenes may also be formed in the competing, temperature controlled deoxygenation. The stereoselectivity and the easy control of $NbCl_3$ (DME) mediated reactions make it a promising reagent for further synthetic applications.*

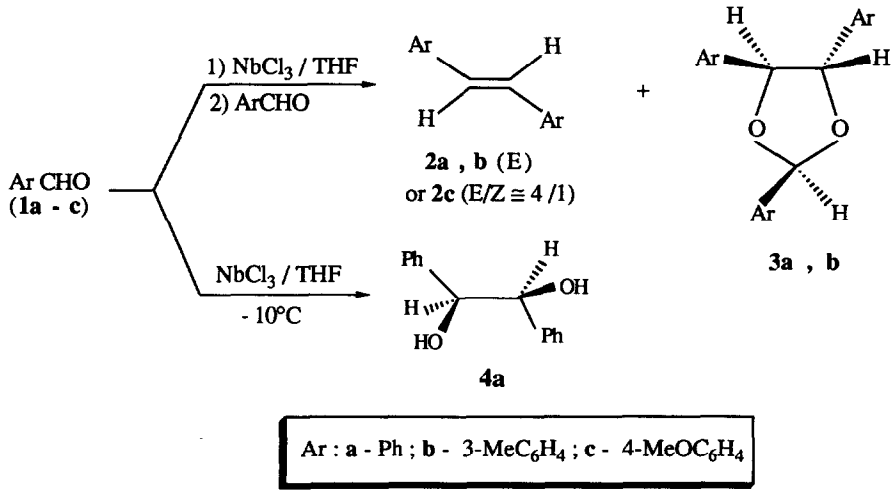
The reductive coupling of aldehydes and ketones leading to vicinal diols and/or alkenes constitutes an important group of carbon-carbon-bond forming reactions. A variety of reagents are employed including early transition metals,[1] and especially the low-valent titanium species generated in situ by the reduction of $TiCl_3$ or $TiCl_4$. Referred to as the McMurry reaction,[2] the latter has greatly extended the scope of the olefin synthesis. The low-valent titanium species are versatile reagents for pinacolizations, in intermolecular as well as in intramolecular reactions.[3] Certain difficulties arose with reproducibility of the titanium slurries, and a lack of selectivity with intermolecular radical dimerization was observed. Low yields were obtained for most of the other transition metals studied.[4] Nevertheless, transition metal reagents which have both well-defined oxidation states and variable coordination chemistry have recently appeared, making it possible to perform more complex and often multistep transformations with high stereoselectivity. The recent preparation and several synthetic applications of the niobium(III) reagent $NbCl_3$(DME)[5] (DME : 1,2-dimethoxyethane) is significant in this respect. The rich coordination chemistry of the d^2 niobium center may be anticipated.

We were interested in using $NbCl_3$(DME) to promote the direct coupling of carbonyl compounds because of the somewhat different course of this reaction anticipated relative to the titanium induced reductive couplings. In fact, the $NbCl_3$(DME) reagent could be considered as a two -and not a one-electron reductant, like the Ti(O) species. Moreover, the presumed differences in oxophilicity[6] and Lewis acidity would make a distinction between the two reactions.

Results and Discussion

We now report the $NbCl_3$(DME) reagent's activity towards model carbonyl compounds : acetophenone and certain benzaldehyde derivatives.

First, benzaldehyde was put together with an equimolar quantity of $NbCl_3$(DME) in THF at room temperature, under argon. After 3 h an additional equimolar portion of benzaldehyde was added. After stirring for 5 h, the reaction mixture was hydrolyzed (10% KOH). The two products separated by flash chromatography were E-stilbene **2a**, and diastereomerically pure threo acetal **3a** (Scheme 1) ; the ratio of **2a**:**3a** was ≈ 1:3 and the overall yield 86% (based on the starting benzaldehyde). Unlike in the reaction with only an equimolar amount of benzaldehyde, no diol was detected in this case. Similarly, the mixture of diastereomerically pure alkene **2b** and acetal **3b** was obtained starting from 2 equivalents of 3-methylbenzaldehyde **1b**. Quite a different result was obtained when 4-methoxybenzaldehyde **1c** was used as the substrate. Only a mixture of alkenes **2c** with the ratio E:Z 4:1 was formed in this reaction.



Scheme 1

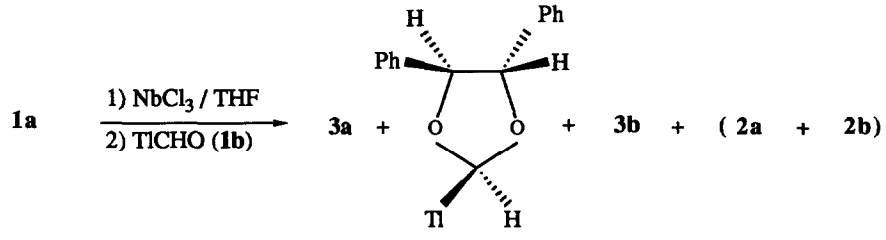
In the Ti-promoted carbonyl coupling reaction, the stereoselectivity is observed in both the diol forming step (dl/meso ratio) and in the deoxygenation of intermediate metallopinacols (E/Z ratio).[2] Although the preference for the thermodynamically favored threo (dl) diols[7] and E-alkenes was often observed in the intermolecular reactions, a mixture of stereoisomers was generally formed, depending on the nature of the titanium reagent[8] and reaction conditions.[9]

In the $NbCl_3$(DME) mediated reductive coupling of benzaldehyde, both the acetal and alkene were formed stereospecifically. Assuming that the pinacolization step is followed by acetalization, the stereochemistry of the diol might be related to the structures of the acetal and alkene[10] obtained.

In order to clarify this question, benzaldehyde **1a** was allowed to react in the presence of an equimolar amount of $NbCl_3$(DME) in THF at low temperature (- 10°C). As a result, only a small amount of acetal **3a** was detected. The threo configuration (> 97%) was found by ^1H NMR in the predominantly formed hydrobenzoin **4a**.[11] On the other hand, the alkene **2a** was obtained as the sole product by refluxing

the equimolar mixture of **1a** and $NbCl_3$(DME) in THF for 6 h. Noteworthy is the easily realized control of these reactions.

The cross-coupling experiment employing benzaldehyde **1a** together with 3-methylbenzaldehyde **1b** (Scheme 2) further contributed to the understanding of the reaction pathways. At the beginning, the mixed acetal **5** (reference) was prepared in 7% yield from the diol **4a** and aldehyde **1b** by the action of $NbCl_3$(DME). The poor yield of this reaction contrasts significantly with the good yields obtained in the direct transformations of aldehydes **1a** and **1b** into acetals **3a** and **3b**. The cross-coupling reactions were then performed at room temperature and at - 15°C. Other reaction conditions were similar to those previously imposed (for the reactions involving separately **1a** or **1b**, see experimental section). For each of the two alternatives, equimolar amounts of **1a** and $NbCl_3$(DME) were put together in THF. After suitable periods, equimolar portions of **1b** were added and the two reactions were continued at constant temperatures, 5 h at r.t. and 16 h at - 15°C, respectively . The products obtained and their molar ratios are given in Scheme 2.



molar ratios

Δ=20°C	10	68	22	16	12
Δ= -15°C	8	67	25	-	-
compound	**3a**	**5**	**3b**	**2a**	**2b**

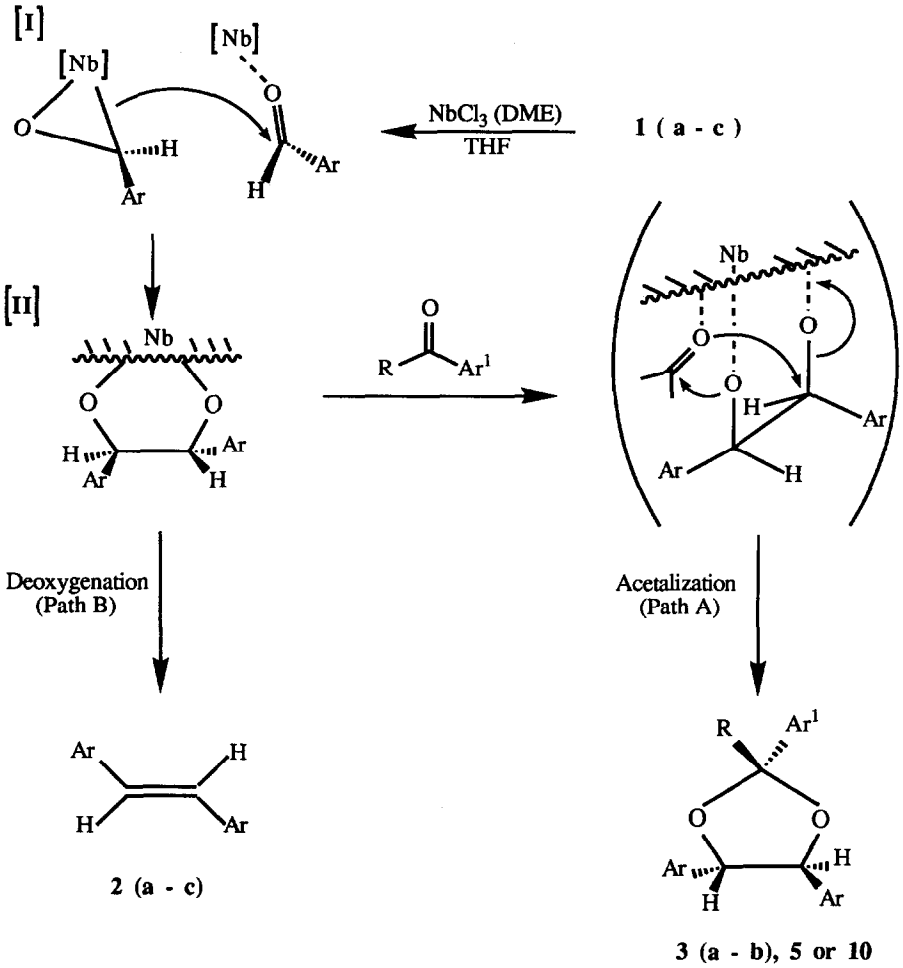
The molar ratio of the acetal mixture (**3a** + **5** + **3b**) and alkenes **2a** and **2b** are related to isolated products. Those of acetals considered separately (**3a** : **5** : **3b**) were established by comparison of peaks heights of the three acetal hydrogen resonances.

Scheme 2

A mixture of three acetals **3a,b** and **5** was formed in each case, with acetal **5** being obtained predominantly (67% and 68%). We therefore concluded that acetalization occurs via the intermediate metallopinacol (vide infra). The reaction was restricted at the pinacol-acetal stages at - 15°C, but by increasing the temperature, alkenes **2a** and **2b** were also formed. The competition between the one - C-O bond cleavage process with the concomitant attack of **1a(b)** leading to the acetals, and the two - C-O bond cleavage deoxygenation takes place (Figure 1).

More detailed studies, particularly in kinetics, are needed to elucidate the mechanism of this reaction. However, an hypothesis accounting for the present results is advanced here (Figure 1). At the first stage the intermediate metalloxirane **I** should be formed starting from the d^2 niobium center. This structure, analogous to niobioaziridine,[5a,b] also has precedents in early transition metal chemistry.[12] The successive insertion of the oxo-group into the metal-carbon bond led to metallopinacol **II**. This process, rather than the

dimerization of the carbonyl radical anions formed by a single electron transfer (Ti),[13] agrees with the enhanced stereoselectivity at the pinacol stage.



2/a, Ar = Ph ; **b,** Ar = 3 -MeC_6H_4 , **c,** Ar = 4 -$MeOC_6H_4$
3/a, Ar = Ar^1 =Ph , R = H , **b,** Ar = Ar^1 = 3 -MeC_6H_4 , R =H
5/ Ar = Ph ; Ar^1 = 3-MeC_6H_4 ; R = H
10/ Ar = Ar^1 = Ph ; R = CH_3

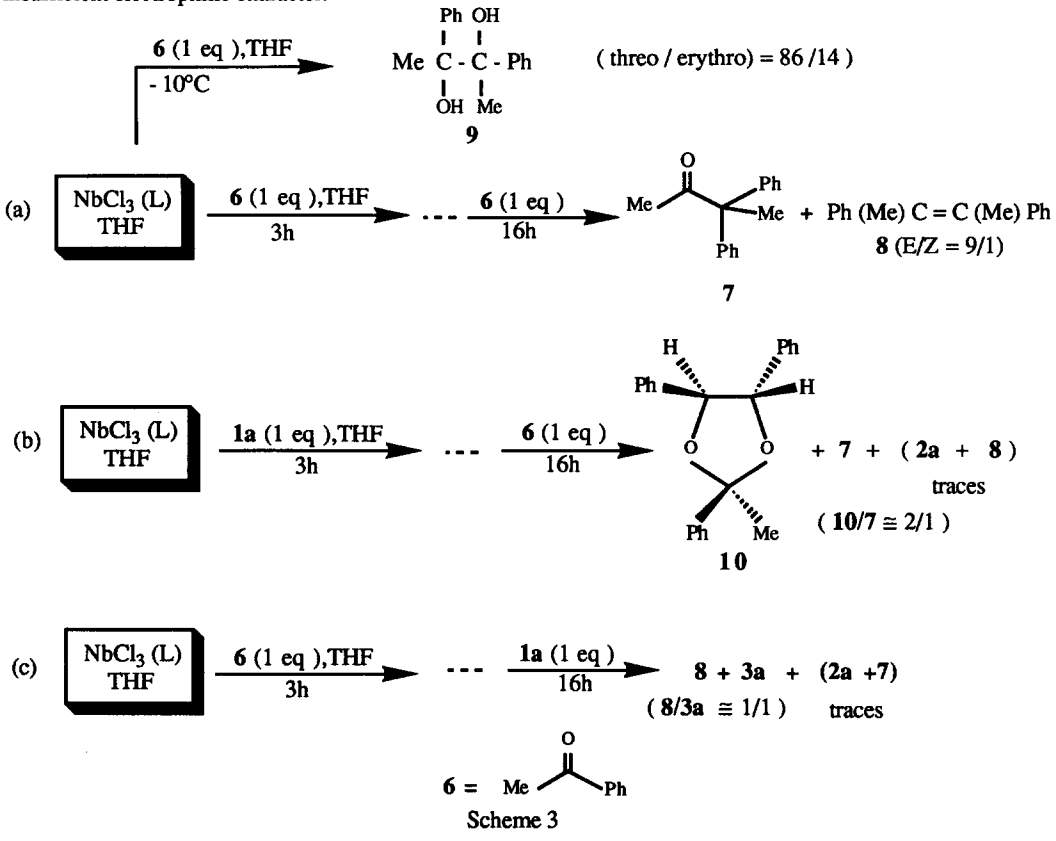
Figure 1

The competition between acetalization (path A) and deoxygenation (path B) governs the next step. The relative kinetics (referring to **II**) of acetalization have marked repercussions on the molar ratio of acetals **3a,b** and **5** (Scheme 2). Before the aldehyde **1b** was added, a significant portion of **1a** had already been transformed into **II(a)**. Consequently, **II(a)** reacted faster with **1b** than with **1a** ; the former reaction gave rise to the major mixed acetal **5**, whereas the latter produced minor amounts of acetal **3a**. The intermediate **II(b)**, formed at the same time, reacted with the remaining **1b** to give acetal **3b**. The

competing deoxygenation may be stopped by decreasing the temperature. On the contrary, the same temperature variation does not significantly affect the acetalization step.

As outlined above : (i) the acetalization accured via the intermediate metallopinacol. (ii) the threo configuration was found in the acetal **3a** as well as in the related diol **4a** (Scheme 1). The chelation-controlled process (Figure 1) could be responsible for the stereochemical outcome of the acetalization, i. e. for the retention of the configuration at the carbon centers. Indeed, the three oxygens should reach the neighboring metal atoms on the same surface [14] of the polymeric niobium reagent [5a].

Acetalization via a metallopinacol intermediate using aldehyde in the presence of $NbCl_3(L)$ may be considered formally similar to the well-known synthesis of acetals from oxiranes and carbonyl compounds. Likewise in the latter in which Lewis acid (BF_3 for example) may be used as a catalyst,[15] $NbCl_3(L)$ would also activate the electrophilic carbonyl center towards the attack of metallopinacol oxygen atom. In this context, a plausible explanation of the inactivity of 4-methoxybenzaldehyde (**1c**) lies in its insufficient electrophilic character.



Scheme 3

Both the oxophilicity and the Lewis acidity of $NbCl_3(L)$ were manifested during the easy acetalization step (Fig. 1, path A). It seemed likely to us that the reaction engaging acetophenone (**6**) in place of benzaldehyde **1a** would occur in an analogous manner. Contrary to our expectation, instead of the anticipated acetal, 3-3-diphenyl-2-butanone (**7**) was formed together with the usual deoxygenation

product : 2,3-diphenyl-2-butene (**8**) (E:Z = 9:1) (Scheme 3, entry a). Furthermore, 2,3-diphenyl-2,3-butanediol (**9**) (dl:meso = 86:14) was obtained when the temperature was lowered to - 10°C.

The ketone **7** was reported[16] as the unique product of acid-catalyzed pinacol- pinacolone rearrangement of the diol **9**. In contrast with the drastic conditions required in this reaction (reflux for 30 min with 50% H_2SO_4), the $NbCl_3(L)$ promoted rearrangement of the intermediate metallopinacol occurred in THF at room temperature. However, none of the isomeric pinacolone, i.e. 2-methyl-1,2-diphenyl-1-propanone was observed. The migration of the phenyl rather than that of the methyl group was strongly favored in both reactions.

The cross-coupling experiments contributed to the clarification of a different course of the reactions involving **6** and **1a**. Two reactions were carried out, in which **6** and **1a** were used in cross-coupling but introduced in opposite order (Scheme 3, entries b and c). Ketal **10** and ketone **7**[17] were obtained when the reaction was carried out according to the scheme 3-b (addition of **1a** prior to **6**). Entirely different products resulted when the addition order was inversed according to scheme 3-c (addition of **6** prior to **1a**), namely alkene **8** and acetal **3a**. In the latter reaction, no mixed acetal **11** (Fig. 2) analogous with **10** was detected.

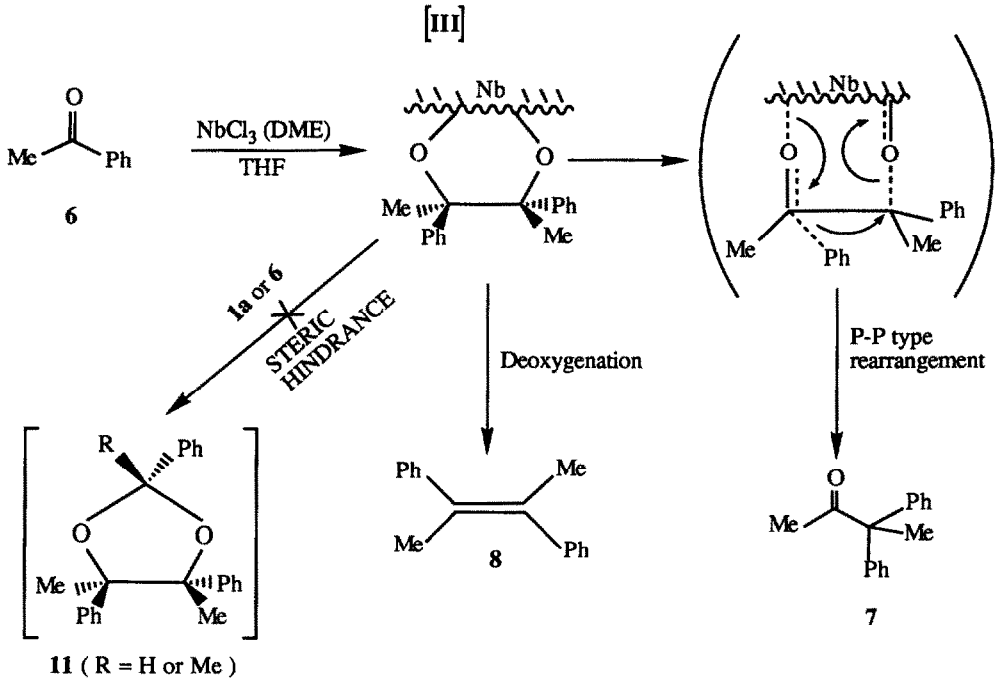


Figure 2

The results are rationalized on the basis of the model presented in Figure 2. The steric control appeared to be responsible for the different pathways of the reactions involving **6** and **1a**. More hindered environment of the metallopinacol **III** as compared to **II(a)** prevents the attack at the carbonyl function leading to the acetal. Instead, another one - C-O bond cleavage transformation may occur, without a concomitant attack of the external carbonyl compound. The tertiary carbonium center can be developed and stabilized afterwards by the migration of the vicinal phenyl group, similarly to the conventional sulfuric

acid-catalyzed rearrangement. Likewise during the acetalization, the competing two - C-O bond cleavage deoxygenation also occurred. It seemed likely that the deoxygenation prevailed over the pinacol-pinacolone type rearrangement at the beginning of the reaction (and vice versa),as supported by the formation of **8** in entry c and of **7** in entry b (Scheme 3).

The multiple properties of $NbCL_3(L)$, its often chameleonic behavior along with its ability to subtly control the reaction selectivity may lead the way to manifold synthetic applications. The enantioselective coupling reactions can be particularly envisaged, due to the high stereoselectivity and the dl-configuration observed. More generally, the ability of niobiopinacols to undergo variable transformations make them interesting targets for future investigations. For example, the reactions analogues to acetalization, but involving attacking agents other than the carbonyl compounds, may be imagined. Further studies dealing with these alternatives are in progress.

Experimental Section

General . All operations were carried out under argon using vaccum line techniques. The solvents used were distilled from sodium benzophenone ketyl under argon atmosphere. Aldehydes **1a-c** and acetophenone were distilled under argon prior to use. $NbCl_3$ (DME) was prepared by a reported procedure.[5a] ^1H and ^{13}C NMR spectra were recorded at 400 and 100.53 MHz, respectively. Mass spectra were obtained by positive ion FAB MS technique employing thioglycerol as the matrix solvent.

General Procedure for Reductive Coupling-(Rearrangement) of Aldehydes 1a-c. A solution of benzaldehyde (**1a**) (0.65 g, 6.13 mmol) in THF (3 mL) was added via syringe to a stirred suspension of $NbCl_3$ (DME) (1.77 g, 6.13 mmol) in 40 mL of THF, at room temperature. After 3 h a second portion of **1a** (0.65 g, 6.13 mmol) in 3 mL of THF was added, and the mixture was stirred for additional 5 h. The reaction mixture was poured into separatory funnel, treated with 10 % KOH (60 mL) and extracted with ether (3 x 70 mL). The combined organics were washed with water, dried ($MgSO_4$) and the solvent was removed in vacuo. Separation by flash chromatography (silica gel, 230-400 mesh, light petroleum-diethyl ether = 9/1) afforded 0.23 g (21 % based on starting **1a**) of E-stilbene (**2a**), and 0.80 g (65 %) of threo-2,4,5-triphenyl-1,3-dioxolane (**3a**) as white crystals : mp 98-100°C. An analytical sample of **3a** was prepared by recrystallization from hexane/ether : mp 100-101°C. **2a** : mp 124-125°C (lit.[18] mp 124-125°C) ; ^1H NMR (C_6D_6) δ 7.33-7.05 (m, 10 H), 7.00 (s, 2H). **3a** : IR (KBr) ν 3065, 3032, 2885, 1498, 1455, 1401, 1358, 1214, 1100, 1067, 1027, 1007, 980 cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 7.70 (br d, J = 7.2 Hz, 2H), 7.47-7.44 (m, 3H), 7.36-7.32 (m, 10H), 6.42 (s, 1H), 5.00 (d, J = 7.8 Hz, 1H), 4.93 (d, J = 7.8 Hz, 1H) ; ^{13}C {^1H} NMR ($CDCl_3$) δ 139.9, 139.4, 137.8, 129.3, 129.2, 129.1, 127.8, 127.6, 127.4, 105.5, 88.3, 86.3 ; DEPT ^{13}C NMR - disappearance of 139.9, 139.4, 137.8 ; none of the two erythro isomers was detected by ^1H and ^{13}C NMR spectroscopy ; MS m/z 303 (MH^+, 48), 197 (100), 179 (56), 167 (74), 152 (21). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.41 ; H, 6.00. Found : C, 83.26 ; H, 6.20. E-3,3'-dimethylstilbene **2b**, methylated threo-acetal **3b** and 4,4'-dimethoxystilbene **2c** were obtained similarly. **2b** : yield 22 % ; mp 56-57 °C (lit.[19] mp 55-56°C) ; ^1H NMR (C_6D_6) δ 7.40-7.36 (m, 4H), 7.25-7.18 (m, 4H), 7.03 (br s, 2H), 2.33 (s, 6H). **3b** : yield 65 % ; oil ; IR (neat) ν 3025, 2958, 2918, 2865, 1488, 1385, 1281, 1160, 1087, 1013, 780 cm^{-1} ; ^1H NMR (CD_3COCD_3) δ 7.50-7.47 (m, 2H), 7.33 (t, J = 6.7 Hz, 1H), 7.25-7.09 (m, 9H), 6.35 (s, 1H), 4.95 (d, J = 7.7 Hz, 1H), 4.88 (d, J = 7.7 Hz, 1H), 2.38 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H) ; ^{13}C {^1H} NMR ($CDCl_3$) δ 139.1, 138.9, 138.7, 137.4, 130.7, 129.9, 129.5, 129.0, 128.2, 128.0, 127.7, 124.8, 124.3, 105.3, 87.8, 85.8, 22.1. **2c** : white crystals of low solubility ; mp 212-214°C (lit.[18] mp 214-215°C). The NMR spectrum is of about 4:1 mixture of E and Z isomers respectively : ^1H NMR (DMSO-d_6) δ 7.57 (d, J = 9.0 Hz, 2H-Z), 7.53 (d, J = 9.1 Hz, 2H-E), 7.07 (s, 2H-E), 7.00 (d, J = 9.0 Hz, 2H-Z), 6.97 (d, J = 9.1 Hz, 2H-E), 5.77 (s, 2H-Z), 3.82 (s, 3H-Z), 3.80 (s, 3H-E).

Pinacol Coupling of Benzaldehyde (1a) : Diol 4a. To a suspension of $NbCl_3$ (DME) (1.70 g, 5.87 mmol) in 25 mL of THF at - 10°C was added a solution of **1a** (0.62 g, 5.87 mmol) in 10 mL

of THF. The resulting mixture was stirred for 8 h at - 10°C. Workup was performed as described above, using 10 % aq. K_2CO_3 (50 mL) instead of 10 % KOH. Flash chromatography (elution with light petroleum-diethyl ether = 9/1 followed by Et_2O alone) yielded 0.49 g (78 %) of 1,2-diphenyl-1,2-ethanediol **4a** : mp 121-122°C (lit.[18] 139-140 (meso), 122-123°C (dl)), together with a small amount of acetal **3a** (0.016 g, 3 %). Threo(dl) configuration was found as predominant for the diol **4a** (threo/erythro > 97/3) by comparison of peak heights of the benzylic PMR resonances, according to the configurational assignment of Seebach et al[20] ($CDCl_3$, dl-δ 4.65, meso-δ 4.77).

Carbonyl Coupling - Deoxygenation of 1a : Alkene 2a. A solution of **1a** (0.22 g, 2.06 mmol) in THF (2 mL) was added via syringe to a stirred suspension of $NbCl_3$ (DME) (0.60 g, 2.06 mmol) in 10 mL of THF. The mixture was heated at reflux for 16 h. The basic workup as described above (20 mL of 10 % aq KOH) followed by flash chromatography purification (elution with 2 % ether-petroleum ether) gave 0.051 g (28 %) of **2a** as white crystals : mp 123-125°C. The ^1H NMR spectrum was identical with that given above.

Threo-2-(3-methylphenyl)-4,5-diphenyl-1,3-dioxolane (5). To a suspension of $NbCl_3$ (DME) (0.72 g, 2.5 mmol) in 10 mL of THF at 0°C was added a solution of diol **4a** (0.36 g, 1.7 mmol) in 5 mL of THF. The mixture was stirred for 15 min., the solution of aldehyde **1b** (0.19 g, 1.7 mmol) in 8 mL of THF was then added in small portions over a 30 min period. After the addition was complete, the reaction was allowed to warm to room temperature and the stirring continued for 3 h. Standard workup (15 mL of 10 % KOH) followed by flash chromatography (light petroleum-diethyl ether = 92/8) of the reaction mixture gave 0.037 g (7 %) of **5** as an oil : IR (neat) ν 3045, 3025, 2918, 2861, 1494, 1454, 1274, 1197, 1164, 1104, 1077, 1003, 765 ; ^1H NMR (CD_3COCD_3) δ 7.58-7.50 (m, 2H), 7.35 -7.08 (m, 12H), 6.38 (s, 1H), 5.01 (d, J = 7.7 Hz, 1H), 4.94 (d, J = 7.8 Hz, 1H), 2.39 (s, 3H) ; ^{13}C {^1H} NMR ($CDCl_3$) δ 140.9, 140.0, 138.8, 138.1, 137.7, 130.9, 130.7, 129.2, 129.0, 128.7; 128.3, 128.0, 127.6, 124.8, 124.4, 105.3, 87.8, 85.9, 21.9.

Mixed Carbonyl Coupling of Aldehydes 1a and 1b. Two experiments were performed at different temperatures : at r.t. and at - 15°C. Equal quantities of substrates and solvents were used in both reactions. A solution of aldehyde **1a** (0.59 g, 5.56 mmol) in THF (3 mL) was added to a stirred suspension of $NbCl_3$ (DME) (1.60 g, 5.56 mmol) in 40 mL of THF. After 3 and 8 h respectively for the reactions at room and lower temperature, aldehyde **1b** (0.66 g, 5.56 mmol) was added in 2 mL of THF. The mixtures were stirred for additional 5 h at r. t. and 16 h at - 15°C. The standard basic workups (60 mL of 10 % aq KOH), followed by flash chromatography (light petroleum-diethyl ether = 9/1) gave products. Only a mixture of three threo-acetals **3a**, **3b** and **5** (1.48 g) was obtained for the low temperature reaction. The mixture of **3a**, **3b** and **5** (1.25 g) together with alkenes **2a** (0.12 g, 12 %) and **2b** (0.10 g, 9 %) were isolated for the r.t. reaction. The molar ratios of acetals were established by comparison of peaks heights of the H-2 resonances. They are **3a** : **5** : **3b** = 8 : 67 : 25 for the - 15°C reaction, and **3a** : **5** : **3b** = 10 : 68 : 22 for the r. t. reaction.

Reductive Coupling-Rearragement of Acetophenone (6). The reaction was performed at 5 mmol (2 x 5 mmol of **6**) scale, using a procedure analogous to that described for the reductive coupling of aldehydes **1a-c**. Flash chromatography (light petroleum-diethyl ether = 96/5) gave 0.79 g (71 %) of 3,3-diphenyl-2-butanone (**7**) and 0.23 g (22 %) of 2,3-diphenyl-2-butene **8** (E/Z = 9/1). Compound **7**[16] : mp 40-41°C (lit. mp 40-41°C) ; IR (CCl_4) 1710 cm^{-1} ; ^1H NMR ($CDCl_3$) δ 7.18-7.03 (m, 10H), 2.11 (s, 3H), 1.89 (s, 3H) ; ^{13}C {^1H} NMR ($CDCl_3$) δ 144.3, 129.0, 127.5, 63.0, 28.2, 27.1 ; MS m/z 225 (MH^+, 100), 181 (25), 165 (10), 147 (21). Alkene **8** : the E/Z = 9/1 ratio was established by comparison of peak heights of the methyl group PMR resonances ($CDCl_3$, E-δ 2.16, Z = δ 1.89)[21] ; ^{13}C {^1H} NMR ($CDCl_3$)[22] δ 145.3(E), 145.2(Z), 133.7(Z), 129.8(E), 128.8(Z), 128.2(E), 126.9(Z), 126.2(E), 23.1(Z), 22.1(E).

Pinacol Coupling of Acetophenone (6) : Diol 9. The reaction was carried out starting from 0.67 g (5.62 mmol) of **6**, as described above for the pinacolization of **1a**. Flash chromatography purification gave 2,3-diphenyl-2,3-butanediol (**9**) ; yield 0.58 g (85 %) ; mp 121-123°C (lit.[23] mp 125°(dl), mp 121°C (meso)). The ^1H NMR spectrum[24] revealed that the product was a mixture of dl and meso diols (dl/meso = 86/14) : ^1H NMR ($CDCl_3$) δ 7.26-7.18 (m, 10H), 2.61 (br s, 2H, D_2O exchange), 1.60 (s, 2H-meso), 1.51 (s, 2H-dl).

Mixed Carbonyl Coupling of Aldehyde 1a and Ketone 6. Two reactions were carried out, which differed only by the order of the introduction of **1a** and **6**. In the first reaction, a solution of **1a** (0.48 g, 4.48 mmol) in 2 mL of THF was added via syringe to a stirred suspension of $NbCl_3$ (DME) (1.30 g, 4.48 mmol) in 35 mL of THF at room temperature. After 3 h a solution of **6** (0.56 g, 4.48 mmol) in 3 mL of THF was added, and the reaction mixture was stirred for additional 16 h. Usual workup for hydrolysis (50 mL of 10 % aq KOH) followed by flash chromatography (light petroleum-diethyl ether = 95/5) gave 0.45 g (63 % based on **1a**) of threo-2-methyl-2,4,5-triphenyl-1,3-dioxolane (**10**) and 0.17 g (34 % based on **6**) of ketone **7**. Moreover, the minor amounts of alkenes **2a** (0.012 g, 3 %) and **8** (0.009 g, 2 %) were isolated. Ketal **10** : mp 41-42°C ; IR (CCl_4) ν 3080, 3040, 2887, 1491, 1455, 1368, 1257, 1187, 1090, 1041, 1021, 957 ; ^1H NMR ($CDCl_3$) δ 7.74 (br d, J = 7.9 Hz, 2H), 7.56-7.11 (m, 13H), 4.94 (d, J = 7.7 Hz, 1H), 4.70 (d, J = 7.7 Hz, 1H), 1.95 (s, 3H) ; ^{13}C {^1H} NMR ($CDCl_3$) δ 139.7, 139.2, 138.2, 129.3, 129.1, 128.9, 128.5, 127.8, 127.5, 125.8, 110.2, 87.1, 86.1, 30.0. When **6** was added prior to **1** alkene **8** (0.30 g, 65 % based on **6**) and acetal **3a** (0.29 g, 64 % based on **1a**) were obtained. Moreover, the minor amounts of alkene **2a** (0.004 g, 1 %) and ketone **7** (0.015 g, 3 %) were isolated.

References

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