# On the Stereoselectivity of γ-Lactol Substitutions with Allyl- and Propargylsilanes − Synthesis of Disubstituted Tetrahydrofuran Derivatives

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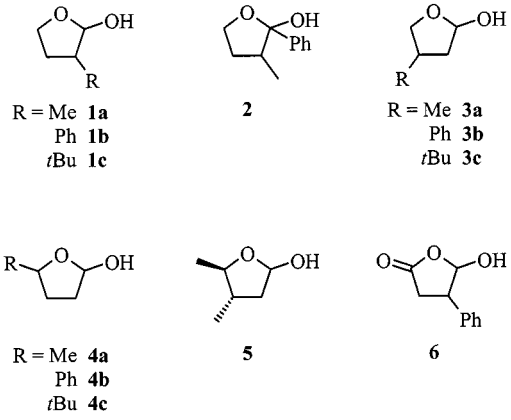
*Dedicated to Prof. Helmut Vorbrüggen on the occasion of his 70th birthday*

**Keywords:** Carbocations / Felkin−Anh model / Lewis acids / Silanes / Tetrahydrofuran

Monosubstituted γ-lactols **1a**–**1c**, **3a**–**3c** and **4a**–**4c**, as well as disubstituted γ-lactol **5** and the γ-hydroxy-substituted γ-lactone **6**, were transformed into disubstituted tetrahydrofuran derivatives by treatment with allyl- and propargylsilanes in the presence of Lewis acids. The diastereoselectivities were moderate to excellent and are interpreted by application of the Felkin–Anh model to cyclic oxocarbenium ions. The effects of the equilibria between conformers of the intermediates are discussed. The surprisingly high diastereoselectivity of 4-substituted γ-lactols **3** can be explained on this basis.

## Introduction

Substituted tetrahydrofuran derivatives are important synthetic intermediates[2] and occur as structural units in many interesting natural products, such as pheromones[3] or polyether antibiotics.[4] Thus, their diastereoselective synthesis is currently receiving much attention.[5] In our group we became interested in Lewis acid-promoted substitution at the anomeric centre of γ-lactols.[6] Although widely employed in carbohydrate chemistry,[7] this methodology is only rarely applied to the synthesis of simple tetrahydrofuran derivatives.[8] This might be due to the lack of information about the stereochemical outcome of this reaction, which makes it difficult to predict the diastereoisomeric distribution. In this paper we wish to report our results regarding the Lewis acid-induced reactions of γ-lactols with allyl- and propargylsilanes.[9] We also propose a model to explain the diastereoselectivities observed in these reactions. For this purpose, γ-lactols **1**−**5** and γ-hydroxy-substituted γ-lactone **6**, bearing substituents of varying steric demand, were treated with a broad variety of silylated nucleophiles under Lewis acid conditions.




## Results

γ-Lactols **1a**−**1c** were treated with propargylsilane **7** and allylsilanes **8**−**10** in the presence of $BF_3{\cdot}OEt_2$. After aqueous workup, 2,3-disubstituted tetrahydrofurans **11**−**14** were isolated as mixtures of *cis* and *trans* isomers (Table 1).

The stereochemical outcome of the reactions depends considerably on the nature of the γ-lactol substituent and on the substitution pattern of the nucleophiles. The influence of substituent R is exemplified by reactions with allylsilane **8** (entries 2−4). A methyl group (**1a**) or a phenyl group (**1b**) both show a similar influence on the diastereoselectivity of the reaction, R = Me being slightly more selective. Not unexpectedly, the *tert*-butyl group (**1c**) directs the attack of the nucleophile exclusively in the *trans* direction (entry 4).

With respect to the nucleophile, substituents at the reactive centre influence the diastereoselectivity of the reaction strongly, while a substituent remote from the carbon involved in bond formation shows no effect. Thus, going from propargylsilane **7** to prenylsilane **10** (entries 1 and 6), the diastereoselectivity of the reactions increases from *trans*/*cis* = 60:40 to 95:5, while reaction of allylsilane **8** and of 1,1-dimethylallylsilane **9** results in equal diastereomer ratios (*trans*/*cis* = 68:32, entries 2 and 5).

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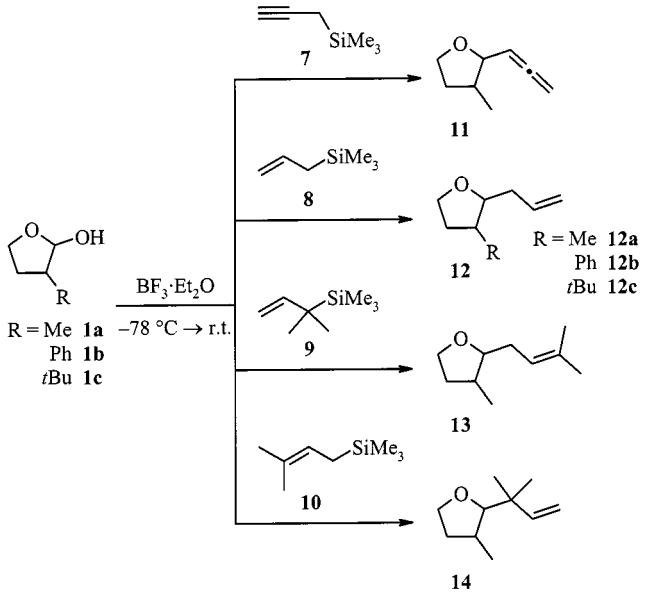
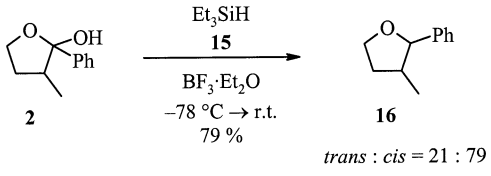



Table 1. $BF_3$-promoted reactions between 3-substituted γ-lactols **1a**–**1c** and silanes **7**–**10**

| Entry | Lactol | Silane | Product | Yield (%) | *trans*:*cis* |
|---|---|---|---|---|---|
| 1 | **1a** | **7** | **11** | 65 | 60:40 |
| 2 | **1a** | **8** | **12a** | 53 | 68:32 |
| 3 | **1b** | **8** | **12b** | 91 | 63:37 |
| 4 | **1c** | **8** | **12c** | 74 | ≥ 98:2 |
| 5 | **1a** | **9** | **13** | 67 | 68:32 |
| 6 | **1a** | **10** | **14** | 50 | 95:5 |

Access to the *cis* series of 2,3-disubstituted tetrahydrofuran derivatives can also be gained by reduction of a 2,3-disubstituted γ-lactol such as **2** with triethylsilane (**15**).[6a–6c,10] As in the other examples, the nucleophile attacks *trans* to the substituent in the 3-position, thus resulting with moderate selectivity (*trans*/*cis* = 21:79) in *cis*-disubstituted tetrahydrofuran **16**.




Compared with those of 3-substituted γ-lactols **1a**–**1c**, the reactions of γ-lactols **3a**–**3c** proceed with significantly higher diastereoselectivity. The nature of the substituent at the γ-lactol ring has a less pronounced influence (entries 2–4 of Table 2). In reaction with allylsilane **8**, a methyl group (**3a**) and a phenyl group (**3b**) induce the same excellent diastereoselectivity (*trans*/*cis* = 95:5), while a *tert*-butyl substituent (**3c**) again directs the attack of the nucleophile exclusively in the *trans* direction (*trans*/*cis* ≥ 98:2). The effect of the substitution pattern in the silane is similar to that observed in reactions of 3-substituted γ-lactols **1**, but at a higher level of selectivity – ranging from *trans*/*cis* = 86:14 with propargylsilane **7** (entry 1) to exclusive formation of *trans*-**19** when using prenylsilane **10** (entry 5).

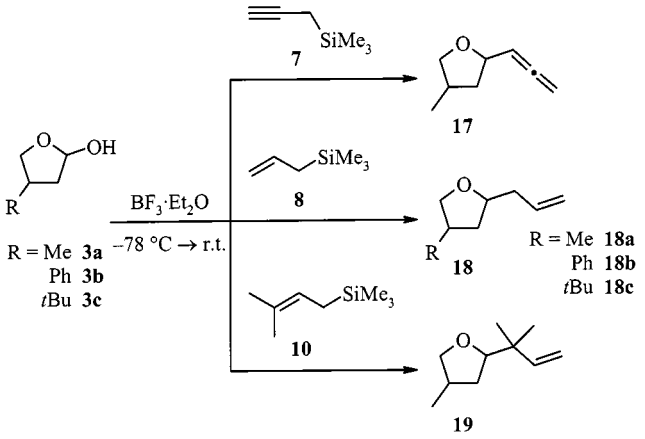



Table 2. $BF_3$-promoted reactions between 4-substituted γ-lactols **3a**–**3c** and silanes **7**, **8** and **10**

| Entry | Lactol | Silane | Product | Yield (%) | *trans*:*cis* |
|---|---|---|---|---|---|
| 1 | **3a** | **7** | **17** | 93 | 86:14 |
| 2 | **3a** | **8** | **18a** | 68 | 95:5 |
| 3 | **3b** | **8** | **18b** | 80 | 95:5 |
| 4 | **3c** | **8** | **18c** | 84 | ≥ 98:2 |
| 5 | **3a** | **10** | **19** | 95 | ≥ 98:2 |

Reactions of 5-substituted γ-lactols **4a**–**4c** with organosilanes seem to be the least predictable transformations. They can lead to preferential formation of either *cis* isomers or *trans* ones, depending on the nature of the substituent at the γ-lactol ring and the steric demand of the attacking nucleophile. Combination of a small substituent (R = Me, **4a**) and low organosilane steric demand leads to good *cis* selectivity (Table 3, entry 1, **21**, *cis*/*trans* = 80:20). Increas-

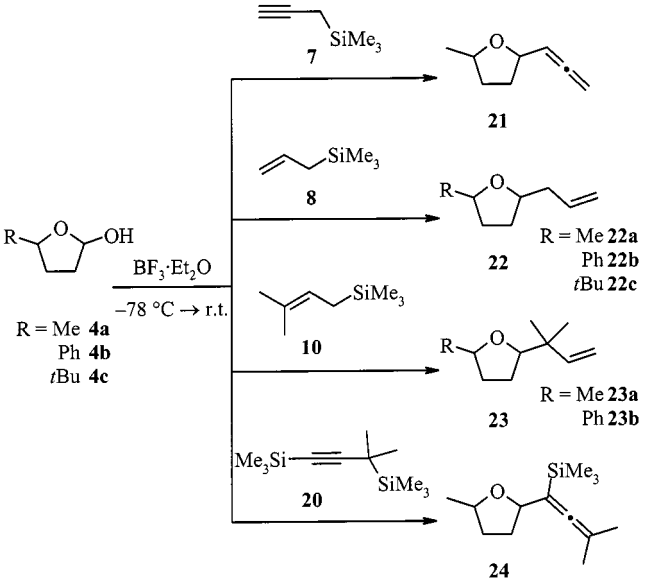


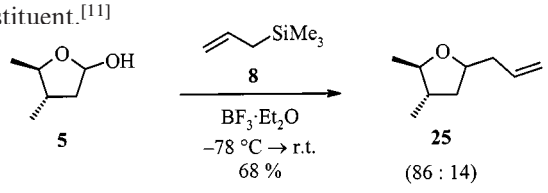
Table 3. $BF_3$-promoted reactions between 5-substituted γ-lactols **4a**−**4c** and silanes **7**, **8**, **10** and **20**

| Entry | Lactol | Silane | Product | Yield (%) | *trans*:*cis* |
|---|---|---|---|---|---|
| 1 | **4a** | **7** | **21** | 82 | 20:80 |
| 2 | **4a** | **8** | **22a** | 70 | 40:60 |
| 3 | **4b** | **8** | **22b** | 80 | 47:53 |
| 4 | **4c** | **8** | **22c** | 72 | 88:12 |
| 5 | **4a** | **10** | **23a** | 93 | 83:17 |
| 6 | **4b** | **10** | **23b** | 84 | 77:23 |
| 7 | **4c** | **20** | **24** | 61[a] | 90:10 |

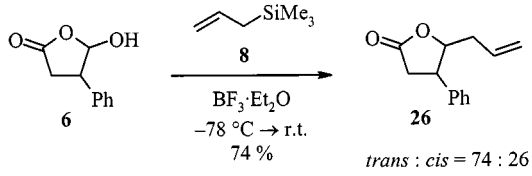
[a] Purity only 83% according to GC.

ing the steric demand of the nucleophile in reaction with γ-lactols bearing small substituents (R = Me, Ph) significantly decreases the *cis* selectivity (entries 2 and 3), while reaction of strongly hindered nucleophiles such as prenylsilane **10** and the silylated propargylsilane **20** leads to preferential formation of the *trans* isomers (entries 5−7). γ-Lactol **4c**, with the large *tert*-butyl substituent, reacted with good selectivity with allylsilane **8**, to form the *trans* isomer (entry 4, *trans*/*cis* = 88:12).

Reaction of the *trans*-4,5-dimethyl-substituted γ-lactol **5** with allylsilane **8** furnished an 86:14 mixture of two diastereomeric tetrahydrofuran derivatives **25**. The major isomer was assigned as 2,4-*trans*-substituted **25**. Thus, the 4-methyl group had the expected effect on the outcome of this reaction, although this was modulated slightly by the 5-methyl substituent.[11]




As well as simple γ-lactols, 5-hydroxy-3,4-dihydrofuran-2-ones such as **6** can also be employed in Lewis acid-promoted reaction with nucleophiles. The corresponding γ-lactone **26** was obtained with moderate *trans* selectivity (*trans*/*cis* = 74:26).



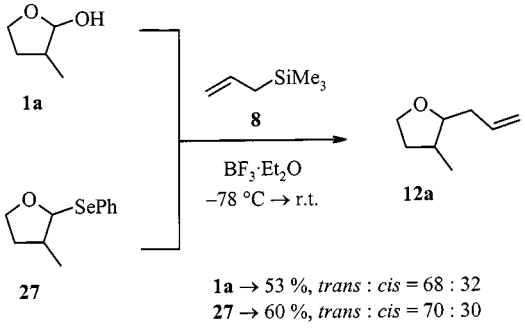

We also studied the influence on the diastereoselectivity of γ-lactol reactions exerted by the Lewis acid and by the leaving group. As shown in Table 4, the nature of the Lewis acid employed to promote the reaction of γ-lactols with organosilanes had no significant influence on the stereochemical outcome. Strong Lewis acids capable of chelate formation result in reduced yields or complex product mixtures, probably due to the formation of open-chain by-products. On the other hand, all monocoordinating Lewis acids employed promoted the reaction equally well, providing fairly similar diastereoselectivities. For the reaction of the 5-hydroxylactone **6**, product **26** was obtained in higher yield but with similar diastereoselectivity when titanium tetrachloride was employed as the Lewis acid, instead of boron trifluoride.

Table 4. Lewis acid dependence of reactions between γ-lactols and silanes **8** and **10**

| Lactol | Silane | Lewis Acid | Product | Yield (%) | *trans*:*cis* |
|---|---|---|---|---|---|
| **1a** | **8** | $BF_3·Et_2O$ | **12a** | 53 | 68:32 |
| **1a** | **8** | $ZnCl_2$ | **12a** | 79 | 69:31 |
| **1a** | **10** | $BF_3·Et_2O$ | **14** | 50 | 95:5 |
| **1a** | **10** | $ZnCl_2$ | **14** | 79 | 95:5 |
| **4a** | **8** | $BF_3·Et_2O$ | **22a** | 79 | 40:60 |
| **4a** | **8** | $TiCl_4$ | —[a] | — | — |
| **4a** | **8** | $SnCl_4$ | **22a** | 34 | 40:60 |
| **4a** | **8** | $EtAlCl_2$ | **22a** | 76 | 40:60 |
| **4b** | **8** | $BF_3·Et_2O$ | **22b** | 80 | 47:53 |
| **4b** | **8** | $TiCl_4$ | —[a] | — | — |
| **6** | **8** | $BF_3·Et_2O$ | **26** | 74 | 74:26 |
| **6** | **8** | $TiCl_4$ | **26** | 99 | 71:29 |

[a] Decomposition.

The effect of the leaving group on the diastereoselectivity of the γ-lactol substitution was also examined. Thus, the reactions of γ-lactol **1a** and of 2-phenylselenenyltetrahydrofuran **27**[12] with allylsilane **8** were studied. In both reactions, the allyl-substituted derivative **12a** was formed in comparable yields and, within the limits of NMR accuracy, identical diastereomer ratios. Thus, the nature of the leaving group showed no influence on the stereochemical outcome.[13]

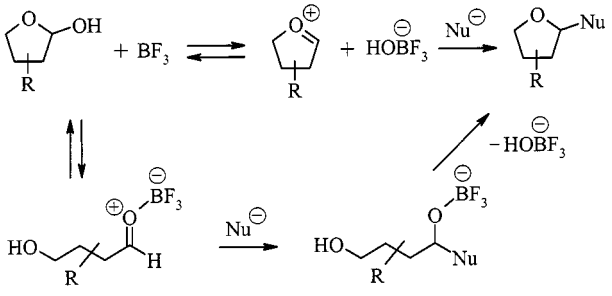



Assignment of the diastereomers, based on $^1H$ and $^{13}C$ NMR spectroscopic data, was unambiguous in most cases. The measurements were supplemented by NOE experiments for some characteristic examples. A more detailed discussion of the configurational assignment has been presented previously.[1,6d]

## Discussion

Two borderline mechanisms for Lewis acid-induced reactions of acetals with nucleophiles are discussed in the literature. The reaction may involve an oxocarbenium ion in an $S_N1$-type process, or it may occur by preliminary formation of an acetal/Lewis acid complex, from which the product is

formed in an $S_N2$-type reaction. In their investigations on Lewis acid-induced substitutions in open-chain acetals, Denmark and co-workers[14] found that the Lewis acids employed exerted a strong influence on the stereochemical outcome, as did the nature of the leaving group. The authors concluded that the reaction mechanism depends on the substrate and the Lewis acid employed. Results for substitution in cyclic acetals reconfirmed these findings.[15] On the other hand, the reaction mechanism for the Lewis acid-promoted reaction of γ-lactols with nucleophiles presented in this report seems unambiguous. Since there is no significant dependence of diastereoselectivity either on the Lewis acid employed or on the leaving group, it seems that neither of them participates in the product-determining step. Hence, the reaction should follow the $S_N1$-mode, via an oxocarbenium ion intermediate. For such a mechanism there are still two possible pathways, since either a cyclic oxocarbenium ion or an open-chain intermediate may be involved. Reaction via the cyclic oxocarbenium ion would lead directly to the isolated tetrahydrofuran derivatives, while addition of the nucleophile to the carbonyl/Lewis acid complex would yield the corresponding 1,4-diol, which could cyclize in the presence of Lewis acids. This pathway can be ruled out, since a smooth cyclization is rather unlikely under the relatively mild conditions employed.[16] Moreover, the high diastereoselectivities recorded for 4-substituted γ-lactols **3** or (in part) for 5-substituted γ-lactols **4** cannot plausibly be explained on the basis of an open-chain intermediate.[17] Thus, to interpret the observed diastereoselectivities, we assume the formation of the cyclic oxocarbenium ion by Lewis acid-assisted dissociation of the hydroxyl group, followed by reaction with the silanes.



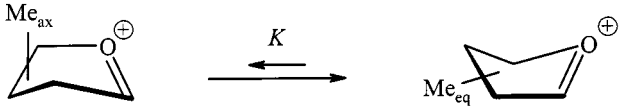

The oxocarbenium ion may exist in two distinct half-chair conformations, which are in rapid equilibrium through pseudorotation.[18] To estimate this conformer equilibrium, we performed MMX-89 force-field calculations,[19] checked by the PIMM-88 force-field as developed by Lindner and co-workers.[20] These calculations supported the assumption that conformers with their substituents in pseudoequatorial position are more stable than those with these substituents in pseudoaxial position. The data obtained for the methyl-substituted oxocarbenium ion are presented in Table 5.

Similarly, the corresponding calculations[1] for phenyl- and *tert*-butyl-substituted oxocarbenium ions show higher

Table 5. MMX-89 force-field calculations on methyl-substituted oxocarbenium ions

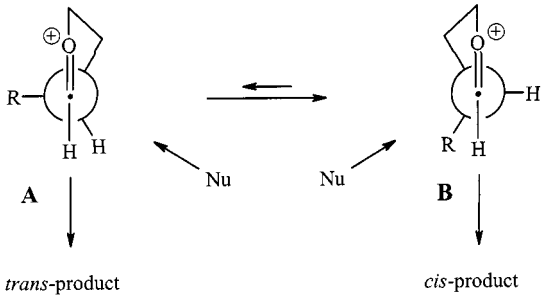
| Oxocarbenium Ion | $\Delta H_f$ [kcal/mol] | $\Delta\Delta H_f$ [kcal/mol] | $K$[a] |
|---|---|---|---|
| 3-$Me_{ax}$ | 153.01 | 0.41 | 2.9 |
| 3-$Me_{eq}$ | 153.42 | | |
| 4-$Me_{ax}$ | 152.95 | 0.75 | 6.7 |
| 4-$Me_{eq}$ | 152.20 | | |
| 5-$Me_{ax}$ | 153.15 | 0.36 | 2.5 |
| 5-$Me_{eq}$ | 152.79 | | |

[a] $K$ was calculated from $\Delta\Delta H_f$ by neglecting $\Delta\Delta S_f$.




stability for the conformer with the substituents in pseudoequatorial position, but the energy differences are considerably larger ($\Delta\Delta H_f$ = 0.86 to 2.32 kcal/mol). The reliability of these calculations is demonstrated by comparison of the bond lengths obtained for the $C{=}O^+$ moiety (1.28 Å) with those calculated by ab initio methods for similar ions (1.26 Å).[21]

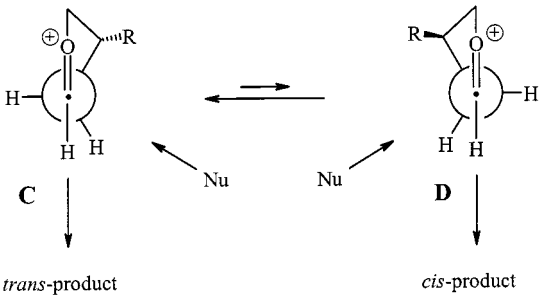
We explain the diastereoselectivities by assuming a Felkin−Anh-type approach of the nucleophile to the cyclic oxocarbenium ion. Thus, the silane attacks the electrophilic carbon opposite to the pseudoaxial (perpendicular) substituent at C-3. For the 3-substituted systems, this stereoelectronic effect should strongly favour formation of *trans* products from **A**, since the alternative attack should be hampered by the equatorial substituent R in conformer **B**.




However, this kinetic effect on the diastereoselectivity[22] must be modified by the slight thermodynamic preference of **B** over **A**. Thus, small nucleophiles such as **7** and **8** may also attack **B** with small substituents (Me, Ph), giving *trans*/*cis* mixtures of the order of 2:1. Only if the nucleophile is bulky (e.g., **10**) or if substituent R is sterically demanding (*tert*-butyl) is almost exclusive formation of *trans* products observed (Table 1).

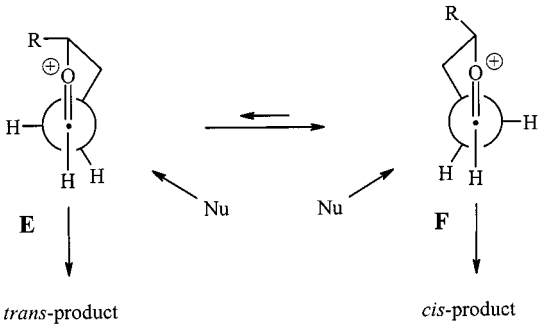
While kinetic (stereoelectronic) and thermodynamic effects are opposed for 3-substituted oxocarbenium ions **A** and **B**, they appear to cooperate for 4-substituted oxocarbenium ions. In a Felkin−Anh approach to the more stable conformer **C**, the pseudoequatorial substituent R is in a more remote position than the pseudoaxial substituent R

in the less stable conformation **D**. In accordance with this interpretation, we obtain very high *trans* selectivities in this series, even with slim nucleophiles and small R substituents (Table 2).




For 5-substituted oxocarbenium ions, conformer **F**, with the pseudoequatorial substituent, is slightly preferred over **E**, but the R substituent is positioned rather remote from the reaction centre. Thus, the thermodynamic effect should gain in importance, compared to the case of the 3-substituted oxocarbenium ions **A/B**.

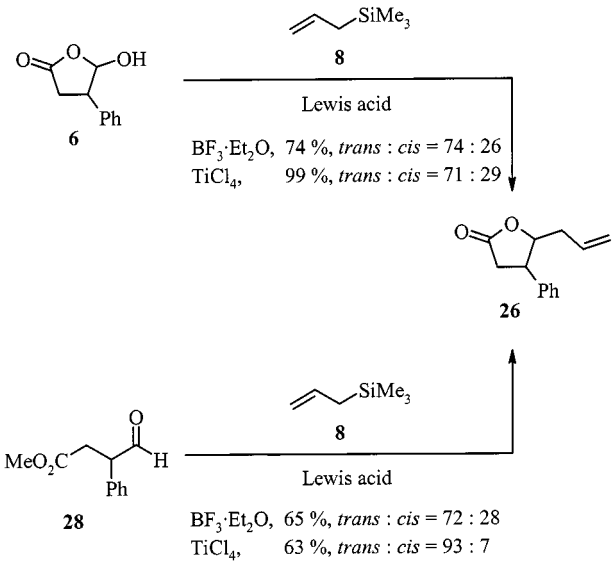
The reaction between the oxocarbenium ion bearing the smallest substituent (R = Me) and the slim (and fast) silane **7** seems to reflect the approximate ratio of the two conformers **F** and **E** ($K \approx 2.5$ according to MMX-89, Table 5), thus leading to considerable *cis* selectivity (entry 1, Table 3).




An increase in steric effects initially leads to the loss of any stereoselectivity (entries 2 and 3, Table 3). However, with bulky groups either on the oxocarbenium ion or in the silane, it is possible to achieve even moderate to good *trans* selectivity (entries 4−7, Table 3). These steric effects seem to promote reaction via conformer **E**.

The stereoselectivity of the reaction between *trans*-4,5-dimethyl-substituted γ-lactol **5** and allylsilane **8** can be rationalized smoothly by comparison of the associated monosubstituted oxocarbenium ions. Thus, the 4-methyl group should induce excellent *trans* selectivity (see conformer **C** and entry 2, Table 2) but the effect is opposed by that due to the 5-methyl group, which exhibits a weak *cis* preference (see conformer **F** and entry 2, Table 3). As would be expected from our interpretation discussed above, the effect due to the 4-methyl group dominates.[23]

The reaction between 5-hydroxylactone **6** and allylsilane **8** may proceed via an open-chain β-formylcarboxylic acid, as discussed for related examples in the literature,[24] or via a highly electrophilic, cyclic, O-acylated oxocarbenium ion. The stereoselectivity of the reaction between β-formyl ester **28** and allylsilane **8** is highly dependent on the Lewis acid employed;[25] this is not the case for the reaction of **6**, which gives nearly identical *trans*/*cis* ratios of γ-lactone **26**. Therefore, we assume that this transformation also proceeds via the cyclic intermediate, as demonstrated for the other γ-lactols in this report.




## Conclusions

These reactions between monosubstituted γ-lactols **1a**−**1c**, **3a**−**3c** and **4a**−**4c** and a variety of allyl- and propargylsilanes in the presence of boron trifluoride−diethyl ether proceed in good yields and − strongly dependent on the substitution pattern − with good to excellent diastereoselectivity. Surprisingly, the 4-substituted γ-lactols **3** furnish their corresponding tetrahydrofuran derivatives with higher diastereoselectivity than do the 3-substituted or 5-substituted γ-lactols **1** and **4**. This behaviour may be explained by the converging or opposing influences of thermodynamic and kinetic (stereoelectronic) effects.[26] Our model study makes disubstituted tetrahydrofurans available in a predictable manner; the results may be applied to the syntheses of more complex products. The interplay of two substituents has been demonstrated by the conversion of disubstituted γ-lactol **5** into trisubstituted tetrahydrofuran derivatives **25**. A further report will deal with Lewis acid-promoted reactions between γ-lactols **1**, **3** and **4** and silyl enol ethers.[27]

## Experimental Section

**General Remarks:** See ref.[6d] NMR spectroscopic data of mixtures of diastereomers are given in the following manner: signal of *trans* isomer/signal of *cis* isomer. The tetrahydrofuran derivatives prepared are very volatile and rather sensitive to oxygen. Therefore,

for a number of products (in particular with 1,2-propadienyl substituents) no correct elemental analysis could be obtained.

**Starting Materials:** Preparations of γ-lactols **1a**, **1b**, **1c**, **3a**, **3b**, **3c**, **4a**, **4b** and **4c** were described with all details in ref.[6d] Compound **6** was prepared according to a known procedure.[28]

**3-Methyl-2-phenyltetrahydrofuran-2-ol (2):** 3-Methyldihydro-2(3*H*)furanone (500 mg, 5.00 mmol) was dissolved in tetrahydrofuran (10 mL) at −78 °C, and a phenyllithium solution (2 M, 2.50 mL, 5.00 mmol) in tetrahydrofuran was added. After stirring for 4.5 h at −78 °C and 30 min at −30 °C, sat. aqueous ammonium chloride solution (10 mL) was added, the mixture was extracted with methyl *tert*-butyl ether, and the organic layers were dried ($MgSO_4$) and concentrated in vacuo. The resulting crude product (1.00 g, 76:24 mixture of anomers) was used without purification. − $^1$H NMR ($CDCl_3$): δ = 8.00−7.50 (m, 5 H, Ph), 4.25 (dt, *J* = 1.5, 9.0 Hz, 0.24 H, 5-H), 4.10 (dt, *J* = 7.0, 9.0 Hz, 0.24 H, 5-H), 3.75−3.57 (m, 2.28 H, 5-H, OH), 2.60−2.45, 2.40−2.28, 2.15−2.00, 1.90−1.85, 1.85−1.77, 1.70−1.58 (6 m, 3 H, 3-H, 4-H), 1.18/1.22 (d/d, *J* = 7.0 Hz, 2.28 H and 0.72 H, 3-Me); several signals may be assigned to the acyclic tautomer of **2**: δ =3.17 (s), 2.95 (broad s), 1.16 (s), 1.06 (d, *J* = 6.0 Hz). − $^{13}$C NMR ($CDCl_3$): δ = 141.1−125.8 (several s and d, Ph and C-2 of both anomers and the acyclic tautomer), 60.2 (t, C-5), 37.2/34.1 (d, C-3), 36.0/30.6 (t, C-4), 17.3/15.1 (q, 3-Me).

***trans*-4,5-Dimethyl-tetrahydrofuran-2-ol (5):** According to the general procedure as described in ref.[6d] *trans*-4,5-dimethyldihydro-2(3*H*)-furan-2-one (*trans*/*cis* = 95:5, 1.14 g, 10.0 mmol) was treated with diisobutylaluminum hydride (12.0 mmol) in toluene to give 0.766 g (66%) of **5** as a 53:47 mixture of anomers. − $^1$H NMR ($CDCl_3$): δ = 5.50−5.35 (m, 1 H, 2-H), 4.52/4.50−4.40 (d/m, *J* = 3.0 Hz, 1 H, OH), 3.76/3.53 (qd, *J* = 6.0, 9.0 Hz/6.0, 8.5 Hz, 1 H, 5-H), 2.50−1.90, 1.75−1.50 (2 m, 2.5 H, 3-H, 4-H), 1.44 (ddd, *J* = 4.0, 9.0, 13.5 Hz, 0.5 H, 3-H), 1.27/1.16 (d, *J* = 6.0 Hz, 3 H, 5-Me), 0.99/0.96 (d, *J* = 6.0 Hz, 3 H, 4-Me); the ratio of the two anomers is strongly dependant on the concentration of the solution. − $^{13}$C NMR ($CDCl_3$): δ = 98.7/97.4 (d, C-2), 79.8/82.8 (d, C-5), 41.4/42.4 (t, C-3), 38.2/40.7 (d, C-4), 18.3/20.4, 15.8 (2 d, 4-Me, 5-Me).

**General Procedure for the Treatment of γ-Lactols with Silanes:** To a solution of the corresponding γ-lactol in dry dichloromethane (2 mL/mmol) was added 2 equivalents of the corresponding silane, and the mixture was cooled to −78 °C. Then, 3 equivalents of the Lewis acid were added via syringe, and the mixture was allowed to warm up to room temperature over 16 h. After addition of water (2 mL/mmol) and extraction with dichloromethane (3 × 20 mL), the organic layers were dried ($MgSO_4$) and concentrated in vacuo. The residue was carefully distilled in a Kugelrohr oven. Boron trifluoride and zinc dichloride were used as etherates. For the amounts of starting materials used and the resulting products, see Table 6.

**3-Methyl-2-phenyltetrahydrofuran (16):** According to the general procedure, unpurified **2** (890 mg, 5.00 mmol) was treated with triethylsilane (**15**) (1.16 g, 10.0 mmol) and boron trifluoride−diethyl ether (2.12 g, 15.0 mmol). After extractive workup, the crude product (1.10 g) was purified by Kugelrohr distillation (100 °C/0.37 Torr) to afford **16** (638 mg, 79%) as an almost pure mixture of the two diastereomers (*trans*/*cis* = 21:79).[16a] The two diastereomers may be separated by HPLC (Hygrosyl 5μ column, hexane/ methyl *tert*-butyl ether = 98:2). − $^1$H NMR ($CDCl_3$): *cis*-**16** δ = 7.33−7.18 (m, 5 H, Ph), 4.95 (d, *J* = 6.5 Hz, 1 H, 2-H), 4.17 (dt, *J* = 6.0, 8.0 Hz, 1 H, 5-H), 3.91 (dt, *J* = 7.0, 8.0 Hz, 1 H, 5-H), 2.50 (broad sept, *J* ≈ 6.5 Hz, 1 H, 3-H), 2.15 (dddd, *J* = 6.0, 7.0, 8.0, 12.0 Hz, 1 H, 4-H), 1.70 (dddd, *J* = 6.0, 7.0, 8.0, 12.0 Hz, 1 H, 4-H), 0.60 (d, *J* = 7.0 Hz, 3 H, 3-Me). − *trans*-**16** δ = 7.33−7.20 (m, 5 H, Ph), 4.27 (d, *J* = 8.0 Hz, 1 H, 2-H), 4.09 (dt, *J* = 7.0,

Table 6. Reactions between γ-lactols and silanes in the presence of Lewis acids, according to the general procedure

| γ-Lactol [mg (mmol)] | Silane [2 equiv.] | Lewis acid [3 equiv.] | Product | Yield [mg (%)] | *trans*/*cis* | b.p. [°C/Torr] |
|---|---|---|---|---|---|---|
| **1a** [400 (3.92)] | **7** | $BF_3{\cdot}OEt_2$ | **11** | 318 (65) | 60:40 | 50/5.5 |
| **1a** [300 (2.94)] | **8** | $BF_3{\cdot}OEt_2$ | **12a** | 195 (53) | 68:32 | 30/6.0 |
| **1b** [300 (1.83)] | **8** | $BF_3{\cdot}OEt_2$ | **12b** | 312 (91) | 63:37 | 55/0.02 |
| **1c** [450 (3.13)] | **8** | $BF_3{\cdot}OEt_2$ | **12c** | 388 (74) | > 98:2 | 60/0.01 |
| **1a** [465 (4.56)] | **9** | $BF_3{\cdot}OEt_2$ | **13** | 472 (67) | 68:32 | 79/6.0[29] |
| **1a** [300 (2.94)] | **10** | $BF_3{\cdot}OEt_2$ | **14** | 225 (50) | 95:5 | 45/4.5 |
| **3a** [400 (3.92)] | **7** | $BF_3{\cdot}OEt_2$ | **17** | 454 (93) | 86:14 | 40/3.0 |
| **3a** [459 (4.50)] | **8** | $BF_3{\cdot}OEt_2$ | **18a** | 388 (68) | 95:5 | 50/6.0 |
| **3b** [400 (2.44)] | **8** | $BF_3{\cdot}OEt_2$ | **18b** | 368 (80) | 95:5 | 70/0.02 |
| **3c** [450 (3.13)] | **8** | $BF_3{\cdot}OEt_2$ | **18c** | 440 (84) | ≥ 98:2 | 60/0.75 |
| **3a** [400 (3.92)] | **10** | $BF_3{\cdot}OEt_2$ | **19** | 574 (95) | ≥ 98:2 | 45/7.5 |
| **4a** [400 (3.92)] | **7** | $BF_3{\cdot}OEt_2$ | **21** | 400 (82) | 20:80 | 40/1.0 |
| **4a** [292 (2.86)] | **8** | $BF_3{\cdot}OEt_2$ | **22a** | 252 (70) | 40:60 | 45/5.0 |
| **4b** [400 (2.44)] | **8** | $BF_3{\cdot}OEt_2$ | **22b** | 365 (80) | 47:53 | 100/0.04 |
| **4c** [330 (2.29)] | **8** | $BF_3{\cdot}OEt_2$ | **22c** | 275 (72) | 88:12 | 60/0.07 |
| **4a** [400 (3.92)] | **10** | $BF_3{\cdot}OEt_2$ | **23**a | 562 (93) | 83:17 | 45/5.0 |
| **4b** [400 (2.44)] | **10** | $BF_3{\cdot}OEt_2$ | **23b** | 442 (84) | 77:23 | 95/0.01 |
| **4a** [400 (3.92)] | **20** | $BF_3{\cdot}OEt_2$ | **24** | 533 (61)[a] | 90:10 | 80/0.75 |
| **5** [160 (1.38)] | **8** | $BF_3{\cdot}OEt_2$ | **25** | 175 (91) | 86:14 | 40/9.0 |
| **6** [400 (2.25)] | **8** | $BF_3{\cdot}OEt_2$ | **26** | 335 (74) | 74:26 | 120/0.01 |
| **6** [500 (2.81)] | **8** | $TiCl_4$ | **26** | 560 (99) | 71:29 | 120/0.01 |
| **1a** [276 (2.71)] | **8** | $ZnCl_2$[b] | **12a** | 270 (79) | 69:31 | 30/6.0 |
| **1a** [197 (1.93)] | **8** | $ZnCl_2$[b] | **14** | 235 (79) | 95:5 | 45/4.5 |
| **4a** [300 (2.95)] | **8** | $SnCl_4$ | **22a** | 126 (34) | 40:60 | 45/5.0 |
| **4a** [143 (1.40)] | **8** | $EtAlCl_2$ | **22a** | 124 (76) | 40:60 | 45/5.0 |
| **27** [600 (2.49)] | **8** | $BF_3{\cdot}OEt_2$ | **12a** | 189 (60) | 70:30 | 30/6.0 |

[a] Purity according to GC and NMR ≈83%; unknown impurities could not be removed by chromatography. − [b] Lewis acid added at 0 °C.

8.5 Hz, 1 H, 5-H), 4.02 (dt, $J$ = 4.5, 8.5 Hz, 1 H, 5-H), 2.20 (dtd, $J$ = 4.5, 7.0, 12.0 Hz, 1 H, 4-H), 2.06 ($m_c$, 1 H, 3-H), 1.69 (tdd, $J$ = 8.5, 9.0, 12.0 Hz, 1 H, 4-H), 1.07 (d, $J$ = 6.5 Hz, 3 H, 3-Me). − $^{13}$C NMR ($CDCl_3$): *cis*-**16** δ = 140.8, 127.8, 126.8, 126.2 (s, 3 d, Ph), 83.6 (d, C-2), 67.2 (t, C-5), 37.3 (d, C-3), 33.7 (t, C-4), 15.4 (q, 3-Me). − *trans*-**16** δ = 142.2, 128.2, 127.4, 126.1 (s, 3 d, Ph), 87.9 (d, C-2), 67.8 (t, C-5), 42.8 (d, C-3), 34.9 (t, C-4), 16.4 (q, 3-Me).

**Analytical and Spectroscopic Data**

**3-Methyl-2-(1,2-propadienyl)tetrahydrofuran (11):** $^1$H NMR ($CDCl_3$): δ = 5.18/5.09 (q, $J$ = 7.0 Hz, 1 H, =CH), 4.85−4.75/4.42−4.36 (m, 2 H, $=CH_2$), 3.97 (dt, $J$ = 5.0, 8.0 Hz, 0.6 H, 5-H, *trans*), 3.89−3.73 (m, 2.4 H, 2-H, 5-H), 2.35 (broad sept, $J \approx 7$ Hz, 0.4 H, 3-H, *cis*), 2.20−2.14 (m, 1.6 H, 3-H, 4-H), 1.67−1.52 (m, 1 H, 4-H), 1.06/1.00 (d, $J$ = 7.0 Hz, 3 H, 3-Me). − $^{13}$C NMR ($CDCl_3$): δ = 208.6/208.5, 89.3/91.4, 76.1/75.8 (s, d, t, $CH=C=CH_2$), 83.5/80.2 (d, C-2), 67.1 (t, C-5), 38.3/37.0 (d, C-3), 34.3 (t, C-4), 16.5/14.7 (q, 3-Me). − IR (neat): $\tilde{\nu}$ = 3000−2840 $cm^{-1}$ (CH), 1955 (C=C=C), 1630 (C=C). − MS (70 eV, EI): *m*/*z* (%) = 124 ($M^+$, 3), 123 ($M^+ - 1$, 6), 85 ($M^+ - [CH_2=C=CH]$, 24), 69 (15), 56 ([cpr·$^+$], 15), 55 ([cpr$^+$], 20), 53 (10), 43 ([$CH_3CO^+$], 53), 41 ([$CH_2=CH-CH_2^+$], 65), 39 ([$CH_2=C=CH^+$], 42), 32 (40). − $C_8H_{12}O$ (124.2): calcd. C 77.38, H 9.74; found C 76.29, H 9.78.

**2-Allyl-3-methyltetrahydrofuran (12a):** $^1$H NMR ($CDCl_3$): δ = 5.92−5.80, 5.15−5.04, 2.35−1.48 (3 m, 1 H, 2 H, 3.68 H, 2-allyl, 4-H), 3.93 (td, $J$ = 6.5, 8.0 Hz, 0.32 H, 5-H, *cis*), 3.88−3.76 (m, 1.68 H, 5-H, *trans*, 2-H, *cis*), 3.73 (td, $J$ = 6.0, 8.0 Hz, 0.32 H, 5-H, *cis*), 3.38 (dt, $J$ = 4.5, 7.5 Hz, 0.68 H, 2-H, *trans*), 1.55−1.35 (m, 0.32 H, 4-H), 1.78/1.46 (broad sept, $J \approx$ 7.0/8.0 Hz, 0.32/0.68 H, 3-H). − $^{13}$C NMR ($CDCl_3$): δ = 135.2/135.6 (d, =CH), 116.4/116.2 (t, $=CH_2$), 85.0/80.9 (d, C-2), 66.7/66.0 (t, C-5), 38.5/35.1 (t, 2-$CH_2$), 38.3/35.2 (d, C-3), 34.6/33.8 (t, C-4), 17.1/14.2 (q, 3-Me). − IR (neat): $\tilde{\nu}$ = 3035 $cm^{-1}$ (=CH), 3000−2800 (CH), 1640 (C=C). − $C_8H_{14}O$ (126.2): calcd. C 76.14, H 11.18; found C 75.74, H 11.37.

**2-Allyl-3-phenyltetrahydrofuran (12b):** $^1$H NMR ($CDCl_3$): δ = 7.32−7.17/7.31−7.14 (m, 5 H, 3-Ph), 5.88−5.75/5.79−5.65, 5.10−5.01/4.98−4.88, 2.39−2.17/2.00−1.78 (3 m, 1 H, 2 H, 2 H, 2-allyl), 4.18 (dt, $J$ = 5.0, 8.5 Hz, 0.37 H, 5-H, *cis*), 4.03−3.94 (m, 1.26 H, 5-H, *trans*), 3.98 (dt, $J$ = 5.5, 8.5 Hz, 0.37 H, 2-H, *cis*), 3.87 (dt, $J$ = 7.0, 8.5 Hz, 0.37 H, 5-H, *cis*), 3.86 (ddd, $J$ = 4.0, 7.0, 8.0 Hz, 0.63 H, 2-H, *trans*), 3.35 (td, $J$ = 5.5, 8.5 Hz, 0.37 H, 3-H, *cis*), 2.94 (q, $J \approx$ 8.5 Hz, 0.63 H, 3-H, *trans*), 2.40 (dtd, $J$ = 5.0, 8.5, 13.0 Hz, 0.37 H, 4-H, *cis*), 2.39−2.30 (m, 0.63 H, 4-H, *trans*), 2.14−1.98 (m, 0.63 H, 4-H, *trans*), 2.12 (dddd, $J$ = 5.5, 7.0, 8.5, 13.0 Hz, 0.37 H, 4-H, *cis*). − $^{13}$C NMR ($CDCl_3$): δ = 141.7/141.9, 128.6/128.5, 127.7/128.2, 126.6/126.4 (s, 3 d, Ph), 134.9/135.4 (d, =CH), 116.9 (t, $=CH_2$), 85.3/82.1 (d, C-2), 67.7/67.0 (t, C-5), 50.3/47.4 (d, C-3), 35.9 (t, 2-$CH_2$), 35.4/33.2 (t, C-4). − IR (neat): $\tilde{\nu}$ = 3080, 3020 $cm^{-1}$ (=CH), 2980−2920 (CH), 1640, 1600, 1490 (C=C). − $C_{13}H_{16}O$ (188.3): calcd. C 82.94, H 8.57; found C 82.08, H 8.64.

**2-Allyl-3-*tert*-butyltetrahydrofuran (12c):** $^1$H NMR ($CDCl_3$): δ = 5.92−5.78, 5.11−5.01, 2.34−2.17 (3 m, 1 H, 2 H, 2 H, 2-allyl), 3.85 (ddd, $J$ = 4.5, 5.5, 8.0 Hz, 1 H, 2-H), 3.80−3.69 (m, 2 H, 5-H), 1.91−1.80, 1.80−1.69 (2 m, 1 H, 2 H, 4-H, 3-H), 0.89 (s, 9 H, *t*Bu). − $^{13}$C NMR ($CDCl_3$): δ = 135.6 (d, =CH), 116.4 (t, $=CH_2$), 79.6 (d, C-2), 67.2 (t, C-5), 54.0 (d, C-3), 40.9 (t, 2-$CH_2$), 31.9, 27.8/29.5 (s, q, 3-*t*Bu). − IR (neat): $\tilde{\nu}$ = 3060 $cm^{-1}$ (=CH), 2980−2820 (CH), 1635 (C=C). − $C_{11}H_{20}O$ (168.3): calcd. C 78.51, H 11.98; found C 78.80, H 11.54.

**3-Methyl-2-prenyltetrahydrofuran (13):** $^1$H NMR ($CDCl_3$): δ = 5.30−5.10, 2.35−2.05, 1.63−1.47, 1.73, 1.64 (3 m, 2 s, 1 H, 0.68 H, 1.32 H, 3 H, 3 H, 2-prenyl), 3.98−3.64 (m, 2.32 H, 2-H, *cis*, 5-H), 3.38 (dt, $J$ = 5.0, 7.0 Hz, 0.68 H, 2-H, *trans*), 2.35−2.05 (m, 2.64 H, 4-H, 3-H, *cis*), 1.92−1.79 (m, 0.68 H, 3-H, *trans*), 1.63−1.47 (m, 0.32 H, 4-H, *cis*), 1.04/0.94 (d, $J$ = 7.0 Hz, 3 H, 3-Me). − $^{13}$C NMR ($CDCl_3$): δ = 132.8/132.6, 120.5/120.7 (s, d, C=CH), 88.0/81.4 (d, C-2), 68.5/65.8 (t, C-5), 38.3/34.9 (d, C-3), 34.5/33.6, 32.5 (2 t, C-4, 2-$CH_2$), 25.8, 17.4 (2 q, $=CMe_2$), 17.9/15.2 (q, 3-Me). − For further analytical data see ref.[29]

**2-(1,1-Dimethylallyl)-3-methyltetrahydrofuran (14):** $^1$H NMR ($CDCl_3$): δ = 5.87−5.78, 4.97−4.91, 0.97/0.90, 0.96/0.88 (2 m, 2 s, 1 H, 2 H, 3 H, 3 H, $H_2C=CH-CMe_2$), 3.79−3.64/3.61−3.55 (m, 2 H, 5-H), 3.15 (d, $J$ = 5.5 Hz, 0.95 H, 2-H, *trans*), 2.11−1.84/1.35−1.09 (m, 2 H, 4-H), 1.43 (broad sept, $J \approx$ 6.0 Hz, 0.95 H, 3-H), 0.99/0.87 (d, $J$ = 7.5/7.0 Hz, 3 H, 3-Me). − $^{13}$C NMR ($CDCl_3$): δ = 145.0, 111.6 (d, t, $CH=CH_2$), 93.1 (d, C-2), 67.3/66.0 (t, C-5), 40.6 (s, 2-*C*$Me_2$), 35.5/34.7 (t, C-4), 33.9 (d, C-3), 23.3, 23.1/15.0, 20.5/13.7 (3 q, 3-Me, 2-C*Me*$_2$). − IR (neat): $\tilde{\nu}$ = 3080 $cm^{-1}$ (=CH), 3000−2810 (CH), 1635 (C=C). − $C_{10}H_{18}O$ (154.3): calcd. C 77.86, H 11.77, found C 77.26, H 11.80.

**4-Methyl-2-(1,2-propadienyl)tetrahydrofuran (17):** $^1$H NMR ($CDCl_3$): δ = 5.21, 5.05−4.09 ($m_c$, m, 3 H, $CH=C=CH_2$), 4.57−4.49/4.45−4.38 (m, 1 H, 2-H), 4.02/3.92 (dd, $J$ = 7.0, 8.0/7.5, 8.0 Hz, 1 H, 5-H), 3.31/3.38 (dd/t, $J$ = 8.0, 7.0/8.0 Hz, 1 H, 5-H), 2.43−2.31 (m, 1 H, 4-H), 1.95, 1.43 (ddd, td, $J$ = 5.5, 7.5, 12.5 and 8.0, 12.5 Hz, 0.86 H each, 3-H, *trans*), 1.05 (d, $J$ = 7.0 Hz, 2.58 H, 4-Me). − $^{13}$C NMR ($CDCl_3$): δ = 207.7, 93.0/92.8, 76.6 (s, d, t, $CH=C=CH_2$), 76.4/76.6, (d, C-2), 74.9/74.6 (t, C-5), 39.8/40.7 (t, C-3), 33.1/34.4 (d, C-4), 17.9/17.5 (q, 4-Me). − IR (neat): $\tilde{\nu}$ = 3080 $cm^{-1}$ (=CH), 2980−2800 (CH), 1955 (C=C=C), 1635 (C=C). − MS (70 eV, EI): *m*/*z* (%) = 124 ($M^+$, 3), 85 ($M^+ - [CH_2=C=CH]$, 100), 79 ($M^+ - [C_2H_5O]$, 12), 77 (10), 67 (19), 57 (41), 55 ([cpr$^+$], 14), 43 ([$CH_3CO^+$], 23), 41 ([$CH_2=CH-CH_2^+$], 71), 39 ([$CH_2=C=CH^+$], 14).

**2-Allyl-4-methyltetrahydrofuran (18a):** $^1$H NMR ($CDCl_3$): δ = 5.90−5.72, 5.15−5.00, 2.40−2.15 (3 m, 1 H, 2 H, 2 H, 2-allyl), 4.03 (qd, $J$ = 6.5, 8.5 Hz, 0.95 H, 2-H, *trans*), 4.00/3.88 (t/dd, $J$ = 8.0/8.0, 7.0 Hz, 1 H, 5-H), 3.26/3.36 (dd, $J$ = 7.0, 8.0 Hz, 1 H, 5-H), 2.26 ($m_c$, 1 H, 4-H), 1.74, 1.57 (2 ddd, $J$ = 6.5, 8.5, 12.5 and 6.5, 7.0, 12.5 Hz, 0.95 each, 3-H, *trans*), 1.02/1.04 (d, $J$ = 7.0 Hz, 3 H, 4-Me). − $^{13}$C NMR ($CDCl_3$): δ = 135.1, 116.7 (d, t, $CH=CH_2$), 78.0/79.4 (d, C-2), 75.1/74.6 (t, C-5), 40.5/40.4, 39.0 (2 t, 2-$CH_2$, C-3), 33.2/34.3 (d, C-4), 18.0/17.9 (q, 4-Me). − IR (neat): $\tilde{\nu}$ = 3035 $cm^{-1}$ (=CH), 3000−2800 (CH), 1640 (C=C). − $C_8H_{14}O$ (126.2): calcd. C 76.14, H 11.18; found C 75.12, H 11.38.

**2-Allyl-4-phenyltetrahydrofuran (18b):** $^1$H NMR ($CDCl_3$): δ = 7.28−7.07 (m, 5 H, Ph), 5.82−5.72, 5.10−4.89, 2.39−2.18 (3 m, 1 H, 2 H, 2 H, 2-allyl), 4.58−4.21 (m, 0.1 H, 2-H, 5-H, *cis*), 4.15 (dd, $J$ = 7.5, 8.5 Hz. 0.95 H, 5-H, *trans*), 4.13 (quint, $J$ = 6.5 Hz, 0. 95 H, 2-H, *trans*), 3.72 (t, $J$ = 8.5 Hz, 0.05 H, 5-H, *cis*), 3.63 (dd, $J$ = 8.0, 8.5 Hz, 0.95 H, 5-H, *trans*), 3.33 (broad quint, $J \approx$ 8.0 Hz, 0.95 H, 4-H, *trans*), 2.83−2.74 (m, 0.05 H, 4-H, *cis*), 2.58−2.49, 2.08−1.91, 1.70−1.56 (3 m, 0.05 H, 1.9 H, 0.05 H, 3-H). − $^{13}$C NMR ($CDCl_3$): δ = 142.5/142.0, 128.5, 127.2, 126.5/126.6 (s, 3 d, Ph), 134.8, 117.0 (d, t, $CH=CH_2$), 78.7/79.6 (d, C-2), 74.6/74.3 (t, C-5), 44.5/45.4 (d, C-4), 40.4, 39.0/40.0 (2 t, 2-$CH_2$, C-3). − IR (neat): $\tilde{\nu}$ = 3080, 3020 $cm^{-1}$ (=CH), 3000−2820 (CH), 1640, 1490 (C=C). − $C_{13}H_{16}O$ (188.3): calcd. C 82.94, H 8.57, found C 82.37, H 8.58.

**2-Allyl-4-*tert*-butyltetrahydrofuran (18c):** $^1$H NMR ($CDCl_3$): δ = 5.90−5.70, 5.15−5.00, 2.45−2.16, 2.11 (3 m, ddd, *J* = 8.0, 9.5, 17.5 Hz, 1 H, 2 H, 1 H, 1 H, 2-allyl), 3.95−3.85 (m, 2 H, 2-H, 5-H), 3.46 (t, *J* = 9.0. Hz, 1 H, 5-H), 2.45−2.16 (m, 1 H, 4-H), 1.76, 1.54 (td, ddd, *J* = 7.5, 12.5 and 6.5, 9.5, 12.5 Hz, 1 H each, 3-H), 0.87 (s, 9 H, *t*Bu). − $^{13}$C NMR ($CDCl_3$): δ = 134.8, 116.4 (d, t, CH=$CH_2$), 78.5 (d, C-2), 69.1 (t, C-5), 49.0 (d, C-4), 40.4, 32.1 (2 t, 2-$CH_2$, C-3), 31.0, 27.4 (s, q, 4-*t*Bu). − IR (neat): $\tilde{\nu}$ = 3060 $cm^{-1}$ (=CH), 3000−2800 (CH), 1635 (C=C). − $C_{11}H_{20}O$ (168.3): calcd. C 78.51, 11.98; found C 78.76, H 11.59.

**2-(1,1-Dimethylallyl)-4-methyltetrahydrofuran (19):** $^1$H NMR ($CDCl_3$): δ = 5.94−5.84, 5.05−4.99, 1.04, 1.00 (2 m, 2 s, l H, 2 H, 3 H, 3 H, $H_2C$=CH−$CMe_2$), 3.94 (dd, *J* = 6.5, 8.0 Hz, 1 H, 5-H), 3.77 (dd, *J* = 7.5, 8.0 Hz, 1 H, 2-H), 3.31 (dd, *J* = 6.5, 8.0 Hz, 1 H, 5-H), 2.28−2.17 (m, 1 H, 4-H), 1.82, 1.42 (td, ddd, *J* = 8.0, 12.5 and 5.5, 7.5, 12.5 Hz, 1 H each, 3-H), 1.03 (d, *J* = 6.5 Hz, 3 H, 4-Me). − $^{13}$C NMR ($CDCl_3$): δ = 145.0, 112.1 (d, t, CH=$CH_2$), 85.7 (d, C-2), 75.4 (t, C-5), 40.4 (s, 2-*C*$Me_2$), 35.0 (t, C-3), 33.7 (d, C-4), 23.7, 22.7 (2 q, 2-C*Me*$_2$), 16.0 (q, 4-Me). − IR (neat): $\tilde{\nu}$ = 3080 $cm^{-1}$ (=CH), 2980−2800 (CH), l635 (C=C). − $C_{10}H_{18}O$ (154.3): calcd. C 77.86, H 11.77; found C 77.59, H 11.97.

**5-Methyl-2-(1,2-propadienyl)tetrahydrofuran (21):** $^1$H NMR ($CDCl_3$): δ = 5.21/5.23, 4.88−4.72 (q, *J* = 6.5 Hz, m, 1 H, 2 H, CH=C=$CH_2$), 4.60−4.50/4.43−4.34 (m, 0.2/0.8 H, 2-H), 4.20−4.08/4.06−3.95 (m, 0.2/0.8 H, 5-H), 2.15−1.95 (m, 2 H, 3-H), 1.85−1.70, 1.60−1.45 (2 m, 1.6 H, 4-H, *cis*), 1.45−1.35 (m, 0.4 H, 4-H, *trans*). − $^{13}$C NMR ($CDCl_3$): δ = 208.0, 93.0/93.1, 76.4 (s, d, t, CH=C=$CH_2$), 77.1, 75.8 (2 d, C-2, C-5), 32.7, 32.2 (2 t, C-3, C-4), 21.2/21.3 (q, 5-Me). − IR (neat): $\tilde{\nu}$ = 3080 $cm^{-1}$ (=CH), 3000−2800 (CH), 1955 (C=C=C), 1640 (C=C). − MS (70 eV, EI): *m*/*z* (%) = 124 ($M^+$, 14), 109 ($M^+$ − $CH_3$, 8), 85 ($M^+$ − [$CH_2$=C=CH], 100), 83 (10), 79 ($M^+$ − [$C_2H_5O$], 20), 67 (20), 57 (25), 55 ([cpr$^+$], 14), 43 ([$CH_3CO^+$], 44), 41 ([$CH_2$=CH−$CH_2^+$], 51), 39 ([$CH_2$=C=$CH^+$], 32).

**2-Allyl-5-methyltetrahydrofuran (22a):** $^1$H NMR ($CDCl_3$): δ = 5.82, 5.07, 2.42−2.16 ($m_c$, $m_c$, m, 1 H, 2 H, 2 H, 2-allyl), 4.09 ($m_c$, 1.4 H, 5-H, 2-H, *trans*), 3.91 ($m_c$, 0.6 H, 2-H, *cis*), 2.08−1.87, 1.61 (m, $m_c$, 3 H, 3-H, 4-H), 1.24/1.21 (d, *J* = 6.0 Hz, 3 H, 5-Me). − $^{13}$C NMR ($CDCl_3$): δ = 135.1, 116.7 (d, t, CH=$CH_2$), 77.9/78.7 (d, C-2), 74.8/75.4 (d, C-5), 40.5 (t, 2-$CH_2$), 33.9/32.8, 31.7/30.7 (2 t, C-3, C-4), 21.4 (q, 5-Me). − IR (neat): $\tilde{\nu}$ = 3070 $cm^{-1}$ (=CH), 3000−2800 (CH), 1640 (C=C). − $C_8H_{14}O$ (126.2): calcd. C 76.14, H 11.18; found C 75.62, H 11.39.

**2-Allyl-5-phenyltetrahydrofuran (22b):** $^1$H NMR ($CDCl_3$): δ = 7.39−7.16/7.43−7.21 (m, 5 H, Ph), 5.93−5.79/5.98−5.85, 5.15−5.03/5.19−5.07, 2.57−2.49, 2.47−2.25 (4 m, 1 H, 2 H, 1 H, l H, 2-allyl), 4.99/4.88 (dd/t, *J* = 6.5, 8.0 and 7.0 Hz, 0.47/0.53 H, 5-H), 4.29−4.21/4.11 (m/broad quint, *J* ≈ 6.5 Hz, 0.47/0.53 H, 2-H), 2.38−2.25, 2.32−2.20, 2.12−2.00, 1.89−1.62 (4 m, 4 H, 3-H, 4-H). − $^{13}$C NMR ($CDCl_3$): δ = 142.4/143.0, 127.4/128.3, 125.7/127.3, 125.8 (s, 3 d, Ph), 134.4, 117.3 (d, t, CH=$CH_2$), 81.3/80.7 (d, C-2), 79.5/79.6 (d, C-5), 40.0/40.1 (t, 2-$CH_2$), 35.1/34.2, 31.5/30.4 (2 t, C-3, C-4). − IR (neat): $\tilde{\nu}$ = 3080, 3020 $cm^{-1}$ (=CH), 3000−2800 (CH), 1640, 1600, 1480 (C=C). − $C_{13}H_{16}O$ (188.3): calcd. C 82.94, H 8.57; found C 82.56, H 8.59.

**2-Allyl-5-*tert*-butyltetrahydrofuran (22c):** $^1$H NMR ($CDCl_3$): δ = 5.96−5.74, 5.29−4.90, 2.42−2.33, 2.23−2.13 (4 m, 1 H, 2 H, 1 H, 1 H, 2-allyl), 3.97−3.88 (m, 1 H, 2-H), 3.65/3.53 (dd, *J* = 6.0, 9.0 and 7.0, 8.0 Hz, 0.88/0.12 H, 5-H), 2.00−1.90, 1.87−1.78, 1.70−1.41 (3 m, 1 H, 1 H, 2 H, 3-H, 4-H), 0.88/0.84 (s, 7.9/1.1 H, *t*Bu). − $^{13}$C NMR ($CDCl_3$): δ = 135.0, 116.2 (d, t, CH=$CH_2$), 86.7/87.2 (d, C-5), 78.7/78.0 (d, C-2), 40.1/40.8 (t, 2-$CH_2$), 33.9/33.3, 25.5/24.7 (s, q, 5-*t*Bu), 31.9/30.5, 26.8/25.7 (2 t, C-3, C-4). − IR (neat): $\tilde{\nu}$ = 3060 $cm^{-1}$ (=CH), 3000−2860 (CH), 1635 (C=C). − $C_{11}H_{20}O$ (168.3): calcd. C 78.51, H 11.98; found C 79.00, H 11.72.

**2-(1,1-Dimethylallyl)-5-methyltetrahydrofuran (23a):** $^1$H NMR ($CDCl_3$): δ = 5.97−5.86, 5.05−4.98, 1.05, 0.99 (2 m, 2 s, 1 H, 2 H, 3 H, 3 H, $CH_2$=CH−$Me_2$), 4.06−3.94 (m, 1 H, 5-H), 3.80/3.65 (dd/t, *J* = 6.5, 9. 0 and 7.5 Hz, 0.83/0.17 H, 2-H), 2.02−1.26 (m, 4 H, 3-H, 4-H), 1.23/1.22 (d, *J* = 6.0 Hz, 3 H, 5-Me). − $^{13}$C NMR ($CDCl_3$): δ = 145.1/145.3, 112.0/111.8 (d, t, CH=$CH_2$), 86.0/86.5 (d, C-5), 75.8/75.3 (d, C-2) 40.8/40.0 (s, 2-*C*$Me_2$), 34.5/34.2, 27.9/26.7 (2 t, C-3, C-4), 23.6, 23.0, 21.2/21.0 (3 q, 2-C*Me*$_2$, 5-Me). − IR (neat): $\tilde{\nu}$ = 3080 $cm^{-1}$ (=CH), 3000−2800 (CH), 1635 (C=C). − $C_{10}H_{18}O$ (154.3): calcd. C 77.86, H 11.77; found C 77.96, H 11.99.

**2-(1,1-Dimethylallyl)-5-phenyltetrahydrofuran (23b):** $^1$H NMR ($CDCl_3$): δ = 7.41−7.18/7.33−7.13 (m, 5 H, Ph), 5.98−5.89, 5.03−4.91, 1.04/1.02, 0.99/0.98 (2 m, 2 s, 1 H, 2 H, 3 H, 3 H, $CH_2$=CH−$CMe_2$), 4.84/4.66 (dd, *J* = 6.0, 8.5 and 6.5, 9.0 Hz, 0.77/0.23 H, 5-H), 3.92/3.68 (dd/t, *J* = 6.5, 9.0 and 7.0 Hz, 0.77/0.23 H, 2-H), 2.35−2.20/2.22−2.12 (m, 1 H, 4-H), 2.00−1.60, 1.53−1.41 (2 m, 2.77 H, 0.23H, 3-H, 4-H). − $^{13}$C NMR ($CDCl_3$): δ = 143.9/142.9, 128.2/127.1, 127.0/125.8, 125.4/125.5 (s, 3 d, Ph), 144.9/145.0, 117.4 (d, t, CH=$CH_2$), 87.1/86.4 (d, C-5), 81.2/80.8 (d, C-2), 40.1/40.3 (s, 2-*C*$Me_2$), 35.8/34.8, 28.0/27.0 (2 t, C-3, C-4), 23.9/23.6, 23.0/23.3 (2 q, 2-C*Me*$_2$). − IR (neat): $\tilde{\nu}$ = 3080, 3020 $cm^{-1}$ (=CH), 2990−2840 (CH), 1635, 1595, 1480 (C=C). − $C_{15}H_{20}O$ (216.3): calcd. C 83.29, H 9.32; found C 82.64, H 9.46.

**5-Methyl-2-(3-methyl-1-trimethylsilyl-1,2-butadienyl)tetrahydrofuran (24):** $^1$H NMR ($CDCl_3$): δ = 4.51/4.31 (t, *J* = 6.0 Hz, 0.1 H, 0.9 H, 2-H), 4.15−4.00/3.95−3.80 (m, 0.1 H, 0.9 H, 5-H), 1.60−1.59 (m, 4 H, 3-H, 4-H), 1.56, 1.55 (2 s, 6 H, Me), 1.13 (d, *J* = 6.0 Hz, 3 H, 5-Me), 0.00 (s, 9 H, $SiMe_3$). − $^{13}$C NMR ($CDCl_3$): δ = 203.6/203.7 (s, =C=), 98.8 (s, =*C*$SiMe_3$), 90.4 (s, =*C*$Me_2$), 78.9/77.9, 75.2/75.9 (2 d, C-2, C-5), 31.4/32.2, 31.2/32.1 (2 t, C-3, C-4), 23.5/26.5, 21.1/20.9, 19.6 (3 q, Me), 0.6/−0.3 (q, $SiMe_3$). − IR (neat): $\tilde{\nu}$ = 3000−2800 $cm^{-1}$ (CH), 1920 (C=C=C), 1625 (C=C).

**2-Allyl-4,5-dimethyltetrahydrofuran (25):** $^1$H NMR ([$D_6$]acetone): δ = 5.88−5.70, 5.58−4.93 (2 m, 1 H, 2 H, CH=$CH_2$), 4.05−3.90 (m, 0.14 H, 2-H), 3.87 (qd, *J* = 6.0, 7.5 Hz, 0.86 H, 2-H), 3.43/3.30 (qd/qd, *J* = 6.0, 9.0 and 6.0, 8.0 Hz, 0.14 H and 0.86 H, 5-H), 2.30−2.10 (m, 2 H, 5-$CH_2$), 1.80−1.60 (m, 0.42 H, 3-H, 4-H), 1.78 (ddd, *J* = 5.5, 8.5, 11.5 Hz, 0.86 H, 3-H), 1.73−1.58 (m, 0.86 H, 4-H), 1.55 (td, *J* = 8.5, 11.5 Hz, 0.86 H, 3-H), 1.13/1.10 (d/d, *J* = 6.0 Hz, 2.58 H and 0.42 H, 5-Me), 0.97/0.95 (d/d, *J* = 6.0 and 6.5 Hz, 0.42 H and 2.58 H, 4-Me). − $^{13}$C NMR ($CDCl_3$): δ = 134.9, 116.6 (d, t, CH=$CH_2$), 82.0/80.9, 77.0/77.4 (2 d, C-2, C-5), 40.9, 39.1 (2 t, C-3, C-6), 40.5/41.9 (d, C-4), 19.2, 16.7/16.0 (2 q, 4-Me, 5-Me). − IR (neat): $\tilde{\nu}$ = 3055 $cm^{-1}$ (=CH), 2980−2810 (CH), 1640 (C=C), 1080−1040 (C−O). − MS (70 eV, EI): *m*/*z* (%) = 99 ($M^+$ −[$C_3H_5$], 100), 76 (42) 55 (66), 43 (83), 41 ([$C_3H_5^+$], 31), 39 (19). − $C_9H_{16}O$ (140.2): calcd. C 77.09, H 11.50; found C 75.25, H 11.51.

**4-Allyl-3-phenyl-γ-butyrolactone (26):** For $^1$H NMR spectroscopic data and other analytical data see ref.[30] − $^{13}$C NMR ($CDCl_3$): δ = 175.3/176.4 (s, C-2), 132.1/132.7, 118.7/117.8 (d, t, CH=$CH_2$), 138.7/137.6, 128.9/128.6, 127.6/127.7, 127.0 (s, 3 d, Ph), 85.5/83.1 (d, C-5), 46.1/44.1 (d, C-4), 37.4/35.5, 37.1/35.4 (2 t, C-3, 5-$CH_2$).

## Acknowledgments

Generous support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is most gratefully acknowledged. We thank Dr. R. Zimmer for his help during the preparation of this manuscript.

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Received June 5, 2000
[O00290]