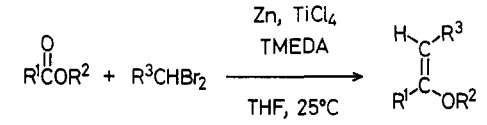
Communications

Alkylidenation of Ester Carbonyl Groups by means of a Reagent Derived from $RCHBr_2$, Zn, $TiCl_4$, and TMEDA. Stereoselective Preparation of (Z)-Alkenyl Ethers

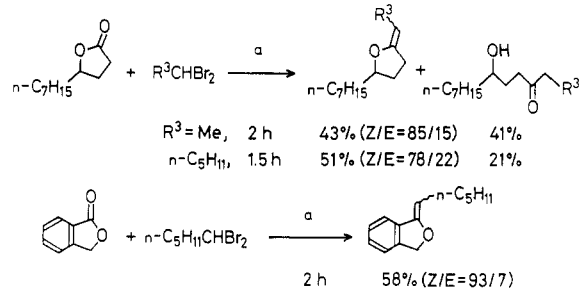
Summary: Reagents prepared by reduction of 1,1-dibromoalkanes (R^3CHBr_2) with zinc and $TiCl_4$ in the presence of *N,N,N',N'*-tetramethylethylenediamine in THF are effective in the conversion of esters ($R^1CO_2R^2$) to the corresponding alkenyl ethers ($R^1(R^2O)C{=}CHR^3$) with high *Z* selectivity.

Sir: Though alkenyl ethers have considerable synthetic utility,[1] the preparation of the ethers is limited to methods which use as starting materials either acetals[2] or acetylenes.[3,4] It is usually difficult to prepare the alkenyl ethers, especially trisubstituted ones, in a regio- and stereoselective manner by these methods. The most promising direct approach to solve these problems is the alkylidenation of ester carbonyl groups, which has remained a persistent challenge in organic synthesis.[5] Recent advances with the Schrock-type metal carbene complexes[6] (**1**, $R^1R^2C{=}MtlL_n$, Mtl = Ta,[7] Zr,[8] Ti,[8b] W[9]) and the Tebbe complex[10] have shown promise. However, the preparation of the complex **1** usually requires special techniques and possesses some restrictions on the substituents R^1 and/or R^2. Moreover, the transformation with **1** does not provide alkenyl ethers under good stereocontrol.[7,8a,11] We report here a simple, general, and stereoselective method for the alkylidenation of ester carbonyl groups by means of a reagent prepared from 1,1-dibromoalkane,[12] zinc, $TiCl_4$, and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in THF (Scheme I).[13]

Scheme I



Scheme II[a]



[a] (a) Zn, $TiCl_4$, TMEDA, THF, 25 °C.

A solution of $TiCl_4$ (1.0 M 4.0 mmol) in dichloromethane was added at 0 °C to THF (10 mL) under an argon atmosphere. To the yellow solution at 25 °C was added TMEDA (1.2 mL, 8.0 mmol) and the mixture was stirred at 25 °C for 10 min. Zinc dust (0.59 g, 9.0 mmol) was added to the mixture. The color of the suspension turned from brownish yellow to dark greenish blue in a slightly exothermic process. After being stirred at 25 °C for 30 min, a solution of methyl pentanoate (0.12 g, 1.0 mmol) and 1,1-dibromohexane[12a] (0.54 g, 2.2 mmol) in THF (2 mL) was added to the mixture. The color of the resulting mixture gradually turned dark brown while being stirred at 25 °C for 2 h. Saturated K_2CO_3 solution (1.3 mL) was added at 0 °C to the mixture. After it was stirred at 0 °C for another 15 min, the mixture was diluted with ether (20 mL) and then passed rapidly through a short column of basic alumina (activity III) using ether–triethylamine (200/1, 100 mL). The resulting clear solution was concentrated and the residue was purified by column chromatography on basic alumina (activity III) with pentane to give the desired 5-methoxy-5-undecene[14] (0.18 g, *Z*/*E* = 91/9) in 96% yield.[15]

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(14) Bp: 109 °C (bath temperature, 24 Torr). IR (neat): 2954, 2926, 2856, 1677, 1458, 1117, 1067 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.88 (t, J = 7 Hz, 3 H), 0.90 (t, J = 7 Hz, 3 H), 1.16–1.53 (m, 10 H), 1.94–2.18 (m, 4 H), 3.47 (s, 3 H (*E*)), 3.52 (s, 3 H (*Z*)), 4.33 (t, J = 7 Hz, 1 H (*E*)), 4.50 (t, J = 7 Hz, 1 H (*Z*)). ^{13}C NMR ($CDCl_3$): *Z* isomer δ 13.9, 14.1, 22.3, 22.6, 24.7, 29.4, 29.8, 31.1, 31.6, 56.4, 110.1 (*C*=CROR'), 155.0 (C=*C*ROR'); *E* isomer δ 96.3 (*C*=CROR'), 156.9 (C=*C*ROR'). MS, *m/e* (relative intensity): 184 (M^+, 14). Anal. Calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 78.09; H, 13.38.

(15) The stereochemistry of the isomers (Table I, runs 9–20) was determined by ^{13}C NMR.[16] As isomerization of alkenyl ethers has been reported to take place in GLPC,[3c] the *Z*/*E* ratios were measured by ^1H NMR (200 MHz).

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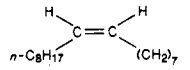
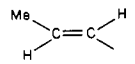
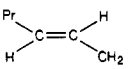
Table I. Preparation of (*Z*)-Alkenyl Ethers from Esters[a]

run	R^1	R^2	R^3	time, h	yield,[b] %	Z/E[c]
1	Ph	Me	Me	2	86	92/8
2			n-C_5H_{11}	2	89	95/5
3			i-Bu	2	79	96/4
4			c-C_6H_{11}	1.5	61	90/10
5		i-Pr	Me	2	88	92/8
6		t-Bu		2	81	71/29
7		Ph		3	76	78/22
8			H	3	16	
9	Me	n-C_8H_{17}	Me	3	68	84/16
10	n-$C_{11}H_{23}$	Me		2	75	88/12
11	Bu		n-C_5H_{11}	2	96	91/9
12			i-Bu	2	95	93/7
13			c-C_6H_{11}	2	69	93/7
14	i-Bu		n-C_5H_{11}	2	88	92/8
15	i-Pr			2	89	100/0
16	CH_2=$CH(CH_2)_8$	Me	Me	3	53	89/11
17				3	70[d]	90/10
18		Et	n-C_5H_{11}	2.5	90	94/6
19	Bu	CH_2=$CHCH_2$		2	52	92/8
20	Pr			3	85	94/6

[a] The ester (1.0 mmol) was treated with 1,1-dibromoalkane (2.2 mmol), Zn (9.0 mmol), $TiCl_4$ (4.0 mmol), and TMEDA (8.0 mmol) in THF at 25 °C. [b] Isolated yields. [c] See ref 15. [d] Partial isomerization of the isolated cis double bond took place. The cis/trans ratio of the double bond at C-11 of the resultant ether was 87/13, which was determined by ^1H NMR after hydrolysis of the alkenyl ether (1 M H_2SO_4, THF)[29] and successive epoxidation with MCPBA.

The results in Table I show the wide applicability and high *Z* selectivity of the process. Several comments can be made concerning the reaction. (1) Steric repulsion by the substituents R^1, R^2, and R^3 influences the Z/E ratios[16] of the products. Thus, as the substituents R^1 or R^3 become bigger or R^2 becomes smaller, higher *Z* selectivity is obtained (except run 4). The results of alkylidenation of esters[17] contrast those with ketones, where low Z/E selectivity was observed.[18] (2) The reagent for methylenation of ketones, a CH_2X_2–Zn–$TiCl_4$ system (X = I or Br),[13] does not affect ester groups.[13b,19] Methylenation of ester carbonyl with CH_2Br_2 in the presence of TMEDA proceeded but the yield was low (run 8). Alkyl substituents of 1,1-dibromo compounds enhance the nucleophilicity of the reagent to add to such an electron-rich carbonyl group. (3) In the case of lactones, the desired exocyclic alkenyl ethers were produced along with hydroxy ketones, resulting from formal hydrolysis of the alkenyl ethers (Scheme II). (4) Esters having terminal double bonds reacted to afford the corresponding alkenyl ethers in about 50% yields (runs 16 and 19). Esters with internal ones gave better yields and the stereochemistry of double bonds of the reactants was retained (runs 18 and 20) except in the case of run 17 where partial isomerization of the isolated cis double bond occurred.[20] Thus the reaction provides a convenient and stereoselective access to allyl vinyl ethers[21] (runs 19 and 20) and oxygen-substituted dienes[22] (run 18).

During the search for the most effective reagent, the following was observed. Geminal diiodoalkanes[23] were also effective for the alkylidenation, but the yields with diiodo compounds were lower than those with the corresponding dibromo ones.[24] Low-valent titanium produced by reduction of $TiCl_4$ with $LiAlH_4$[25] was slightly effective. The use of TMEDA was crucial to the success of the reactions,[26] since in its absence considerable amounts of ketone (hydroxy ketones in the case of lactones) were produced. For example, treatment of methyl dodecanoate (**2**) with a reagent derived from 1,1-dibromoethane, Zn, and $TiCl_4$ in THF at 25 °C for 2 h afforded the desired 3-methoxy-2-tetradecene (**3**) in only 5% yield (Z/E = 85/15) and 3-tetradecanone (**4**) was the major product (70% yield).

Although the reactive species is still unknown,[27] the method has unprecedented generality and stereoselectivity and should find numerous synthetic applications. The scope of the alkylidenation reagent with regard to other carbonyl functions is under investigation.[17]

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(17) Reactions with such electron-rich carbonyl compounds as *S*-alkyl thio esters, trimethylsilyl carboxylates, and amides took place to generate alkenyl sulfides, silyl enol ethers, and enamines, respectively. The two former substrates showed almost the same *Z* selectivity as the present reaction.

(18) Treatment of 4-phenyl-2-butanone with the alkylidenation reagent derived from $C_5H_{11}CHBr_2$, Zn, and $TiCl_4$ in THF afforded 3-methyl-1-phenyl-3-nonene in 78% yield. The Z/E ratio of the olefin was about 45/55 regardless of the addition of TMEDA.

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(24) Treatment of methyl dodecanoate (**2**) in THF with the reagent derived from CH_3CHI_2,[23b] zinc, $TiCl_4$, and TMEDA at 25 °C for 4 h gave the desired ether **3** (22% yield, Z/E = 88/12), ketone **4** (10%), and the reactant **2** (53% recovery).

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(26) Addition of such Lewis bases as Et_3N, $Ph_2PCH_2CH_2PPh_2$, pyridine, or 2,2′-bipyridine instead of TMEDA did not improve the yield of alkenyl ethers.

(27) We are tempted to assume that the Schrock-type metal carbene complex (R^3CH=TiL_n) or geminal dimetallic compounds[28] ($R^3CH(Mtl)_2$, $(Mtl)_2$ = $(TiL_n)_2$ or $(TiL_n)(ZnL_n)$) are the reactive species of the reaction.

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Registry No. **2**, 111-82-0; (*Z*)-**3**, 109585-97-9; (*E*)-**3**, 109585-96-8; **4**, 629-23-2; $PhCO_2Me$, 93-58-3; $PhCO_2Pr$-*i*, 939-48-0; $PhCO_2Bu$-*t*, 774-65-2; $PhCO_2Ph$, 93-99-2; $MeCO_2C_8H_{17}$, 112-14-1; $BuCO_2Me$, 624-24-8; *i*-$BuCO_2Me$, 556-24-1; *i*-$PrCO_2Me$, 547-63-7; $H_2C{=}CH(CH_2)_8CO_2Me$, 111-81-9; $C_8H_{17}CH{=}CH(CH_2)_7CO_2Me$, 112-62-9; $MeCH{=}CHCO_2Et$, 623-70-1; $BuCO_2CH_2CH{=}CH_2$, 6321-45-5; $PrCO_2CH_2CH{=}CHPr$, 53398-83-7; $MeCHBr_2$, 557-91-5; $C_5H_{11}CHBr_2$, 58133-26-9; *i*-$BuCHBr_2$, 62127-59-7; *c*-$C_6H_{11}CHBr_2$, 52470-92-5; CH_2Br_2, 74-95-3; CH_3CHI_2, 594-02-5; (*Z*)-MeCH=C(Ph)OMe, 4518-65-4; (*E*)-MeCH=C(Ph)OMe, 4541-69-9; (*Z*)-Ph(OMe)C=CHC_5H_{11}, 109612-96-6; (*E*)-Ph(OMe)C=CHC_5H_{11}, 109612-97-7; (*Z*)-*i*-BuCH=C(OMe)Ph, 109585-87-7; (*E*)-*i*-BuCH=C(OMe)Ph, 109585-88-8; (*Z*)-*c*-C_6H_{11}CH=C(OMe)Ph, 109585-89-9; (*E*)-*c*-C_6H_{11}CH=C(OMe)Ph, 109585-90-2; (*Z*)-MeCH=C(OPr-*i*)Ph, 70812-87-2; (*E*)-MeCH=C(OPr-*i*)Ph, 70812-88-3; (*Z*)-MeCH=C(OBu-*t*)Ph, 109585-91-3; (*E*)-MeCH=C(OBu-*t*)Ph, 109585-92-4; (*Z*)-MeCH=C(OPh)Ph, 109585-93-5; (*E*)-MeCH=C(OPh)Ph, 109585-94-6; $H_2C{=}C$(OPh)Ph, 19928-57-5; (*Z*)-MeCH=C(Me)OC_8H_{17}, 109585-95-7; $MeCO(CH_2)_2Ph$, 2550-26-7; (*E*)-MeCH=C(OMe)$C_{11}H_{23}$, 109585-98-0; (*Z*)-C_5H_{11}CH=C(OMe)Bu, 109585-99-1; (*E*)-C_5H_{11}CH=C(OMe)Bu, 109586-00-7; (*Z*)-*i*-BuCH=C(OMe)Bu, 109586-01-8; (*E*)-*i*-BuCH=C(OMe)Bu, 109586-02-9; (*Z*)-*c*-C_6H_{11}CH=C(OMe)Bu, 109586-03-0; (*E*)-*c*-C_6H_{11}CH=C(OMe)Bu, 109586-04-1; (*Z*)-C_5H_{11}CH=C(OMe)Bu-*i*, 109586-05-2; (*E*)-C_5H_{11}CH=C(OMe)Bu-*i*, 109586-06-3; (*Z*)-C_5H_{11}CH=C(OMe)Pr-*i*, 109586-07-4; (*Z*)-MeCH=C(OMe)$(CH_2)_8CH{=}CH_2$, 109586-08-5; (*E*)-MeCH=C(OMe)$(CH_2)_8CH{=}CH_2$, 109586-09-6; (*Z,Z*)-$C_8H_{17}CH{=}CH(CH_2)_7$(MeO)C=CHMe, 109586-11-0; (*E,E*)-$C_8H_{17}CH{=}CH(CH_2)_7$(MeO)C=CHMe, 109586-10-9; (*Z,E*)-$C_8H_{17}CH{=}CH(CH_2)_7$(MeO)C=CHMe, 109586-20-1; (*E,Z*)-$C_8H_{17}CH{=}CH(CH_2)_7$(MeO)C=CHMe, 109586-21-2; (*Z,E*)-C_5H_{11}CH=C(OEt)CH=CHMe, 109586-12-1; (*E,E*)-C_5H_{11}CH=C(OEt)CH=CHMe, 109586-13-2; (*Z*)-C_5H_{11}CH=C(Bu)-$OCH_2CH{=}CH_2$, 109586-14-3; (*E*)-C_5H_{11}CH=C(Bu)$OCH_2CH{=}CH_2$, 109586-15-4; (*Z,E*)-C_5H_{11}CH=C(Pr)CH_2CHCHPr, 109586-16-5; (*E,E*)-C_5H_{11}CH=C(Pr)CH_2CHCHPr, 109586-17-6; (*Z*)-Ph-$(CH_2)_2$(Me)C=CHC_5H_{11}, 109586-18-7; (*E*)-Ph$(CH_2)_2$(Me)C=CHC_5H_{11}, 109586-19-8; C_7H_{15}CH(OH)$(CH_2)_2$COEt, 109586-24-5; C_7H_{15}CH(OH)$(CH_2)_2COC_6H_{13}$, 109586-27-8; (*Z*)-2-ethylidene-4-heptyl-2,3,4,5-tetrahydrofuran, 109586-22-3; (*E*)-2-ethylidene-4-heptyl-2,3,4,5-tetrahydrofuran, 109586-23-4; (*Z*)-4-heptyl-2-hexylidene-2,3,4,5-tetrahydrofuran, 109586-25-6; (*E*)-4-heptyl-2-hexylidene-2,3,4,5-tetrahydrofuran, 109586-26-7; (*Z*)-1,3-dihydro-1-hexylideneisobenzofuran, 109586-28-9; (*E*)-1,3-dihydro-1-hexylideneisobenzofuran, 109586-29-0; 5-heptyl-2(3*H*)-furanone, 104-67-6; 1(3*H*)-isobenzofuranone, 87-41-2.

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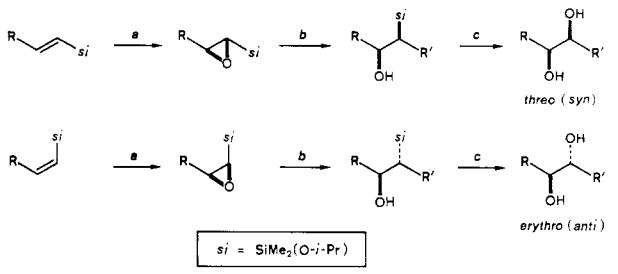
Silafunctional α,β-Epoxy Silanes: Transformation into Erythro and Threo 1,2-Diol Skeletons and Its Application to the Synthesis of (±)-*exo*-Brevicomin[1]

Summary: Stereodefined *E* and *Z* α,β-epoxy silanes containing an isopropoxy group on silicon can be transformed into threo and erythro 1,2-diol skeletons, respectively, by regioselective ring opening with carbon nucleophiles followed by hydrogen peroxide oxidation of the carbon–silicon bonds; application to the synthesis of (±)-*exo*-brevicomin is also reported.

Sir: Epoxidation of stereodefined olefins and the subsequent ring opening with nucleophiles have provided one of the most efficient methods for stereoselective synthesis of polyfunctional compounds.[2] However, it is not an easy task to control the regioselectivity of the ring opening in unsymmetrical epoxides.[2] It is noteworthy in this respect that α,β-epoxy silanes react with carbon or heteroatom nucleophiles regioselectively at carbon α to silicon exclusively to form β-hydroxy silanes.[3] This unique chemistry, however, has so far been applied only to the stereoselective synthesis of olefins,[3a,4c,f] haloolefins,[4a] enol ethers,[4a] enol esters,[4a,b,d] enamides,[4a] and enamines,[4e] as well as conversion to carbonyl functionalities.[5] Reported herein is a new transformation of α,β-epoxy silanes to 1,2-diol derivatives. Thus, as shown in Scheme I, stereodefined *E* and *Z* epoxy silanes undergo regioselective ring opening with carbon nucleophiles and the subsequent stereospecific oxidative cleavage of the carbon–silicon bond with retention of configuration[6] to form unambiguously threo and erythro 1,2-diol skeletons, respectively.[7] The presence of an alkoxy group on silicon is essential for the present process.[8]

Scheme I[a]



[a] (a) MCPBA (1 equiv)/CH_2Cl_2/room temperature/12 h; (b) R′MgX (3 equiv)/CuCN (0.3 equiv)/Et_2O/−20∼−30 °C/2–3 h; (c) 30% H_2O_2 (5–20 equiv)/KF (3 equiv)/$KHCO_3$ (3 equiv)/MeOH/THF/room temperature/12 h.

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