A New Method for the Preparation of δ-Alkoxy-α,β-unsaturated Aldehydes and Polyenals

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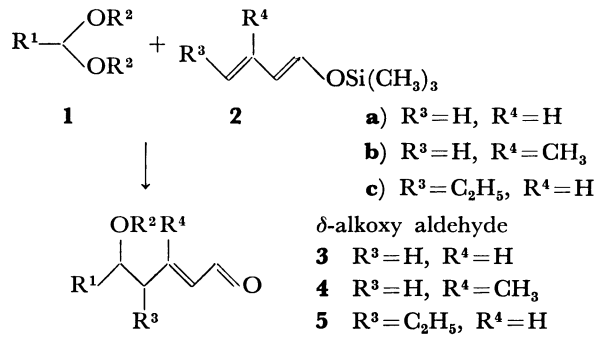
Dienoxysilanes (**2**) react with acetals in the presence of $TiCl_4$ and also in the coexistence of $TiCl_4$ and $Ti(O^iPr)_4$ to give δ-alkoxy-α,β-unsaturated aldehydes (**3**—**5**) in good yields. In the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene or 1,5-diazabicyclo[4.3.0]non-5-ene and molecular sieves 3A or 4A, the elimination reaction of δ-alkoxyl group of α,β-unsaturated aldehydes (**3**—**5**) proceeds smoothly to afford the corresponding polyenals in good yields.

In previous papers,[1,2] it was reported that the reaction of 1-trimethylsiloxy-1,3-butadiene (**2a**)[3] with various acetals (**1**) in the coexistence of $TiCl_4$ and $Ti(O^iPr)_4$ gives δ-alkoxy-α,β-unsaturated aldehydes (**3**), and that the aldehydes (**3**) are converted into polyenals by the elimination of δ-alkoxyl group with tertiary amines as 1,8-diazabicyclo[5.4.0]undec-7-ene (DUB) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in the presence of molecular sieves 3A and 4A. In the present paper, the preparation of δ-alkoxy-α,β-unsaturated aldehydes and polyenals is described in detail.

Results and Discussion

Preparation of δ-Alkoxy-α,β-unsaturated Aldehydes. Dienoxysilanes (**2**) reacted exclusively at their terminal sp^2 carbon atoms with acetals (**1**) activated by $TiCl_4$ to give the corresponding δ-alkoxy-α,β-unsaturated aldehydes (**3**—**5**) without the accompanying competitive products, β-alkoxy aldehydes[4] as shown in the following scheme 1.



Scheme 1.

Dienoxysilanes (**2**) are very sensitive toward $TiCl_4$ readily undergoing polymerization. When the reaction was carried out in solvents inert to $TiCl_4$, such as dichloromethane and toluene, dienoxysilanes (**2**) instantaneously afforded polymeric substance instead of the desired δ-alkoxy-α,β-unsaturated aldehydes (**3**—**5**). The difficulty was overcome by diminishing the effect of $TiCl_4$ on dienoxysilanes (**2**) by a proper choice of solvents or addition of $Ti(O^iPr)_4$. Aldehydes (**3**—**5**) were prepared according to methods A, B, and C as follows.

Method A). $TiCl_4$-THF + **1** $\xrightarrow[-78\,°C\ THF]{2}$ **3**—**5**

Method B). **1** + $TiCl_4$ + $Ti(O^iPr)_4$ $\xrightarrow[-40\,°C\ CH_2Cl_2]{2}$ **3**—**5**

Method C). $TiCl_4$ + $Ti(O^iPr)_4$ $\xrightarrow[-40\,°C\ CH_2Cl_2]{1+2}$ **3**—**5**

Method A. $TiCl_4$ formed a yellow complex with tetrahydrofuran (THF). The complex still possessed sufficient ability to activate unsaturated acetals (**1d**—**f**), the reaction proceeding smoothly at −78 °C to give the desired aldehydes (**3**—**5**) in good yields. The saturated acetals (**1a** and **1c**), however, gave unsatifactory results. The results are summarized in Table 1.

Method B. In order to moderate the activity of $TiCl_4$, $Ti(O^iPr)_4$ was added to a mixture of $TiCl_4$ and acetals (**1**) in dichloromethane at −40 °C followed by the addition of dienoxysilane (**2**). Combined use of $TiCl_4$ and

TABLE 1. YIELDS OF δ-ALKOXY-α,β-UNSATURATED ALDEHYDES (METHOD A)

	Acetal (**1**)		Dienoxy-silane	Product		Isolated yield (%)
	R^1	R^2			R^2	
a	$C_6H_5CH_2CH_2$	CH_3	**2a**	**3a**	CH_3	trace
c	C_6H_5	CH_3	**2a**	**3c**	CH_3	16
d	$C_6H_5CH{=}CH$	CH_3	**2a**	**3d**	CH_3	88
d	$C_6H_5CH{=}CH$	C_2H_5	**2a**	**3d**	C_2H_5	82
d	$C_6H_5CH{=}CH$	$-CH_2-$	**2a**	**3d**	CH_2CH_2OH	60
d	$C_6H_5CH{=}CH$	CH_3	**2b**	**4d**	CH_3	85
d	$C_6H_5CH{=}CH$	CH_3	**2c**	**5d**	CH_3	69
e	$CH_3CH{=}CH$	CH_3	**2a**	**3e**	CH_3	86
f	n-$C_3H_7CH{=}CH$	CH_3	**2b**	**4f**	CH_3	70

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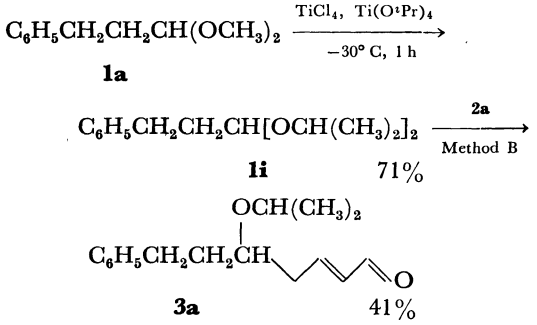
Table 2. Yields of δ-alkoxy-α,β-unsaturated aldehydes (Method B)

	Acetals (1)		Dienoxy-silane	Product	Isolated yield (%)	
	R^1	R^2			$R^2=CH(CH_3)_2$,	R^2
a	$C_6H_5CH_2CH_2$	CH_3	**2a**	**3a**	80	5
a	$C_6H_5CH_2CH_2$	C_2H_5	**2a**	**3a**	79	5
a	$C_6H_5CH_2CH_2$	CH_3	**2b**	**4a**	76	trace
b	n-C_5H_{11}	CH_3	**2a**	**3b**	75	5
c	C_6H_5	CH_3	**2a**	**3c**	83	3
d	$C_6H_5CH=CH$	CH_3	**2a**	**3d**	90	trace
g		CH_3	**2b**	**4g**	—	81
h		CH_3	**2a**	**3h**	—	69
		CH_3	**2b**	**4h**	—	68

$Ti(O^iPr)_4$ enabled us to use dichloromethane as a solvent. The saturated acetals (**1a**, **c**) also gave the corresponding δ-alkoxy-α,β-unsaturated aldehydes (**3**—**5**) in good yields (Table 2). However, the δ-alkoxyl group of most products prepared according to Method B was replaced by the isopropoxyl group originated from $Ti(O^iPr)_4$. In the case of sterically blocked α- and β-cyclocitral dimethyl acetal (**1g** and **1h**), no replacement of a methoxyl group of the parent acetal by an isopropoxyl group took place, and the normal δ-methoxy aldehydes could be obtained.



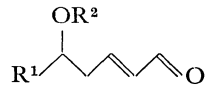
3-Phenylpropionaldehyde dimethyl acetal (**1a**) was readily converted into the diisopropyl acetal (**1i**)[5] in 71% yield by treatment with a mixture of $TiCl_4$ and $Ti(O^iPr)_4$ at −30 °C for 1 h under an argon atmosphere. When the diisopropyl acetal (**1i**) was treated with dienoxysilane (**2a**) under the conditions of Method B, 5-isopropoxy-7-phenyl-2-heptenal (**3a**) was isolated only in 41% yield. The lower yield of **3a** from **1i** might indicate that the reaction according to Method B proceeded through an intermediate, monoisopropyl acetal (**6**) rather than diisopropyl acetal (**1i**).

Method C. By changing the order of addition of the reagents, the replacement of the alkoxyl groups of starting acetals (**1**) with the isopropoxyl group of $Ti(O^iPr)_4$ could be easily prevented. A mixture of dienoxysilanes (**2**) and acetals (**1**) was added to a solution of $TiCl_4$ and $Ti(O^iPr)_4$ in dichloromethane at −40 °C. Various kinds of δ-alkoxy-α,β-unsaturated aldehydes (**3**—**5**) could be obtained in satisfactory yields without exchanging the alkoxyl groups of the parent acetals during the course of reaction (Table 3).

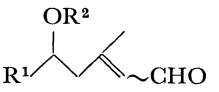
Table 3. Yields of δ-alkoxy-α,β-unsaturated aldehydes (Method C)

	Acetals(1)		Dienoxy-silane	Product	Isolated yields (%)
	R^1	R^2			
a	$C_6H_5CH_2CH_2$	CH_3	**2a**	**3a**	51
a	$C_6H_5CH_2CH_2$	C_2H_5	**2a**	**3a**	50
b	n-C_5H_{11}	CH_3	**2a**	**3b**	54
c	C_6H_5	CH_3	**2a**	**3c**	80
c	C_6H_5	C_2H_5	**2a**	**3c**	80
c	C_6H_5	CH_3	**2b**	**4c**	75
c	C_6H_5	CH_3	**2c**	**5c**	69
d	$C_6H_5CH=CH$	CH_3	**2a**	**3d**	85
d	$C_6H_5CH=CH$	C_2H_5	**2a**	**3d**	83
d	$C_6H_5CH=CH$	CH_3	**2b**	**4d**	76
d	$C_6H_5CH=CH$	CH_3	**2c**	**5d**	71
e	$CH_3CH=CH$	CH_3	**2a**	**3e**	80
f	n-$C_3H_7CH=CH$	CH_3	**2a**	**3f**	84
f	n-$C_3H_7CH=CH$	CH_3	**2b**	**4f**	74
g		CH_3	**2b**	**4g**	62
h		CH_3	**2a**	**3h**	80
		CH_3	**2b**	**4h**	80

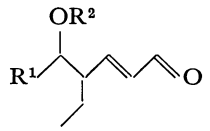
The δ-alkoxy-α,β-unsaturated aldehydes (Tables 1, 2, and 3) can be classified into three groups: i) α,β-Unsaturated aldehydes, **3**(**a**—**f**, **h**); ii) 3-Methyl-α,β-unsaturated aldehydes, **4**(**a**, **c**, **d**, **f**, **g**); iii) 4-Ethyl-α,β-unsaturated aldehydes, **5**(**c**, **d**). The configuration of each aldehyde was determined mainly on the basis of NMR spectroscopy.



3 $J_{1,2}=8$Hz
$J_{2,3}=16$Hz



4 C_3-CH_3 group
2*E* δ 2.15—2.25
2*Z* δ 1.95—2.05



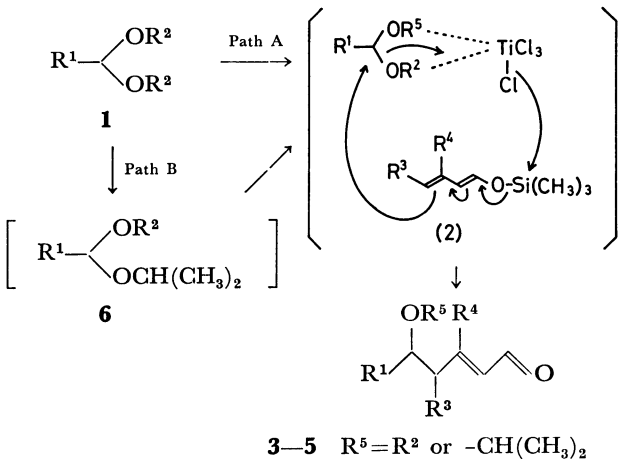
5 $J_{1,2}=8$Hz
$J_{2,3}=16$Hz

The aldehydes (**3**) of the first group were obtained as the sole product by this reaction, exhibiting peaks due to α,β-olefinic protons in the region of δ 5.00—6.10(C_2–H) and δ 6.75—6.80(C_3–H) with large coupling constants($J_{2,3}=16$ Hz), which supported the *trans* configuration of the double bonds in aldehydes (**3**).

On the other hand, the aldehydes (**4**) of the second group were mixtures of 2*E* and 2*Z* isomer(2*E* : 2*Z*=*ca.* 3—5 : 1). 3-Methyl group of 2*Z* isomers showed the signal in the region of δ 1.95—2.05 as a singlet or a doublet. In 2*E* isomers, the corresponding signal shifted to δ 2.15—2.25 as expected.[6]

The aldehydes (**5**) of the final group were found to be mixtures of *threo* and *erythro* isomers from their NMR spectra. No double bond isomer was detected. Without separation, these diasteromeric mixtures were subjected to the subsequent elimination reaction discussed later.

From the results, the reaction is assumed to proceed through a similar pathway proposed in the reaction of acetals with various nucleophiles,[7] *viz.*, the acetals (**1**) activated by $TiCl_4$ react with dienoxysilanes (**2**) to afford aldehydes (**3**—**5**) (path A of Scheme 2). The formation of δ-isopropoxy aldehydes by Method B could be explained by assuming an initial formation of monoisopropyl acetals (**6**) (path B).

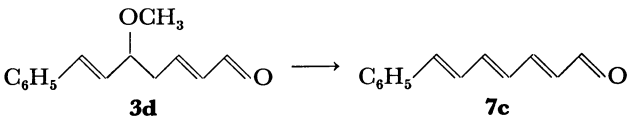


3—**5** $R^5=R^2$ or $-CH(CH_3)_2$

Scheme 2.

Preparation of Polyenals: The conversion of δ-alkoxy-α,β-unsaturated aldehydes into polyenals was examined under acidic[8-11] and basic conditions.[12] The results obtained by use of 5-methoxy-7-phenyl-2,6-heptadienal (**3d**) as a substrate are summarized in Table 4. Besides low yields, disadvantage of the use of acids might be expected when the reaction is undertaken with 5-methoxy-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-pentenals (**3h**, **4h**), since a double bond of 2,6,6-trimethyl-1-cyclohexenyl group of these compounds is very labile to acids and the double bond migration takes place readily.[13]

Table 4. Yield of 7-phenyl-2,4,6-heptatrienal (**7c**)



3d **7c**

	Acid or Base	Conditions	Yield (%)
1)	*p*-TsOH-C_6H_6	refl. 5 h	46
2)	CH_3CO_2Na-CH_3CO_2H	refl. 2 h	13
3)	$BF_3\cdot O(C_2H_5)_2$-$(CH_3CO)_2O$	−10 °C 0.5 h	26(63)[a]
4)	$BF_3\cdot O(C_2H_5)_2$-CH_2Cl_2	−10 °C 1 h	63
5)	*t*-BuOH-THF	−10 °C 1 h	59

a) 7-Phenyl-1,1,5-triacetoxy-2,6-heptadiene is obtained as a major product and converted into **7c** in 37% yield based on **3d**.

After several experiments on the elimination under basic conditions,[2] we found that 5-methoxy-7-phenyl-2,6-hetadienal (**3d**) gives the desired trienal (**7c**) in 92% yield by treatment with 2 molar amounts of DBU or DBN in the presence of molecular sieves 3A or 4A. There is no singificant difference either between the yields of DBU and DBN, or those of molecular sieves 3A and 4A. The longer reaction time was required when the reaction was carried out in the absence of molecular sieves.

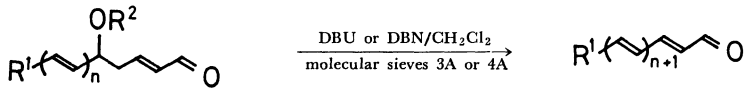
In a similar manner, various δ-alkoxy-α,β-unsaturated aldehydes can be easily converted into corresponding polyenals (**7a**—**f**). **3h** also gave 5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4-pentadienal (**7f**) in 78% yield without the migration of double bond. The reactions usually proceed at room temperature in a short reaction time. The results are summarized in Table 5.

Although the method is applicable to the preparation of various polyenals from δ-alkoxy-α,β-unsaturated aldehydes, the results with 3-methyl-5-alkoxy-α,β-unsaturated aldehydes (**4**) (Table 6) were unsatisfactory even after prolonged refluxing. For conversion of **4** into polyenals (**8**, **9**), 4 molar amounts of DBU and addition of CH_3CN were required.

By this procedure, 5-methoxy-3-methyl-7-phenyl-2,6-heptadienal (**4d**) gave a mixture of (2*E*,4*E*,6*E*)-3-methyl-7-phenyl-2,4,6-heptatrienal (**8b**) and its (2*Z*,4*E*,6*E*)-isomer (**9b**). **8b** and **9b** were isolated by preparative TLC in 78% and 15% yields, respectively. Their configurations were easily determined by a comparison of the chemical shift of the 3-methyl group; 2*E* isomer (**8b**) has a signal due to 3-methyl protons at δ 2.30 and 2*Z* isomer (**9b**) has the corresponding signal at δ 2.10. The NMR data are consistent with the assigned configurations.

9b can be converted into thermodynamically stable **8b** in 67% yield by treating with a catalytic amount of iodine[12] in benzene–ether (1 : 1) at room temperature for 7 h. Oxidation of **8b** with silver oxide[14] afforded (2*E*,4*E*,6*E*)-3-methyl-7-phenyl-2,4,6-heptatrienoic acid (**10a**). The melting point of the acid (**10a**) and the NMR spectrum of its methyl ester (**10b**) coincide with those reported.[15,16]

Table 5. Elimination reaction of δ-alkoxy group of α,β-unsaturated aldehyde with DBU or DBN

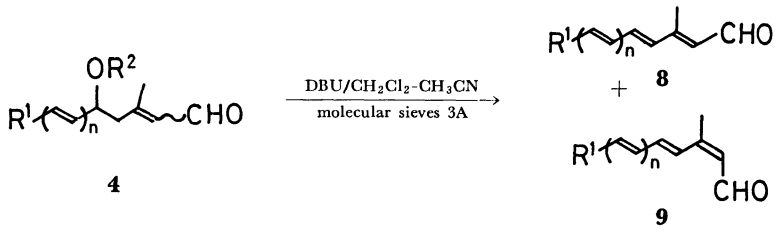


3 7

δ-Alkoxy aldehyde (3)			Conditions		Product	Yield of 7 (%)		
R^1	R^2	n	Temp	Time(h)		A[a]	B[b]	C[c]
n-C_3H_7	CH_3	1	r. t.	3.0	**7a**	81	82	80
C_6H_5	CH_3	0	r. t.	1.0	**7b**	82	80	80
C_6H_5	C_2H_5	0	r. t.	1.5	**7b**	79	79	—
C_6H_5	CH_3	1	r. t.	1.0	**7c**	92	92	89
C_6H_5	C_2H_5	1	r. t.	1.5	**7c**	92	—	—
C_6H_5	$CH(CH_3)_2$	1	refl.	2.0	**7c**	65	—	—
C_6H_5	CH_3	2	r. t.	1.0	**7d**	90	—	—
C_6H_5	CH_3	3	r. t.	1.0	**7e**	84	—	—
	CH_3	0	r. t.	4.0	**7f**	78	78	—

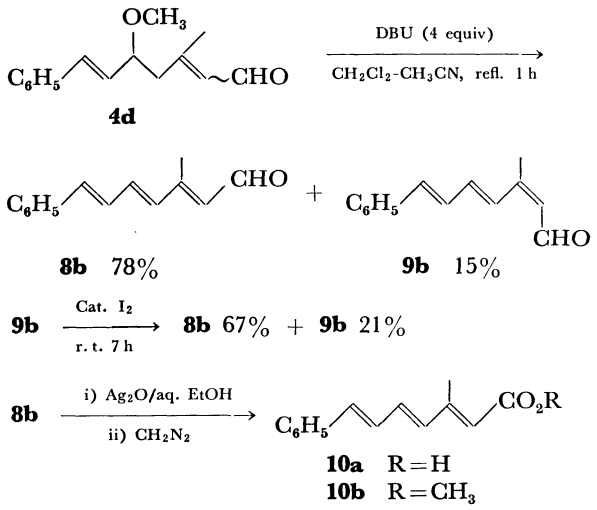
a) DBU-molecular sieves 3A. b) DBN-molecular sieves 3A. c) DBU-molecular sieves 4A.

Table 6. Yield of 3-methyl polyenal



4

δ-Alkoxy aldehyde (4)		Conditions		Yield (%) of 8 and 9			
R^1	n	Temp	Time (h)	Product 2E		Product 2Z	
C_6H_5	0	refl.	4.0	**8a**	54	**9a**	10
C_6H_5	1	refl.	1.5	**8b**	78	**9b**	15
	0	refl.	5.0	**8c**	56	**9c**	19

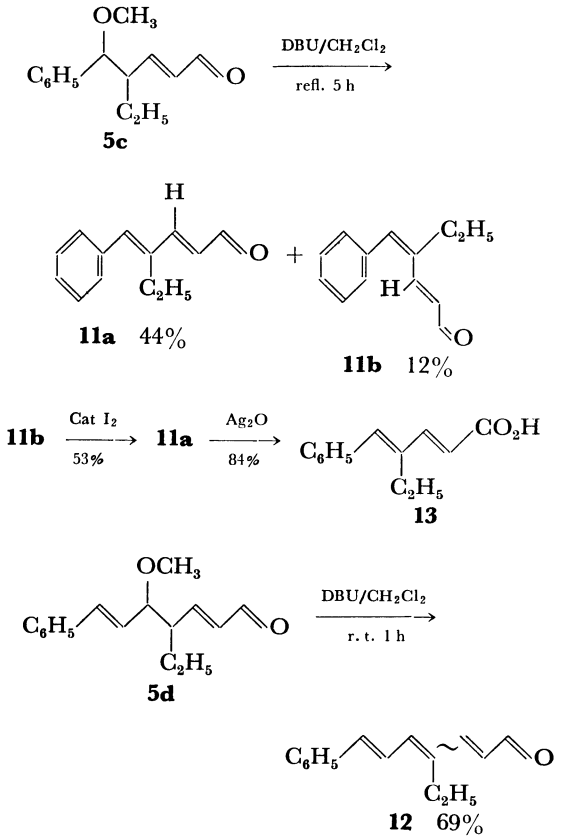


10a R=H
10b R=CH_3

Similarly, 5-methoxy-3-methyl-5-phenyl-2-pentenal (**4c**) and 5-methoxy-3-methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-pentenal (**4h**) were converted into the corresponding polyenals **8a** and **8c** (Table 6). The product **8c** is a useful intermediate for the syntheses of vitamin A and β-carotene.[17,18]

Elimination of a methoxyl group of 4-ethyl-5-methoxy-α,β-unsaturated aldehydes (**5**) proceeded smoothly under the conditions described for compounds **3a**—**f** in Table 5, as shown in the following Scheme 3.

4-Ethyl-5-methoxy-5-phenyl-2-pentenal (**5c**) gave (2E, 4E)-dienal (**11a**) and its (2E,4Z)-isomer (**11b**) in 44% and 12% yields, respectively. The configuration of **11a** and **11b** were deduced from their NMR data. The NMR spectrum of **11a** showed a doublet centered at δ7.25 (J=16 Hz) due to the C_3-vinyl proton and a quartet centered at δ 2.57 due to methylene protons of



Scheme 3.

a 4-ethyl group, whereas the corresponding signals of **11b** appeared at δ 7.63(J=16 Hz) and δ 2.47. The differences in the chemical shifts of the corresponding signals could be produced from the anisotropic effect of the benzene ring at C-5. The data obtained are in line with the assigned stuctures.

Isomerization of **11b** by iodine also indicates that **11a** has a stable (2*E*,4*E*)-configuration. Further proof of the structure was provided by a comparision of the NMR spectrum of the dienoic acid (**13**) derived from **11a** with that of (2*E*,4*E*)-4-methyl-5-phenyl-2,4-pentadienoic acid.[19] Both spectra are almost the same except for the peaks due to 4-substituents.

Similarly, 4-ethyl-5-methoxy-7-phenyl-2,6-heptadienal (**5d**) was easily converted into the polyenal (**12**) in 69% yield at room temperature.

By a proper choice of conditions (Method A, B, or C) various δ-alkoxy-α,β-unsaturated aldehydes (**3**—**5**) can be easily synthesized in good yields by the reaction of dienoxysilanes (**2**) and acetals (**1**) activated by $TiCl_4$. Elimination of the resulting δ-alkoxy-α,β-unsaturated aldehydes was found to proceed in satiafsctory yields by the use of tertiary amines in the presence of molecular sieves 3A or 4A. The present work would provide a simple and useful route for the synthesis of polyenals.

Experimental[20]

Materials. Commercial $TiCl_4$ and $Ti(O^iPr)_4$ were distilled under an argon atmosphere before use.

Perparation of 1-Trimethylsiloxy-1,3-butadiene (2a).[3] To a solution of crotonaldehyde(8.4 g, 120 mmol) and triethylamine (12.6 g, 125 mmol) in anhydrous C_6H_6(15 ml) were added quickly anhydrous $ZnCl_2$ (120 mg), hydroquinone (200 mg), and trimethylchlorosilane(12.7 g, 125 mmol). The mixture was heated at 70 °C for 8 h in a sealed tube and quenched with aqueous $NaHCO_3$ solution at 0 °C. After filtration of undissolved substance filtrate was washed with 10% $KHSO_4$ solution and water, and dried over anhydrous Na_2SO_4. The solvent was removed and the residual oil was distilled. 1-Trimethylsiloxy-1,3-butadiene (**2a**) was obtained in 65% yield (10.4 g, bp 57—60 °C/50 Torr).

In a similar way, dienoxysilanes (**2b** and **2c**) were obtained in 70% and 65% yields, respectively. **2b**: bp 68—70 °C/40 Torr; **2c**: bp 80—83 °C/28 Torr.

Reaction of Dienoxysilane (2a) with Cinnamaldehyde Dimethyl Acetal (1d) by Method A. To a mixture of $TiCl_4$(3.0 mmol) and cinnamaldehyde dimethyl acetal(455 mg, 2.5 mmol) in 10 ml of dry THF was added a solution of dienoxysilane (**2a**) (426 mg, 3.0 mmol) in 4 ml of dry THF at −78 °C under an argon atmosphere. The mixture was stirred for 4 h at the same temperature and quenched with K_2CO_3 (3.0 g, in 10 ml of water). The resulting precipitate was filtered off and the filtrate was extracted with ether. The extract was washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. 5-Methoxy-7-phenyl-2,6-heptadienal (475 mg) was isolated in 88% yield by preparative TLC on silica gel developing with hexane–ethyl acetate (4 : 1). IR(neat): 1695, 1640, 1600 cm^{-1}; NMR(CCl_4): δ 9.45(1H, d, J=8 Hz, aldehyde H), 7.25(5H, s, aryl CH), 5.7—7.2(4H, m, olefinic H), 3.6—3.9(1H, br. q, C_5–H), 3.25 (3H, s, $-OCH_3$), 2.4—2.7(2H, br. t, $-CH_2-$); Found: C, 77.89; H, 7.41%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

The IR and NMR spectra of the other δ-alkoxy-α,β-unsaturated aldehydes (**3c**—**e**, **4d**—**f**, and **5d**) prepared by Method A are consistent with the assigned structures. **3c**(R^2=CH_3): bp 80 °C/0.05 Torr (bath temperature); IR(neat): 1690, 1640 cm^{-1}; NMR(CCl_4): δ 9.50(1H, d, J=8 Hz, aldehyde H), 7.30(5H, s, aryl CH), 6.80(1H, ddd, J=16, 8, 8 Hz, C_3–H), 6.05(1H, dd, J=8,16 Hz, C_2–H), 4.1—4.4(1H, br. t, C_5–H), 3.20(3H, s, $-OCH_3$), 2.45—2.80(2H, m, $-CH_2-$); Found: C, 75.91; H, 7.55%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%. **3d**(R^2=C_2H_5): IR(neat): 1690, 1640 cm^{-1}; NMR(CCl_4): δ 9.45(1H, d, J=8 Hz, aldehyde H), 7.30(5H, s, aryl CH), 5.8—7.5(4H, m, olefinic H), 3.7—4.1 (1H, q, C_5–H), 3.2—3.7(2H, br. q, $-OCH_2-$), 2.4—2.7(2H, br. t, $-CH_2-$), 1.20(3H, t, CH_3). **3d**(R^2=CH_2CH_2OH): IR (neat): 3430, 1690, 1640 cm^{-1}; NMR(CCl_4): δ 9.45(1H, d, J=8 Hz, aldehyde H), 7.30(5H, s, aryl CH), 5.6—7.1(4H, m, olefinic H), 3.8—4.1(1H, m, C_5–H), 3.0—3.8(5H, m, $-OCH_2CH_2OH$), 2.5—2.8(2H, $-CH_2-$). **3e**(R^2=CH_3): bp 70 °C/0.5 Torr(bath temperature); IR(neat): 1690, 1630 cm^{-1}; NMR(CCl_4): δ 9.55(1H, d, J=8 Hz, aldehyde H), 6.85(1H, ddd, J=16, 8, 8 Hz, C_3–H), 6.10(1H, dd, J=16,8 Hz, C_2–H), 5.2—5.8(2H, m, olefinic H), 3.4—3.8(1H, br. q, C_5–H), 3.20(3H, s, $-OCH_3$), 2.4—2.7(2H, t, $-CH_2-$), 1.75(3H, d, J=6 Hz, CH_3). **4d**(R^2=CH_3, a mixture of 2*E* and 2*Z* isomers): IR(neat): 1670, 1630 cm^{-1}; NMR(CCl_4): δ 10.00(1H, d, J=8 Hz, aldehyde H), 7.35(5H, s, aryl CH), 6.63(1H, d, C_7–H), 5.8—6.3(2H, br, C_6–H, C_2–H), 3.7—4.2 (1H, br. C_5–H), 3.30(3H, s, $-OCH_3$), 2.20(s, 2E, C_3-CH_3), 2.05(s, 2*Z*, C_3-CH_3), 2.35—2.5(2H, $-CH_2-$). **4f**(R^2=CH_3) 2*E* isomer: bp 80 °C/0.05 Torr (bath temperature): IR (neat): 1670, 1630 cm^{-1}; NMR(CCl_4): δ 9.95(1H, d, J= 8 Hz, aldehyde H), 5.65—5.95(1H, br, C_2–H), 5.00—5.65 (2H, m, olefinic H), 3.5—3.9(1H, m, C_5–H), 3.15(3H, s, $-OCH_3$), 2.15(3H, s, C_3-CH_3), 0.7—2.5(9H, aliphatic H); Found: C, 73.56; H, 9.98%. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%. **4f**(R^2=CH_3) 2*Z* isomer: bp 80 °C/0.05 Torr(bath temperature); IR(neat): 1670, 1630 cm^{-1}; NMR

(CCl_4): δ 9.80(1H, d, J=8 Hz, aldehyde H), 5.70—5.95 (1H, br, C_2–H), 5.0—5.7(2H, m, olefinic H), 3.45—3.90(1H, m, C_5–H), 3.20(3H, s, $-OCH_3$), 1.95(3H, s, C_3-CH_3), 0.7—2.8(9H, aliphatic H), Found: C, 73.53; H, 10.05%. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%. **5d**($R^2=CH_3$, a mixture of *threo* and *eythro* isomers): IR(neat): 1690, 1640, 1600 cm^{-1}; NMR(CCl_4): δ 9.63(1H, d, J=8 Hz, aldehyde H), 7.40(5H, s, aryl CH), 5.8—7.7(4H, olefinic H), 3.6—3.9 (1H, C_5–H), 3.33(3H, s, $-OCH_3$), 1.2—2.7(3H, aliphatic H), 0.90(3H, t, CH_3); Found: C, 78.82; H, 8.33%. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25%.

*Reaction of Dienoxysilane (**2a**) with Cinnamaldehyde Dimethyl Acetal (**1d**) by Method B.* To a mixture of $Ti(O^iPr)_4$ (2.0 mmol) and 356 mg(2.0 mmol) of cinnamaldehyde dimetl yl acetal (**1d**) in 25 ml of CH_2Cl_2 was added $TiCl_4$ (2.3 mmol) in 1 ml of CH_2Cl_2 at -40 °C under an argon atmosphere. After stirring for a minute, dienoxysilane (**2a**, 355 mg, 2.5 mmol in 4 ml of CH_2Cl_2) was added to the mixture. The mixture was kept at -40 °C for 30 min, quenched with K_2CO_3 (2 g in 10 ml of H_2O) and worked up in the usual way. 5-Isopropoxy-7-phenyl-2,6-heptadienal(441 mg) was isolated in 90 % yield by preparative TLC on silica gel developing with hexane–ethyl acetate(4 : 1). IR(neat): 1690, 1640, 1600 cm^{-1}; NMR(CCl_4): δ 9.50(1H, d, J=8 Hz, aldehyde H), 7.30(5H, s, aryl CH), 5.8—7.2(4H, m, olefinic H), 3.4—4.3 (2H, m, $-OCH<$, C_5–H), 2.4—2.8(2H, m, $-CH_2-$), 1.15(6H, d, $2\times CH_3$).

The IR and NMR spectra of other δ-alkoxy-α,β-unsaturated aldehydes (**3a—h** and **4a—h**) prepared by Method B are consistent with the assigned structures. **3a** ($R^2=i$-pr): IR (neat): 1690, 1630, 1600 cm^{-1}; NMR(CCl_4): δ 9.50(1H, d, J=8 Hz, aldehyde H), 7.20(5H, s, aryl CH), 6.80(1H, ddd, J=16, 8, 8 Hz, C_3–H), 6.05(1H, dd, J=16, 8 Hz, C_2–H), 3.2 —3.8(2H, m, $2\times$–O–CH<), 2.2—2.8(4H, m, $-CH_2-$), 1.5—1.9(2H, m, $-CH_2-$), 1.10(6H, d, $2\times CH_3$). **3b**($R^2=i$-pr): bp 140 °C/0.2 Torr (bath temperature); IR(neat); 1680, 1625 cm^{-1}; NMR(CCl_4); δ 9.55(1H, d, J=8 Hz, aldehyde H), 6.80 (1H, ddd, J=16, 8, 8 Hz, C_3–H), 6.05(1H, dd, J=16, 8 Hz, C_2–H), 3.2—3.8(2H, m, $2\times$–O–CH<), 2.3—2.7(2H, m, $-CH_2-$), 0.7—1.6(17H); Found: C, 73.23; H, 11.35%. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39%. **3c**($R^2=i$-pr): IR(neat): 1695, 1640 cm^{-1}; NMR(CCl_4): δ 9.45(1H, d, J=8 Hz, aldehyde H), 7.30(5H, s, aryl CH), 6.80(1H, ddd, J=16, 8, 8 Hz, C_3–H), 6.00(1H, dd, J=16, 8 Hz, C_2–H), 4.2 —4.65 (1H, m, C_5–H), 3.3—3.7 (1H, m, $-OCH<$), 2.5—2.8 (2H, $-CH_2-$), 1.00—1.30(6H, $2\times CH_3$). **3h**($R^2=CH_3$): IR (neat); 1690, 1635 cm^{-1}; NMR(CCl_4): δ 9.50(1H, d, J=8 Hz, aldehyde H), 6.85(1H, ddd, J=16, 8, 8 Hz, C_3–H), 6.05 (1H, dd, J=16, 8 Hz, C_5–H), 3.15(3H, s, $-OCH_3$), 1.75(3H, s, C=C–CH_3), 0.95—1.00(6H, 2s, $2\times CH_3$), 1.20—2.90(7H, aliphatic H), **4a**($R^2=i$-pr, a mixture of 2*E* and 2*Z* isomers): IR(neat): 1680, 1630, 1600 cm^{-1}; NMR(CCl_4): δ 9.90(1H, d, J=8 Hz, aldehyde H), 7.15(5H, s, aryl CH), 5.7—6.0(1H, br. d, C_2–H), 3.25—3.8(2H, m, $2\times$–O–CH<), 1.5—3.0(5H, m, aliphatic H), 1.10(6H, d, $2\times CH_3$), 2.15(s, 2*E*, C_3-CH_3), 1.95(s, 2*Z*, C_3-CH_3). **4g**($R^2=CH_3$): 2*E* isomer: IR(neat): 1680, 1625 cm^{-1}; NMR(CCl_4); δ 9.95(1H, d, J=8 Hz, aldehyde H), 5.6—5.9(1H, br. d, C_2–H), 5.2—5.9(1H, br, olefinic H), 3.0—3.3(1H, br, C_5–H), 3.25(3H, s, $-OCH_3$), 1.75 (3H, s, C=C–CH_3), 1.00, 0.85(6H, 2s, $2\times CH_3$), 0.5—2.5(7H, aliphatic H), 2.20(3H, s, C_3-CH_3). 2*Z* isomer: IR(neat): 1680, 1625 cm^{-1}; NMR(CCl_4): δ 9.90(1H, d, J=8 Hz, aldehyde H), 5.65—5.95(1H, br. d, C_2–H), 5.3—5.6(1H, br, olefinic H), 3.25(3H, s, $-OCH_3$), 2.00(3H, s, C_3-CH_3), 1.75 (3H, s, C=C–CH_3), 1.05, 0.90(6H, 2s, $2\times CH_3$).

*Reaction of Dienoxysilane(**1a**) with 3-Phenylpropionaldehyde Dimethyl Acetal (**1a**) by Method C.* To a stirred solution of $TiCl_4$(1.5 mmol) and $Ti(O^iPr)_4$ (1.5 mmol) in 10 ml of CH_2Cl_2 was added a solution of 3-phenylpropionaldehyde dimethyl acetal(180 mg, 1.0 mmol) and dienoxysilane (**2a** 170 mg, 1.2 mmol) in 5 ml of CH_2Cl_2 at -40 °C under an argon atmosphere. After being stirred for 30 min at the same temperature, the mixture was quenched with K_2CO_3 (1.5 g in 10 ml of H_2O), and the resulting precipitate was filtered off. The filtrate was extracted with ether and the resulting solution was dried over anhydrous Na_2SO_4. After removal of the solvent, the residual oil was chromatographed on silica gel developing with hexane–ethyl acetate(4 : 1) to give 5-methoxy-7-phenyl-2-heptenal (112 mg) in 51% yield. IR(neat): 1690, 1640, 1600 cm^{-1}; NMR(CCl_4): δ 9.55(1H, d, J=8 Hz, aldehyde H), 7.20(5H, s, aryl CH), 6.80(1H, ddd, J=16, 8, 8 Hz, C_3–H), 6.05(1H, dd, J=16, 8 Hz, C_2–H), 3.35(3H, s, $-OCH_3$), 3.0—3.4(1H, br, C_5–H), 2.3—2.9(4H, m, $-CH_2-$), 1.5—2.0(2H, m, $-CH_2-$).

2,4-Dinitrophenylhydrazone: mp 123—124 °C; Found: C, 60.29; H, 5.57; N, 14.06%. Calcd for $C_{20}H_{22}O_5N_4$: C, 60.06; H, 5.76; N, 13.96%.

The IR and NMR spectra of other δ-alkoxy-α,β-unsaturated aldehydes (**3a—h**, **4c—h** and **5c—d**), prepared by Method C are consistent with the assigned structures. **3a**($R^2=C_2H_5$): IR (neat): 1685, 1630, 1600 cm^{-1}; NMR(CCl_4): δ 9.50(1H, d, J=8 Hz, aldehyde H), 7.20(5H, s, aryl CH), 6.75(1H, ddd, J=16, 8, 8 Hz, C_3–H), 6.00(1H, dd, J=16, 8 Hz, C_2–H), 3.2 —3.7(3H, m, $-OCH_2-$, C_5–H), 2.3—2.9(4H, m, $-CH_2-$), 1.5 —2.0(2H, m, $-CH_2-$), 1.20(3H, t, $-CH_3$). **3b**($R^2=CH_3$): bp 125 °C/0.1 Torr(bath temperature); IR(neat): 1695, 1640 cm^{-1}; NMR(CCl_4): δ 9.50(1H, d, J=8 Hz, aldehyde H), 6.80(1H, ddd, J=16, 8, 8 Hz, C_3–H), 6.05(1H, dd, J=16, 8 Hz, C_2–H), 3.30(3H, s, $-OCH_3$), 3.1—3.5(1H, br, C_5–H), 2.4 —2.7(2H, m, $-CH_2-$), 0.7—1.6(11H); Found: C, 71.84; H, 11.18%. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94%. **3c** ($R^2=C_2H_5$): IR(neat): 1690, 1640 cm^{-1}; NMR(CCl_4): δ 9.40(1H, d, J=8 Hz, aldehyde H), 7.25(5H, s, aryl CH), 6.75(1H, ddd, J=16, 8, 8 Hz, C_3–H), 6.00(1H, dd, J=16, 8 Hz, C_2–H), 4.25(1H, t, C_5–H), 3.5(2H, q, $-OCH_2-$), 2.5—2.8(2H, br. t, $-CH_2-$), 1.15(3H, t, CH_3). **3d**($R^2=C_2H_5$): IR(neat): 1690, 1640 cm^{-1}; NMR(CCl_4): δ 9.45(1H, d, J=8 Hz, aldehyde H), 7.30(5H, s, aryl CH), 5.8—7.5(4H, m, olefinic H), 3.7—4.1(1H, q, C_5–H), 3.2—3.7(2H, q, $-OCH_2-$), 2.4—2.7(2H, br. t, $-CH_2-$), 1.20(3H, t, CH_3). **3f**($R^2=CH_3$): bp 85 °C/0.1 Torr (bath temperature); IR(neat): 1685, 1635 cm^{-1}; NMR(CCl_4): δ 9.45(1H, d, J=8 Hz, aldehyde H), 6.75(1H, ddd, J=16, 8, 8 Hz, C_3–H), 6.00(1H, dd, J=16, 8 Hz, C_2–H), 5.1—5.8(2H, m, olefinic H), 3.4—3.8(1H, m, C_5–H), 3.20(3H, s, $-OCH_3$), 0.7—2.7(9H, aliphatic H); Found: C, 72.29; H, 10.09%. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96%. **4c**($R^2=CH_3$): 2*E* isomer; IR(neat): 1670, 1630 cm^{-1}; NMR(CCl_4): δ 10.00(1H, d, J=8 Hz, aldehyde H), 7.35(5H, s, aryl CH), 5.8—6.1(1H, br. d, C_2–H), 4.25—4.55(1H, C_5–H), 3.21(3H, s, $-OCH_3$), 2.5—2.8(2H, $-CH_2-$), 2.18(3H, d, J=1.2 Hz, C_3-CH_3). 2*Z* isomer: IR (neat): 1670, 1630 cm^{-1}; NMR(CCl_4): δ 9.80(1H, d, J= 8 Hz, aldehyde H), 7.33(5H, s, aryl CH), 5.8—6.1(1H, br. d, C_2–H), 4.25—4.55(1H, C_5–H), 3.21(3H, s, $-OCH_3$), 2.8—3.3 (2H, $-CH_2-$), 1.96(3H, d, J=1.2 Hz, C_3-CH_3). **5c**($R^2=CH_3$, a mixture of *threo* and *erythro* isomers): bp 85 °C/ 0.05 Torr(bath temperature); IR (neat): 1700, 1640 cm^{-1}; Found: C, 76.92; H, 8.37%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%. isomer A: NMR($CDCl_3$): δ 9.48(d, J=8 Hz, aldehyde H), 7.35(s, aryl CH), 6.85(dd, J=16, 8 Hz, C_3–H), 6.04(dd, J=16, 8 Hz, C_2–H), 4.18(d, C_5–H), 3.24(s, $-OCH_3$). Isomer B: NMR($CDCl_3$): δ 9.60(d, J=8 Hz, aldehyde H), 7.35(s, aryl CH), 6.65(dd, J=16, 8 Hz, C_3–H), 5.98(dd, J=16, 8 Hz, C_2–H), 4.18(d, C_5–H), 3.21(s, $-OCH_3$).

*Conversion of 3-Phenylpropionaldehyde Dimethyl Acetal (**1a**) into Diisopropyl Acetal (**1i**) in the Presence of $TiCl_4$ and $Ti(O^iPr)_4$*[4]. To a mixture of 3-phenylpropionaldehyde dimethyl acetal (360 mg, 2.0 mmol) and $Ti(O^iPr)_4$ (2.0 mmol) in 25 ml of CH_2Cl_2 was added a solution of $TiCl_4$(2.4 mmol) in 5 ml of CH_2Cl_2 at −30 °C under an argon atmosphere. The mixture was stirred for 1 h and quenched with K_2CO_3(2 g in 10 ml of water). The precipitate was filtered off and the filtrate was extracted with ether. The extract was washed with water and dried over anhydrous Na_2SO_4. After removal of the solvent, the resulting oil was distilled. 3-Phenyl propionaldehyde diisopropyl acetal(335 mg) was obtained in 71% yield. bp 135 °C/11 Torr; NMR(CCl_4): δ 7.25(5H, s, aryl CH), 4.6(1H, t, $-CH\langle^{O-}_{O-}\rangle$), 3.7—4.1(1H, m, 2×$-OCH\langle$), 2.6—2.9, 1.7—2.2(4H, m, $-CH_2-$), 1.12, 1.22(12H, 2d, 4×CH_3). The IR and NMR spectra of this diisopropyl acetal (**1i**) are identical with those of the sample prepared from 3-phenylpropionaldehyde and isopropyl alcohol according to the method of Roelofsen and Bekkum.[5]

*Conversion of 5-Methoxy-7-phenyl-2,6-heptadienal (**3d**) into 7-Phenyl-2,4,6-heptatrienal (**7c**) under Acidic and Basic Conditions.* p-*TsOH–C_6H_6*: A solution of **3d** (108 mg, 0.5 mmol) and *p*-toluensulfonic acid(5 mg) in 10 ml of abs. C_6H_6 was refluxed for 3 h under an agron atmosphere. The C_6H_6 solution was washed with 10% $NaHCO_3$ solution and water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting solid was chromatographed on silica gel and eluted with hexane–ethyl acetate(4 : 1) to afford **7c**(42 mg) in 46% yield. IR(KBr): 1670, 1605, 1595 cm^{-1}; NMR (CCl_4): δ 9.55(1H, d, J=8 Hz, aldehyde H), 7.35(5H, s, aryl CH), 6.4—7.5(5H, m, olefinic H), 6.15(1H, dd, J=8,16 Hz, C_2–H).

AcONa-AcOH: A solution of **3d**(108 mg, 0.5 mmol) and sodium acetate(30 mg) in 1 ml of acetic acid was refluxed for 2 h under an argon atmosphere. The reaction mixture was poured into 10% $NaHCO_3$ solution at 0 °C and extracted with ether. After being worked up in the usual way, **7c**(12 mg) was obtained in 13% yield.

$BF_3\cdot O(C_2H_5)_2$-Ac_2O: To a solution of **3d**(216 mg, 1 mmol) in 1 ml of acetic anhydride was added one drop of $BF_3\cdot O(C_2H_5)_2$ at −10 °C under an argon atmosphere. The mixture was stirred for 0.5 h at −10 °C, poured into ice cold water and extracted with ether. The extract was washed with 10% $NaHCO_3$ solution and water, dried and worked up in the usual way. **7c**(48 mg) and 7-phenyl-1,1,5-triacetoxy-2,6-heptadiene(150 mg) were obtained in 26% and 43% yields, respectively. 7-Phenyl-1,1,5-triacetoxy-2,6-heptadiene: IR (neat), 1760, 1740, 1600, 1240, 1200 cm^{-1}; NMR(CCl_4): δ 7.20(5H, s, aryl CH), 5.2—7.5(6H), 2.3—2.6(2H, $-CH_2-$), 2.00(9H, s, 3×$-COCH_3$). A mixture of the above triacetate (150 mg) in 3 ml of CH_3OH and 20% KOH solution(0.5 ml) was stirred for 15 h at room temperature under an argon atmosphere. After removal of CH_3OH, the residual aqueous solution was neutralized with dil. HCl and extracted with ether. The ether layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Another crop of crystals, **7c**(68 mg), was obtained in 37% yield based on **3d**, the total yield of **7c** being 63%.

$BF_3\cdot O(C_2H_5)_2$-CH_2Cl_2: To a solution of **3d** (108 mg, 0.5 mmol) in 3 ml of CH_2Cl_2 was added a solution of $BF_3\cdot O(C_2H_5)_2$ (1 mmol) in 2 ml of CH_2Cl_2 at −10 °C under an argon atmosphere. The mixture was stirred for 1 h and quenched with 10% K_2CO_3 solution. After the usual work up, **7c** (58 mg) was isolated in 63% yield.

t-*BuOK–THF*: To a solution of *t*-BuOK (125 mg, 1.1 mmol) in 5 ml of dry THF was added a solution of **3d** (108 mg, 0.5 mmol) in 3 ml of dry THF at −10 °C under an argon atmosphere. The mixture was stirred for 1 h at −10 °C and poured into ice cold water containing hydrochloric acid. After being worked up in the usual way, **7c** (54 mg) was obtained in 59% yield.

*Conversion of 5-Methoxy-7-phenyl-2,6-heptadienal(**3d**) to 7-Phenyl-2,4,6-heptatrienal (**7c**) with DBU.* To a solution of 5-methoxy-7-phenyl-2,6-heptadienal(350 mg, 1.6 mmol) in 10 ml of CH_2Cl_2 were added a solution of DBU(492 mg, 3.2 mmol) in 5 ml of CH_2Cl_2 and molecular sieves 3A(500 mg) at room temperature under an argon atmosphere. The mixture was stirred for 1 h and poured into ice cold brine containing acetic acid. The organic layer was separated, washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residual solid was chromatographed on silica gel and eluted with hexane–ethyl acetate(4 : 1) to afford 274 mg of 7-phenyl-2,4,6-heptatrienal(**7c**) in 92% yield. mp 114—115 °C, (lit,[21] mp 116 °C).

The IR, UV, and NMR spectra of polyenals(**7a—f**) are consistent with the assigned structures: **7a**: bp 70 °C/0.5 Torr(bath temperature), (lit,[22] bp 70 °C/0.7 Torr); IR(neat): 1680, 1610 cm^{-1}; NMR(CCl_4): δ 9.50(1H, d, J=8 Hz, aldehyde H), 5.8—7.3(6H, m, olefinic H), 2.0—2.5(2H, m, $-CH_2-$), 1.2—1.7(2H, m, $-CH_2-$), 0.8—1.2(3H). **7b**: mp 39—41 °C(lit,[23] mp 37—39 °C); IR(KBr): 1670, 1615 cm^{-1}; NMR(CCl_4): δ 9.60(1H, d, J=8 Hz, aldehyde H), 7.35(5H, s, aryl CH), 5.9—7.4(4H, m, olefinic H). **7d**: mp 141—142 °C(lit,[24] mp 139—141 °C); IR(Nujol): 1680, 1595, 1560 cm^{-1}; NMR(d_6-DMSO): δ 9.55(1H, d, J=8 Hz, aldehyde H), 7.35(5H, s, aryl CH), 6.4—7.4(7H, m, olefinic H), 6.10 (1H, dd, J=8,16 Hz, C_2–H); UV λ_{max}^{EtOH} 382 nm(ε 5.6×10⁴), 275 nm(ε 1.1×10⁴); Mass: *m/e* 210(M^+). **7e**: mp 185—186 °C(lit,[25] mp 183 °C); IR(KBr): 1660, 1600, 1560 cm^{-1}; UV λ_{max}^{EtOH} 406 nm(ε 7.49×10⁴), 295 nm(ε 1.49×10⁴); Mass: *m/e* 236 (M^+). **7f**: IR(neat): 1680, 1610 cm^{-1}; NMR (CCl_4): δ 9.55(1H, d, J=8 Hz, aldehyde H), 5.85—7.30 (4H, m, olefinic H), 1.75(3H, s, C=C–CH_3), 1.05(6H, s, 2×CH_3), 0.9—2.4(6H, aliphatic H).

*Conversion of 5-Methoxy-3-methyl-7-phenyl-2,6-heptadienal (**4d**) to 3-Methyl-7-phenyl-2,4,6-heptatrienal with DBU.* To a solution of 5-methoxy-3-methyl-7-phenyl-2,6-heptatrienal (450 mg, 1.96 mmol) in 8 ml of CH_2Cl_2 were added a solution of DBU(1.0 g) in 8 ml of CH_3CN and molecular sieves 3A (1.0 g) under an argon atmosphere. The mixture was refluxed for 1.5 h and poured into ice cold brine containing acetic acid, and worked up in the usual way. After separation by preparative TLC on silica gel [hexane–ethyl acetate(4 : 1)], (2*E*, 4*E*,6*E*)-3-methyl-7-phenyl-2,4,6-heptatrienal (**8b**) (303 mg) and (2*Z*,4*E*,6*E*)-isomer (**9b**) (58 mg) were obtained in 78% and 15% yields, respectively. **8b**: mp 76—77 °C; IR (Nujol) 1650, 1600, 1580 cm^{-1}; NMR($CDCl_3$): δ 10.15(1H, d, J= 8 Hz, aldehyde H), 6.4—7.7(9H, aryl CH, olefinic H), 6.00 (1H, d, C_2–H), 2.30(3H, s, CH_3); Found: C, 85.06; H, 7.19%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%. **9b**: IR(neat): 1650, 1600, 1580 cm^{-1}; NMR($CDCl_3$): δ 10.20 (1H, d, J=8 Hz, aldehyde H), 6.4—7.6(9H, aryl CH, olefinic H), 5.90(1H, d, C_2–H), 2.15(3H, s, CH_3).

The IR and NMR spectra of other 3-methyl polyenals (**8a—c** and **9a—c**) are consistent with the assigned structures. **8a**: IR(neat): 1660, 1615, 1590 cm^{-1}; NMR($CDCl_3$): δ 10.23(1H, d, J=8 Hz, aldehyde H), 6.99—7.80(7H, m, aryl CH, olefinic H), 6.11(1H, d, J=8 Hz, C_2–H), 2.37(3H, s, C_3–CH_3). **9a**: NMR($CDCl_3$): δ 10.33(1H, d, J=8 Hz, aldehyde H), 7.1—7.8(7H, m,) 5.98(1H, d, J=8 Hz, C_2–H), 2.21 (3H, s, C_3–CH_3). **8c**: IR(neat): 1660, 1600 cm^{-1}; NMR (CCl_4); δ 10.20(1H, d, J=8 Hz, aldehyde H), 6.10, 6.65 (2H, 2d, J=16 Hz, C_4–H, C_5–H), 5.85(1H, d, J=8 Hz, C_2–

H), 2.30(3H, s, C_3–CH_3), 1.70(3H, s, C=C–CH_3), 1.50—2.20 (6H, aliphatic CH_2), 1.05(6H, s, 2×CH_3). **9c**: IR(neat): 1670, 1610 cm^{-1}; NMR(CCl_4): δ 10.15(1H, d, J=8 Hz, aldehyde H), 6.50, 7.10(2H, 2d, J=16 Hz, C_4–H, C_5–H), 5.75(1H, d, J=8 Hz, C_2–H), 2.10(3H, s, C_3–CH_3), 1.75(3H, s, C=C–CH_3), 1.50—2.20(6H, aliphatic H), 1.05(6H, s, 2×CH_3).

*Conversion of 4-Ethyl-5-methoxy-5-phenyl-2-pentenal (**5c**) to 4-Ethyl-5-phenyl-2,4-pentadienal (**11**) with DBU.* To a solution of 4-ethyl-5-methoxy-5-phenyl-2-pentenal(218 mg, 1 mmol) in CH_2Cl_2 (5 ml) were added a solution of DBU (304 mg, 2 mmol) in CH_2Cl_2 (5 ml) and molecular sieves 3A (500 mg) under an argon atmosphere. The mixture was refluxed for 5 h and the solvent was removed at 20 °C under reduced pressure. The residual oil was chromatographed on silica gel using hexane–ethyl acetate(8 : 1) as an eluent. (2*E*,4*E*)-4-Ethyl-5-phenyl-2,4-pentadienal (**11a**) (82 mg) and (2*E*, 4*Z*) isomer (**11b**) (23 mg) were obtained in 44% and 12% yields, respectively. **11a**: IR(neat): 1680, 1600 cm^{-1}; NMR($CDCl_3$): δ 9.75(1H, d, J=8 Hz, aldehyde H), 7.24(5H, s, aryl CH), 7.25(1H, d, J=16 Hz, C_3–H), 6.93(1H, s, C_5–H), 6.38 (1H, dd, J=16, 8 Hz, C_2–H), 2.57(2H, q, –CH_2–), 1.21(3H, t, CH_3). **11b**: IR(neat): 1680, 1610 cm^{-1}; NMR($CDCl_3$): δ 9.76(1H, d, J=8 Hz, aldehyde H), 7.38(5H, s, aryl CH), 7.63(1H, d, J=16 Hz, C_3–H), 6.93(1H, s, C_5–H), 6.35(1H, dd, J=16,8 Hz, C_2–H), 2.47(2H, q, –CH_2–), 1.20(3H, t, CH_3).

4-Ethyl-5-methoxy-7-phenyl-2,6-heptadienal (**5d**) was convered into 4-ethyl-7-phenyl-2,4,6-heptatrienal (**12**) in 69% yield by treating with DBU(4 equiv) at room temperature for 1 h. **12**: mp 93—94 °C: IR(Nujol): 1660, 1600, 1580 cm^{-1}; NMR($CDCl_3$): δ 9.75(1H, d, J=8 Hz, aldehyde H), 5.5—7.7(9H, aryl CH, olefinic H), 6.25(1H, dd, J=8, 16 Hz, C_2–H), 2.52(2H, q, –CH_2–), 1.12(3H, t, CH_3). Found: C, 84.97; H, 7.65%. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60%.

*Isomerization of (2Z,4E,6E)-3-Methyl-7-phenyl-2,4,6-heptatrienal(**9b**) to (2E,4E,6E)-3-Methyl-7-pehnyl-2,4,6-heptatrienal (**8b**) with Iodine.* A solution of (2*E*,4*Z*,6*E*)-3-methyl-7-phenyl-2,4,6-heptatrienal (106 mg) in 10 ml of abs. C_6H_6–ether(1 : 1) was treated with a catalytic amount of iodine at room temperature under an argon atmosphere. After stirring for 7 h, the reaction mixture was washed with aqueous $Na_2S_2O_3$ solution and dried over anhydrous Na_2SO_4. The solvent was removed and the crystalline residue was chromatographed on silica gel and eluted with hexane–ethyl acetate (4 : 1) to afford 71 mg of **8b** and 21 mg of **9b** in 67% and 21% yields, respectively.

(2*E*,4*Z*)-4-Ethyl-5-phenyl-2,4-pentadienal (**11a**) and the recovered (2*E*,4*Z*)-isomer(**11b**) were obtained in 53% and 14% yields, respectively, by treating (2*E*,4*Z*)-isomer(**11b**) with iodine under similar conditions.

*Oxidation of (2E,4E,6E)-3-Methyl-7-phenyl-2,4,6-heptatrienal (**8b**) to (2E,4E,6E)-3-Methyl-7-phenyl-2,4,6-heptatrienoic Acid (**10a**).* To a solution of silver nitrate(123 mg, 0.72 mmol) in 1.5 ml of water were added a solution of (2*E*,4*E*,6*E*)-3-methyl-7-phenyl-2,4,6-heptatrienal(120 mg, *ca.* 0.6 mmol) in ethanol(2.5 ml) and NaOH(112 mg in 1.5 ml of water). The mixture was stirred for 15 h at room temperature in the dark and the precipitate was filtered off. Ethanol was removed under reduced pressure. The residual aqueous solution was acidified with dil. HCl and extracted with ethyl acetate. (2*E*,4*E*,6*E*)-3-Methyl-7-phenyl-2,4,6-heptatrienoic acid (**10a**) (116 mg) was obtained in 89% yield. mp 201—203 °C, (lit,[15] mp 203 °C); IR(Nujol): 1660, 1590 cm^{-1}; NMR($CDCl_3$): δ 6.27—7.6(10H), 5.88(1H, br. s, C_2–H), 2.35(3H, s, C_3–CH_3); UV λ_{max}^{EtOH} 329 nm(ε 6.0×10^4), 242 nm(ε 1.0×10^4).

Acid (**10a**) was converted into the corresponding methyl ester (**10b**) in 90% yield according to the method of Wiley *et al.*,[16] **10b**: mp 56—57 °C; IR(Nujol): 1700, 1600 cm^{-1}; NMR(CCl_4): δ 7.26(5H, br. s, aryl CH), 6.3—6.9(4H, olefinic H), 5.72(1H, br. s, C_2–H), 3.60(3H, s, –OCH_3), 2.29 (3H, s, C_3–CH_3); UV λ_{max}^{MeOH} 336 nm(ε 5.06×10^4), 245 nm(ε 9.66×10^3).

Similarly, (2*E*,4*E*)-4-ethyl-5-phenyl-2,4-pentadienoic acid (**13**) was obtained in 84% yield by treating with silver oxide in the dark. **13**: mp 98—99 °C; IR(KBr): 1670, 1600 cm^{-1}; UV λ_{max}^{hexane} 302 nm(ε 2.76×10^4), 225 nm(ε 6.65×10^3); NMR($CDCl_3$): δ 10.56(1H, br. –CO_2H), 7.56(1H, d, J= 16 Hz, C_3–H), 7.41(5H, s, aryl CH), 6.87(1H, s, C_5–H), 6.06 (1H, d, J=16 Hz, C_2–H), 2.55(2H, q, –CH_2–), 1.21(3H, t, CH_3); Found: C, 71.75; H, 6.37%. Calcd for $C_{13}H_{14}O_2$: C, 71.54; H, 6.47%.

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