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(2*E*)-4,4-Dimethoxy-2-butenal in the Synthesis of Conjugated Dienes and Dienals

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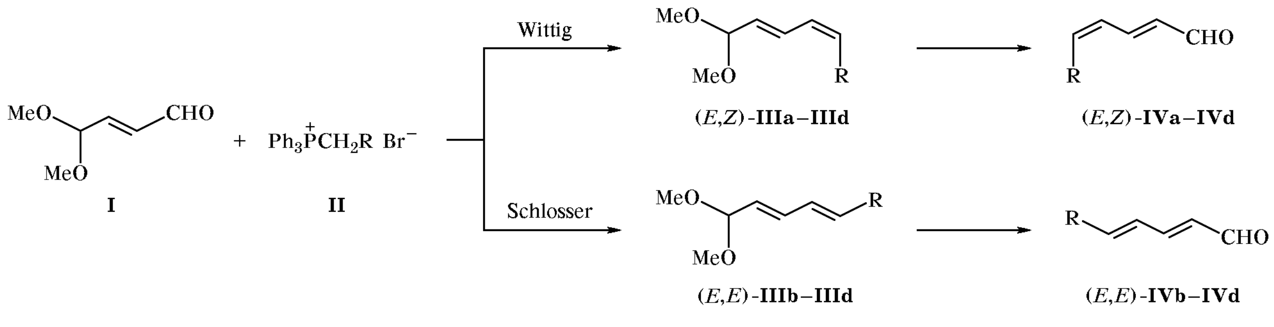
Abstract—Using (2*E*)-4,4-dimethoxy-2-butenal as starting compound, methods were developed for synthesis of (2*E*,4*E*)- and (2*E*,4*Z*)-dimethoxyalkadienes. Deacetalization of the latter gives with high yield the corresponding dienals which are naturally occurring compounds and also synthons for preparation of conjugated dienes as key compounds for building up other natural products.

(2*E*)-4,4-Dimethoxy-2-butenal (**I**) is a convenient building block for synthesis of conjugated dienes. The presence of a double bond having *E*-configuration and latent aldehyde functionality provides the possibility for constructing a diene and polyene fragments which are incorporated into carbon skeleton of various organic compounds and natural molecules, such as undecatrienes, leucotrienes, pheromones, etc. The synthetic potential of compound **I** has been explored insufficiently [1]. This makes (2*E*)-4,4-dimethoxy-2-butenal very promising subject for study. For example, compound **I** was used to synthesize pheromones of the codling moth *Cydia pomonella* and European grapevine moth *Lobesia botrana*, as well as optically active pheromone of the dried bean beetle *Acanthoscelides obtectus* [2, 3].

(2*E*)-4,4-Dimethoxy-2-butenal is involved in the synthesis of conjugated dienes and dienals via Wittig or Schlosser reactions shown in Scheme 1. This scheme turned out to be very convenient for building up functionally substituted conjugated systems.

Initially, we have examined the behavior of butenal **I** in the reaction with phosphonium salts **II** in the presence of various bases; various reaction conditions and reactant ratios were tried (Tables 1, 2). By the Wittig reaction of aldehyde **I** with phosphorane generated from the phosphonium salt $Ph_3\overset{+}{P}CH_2R\,Br^-$ (**II**) by the action of sodium amide (heating in THF under reflux, 1–2 h) we obtained dimethoxydienes (*E*,*Z*)-**III**. The rate of phosphorane generation depends on the solvent (THF) amount. It was necessary to take 1 ml of the solvent per gram of the phosphonium salt.

Scheme 1.



R = Me (**a**), Et (**b**), Pr (**c**), C_5H_{11} (**d**).

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Table 1. Wittig olefination of (2*E*)-4,4-dimethoxy-2-butenal **(I)**

Product no.	Method	Isomer ratio *E*,*Z* : *E*,*E* (*E*,*Z* : *E*,*E* : X : Y),[a] %	Overall yield, %
IIIa	A^b	– (93.0 : 0 : 0 : 7.0)	70
IIIb	A^b	95.0 : 1.5 –	73
IIIc	A^b	98.5 : 1.5 (92.0 : 1.4 : 6.6 : 0)	66
IIId	A^b	99.4 : 0.4 (96.6 : 0.6 : 1.7 : 0.9)	60
IIIa	A'^c	– (94.0 : 0 : 0 : 6.0)	82
IIIb	A'^c	96.0 : 4.0 (96.0 : 4.0 : 0 : 0)	90
IIIc	A'^c	94.0 : 6.0 (87.2 : 5.5 : 7.3 : 0)	88
IIId	A'^c	99.4 : 0.6 (91.6 : 0.5 : 6.3 : 1.6)	86
IIIa	B^d	– (99.6 : 0 : 0 : 0.4)	78
IIIb	B^d	92.0 : 8.0 –	88
IIIc	B^d	93.1 : 6.9 (85.0 : 6.4 : 7.7 : 0)	72
IIId	B^d	98.4 : 1.6 (94.0 : 1.5 : 8.1 : 0)	79
IIIc	B'^e	80.0 : 20.0 (77.0 : 20.0 : 3.0 : 0)	75
IIId	B'^e	87.0 : 13.0 (84.0 : 12.0 : 4.0 : 0)	73

[a] X and Y are likely to be (*Z*,*Z*)- and (*Z*,*E*)-dimethoxydienes **III**; the ratios were quantitated from the GLC data.

[b] Method *A*: $NaNH_2$, –78°C, 1 h.

[c] Method *A*′: $NaNH_2$, 0°C, 30 min.

[d] Method *B*: C_4H_9Li, –78°C, 30 min.

[e] Method *B*′: C_4H_9Li, 0°C, 30 min.

The effect of temperature was studied using sodium amide as a base. Addition of aldehyde **I** at –78°C (method *A*) to the phosphorane generated from salt **II** leads to formation of 60–73% of a mixture of (*E*,*Z*)- and (*E*,*E*)-dimethoxydienes **III**, the fraction of the *E*,*Z*-isomer being 93–98.5%. This follows from the ^1H, ^{13}C, and two-dimensional NMR spectra, as well as from GLC analysis using an HP-5 column. The 3-H signal from isomer (*E*,*E*)-**IIIa** appears in the ^1H NMR spectrum at δ 6.27 ppm, and the same signal from (*E*,*Z*)-**IIIa**, at δ 6.63 ppm.

The length of the hydrocarbon chain in salt **II** does not essentially affect the isomer ratio of products **III**. By varying the salt-to-base ratio from 1 : 1 to 1 : 1.5 we found that the best results were obtained at a ratio of 1 : 1.3, the stereoisomeric composition of the products remaining almost unchanged. Similar results were obtained when the reaction was carried out at 0°C (Table 1, method *A*′): the yield of isomeric (*E*,*Z*)- and (*E*,*E*)-dimethoxydienes **III** was greater (82–90%), and their stereoisomeric purity was 94–99%. Comparison of our data with those reported in [4] shows that the temperature factor is not essential.

With the use of butyllithium instead of sodium amide (Table 1, method *B*) at –78°C in THF, 72–88% of isomeric dienes **III** was formed, the *E*,*Z* isomer prevailing (stereoisomeric purity 93–99%). These data differ from those given in [5], according to which the isomer ratio *E*,*Z* : *E*,*E* is 55 : 45. Raising the temperature to 0°C (Table 1, method *B*′) does not lead to appreciable change in the product yield but strongly affects their stereoisomeric composition (80 : 20) due to increase of the fraction of (*E*,*E*)-**III**. In analogous reaction with butyllithium at –30°C or 0°C in THF the isomer ratio *E*,*Z* : *E*,*E* was 85 : 15 [4, 6]. The products were purified by column chromatography on silica gel. Dimethoxydienes underwent considerable deacetalization during chromatographic purification; therefore, the isolated products contained the corresponding dienals. To avoid deacetalization, silica gel was replaced by neutral aluminum oxide. In this case we succeeded in isolating isomeric dimethoxydienes **III** in the pure form.

Thus, the Wittig reaction of (2*E*)-4,4-dimethoxy-2-butenal in the presence of sodium amide, butyllithium, and sodium silazide [2] can be recommended for the synthesis of (*E*,*Z*)-dimethoxyalkadienes.

It was also interesting to involve (2*E*)-4,4-dimethoxy-2-butenal in the Schlosser reaction with the goal of obtaining (*E*,*E*)-dimethoxydienes. It is known that the use of a double amount of base in the Wittig reaction increases several times the yield of the *E* isomer [4] and that in some cases the *E* isomer becomes the major product [7–9]. As follows from the data in Table 2, the reaction performed at –78°C affords mixtures of (*E*,*E*)-dienes **III** with the corresponding (*E*,*Z*)-isomers, the fraction of the former attaining 90–96% (yield 57–85%). With phosphonium salt **IIc** as an example we examined the effect of the temperature and reaction time. No appreciable change in the product yield and isomeric composition was observed in the reactions performed at –78, –50, and –20°C, the reaction time being varied from 20 min to 1.5 h. However, after 2 h, the yield increased to 66%, and the fraction of the (*E*,*E*)-isomer decreased to 94%. These data indicate that the Schlosser reaction of (2*E*)-4,4-dimethoxy-2-butenal can successfully be applied to synthesis of (2*E*,4*E*)-4,4-dimethoxyalkadienes.

Our further study was aimed at elucidating the course of deacetalization of dimethoxydienes **III** (Table 3). The reaction in acetone in the presence of a catalytic amount of *p*-toluenesulfonic acid at 0°C was accompanied by appreciable change of configuration of the (4*Z*)-double bond. The ratio of (*E*,*Z*)- and (*E*,*E*)-dienals obtained from compound **IIIc** was 83 : 17 against the initial ratio 98 : 2. In the ^{1}H NMR spectrum of aldehyde **IVc** the 3-H signals were observed at δ 6.74 (*E*,*E*) and 7.30 ppm (*E*,*Z*) (Tables 4–6). We also examined the effect of temperature and solvent nature on the reaction direction. In the reaction with acetal **IIId** raising the temperature from –10 to 20°C led to isomerization toward dienal (*E*,*E*)-**IV**; its fraction increased from 29 to 89%. According to published data [10, 11], this isomer is thermodynamically more stable. The hydrolysis of acetal **IIId** in acetone with an equimolar amount of water (20°C, 15 min) also gave a 89% fraction of isomer (*E*,*E*)-**IV**. The *cis–trans*-isomerization is essentially suppressed by adding diethyl ether: the fraction of the *E*,*E* isomer decreases to 24% when the ether–acetone ratio is 2.5 : 1. We also succeeded in avoiding the isomerization completely by raising the acetone–water ratio to 2.5 : 1 and excluding diethyl ether from the solvent mixture. As a result, the ratio of (*E*,*Z*)-**IV** and (*E*,*E*)-**IV** became 93 : 7 against the initial fraction of (*E*,*Z*)-**III** equal to 99%. However, increase in the reaction time from 15 to 60 min, as well as addition of further portions of water (to an acetone–water ratio of 2 : 1), had no appreciable effect at room temperature. Deacetalization of dimethoxydiene **IIIc**, which was obtained by the Schlosser reaction, gave aldehyde (*E*,*E*)-**IV** with a stereoisomeric purity of 97% (after chromatographic purification) in 90% yield.

It should be noted that products of both Wittig and Schlosser reactions, apart from the major *E*,*E* and *E*,*Z* isomers, contained two more substances (according to the GLC data). Taking into account published data [4, 8], these substances are most likely to be (*Z*,*Z*)- and (*Z*,*E*)-dimethoxydienes **III**. The reaction mixture obtained after deacetalization contained only isomeric alkadienes (*E*,*Z*)-**IV** and (*E*,*E*)-**IV** (GLC and NMR data). Despite a very small difference in R_f values between isomers (*E*,*Z*)-**IV** and (*E*,*E*)-**IV** (Table 7), we succeeded in effectively separating them by column chromatography. For compound **IVc**, the *E*,*Z*/*E*,*E* isomer ratio (after deacetalization) was 87 : 13. By column chromatography on silica gel we isolated two fractions. The first of these contained 91% of the (*E*,*Z*)-aldehyde (yield 86%), and in the second fraction the major isomer was *E*,*E* (85%, yield 9%); overall yield 95%.

Table 2. Schlosser olefination of (2*E*)-4,4-dimethoxy-2-butenal (**I**)

Product no.	Temp., °C	Time, h	Isomer ratio *E*,*Z* : *E*,*E* (*E*,*Z* : *E*,*E* : X : Y),[a] %	Overall yield, %
IIIb	–78	1	95.6 : 4.4 (88.5 : 4.1 : 2.3 : 5.1)	85
IIIc	–78	0.3	93.0 : 7.0 (87.6 : 6.6 : 1.8 : 3.8)	56
IIIc	–78	1	96.0 : 4.0 (90.3 : 3.7 : 0.9 : 5.1)	61
IIIc	–78	1.5	95.7 : 4.3 (88.9 : 5.1 : 3.7 : 2.3)	60
IIIc	–50	1	95.1 : 4.9 (89.0 : 5.3 : 0 : 5.6)	64
IIIc	–20	1	95.6 : 4.4 (91.9 : 4.3 : 0 : 3.8)	61
IIIc	–20	2	93.6 : 6.4 (84.0 : 7.7 : 0 : 6.5)	66
IIId	–78	1	90.0 : 10.0 (83.7 : 9.3 : 0 : 7.0)	57

[a] X and Y are likely to be (*Z*,*Z*)- and (*Z*,*E*)-dimethoxydienes **III**; the ratios were quantitated from the GLC data.

Alkadienals **IV** attract considerable interest not only as naturally occurring compounds but also as synthons for design of natural products. (2*E*,4*Z*)-Hexa-, -octa-, -nona-, and -decadienals are among 21 aldehydes constituting volatile components of black and green tea [12, 13]. (2*E*,4*Z*)-Heptadienal was detected in tomato flowers and cranberry [13–15]; this compound and its (2*E*,4*E*)-isomer are volatile components responsible for a specific odor of yellow–green algae *Uroglena americana* which causes florescence of water [16, 17]. (2*E*,4*Z*)-Nonadienal was found in potato [13]; (2*E*,4*Z*)-decadienal is a fragrant component of carrot and green nut flowers [14, 15] and also a component of natural codling moth pheromone [18]; the corresponding (2*E*,4*E*)-isomer is a volatile component determining the odor of *Prunus armeniaca* [19]. (2*E*,4*Z*)-Decadienal was also detected in pepper, tomato, potato, boiled apples, bread, and cranberry [12, 14, 15].

Thus, our results demonstrate the possibility for successful application of (2*E*)-4,4-dimethoxy-2-

Table 3. Deacetalization of dimethoxydienes **III**

Compound no.	Temperature, °C	Time, min	Ratio (*E*,*Z*)-**IV**:(*E*,*E*)-**IV**, % (GLC)	Solvent	Overall yield, %
IIIa	0 to –5	20	83:17	Acetone[a]	70
IIIb[b]	–40	180	85:15	Acetone[a]	95
IIIb[b]	–20	20	85:15	Acetone[a]	95
IIIc[c]	0 to –5	20	83:17	Acetone[a]	82
IIId[b]	0 to –5	20	26:74	Acetone[a]	81
IIId[c]	–10	30	71:29	Acetone[a]	72
IIId[d]	20	15	11:89	Acetone[a]	–
IIId[d]	20	15	76:24	Acetone–ether,[a] 2.5:1	–
IIId[d]	20	15	93:7	Acetone–water, 2.5:1	–
IIIb[d]	20	15	83:17	Acetone–water, 2.5:1	–
IIIb[d]	20	60	86:14 (95:5)[e]	Acetone–water, 2.5:1	–
IIIb[d]	20	5	86:14 (91:9)[e]	Acetone–water, 2:1	–
IIIc[d]	20	10	87:13	Acetone–water, 2:1	–
IIIc[f]	20	10	7:93 (3:97)[e]	Acetone–water, 2:1	90

[a] Equimolar amount of water. The initial *E*,*Z*:*E*,*E* ratio is given in Table 1.
[b] Method *A*.
[c] Method *B*.
[d] Method *A*′.
[e] Isomer ratio after chromatographic separation.
[f] Initial *E*,*Z*:*E*,*E* ratio 96:4.

butenal as a building block for synthesis of 4,4-dimethoxy-2,4-alkadienes and the corresponding 2,4-alkadienals.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-250 (250 MHz; C_6D_6–$CDCl_3$, 80:20 by volume) and Varian Mercury-300* spectrometers [300 MHz, acetone-d_6, aldehyde (*E*,*E*)-**IV**] using TMS as internal reference. The IR spectra were recorded on a UR-20 spectrometer. GLC analysis was performed on a Chrom-5 chromatograph equipped with a flame-ionization detector (glass capillary column, 25 m × 0.2 mm, stationary phase SE-30, carrier gas nitrogen, flow rate 30 ml/min). Silica gel (L 40/100 μm) and aluminum oxide (neutral, L 40/250 μm) were used for column chromatography. TLC was performed on Silufol UV-254 plates; spots were visualized by treatment with iodine vapor and a solution of $KMnO_4$.

Wittig olefination. *Methods A and A*′. Alkyltriphenylphosphonium bromide (**II**), 10 mmol, was added to a mixture of 13 mmol of sodium amide in 4 ml of dry ether, stirred under argon at 20°C. The mixture was refluxed for 1 h and cooled to –78°C (or 0°C), and a solution of 10 mmol of aldehyde **I** in 5 ml of dry THF was added dropwise. The mixture was stirred for 0.5 h at –78°C (or 0°C), allowed to slowly warm up to room temperature, poured into 50 ml of ice water, and extracted with ether–hexane, 1:1. The extract was dried over anhydrous sodium sulfate and evaporated, and the residue was subjected to column chromatography on neutral aluminum oxide. Some physical and spectral properties of the isolated dimethoxydienes **III** are given in Tables 1, 4, 5, and 7.

Methods B and B′. To a suspension of 10 mmol of alkyltriphenylphosphonium bromide **II** in 5 ml of dry THF we added dropwise while stirring under argon at 20°C 10 ml of a 1 N solution of butyllithium in hexane. The mixture was stirred for 1 h at 20°C and cooled to –78°C (or 0°C), and a solution of 10 mmol

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Table 4. ^{1}H NMR spectra (δ, ppm) of dimethoxydienes **III**[a–c]

Comp. no.	Isomer	1-H	2-H	3-H	4-H	5-H	OCH_3	R
IIIa [2]	2*E*,4*Z*	4.79	5.55	6.63	5.97	5.53	3.24	1.70
	2*E*,4*E*	4.79	5.44	6.27	6.00	5.69	3.22	1.70
IIIb	2*E*,4*Z*	4.79	5.51	6.60	5.92	5.46	3.24	0.94, 2.15
	2*E*,4*E*	4.74	5.46	6.27	5.98	5.73	3.23	0.95, 2.03
IIIc	2*E*,4*Z*	4.81	5.57	6.66	6.00	5.48	3.24	0.97, 1.36, 2.13
	2*E*,4*E*	4.77	5.50	6.30	6.00	5.69	3.23	0.96, 1.36, 2.00
IIId	2*E*,4*Z*	4.83	5.58	6.63	5.98	5.50	3.28	0.88, 1.30, 2.18
	2*E*,4*E*						3.27	

[a] The chemical shifts are given relative to TMS; solvent C_6D_6–$CDCl_3$ (volume ratio 3:1); room temperature.

[b] The vicinal coupling constants for all compounds are as follows: $J_{1,2} \approx 5.0$, $J_{2,3} \approx 15.5$, $J_{3,4} \approx 11.2$, $J_{4,5} \approx 11.1$ Hz (2*E*,4*Z*), $J_{4,5} \approx 15.0$ Hz (2*E*,4*E*).

[c] The signals were assigned using two-dimensional NMR techniques (^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY, and TOCSY).

Table 5. ^{13}C NMR spectra (δ_C, ppm) of dimethoxydienes **III**[a, b]

Comp. no.	Isomer	C^1	C^2	C^3	C^4	C^5	OCH_3	R
IIIa	2*E*,4*Z*	102.64	128.49	128.63	128.19	128.34	52.4	13.36
	2*E*,4*E*	102.69	126.21	133.90	130.39	131.46	52.4	18.06
IIIb	2*E*,4*Z*	102.56	126.51	133.97	128.08	138.30	52.3	14.03, 21.03
	2*E*,4*E*	102.69	128.76	128.65	127.43	133.85	52.08	13.20, 25.54
IIIc	2*E*,4*Z*	102.36	128.76	128.65	127.43	133.85	52.08	13.48, 22.56, 29.61
	2*E*,4*E*	102.50	126.48		129.17	136.49	52.08	13.48, 22.13, 34.53
IIId	2*E*,4*Z*	102.46	128.81	128.96	127.22	134.23	52.18	13.88, 22.41, 27.63, 29.13, 31.30
	2*E*,4*E*	102.58	126.39	133.94	128.57	136.89	51.95	13.88, 22.41, 28.69, 31.25, 32.49

[a] The chemical shifts were measured in C_6D_6–$CDCl_3$ (3:1, by volume) at room temperature relative to TMS.

[b] The signals were assigned using two-dimensional NMR techniques (^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY, and TOCSY).

Table 6. ^{1}H NMR spectra (δ, ppm) of dienals **IV**[a–c]

Comp. no.	Isomer	1-H	2-H	3-H	4-H	5-H	R
IVb [15]	2*E*,4*Z*	9.42	5.93	7.22	6.05	5.79	0.91, 2.18
	2*E*,4*E*	9.36	5.93	6.82	5.95	6.10	0.91, 2.07
IVc	2*E*,4*Z*	9.45	5.95	7.30	6.02	5.75	0.83, 1.32, 2.21
	2*E*,4*E*	9.42		6.74	5.90	6.10	0.83, 1.35, 1.98
IVd [15]	2*E*,4*Z*	9.41	5.97	7.19	5.98	5.75	0.81, 1.20, 2.16
	2*E*,4*E*	9.35	5.92	6.76	6.05	6.00	0.81, 1.20, 2.02
IVc[d]	2*E*,4*E*	9.55	6.05	7.23	6.40	6.35	0.93, 1.50, 2.22

[a] The chemical shifts are given relative to TMS; solvent C_6D_6–$CDCl_3$ (volume ratio 3:1) or acetone-d_6 for (*E*,*E*)-**IVc**; room temperature.

[b] The vicinal coupling constants for all compounds are as follows: $J_{1,2} \approx 8.0$, $J_{2,3} \approx 15.0$, $J_{3,4} \approx 10.0$, $J_{4,5} \approx 10.8$ Hz (2*E*,4*Z*), $J_{4,5} \approx 15.2$ Hz (2*E*,4*E*).

[c] The signals were assigned using two-dimensional NMR techniques (^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY, and TOCSY).

[d] (*E*,*E*)-Isomer of **IVc**.

Table 7. GLC and TLC data and IR spectra of methoxydienes **III** and dienals **IV**

Comp. no.	Retention time, min (oven temperature, °C) Y : *E,Z* : X : *E,E*	R_f[a] *E,Z* : *E,E*	IR spectrum, ν, cm^{-1}
IIIa	10.43 : 11.04 : 0 : 0 (92)	0.23	970, 1065, 1080, 1130, 1160, 1195, 1620, 1660
IIIb	15.64 : 16.38 : 0 : 17.70 (90)	0.25	960, 1060, 1075, 1125, 1160, 1195, 1620, 1650
IIIc	17.02 : 17.76 : 18.28 : 19.48 (102)	0.27	970, 1065, 1080, 1095, 1110, 1130, 1180, 1195, 1630, 1670
IIId	17.19 : 18.64 : 19.71 : 21.36 (125)	0.32	980, 1030, 1070, 1110, 1190, 1620, 1660
IVa	0 : 9.6 : 0 : 0 (80)	0.10	975, 1600, 1620, 1680, 2710
IVb [13]	0 : 8.73 : 0 : 0 (90)	0.12 : 0.10	957, 1010, 1595, 1620, 1680, 2720
IVc	0 : 11.21 : 0 : 11.31 (102)	0.19 : 0.13	975, 1600, 1630, 1680, 2720
IVd [13]	0 : 11.96 : 0 : 12.73 (125)	0.24 : 0.18	980, 1600, 1628, 1675, 2730

[a] Eluent ether–hexane, 1 : 10.

of aldehyde **I** in 6 ml of dry THF was added dropwise. The mixture was stirred for 1 h at –78°C or for 30 min at 0°C and was treated as described above in *A* and *A'*. Some physical properties and spectral parameters of the resulting dimethoxydienes **III** are given in Tables 1, 4, 5, and 7.

Schlosser olefination. To a suspension of 10 mmol of alkyltriphenylphosphonium bromide **II** in 24 ml of anhydrous THF and 12 ml of dry ether, stirred at 20°C under argon, we added dropwise 9.1 ml of a 1.1 N solution of butyllithium in hexane (10 mmol). The mixture was kept for 1 h at that temperature and cooled to –78°C, and a solution of 10 mmol of aldehyde **I** in 12 ml of anhydrous THF and 6 ml of dry ether was added dropwise. The mixture was stirred for 30 min at –78°C, 10 mmol of anhydrous methanol was added dropwise, and 1 h after the temperature was raised to 0°C. The mixture was then treated as described above. The physical properties and spectral parameters of the isolated products are given in Tables 2, 4, 5, and 7.

Deacetalization of dimethoxydienes (III). To a mixture of 1.2 g (7 mmol) of dimethoxydiene **III**, 10 ml of acetone, and 5 ml of water we added 36 mg (0.2 mmol) of *p*-toluenesulfonic acid. The mixture was stirred for 10 min at 20°C (the progress of the reaction was monitored by TLC) and neutralized with sodium carbonate, acetone was evaporated, the mixture was extracted with ether, and the extract was dried over sodium sulfate. The solvent was removed, and the residue was subjected to column chromatography using hexane–ether (10 : 1) as eluent. The first fraction was 750 mg (86%) of a mixture of (*E,Z*)- and (*E,E*)-dienals **IV** at a ratio of 91 : 9; the second fraction was 80 mg (9%) of a mixture of (*E,Z*)- and (*E,E*)-dienals **IV** at a ratio of 15 : 85. Overall yield of isomeric dienals **IVc** 95% (Tables 3, 6, 7).

REFERENCES

1. Gree, R., Tourbah, H., and Carrie, R., *Tetrahedron Lett.*, 1986, vol. 27, no. 41, pp. 4983–4986; Meyers, A.I. and Brinkmeyer, R.S., *Tetrahedron Lett.*, 1975, no. 21, pp. 1749–1752.
2. Khrimyan, A.P., Ovanesyan, A.L., Streinz, L., Svatos, A., Khrimyan, E.P., Makaryan, G.M., and Badanyan, Sh.O., *Zh. Bioorg. Khim.*, 1992, vol. 18, no. 7, pp. 969–978.
3. Khrimian, A.P., Ovanessian, A.L., Streinz, L., Svatos, A., Romanuk, M., and Badanian, Sh.H., *Proc. Conf. on Insecticide Chemistry and Ecology*, Tabor, 1990, pp. 137–140.
4. Ideses, R. and Shani, A., *Tetrahedron*, 1989, vol. 45, no. 11, pp. 3523–3534.
5. Naff, F., Decorzant, R., Thommen, W., Willhalm, B., and Ohloff, G., *Helv. Chim. Acta*, 1975, vol. 58, nos. 109–110, pp. 1016–1037.
6. Ohloff, G. and Pawlak, M., *Helv. Chim. Acta*, 1973, vol. 56, no. 3, pp. 1176–1179.
7. Li Han-Dong, Deng Jan-Neng, Xu Han-Sbeog, Iao Li, and Qu Hai-Sheng, *Chin. J. Org. Chem.*, 1988, vol. 8, no. 2, pp. 167–168.
8. Kovalev, B.G., Rastegaeva, V.M., Kurts, A.L., and Bundel', Yu.G., *Zh. Org. Khim.*, 1986, vol. 22, no. 9, pp. 1818–1824.
9. Christmann, K.F., *Synthesis*, 1969, no. 1, pp. 38–39.
10. Viola, A. and MacMillan, J.H., *J. Am. Chem. Soc.*, 1970, vol. 92, no. 8, pp. 2404–2410.
11. Ingham, S., Turner, R.W., and Wallace, T.W., *J. Chem. Soc., Chem. Commun.*, 1985, no. 23, pp. 1664–1666.
12. Renold, W., Naf-Muller, R., Keller, U., Wilhalm, B., and Ohloff, G., *Helv. Chim. Acta*, 1974, vol. 57, no. 144, pp. 1301–1308.

13. Naf, F. and Decorzant, R., *Helv. Chim. Acta*, 1974, vol. 57, no. 145, pp. 1309–1317.
14. Goldbach, M., Jakel, E., and Schneider, M.P., *J. Chem. Soc., Chem. Commun.*, 1987, no. 19, pp. 1434–1435.
15. Tsuboi, S., Masuda, T., and Takedo, A., *J. Org. Chem.*, 1982, vol. 47, no. 23, pp. 4478–4482.
16. Nakahara, M., Takano, R., Ito, H., Yano, H., Hirase, S., and Harimaya, K., *J. Agric. Chem. Soc. Jpn.*, 1988, vol. 62, no. 2, pp. 157–159; *Ref. Zh., Khim.*, 1989, no. 6 E 379.
17. Hara, T., Kubota, E., and Horita, H., *J. Agric. Chem. Soc. Jpn.*, 1987, vol. 61, no. 4, pp. 471–473; *Ref. Zh., Khim.*, 1988, no. 14 R 436.
18. Einhorn, J., Beauvais, J., Gallois, M., Descoins, Ch., and Chausse, R., *C.R. Acad. Sci.*, 1984, vol. 299, no. 19, pp. 773–778.
19. Takeoka, E.R., Flath, R.A., Mon, T.R., Teranishi, R., and Euenert, M., *J. Agric. Food Chem.*, 1990, vol. 38, no. 2, pp. 471–477; *Ref. Zh., Khim.*, 1990, no. 20 E 16.