ω-Halogeno polyenals: preparation and application to a one-pot synthesis of polyenals from carbonyl compounds

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Syntheses of 5-halogeno-2,4-dienals 1a–c are described starting either from the glutaconaldehyde potassium salt or from furan. The 5-bromopenta-2,4-dienal 1b can be transformed efficiently into homologous ω-bromo polyenals 2–4, precursors of ω-bromo polyenol ethers 5b,d, 6 and 7. After bromine–lithium exchange, followed by condensation with carbonyl compounds, 1-bromo-6-methoxyhexa-1,3,5-triene 5b, 1-bromo-8-methoxyocta-1,3,5,7-tetraene 6 and 1-bromo-10-methoxydeca-1,3,5,7,9-pentene 7 lead to various conjugated tri-, tetra- and penta-enals in good yields, in a one-pot procedure.

Introduction

ω-Halogeno polyenals can be considered as valuable intermediates owing to their reactive terminal functions, but only a few compounds in this family have been described.[1–4] 3-Bromo-2-methylpropenal[1] and its homologues[1c,d] are useful reagents in terpene synthesis. Although 3-chloro-,[2] 3-bromo-[2b,3] and 3-iodo-propenals[4] have been prepared, only one vinylogue, 5-chloropentadienal **1a**, was previously known.[2b]

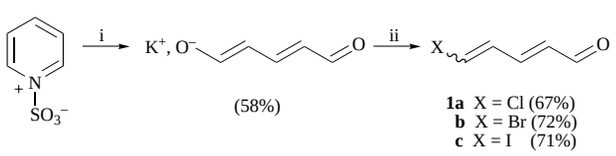
ω-Lithio polyenol ethers conveniently prepared by bromine–lithium exchange are efficient reagents for polyvinylogation of carbonyl compounds.[1d,5] The presence of conjugated linear polyenic chains in various natural products prompted us to develop a new strategy to obtain unsubstituted ω-bromo polyenol ethers starting from ω-halogeno polyenals.[6]

In this work, we report an efficient synthesis of ω-halogeno polyenals **1–4** and their use as precursors for ω-halogeno polyenol ethers **5–7** (Table 1); we illustrate their use in convergent syntheses of polyenals.

Results and discussion

ω-Halogeno polyenals 1–4

We prepared ω-halogenopentadienals **1a–c** from the glutaconaldehyde potassium salt,[6] a compound easily obtained from commercial pyridinium-1-sulfonate and which, unlike the corresponding sodium and ammonium salts, crystallizes without any molecules of water of crystallization.[7] When treated with thionyl dichloride in methylene dichloride, it leads to 5-chloropentadienal **1a** (yield: 67%), previously obtained by reaction of phosgene with glutaconaldehyde sodium salt.[2b] Reaction with triphenylphosphine–bromine complex and triphenylphosphine–iodine complex prepared in CH_2Cl_2 *in situ* yielded bromo- and iodo-pentadienal **1b** and **1c** (yields: 71–72%) (Scheme 1).

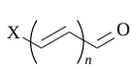


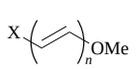
Scheme 1 *Reagents:* i, KOH (ref. 7); ii, $SOCl_2$ or Ph_3PX_2

These aldehydes were obtained as mixtures of 2*E*,4*E* and 2*E*,4*Z* isomers. Following our experimental conditions, isomer 2*E*,4*E* is predominant for bromo and iodo aldehydes **1b** and **1c** while chloro aldehyde **1a** is obtained as a 50:50 mixture. Isomers 2*E*,4*E* and 2*E*,4*Z* can be easily separated by crystallization or by chromatography on silica gel (Table 2).

Starting from pure 2*E*,4*E* and pure 2*E*,4*Z* isomers, we studied their isomerization by ^{1}H NMR spectroscopy in deuteriochloroform ($CDCl_3$) and obtained the same equilibrium state (2*E*,4*E*/2*E*,4*Z* = 50:50) at room temperature after 2 days for the bromo aldehyde **1b** and 8 days for the iodo compound **1c**. In hexadeuteriobenzene (C_6D_6), the isomerization was

Table 1 ω-Halogeno polyenals **1–4** and ω-halogeno polyenol ethers **5–7**





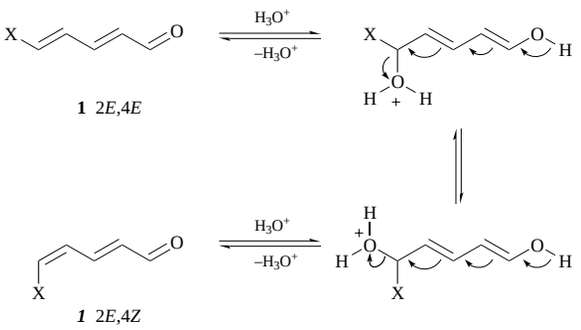
n	2			3	4	5	*n*	3			4	5
X	Cl	Br	I	Br	Br	Br	X	Cl	Br	I	Br	Br
Compound	**1a**	**1b**	**1c**	**2**	**3**	**4**	Compound	**5a**	**5b**	**5c**	**6**	**7**

Table 2 Separation of isomers of halogenopentadienals **1b** and **1c**

	X = Br, **1b**			X = I, **1c**		
	2*E*,4*E* (%)	2*E*,4*Z* (%)	Global yield (%)	2*E*,4*E* (%)	2*E*,4*Z* (%)	Global yield (%)
Starting material	75	25	72[a]	55	45	71[a]
Yield after crystallization	49	19	68[b]	33	29	62[c]
Yield after chromatography	50	18	68	35	29	64

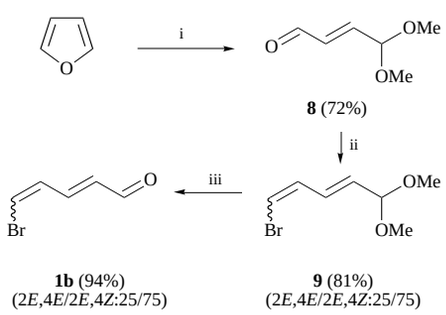
[a] From glutaconaldehyde potassium salt. [b] Crystallization from diethyl ether. [c] Crystallization from light petroleum.

slower for bromo compound **1b** and was not detected for the iodo analogue **1c**. We noticed that when these solvents were dried beforehand on magnesium sulfate, the isomerization was strongly reduced for compound **1b** (<5% after a week) and was not observed for **1c**. Thus an addition–elimination mechanism involving traces of water can be suggested (Scheme 2).



Scheme 2

For the preparation of bromopentadienal **1b**, we envisaged a second approach based on furan (Scheme 3). The known aldo



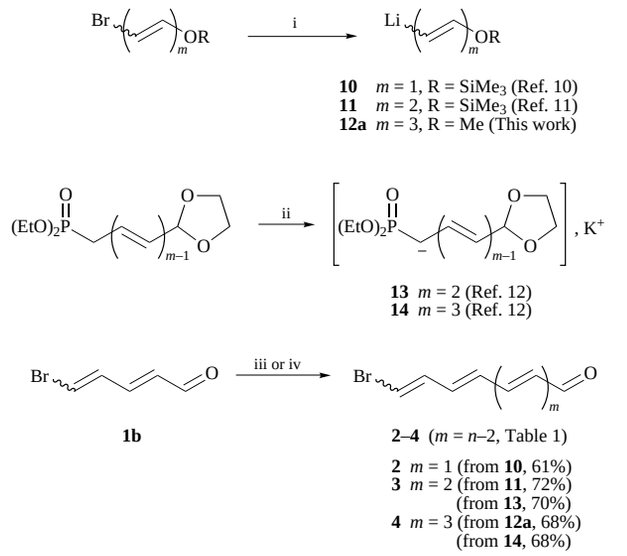
Scheme 3 *Reagents and conditions:* i, Br_2, CH_3OH, Amberlyst 15 (ref. 8); ii, Ph_3P=CHBr, THF, −70 °C; iii, Amberlyst 15, aq. acetone, room temp., 10 min

acetal **8** was obtained as described by R. Grée *et al.*,[8] by brominating furan in methanol and then selectively hydrolysing the resulting furanaldehyde bis(dimethyl acetal). Condensation of aldehyde **8** with bromomethylene(triphenyl)phosphorane generated *in situ* yielded bromo acetal **9** in which the newly formed double bond is predominantly *Z*.[9] Hydrolysis of bromo acetal **9** led to the expected bromopentadienal **1b** (2*E*,4*E*/2*E*,4*Z*: 25/75).

Thus, two routes have proven practical for the synthesis of bromopentadienal **1b**. The first leads mainly to the all-*E* isomer in two steps from commercial pyridinium-1-sulfonate. The second provides mainly the 2*E*,4*Z* isomer in four steps from furan.

The preparation of homologous ω-bromo polyenals **2**–**4** was accomplished by condensation of bromopentadienal **1b** with mono-, di- or tri-vinylogation reagents **10**–**14**. These reagents prepared *in situ* have already been described by us[10–12] (Scheme 4).

Lithio enol ethers **10**, **11** and **12a** were easily obtained from their bromo precursors[10,11] by halogen–metal exchange, whereas metallation of unsaturated phosphonodioxolanes led to reagents **13** and **14**[12] (Scheme 4). The condensation products, *viz*. hydroxy enol ethers (using lithio enol ethers **10**–**12a**) or polyunsaturated dioxolanes (using phosphonodioxolanes **13** and **14**), were easily transformed *in situ*, by mild acidic treatment, into ω-bromo polyenals **2**–**4**, with good yields (Scheme 4). As these ω-bromo polyenals were prepared in view of their potential transformation into bromo polyenol ethers **5**–**7**, we used the starting bromopentadienal **1b** as a mixture of 2*E*,4*E*/2*E*,4*Z* isomers. Indeed, it is well known that the configuration of the bromo enol ethers and consequently of the corresponding lithio reagents is of no importance in the configuration of the

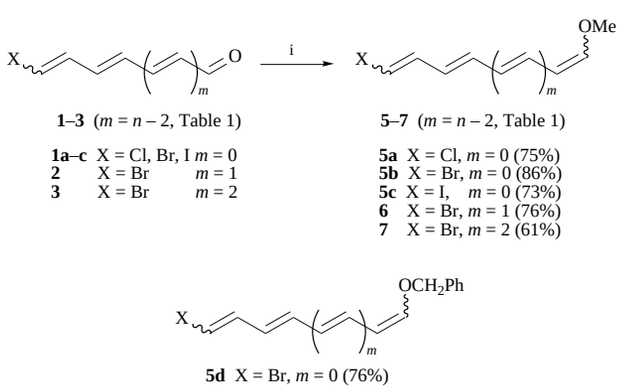


Scheme 4 *Reagents and conditions:* i, Bu^{t}Li, Et_2O, −70 °C; ii, Bu^{t}OK, THF, −70 °C; iii, **10**, **11** or **12a**, Et_2O, −70 °C; 1 M HCl, room temp., 2 h; iv, **13** or **14**, THF, −70 °C; 3 M HCl, 0 °C, 1 h

polyenic aldehyde obtained after condensation.[5c,d] Thus, bromo polyenals **2**–**4** were isolated as mixtures of two isomers, one with an all-*E* configuration and the second with the same all-*E* configuration except for the last carbon–carbon double bond.

ω-Halogeno polyenol ethers 5–7

Access to ω-halogeno polyenol ethers **5**–**7** was attained as follows. ω-Halogeno polyenals **1**–**3** were treated with methoxymethylene(triphenyl)phosphorane prepared *in situ* from commercial methoxymethyl(triphenyl)phosphonium chloride and potassium *tert*-butoxide (Bu^{t}OK), and the resulting methyl bromo polyenol ethers **5**–**7** were isolated after flash chromatography. 1-Benzyloxy-6-bromohexatriene **5d** was similarly prepared from bromopentadienal **1b** and benzyloxymethylene(triphenyl)phosphorane (Scheme 5).



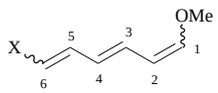
Scheme 5 *Reagents and conditions:* i, Ph_3P=CHOMe, THF, −70 °C

These halogeno enol ethers were obtained as mixtures of four stereoisomers: the last two double bonds were non-controlled, unlike the others which were all-*E*. The newly introduced double bond bearing the alkoxy substituent was mainly *Z*. A complete ^{1}H NMR analysis of 1-halogeno-6-methoxyhexatrienes **5a**–**c** thus prepared is reported in Table 3.

Polyenic aldehydes 17–20

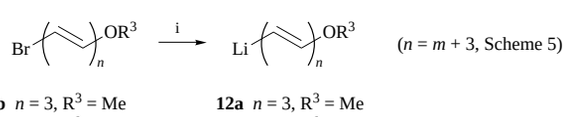
Bromo enol ethers **5b**,**d**, **6** and **7** were treated with *tert*-butyllithium in diethyl ether and transformed into lithio enol ethers **12a**,**b**, **15** and **16**, which were then condensed with aldehydes and ketones at −70 °C. When treated with 1 M HCl solution at room temperature (Scheme 6), the resulting adducts were converted by a dehydration–hydrolysis sequence into polyenic

Table 3 Isomer abundance and ^{1}H NMR data (δ; J/Hz) of the halogeno enol ethers **5a–c** (n = 3)



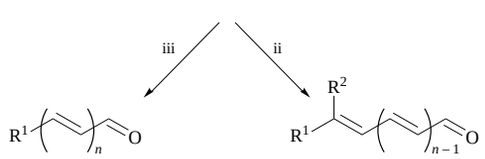
Compound (X)	Isomer (%)	CH_3	H^1	H^2	H^3	H^4	H^5	H^6
5a[a](Cl)	1*Z*,3*E*,5*Z*	3.06	5.57	4.92	6.62	5.78	6.33	6.60
	(29)		*J* 6.1	*J* 6.1; 11.2	*J* 11.2; 15.4	*J* 15.4; 10.8	*J* 10.8; 7.5	*J* 7.5
	1*Z*,3*E*,5*E*	3.04	5.52	5.02	6.80	6.68	6.01	5.58
	(35)		*J* 6.1	*J* 6.1; 11.1	*J* 11.1; 15.3	*J* 15.3; 10.9	*J* 10.9; 13.4	*J* 13.4
	1*E*,3*E*,5*Z*	3.08	6.35	5.32	5.74	5.65	6.32	5.77
	(17)		*J* 12.4	*J* 12.4; 10.5	*J* 10.5; 15.0	*J* 15.3; 11.0	*J* 11.0; 7.4	*J* 7.4
	1*E*,3*E*,5*E*	3.04	6.40	5.37	5.92	6.55	5.95	5.59
	(19)		*J* 12.4	*J* 12.4; 11.1	*J* 11.1; 15.0	*J* 15.0; 11.1	*J* 11.1; 12.8	*J* 12.8
5b[b](Br)	1*Z*,3*E*,5*Z*	3.03	5.52	4.92	6.64	5.72	6.28	6.60
	(18)		*J* 6.0	*J* 6.0; 10.9	*J* 10.9; 15.5	*J* 15.5; 10.8	*J* 10.8; 7.0	*J* 7.0
	1*Z*,3*E*,5*E*	2.99	5.48	5.00	6.89	6.60	6.58	5.83
	(34)		*J* 6.0	*J* 6.0; 11.0	*J* 11.0; 15.5	*J* 15.5; 10.8	*J* 10.8; 14.0	*J* 14.0
	1*E*,3*E*,5*Z*	3.00	6.40	5.32	5.95	6.52	6.28	5.70
	(16)		*J* 12.4	*J* 12.4; 11.2	*J* 11.2; 14.8	*J* 14.8; 10.4	*J* 10.4; 7.2	*J* 7.2
	1*E*,3*E*,5*E*	3.01	6.33	5.29	5.72	6.58	5.60	5.71
	(32)		*J* 12.5	*J* 12.5; 10.6	*J* 10.6; 13.7	*J* 13.7; 11.2	*J* 11.2; 14.9	*J* 14.9
5c[c](I)	1*Z*,3*E*,5*Z*	3.01	5.50	5.00	6.95	6.48	6.41	5.78
	(25)		*J* 6.1	*J* 6.1; 11.2	*J* 11.2; 15.5	*J* 15.5; 10.8	*J* 10.8; 6.9	*J* 6.9
	1*Z*,3*E*,5*E*	3.03	4.90	4.90	6.62	5.75	6.33	6.60
	(24)		*J* 6.1	*J* 6.1; 11.2	*J* 11.2; 15.0	*J* 15.0; 10.8	*J* 10.8; 10.3	*J* 10.3
	1*E*,3*E*,5*Z*	3.01	6.43	5.35	6.02	6.38	6.40	5.77
	(31)		*J* 12.5	*J* 12.5; 11.1	*J* 11.1; 14.1	*J* 14.1; 10.6	*J* 10.6; 7.1	*J* 7.1
	1*E*,3*E*,5*E*	3.06	6.33	5.28	5.70	6.90	5.82	6.90
	(20)		*J* 12.4	*J* 12.4; 10.3	*J* 10.3; 14.3	*J* 14.3; 10.2	*J* 10.3; 10.2	*J* 10.2

[a] Prepared from chloropentadienal **1a** (2*E*,4*E*/2*E*,4*Z*: 50/50). [b] Prepared from bromopentadienal **1b** (2*E*,4*E*/2*E*,4*Z*: 75/25). [c] Prepared from iodopentadienal **1c** (2*E*,4*E*/2*E*,4*Z*: 55/45).



5b n = 3, R^3 = Me
5d n = 3, R^3 = CH_2Ph
6 n = 4, R^3 = Me
7 n = 5, R^3 = Me

12a n = 3, R^3 = Me
12b n = 3, R^3 = CH_2Ph
15 n = 4, R^3 = Me
16 n = 5, R^3 = Me



17$_3$ n = 3, R^1 = Ph (62% from **12a**) (64% from **12b**)
17$_4$ n = 4, R^1 = Ph (59%)
17$_5$ n = 5, R^1 = Ph (69%)
18$_4$ n = 4, R^1 = Pr^i (56%)
18$_5$ n = 5, R^1 = Pr^i (59%)

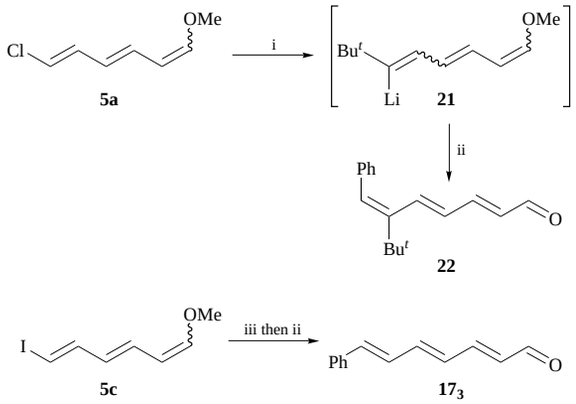
19$_4$ n = 4, R^1,R^2 = $[CH_2]_5$ (56%)
19$_5$ n = 5, R^1,R^2 = $[CH_2]_5$ (60%)
20$_4$ n = 4, R^1 = Ph, R^2 = Me (54%)
20$_5$ n = 5, R^1 = Ph, R^2 = Me (50%)

Scheme 6 *Reagents and conditions:* i, Bu^{t}Li, Et_2O, −70 °C; ii, R^1COR^2, 1 M HCl, room temp.; iii, R^1CHO, 1 M HCl, room temp.

aldehydes **17**–**20**. These polyenals were isolated with an all-*E* configuration (**17**–**19** from aldehydes or symmetric ketones) or predominantly *E* configuration (**20** from dissymmetric ketones).

1-Lithio-6-methoxyhexatriene **12a** and 1-benzyloxy-6-lithiohexatriene **12b** have the same behaviour as analogous 1-ethoxy-6-lithiohexatriene, previously reported,[5c,d] and allow the direct trivinylogation of carbonyl compounds. Moreover, it confirms that the configuration of the starting bromo enol ether is not of prime importance for this type of reaction. Indeed, the proportions of the stereoisomers of 1-bromo-6-ethoxyhexatriene (1*E*,3*E*,5*E*/1*Z*,3*E*,5*E*/1*E*,3*E*,5*Z*/1*Z*,3*E*,5*Z*: 12/12/33/43), precursors to 1-ethoxy-6-lithiohexatriene, were different from those of methyl and benzyl bromo enol ethers **5b** and **5d**, precursors to reagents **12a** and **12b**. However, the yields of the condensation with benzaldehyde are similar. Such one-pot trivinylogation reagents[13] reacting with enolizable carbonyl compounds and with ketones as well as with aldehydes are not frequently observed.[13a] We have recently provided an illustration of the synthetic potential of these reagents by applying them to one-pot syntheses of navenones A, B and C from aromatic aldehydes.[13b] To our knowledge lithio enol ethers **15** and **16** are the first reagents reported for the direct tetravinylogation[14] and pentavinylogation[15] of carbonyl compounds.

Finally, chloro- and iodo-(methoxy)hexatrienes **5a** and **5c** were treated with alkyllithiums. No halogen–lithium exchange could be observed with chloro polyenol ether **5a** but instead a metallation reaction took place and the resulting carbenoid reacted with Bu^{t}Li, leading to a new alkylated



Scheme 7 *Reagents and conditions:* i, Bu^{t}Li, Et_2O, −70 °C; ii, PhCHO, 1 M HCl, room temp.; iii, Bu–Li, Et_2O, −70 °C

lithium polyenol ether **21**, which after condensation with benzaldehyde yielded polyene aldehyde **22** with an all-*E* configuration. On the other hand, iodo polyenol ether **5c** smoothly gave the exchange when treated with butyllithium in Et_2O and the resulting anion **12a** led to the expected phenylheptatrienal **17$_3$** in 68% yield, after reaction with benzaldehyde and work-up (Scheme 7).

Conclusions

Halogenopentadienals **1** are valuable intermediates for the synthesis of compounds with long polyenic chains. Especially worthy of note is bromopentadienal **1b**, a starting material for homologous polyenals **2**–**4** and for bromo enol ethers **5**–**7** which are precursors to powerful tri-, tetra- and penta-vinylogation reagents of carbonyl compounds.

Experimental

General

IR spectra were recorded on a Perkin-Elmer FT IR 16 PC spectrometer as thin films. Mass spectra were recorded on a JEOL JMS AX 500 mass spectrometer (EI: electronic impact; CI: chemical ionization with CH_4) at 30 to 70 eV. NMR spectra were obtained for solutions in $CDCl_3$ unless otherwise stated, with a Bruker AM 400 MHz operating at 400 MHz for proton and at 100 MHz for carbon, or a Bruker AC 200 operating at 200 MHz for proton spectra. No $SiMe_4$ was added; rather, shifts were referenced to the line for $CDCl_3/CHCl_3$ (chemical shifts in ppm and coupling constants *J* in Hz). UV spectra were recorded on a Kontron Uvikon 940 ($CHCl_3$ as solvent except where stated otherwise), ε values are given in units of $dm^3\ mol^{-1}\ cm^{-1}$. All reactions were carried out under dry Ar. TLC was performed on silica gel 60F-254 plates. Flash chromatography was performed with Merck Kieselgel 60 (over 230–400 mesh ASTM) support with light petroleum (distillation temp. <60–65 °C)–diethyl ether mixtures as eluent. Microanalyses were performed by INSA Laboratories, Rouen. Mps were measured on a Reichert-Jung microscope and are uncorrected. Solvents were purified, when necessary, according to standard procedures.

5-Chloropenta-2,4-dienal 1a

To a mixture of glutaconaldehyde potassium salt[7] (2.3 g, 17.6 mmol) in CH_2Cl_2 (80 ml) at 0 °C was added thionyl chloride (3.2 g, 27 mmol) as a solution in CH_2Cl_2 (20 ml). The mixture was warmed to room temperature and stirred for 12 h. Then, after being cooled to 0 °C, the mixture was treated with aq. $NaHCO_3$ (5% w/v; 50 ml). After extraction of the aqueous layer with CH_2Cl_2 (3 × 20 ml), the organic layer was dried ($MgSO_4$). Evaporation gave a crude product, which was chromatographed over silica gel [light petroleum (distilled 50–65 °C)–Et_2O (70/30 v/v)]. 5-Chloropenta-2,4-dienal **1a**[2b] was obtained as a yellow solid (1.4 g, 67%) (2*E*,4*E*/2*E*,4*Z*: 50/50), mp 48 °C; ν_{max} 1680 and 1625 cm^{-1}; δ_H 2*E*,4*E*: 50% 6.15 (dd, *J* 7.7 and 15.3, 2-H), 6.70 (dd, *J* 9.6 and 11.1, 4-H), 6.72 (d, *J* 11.1, 5-H), 7.03 (dd, *J* 15.3 and 9.6, 3-H) and 9.58 (d, *J* 7.7, 1-H); δ_C 131.16 (d, C-5), 131.69 (C-4), 132.00 (C-2), 146.89 (C-3) and 193.11 (C-1); δ_H 2*E*, 4*Z*: 50% 6.24 (dd, *J* 8.1 and 15.3, 2-H), 6.49 (d, *J* 7.1, 5-H), 6.58 (dd, *J* 10.3 and 7.1, 4-H), 7.51 (dd, *J* 15.3 and 10.3, 3-H) and 9.62 (d, *J* 8.1, 1-H); δ_C 127.72 (d, C-4), 128.36 (C-5), 133.87 (C-2), 143.49 (C-3) and 193.63 (C-1); *m*/*z* 118–116 ($M^{\bullet+}$, 45%) and 81 ($M^{\bullet+}$ − Cl, 100) (Found: M^+, 117.9997–116.0031. C_5H_5ClO requires M, 118.0000–116.0031) (Found: C, 51.53; H, 4.12. C_5H_5ClO requires C, 51.28; H, 4.27%).

Other halogeno polyenals

Method A: from glutaconaldehyde potassium salt. 5-*Bromopenta*-2,4-*dienal* **1b**.—To a solution of triphenylphosphine (5.1 g, 19.4 mmol) in CH_2Cl_2 (80 ml) at 0 °C was added bromine (3.1 g, 19.4 mmol) as a solution in CH_2Cl_2 (20 ml). Then, glutaconaldehyde potassium salt (2.3 g, 17.6 mmol) was added to this solution. The mixture was warmed to room temperature and stirred for 12 h. After treatment with aq. $NaHCO_3$ (5% w/v; 50 ml) and the usual work-up, the crude product was chromatographed on silica gel [light petroleum (distilled 50–65 °C)–Et_2O (70/30 v/v)]. 5-Bromopenta-2,4-dienal **1b** was obtained as a yellow solid (5.1 g, 72%) (2*E*,4*E*/2*E*,4*Z*: 75/25). With the same eluent in another ratio (98/2 v/v) the two isomers were separated (2*E*,4*E*: 1.18 g, 50%; 2*E*,4*Z*: 0.38 g, 18%).

Purification by crystallization was also performed according to the following protocol. At room temperature, anhydrous Et_2O (20 ml) was added to the crude product. The solution was stirred for 20 min at 0 °C. After filtration, the 2*E*,4*E* isomer was separated as pure crystals and the operation was repeated twice. The ethereal solutions were collected and evaporated to obtain a mixture of isomers 2*E*,4*Z*/2*E*,4*E*: 95/5. Finally, the 2*E*,4*Z* isomer was obtained pure by chromatography on silica gel [light petroleum (distilled 50–65 °C)–Et_2O (98/2 v/v)]. Thus, the *two isomers* were separated (2*E*,4*E*: 1.15 g, 49%; 2*E*,4*Z*: 0.40 g, 19%); ν_{max} 1676 and 1626 cm^{-1}; λ_{max} 279 nm (ε 33 720); 2*E*,4*E*: yellow solid; mp 65–68 °C; δ_H 6.10 (dd, *J* 8.0 and 15.0, 2-H), 6.86–7.03 (m, 3-, 4- and 5-H) and 9.50 (d, *J* 8.0, 1-H); δ_C 119.76 (C-5), 131.67 (C-2), 135.37 (C-4), 147.68 (C-3) and 193.00 (C-1); and 2*E*,4*Z*: red oil; δ_H 6.23 (dd, *J* 8.0 and 15.5, 2-H), 6.70 (d, *J* 7.0, 5-H), 6.90 (dd, *J* 10.5 and 7.0, 4-H), 7.40 (dd, *J* 15.5 and 10.5, 3-H) and 9.60 (d, *J* 8.0, 1-H); δ_C 118.90 (C-5), 130.56 (C-4), 134.26 (C-2), 145.51 (C-3) and 193.42 (C-1); *m*/*z* 162–160 ($M^{\bullet+}$, 34%) and 81 ($M^{\bullet+}$ − Br, 100) (Found: M^+, 161.9493–159.9477. C_5H_5BrO requires M, 161.9504–159.9524) (Found: C, 37.48; H, 2.96. C_5H_5BrO requires C, 37.27; H, 3.11%).

Method B: from furan. 5-*Bromo*-1,1-*dimethoxypenta*-2,4-*diene* **9**.—To a mixture of bromomethyl(triphenyl)phosphonium bromide (7.3 g, 16.1 mmol) in tetrahydrofuran (THF) (70 ml) at −70 °C was slowly added potassium *tert*-butoxide (1.82 g, 16.3 mmol). The mixture was stirred for 90 min to allow the formation of the ylide, and the keto acetal **8** (1.8 g, 13.7 mmol) was added as a solution in 8 ml of THF. The mixture was warmed to 0 °C for 1 h and then was stirred at room temperature for 90 min. After hydrolysis by water, extraction with Et_2O and the usual treatment, the crude product was chromatographed on silica gel [light petroleum (distilled 50–60 °C)–Et_2O (95/5 v/v)]. The 5-bromo-1,1-dimethoxypenta-2,4-diene **9** was obtained as an orange oil (2.3 g, 81%) (2*E*,4*Z*/2*E*,4*E*: 75/25), ν_{max} 1932 and 1648 cm^{-1}; δ_H 3.31 (s, OCH_3), 4.84 (d, *J* 4.5, 1-H), 5.81 (dd, *J* 4.5 and 14.6, 2-H), 6.23 (dd, *J* 8.4 and 11.0, 4-H), 6.62 (d, *J* 8.4, 5-H) and 6.65 (dd, *J* 14.6 and 11.0, 3-H); δ_C 52.71 (OCH_3), 102.17 (C-1), 110.06 (C-5), 129.01, 131.40 and 133.12 (C-2, -3 and -4); and 2*E*,4*Z*: δ_H 3.28 (s, OCH_3), 4.80 (d, *J* 4.5, 1 H), 5.61 (dd, *J* 4.5 and 15.4, 2-H), 6.23 (dd, *J* 15.4 and 11.0, 3-H), 6.38 (d, *J* 13.5, 5-H) and 6.70 (dd, *J* 11.0 and 13.5, 4-H); δ_C 52.47 (OCH_3), 101.67 (C-1), 110.66 (C-5), 130.11,

130.70 and 136.22 (C-2, -3 and -4); *m*/*z* 208–206 ($M^{\cdot+}$, 38%) and 127 ($M^{\cdot+}$ − Br, 100) (Found: C, 40.82; H, 5.22. $C_7H_{11}BrO_2$ requires C, 40.58; H, 5.31%).

5-*Bromopenta*-2,4-*dienal* **1b**.—To a solution of 5-bromo-1,1-dimethoxypenta-2,4-diene **9** (2.07 g, 10 mmol) in acetone (40 ml) and water (0.6 ml) was added Amberlyst-15 (0.4 g) at room temperature. The solution was stirred for 15 min and was then quenched by addition of Na_2CO_3 (3 g). After filtration and evaporation off of the solvents, the 5-bromopenta-2,4-dienal **1b** was obtained as an orange oil (1.5 g, 94%) (2*E*,4*E*/2*E*,4*Z*: 25/75).

5-*Iodopenta*-2,4-*dienal* **1c**.—The first procedure described above for bromo analogue **1b** from the glutaconaldehyde potassium salt was applied for compound **1c**, using iodine (4.9 g, 19.4 mmol) and stirring for 72 h. The crude product was chromatographed over silica gel [light petroleum (distilled 50–65 °C)–Et_2O (70/30 v/v)]. 5-Iodopenta-2,4-dienal **1c** was obtained as a yellow solid (2.3 g, 72%) (2*E*,4*E*/2*E*,4*Z*: 55/45). With the same eluent in another ratio (98/2 v/v) the two isomers were separated (2*E*,4*E*: 1.14 g, 35%; 2*E*,4*Z*: 0.95 g, 29%).

Purification by crystallization was also attempted according to the following protocol. At room temperature, light petroleum (20 ml) was added to the crude product. The solution was stirred for 20 min at 0 °C. After filtration, the 2*E*,4*E* isomer was separated as pure crystals and the operation was repeated twice. The ethereal solutions were collected and evaporated to obtain a mixture of isomers 2*E*,4*Z*/2*E*,4*E*: 93/7. Finally, the 2*E*,4*Z* isomer was obtained pure by chromatography on silica gel [light petroleum (distilled 50–65 °C)–Et_2O (98/2 v/v)]. Thus, the *two isomers* were separated (2*E*,4*E*: 1.06 g, 33%; 2*E*,4*Z*: 0.94 g, 29%); ν_{max} 1676 and 1612 cm^{-1}; 2*E*,4*E*: yellow solid, mp 58–62 °C; δ_H 6.12 (dd, *J* 8.0 and 15.3, 2-H), 6.96 (dd, *J* 10.9 and 15.3, 3-H), 7.13 (d, *J* 14.6, 5-H), 7.30 (dd, *J* 10.9 and 14.6, 4-H) and 9.97 (d, *J* 8.0, 1-H); δ_C 92.20 (C-5), 131.02 (C-2), 143.07 (C-4), 149.52 (C-3) and 193.19 (C-1); and 2*E*,4*Z*: yellow solid, mp 37 °C; δ_C 6.35 (dd, *J* 8.0 and 15.4, 2-H), 7.01 (d, *J* 8.2, 5-H), 7.02 (dd, *J* 10.6 and 8.2, 4-H), 7.23 (dd, *J* 15.4 and 10.6, 3-H) and 9.68 (d, *J* 8.0, 1-H); δ_C 95.12 (C-5), 134.79 (C-2), 136.53 (C-4), 149.74 (C-3) and 193.48 (C-1); *m*/*z* 208 ($M^{\cdot+}$, 26%) 81 ($M^{\cdot+}$ − I, 100) (Found: M^+, 207.9384; C, 28.67; H, 2.66%. C_5H_5IO requires M, 207.9385; C, 28.85; H, 2.40%).

ω-Bromo polyenals 2–4

Using ω-lithio enol ethers 10, 11, 12a. To a solution of an ω-bromo enol ether (5 mmol) [respectively 1-bromo-2-(trimethylsilyloxy)ethylene,[10] 1-bromo-4-(trimethylsilyloxy)buta-1,3-diene[11] or 1-bromo-6-methoxyhexa-1,3,5-triene **5b**] in anhydrous Et_2O (20 ml) at −70 °C was added a solution of Bu^{t}Li (5 ml of a 1.8 M solution in pentane; 9 mmol). After 90 min at −70 °C, a solution of 5-bromopenta-2,4-dienal (4*E*/4*Z*: 75/25) **1b** (0.65 g, 4 mmol) in anhydrous Et_2O (3 ml) was added. The mixture was warmed to 0 °C and stirred for 2 h. The solution was then cooled to −50 °C and hydrolysed by aq. HCl (10 ml; 1 M). After return to room temperature, the mixture was stirred for 2 h; the organic layer was separated and dried ($MgSO_4$). Evaporation gave the crude product, which was chromatographed over silica gel [light petroleum (distilled 50–65 °C)–Et_2O (70/30 v/v)].

7-*Bromohepta*-2,4,6-*trienal* **2**.—(2*E*,4*E*,6*E*/2*E*,4*E*,6*Z*: 65/35); *yellow solid* (0.46 g, 61%), mp 48 °C; ν_{max} 1688 and 1608 cm^{-1}; λ_{max} 313 nm (ε 48 720); 2*E*,4*E*,6*E*: δ_H 6.20 (dd, *J* 7.8 and 15.4, 2-H), 6.42 (dd, *J* 10.7 and 14.9, 4-H), 6.55 (dd, *J* 14.9 and 10.6, 5-H), 6.62 (d, *J* 13.6, 7-H), 6.81 (dd, *J* 10.6 and 13.6, 6-H), 7.04 (dd, *J* 15.4 and 10.7, 3-H) and 9.58 (d, *J* 7.8, 1-H); δ_C 115.30 (C-7), 130.37 (C-4), 132.40 (C-2), 136.57 (C-6), 138.55 (C-5), 150.57 (C-3) and 193.29 (C-1); 2*E*,4*E*,6*Z*: δ_H 6.23 (dd, *J* 7.8 and 15.4, 2-H), 6.49 (d, *J* 7.2, 7-H), 6.61 (dd, *J* 11.0 and 14.7, 4-H), 6.76 (dd, *J* 10.4 and 7.2, 6-H), 6.98 (dd, *J* 14.7 and 10.4, 5-H), 7.18 (dd, *J* 15.4 and 11.0, 3-H) and 9.60 (d, *J* 7.8, 1-H); δ_C 114.29 (C-7), 131.56 (C-4), 132.76 (C-2), 132.95 (C-6), 136.79 (C-5), 150.65 (C-3) and 193.32 (C-1); *m*/*z* 188–186 ($M^{\cdot+}$, 35%) and 107 ($M^{\cdot+}$ − Br, 65) (Found: M^+, 187.9684–185.9690; C, 44.81; H, 3.72%. C_7H_7BrO requires M, 187.9660–185.9680; C, 44.92; H, 3.74%).

9-*Bromonona*-2,4,6,8-*tetraenal* **3**.—(2*E*,4*E*,6*E*,8*E*/2*E*,4*E*,6*E*,8*Z*: 70/30); *brown solid* (0.62 g, 72%), mp 78 °C; ν_{max} 1664 and 1598 cm^{-1}; λ_{max} 344 nm (ε 27 640); 2*E*,4*E*,6*E*,8*E*: 70% δ_H 6.16 (dd, *J* 7.9 and 15.1, 2-H), 6.31 (dd, *J* 10.5 and 14.9, 6-H), 6.48 (dd, *J* 14.9 and 10.9, 4-H), 6.50 (d, *J* 13.4, 9-H), 6.53 (dd, *J* 13.4 and 10.1, 8-H), 6.61 (dd, *J* 14.9 and 10.1, 7-H), 6.81 (dd, *J* 10.5 and 14.9, 5-H), 7.10 (dd, *J* 15.1 and 10.9, 3-H) and 9.57 (d, *J* 7.9, 1-H); δ_C 112.53 (C-9), 131.23 (C-4), 131.60 (C-2), 132.27 (C-8), 134.85 (C-6), 137.05 (C-7), 141.45 (C-5), 151.14 (C-3) and 193.39 (C-1); 2*E*,4*E*,6*E*,8*Z*: 30% δ_H 6.17 (dd, *J* 8.0 and 15.2, 2-H), 6.32 (d, *J* 6.0, 9-H), 6.48 (dd, *J* 11.0 and 14.0, 7-H), 6.52 (dd, *J* 11.5 and 13.7, 4-H), 6.70 (dd, *J* 10.5 and 6.0, 8-H), 6.74 (dd, *J* 13.7 and 10.5, 5-H), 6.77 (dd, *J* 10.5 and 13.2, 6-H), 7.12 (dd, *J* 15.2 and 11.5, 3-H) and 9.58 (d, *J* 8.0, 1-H); δ_C 111.84 (C-9), 131.68 (C-4), 131.88 (C-2), 132.09 (C-8), 133.13 (C-6), 134.65 (C-7), 141.66 (C-5), 151.01 (C-3) and 193.40 (C-1); *m*/*z* 214–212 ($M^{\cdot+}$, 40%) and 133 ($M^{\cdot+}$ − Br, 97) (Found: 213.9843–211.9837; C, 50.86; H, 4.14%. C_9H_9BrO requires M, 213.9817–211.9837; C, 50.70; H, 4.23%).

11-*Bromoundeca*-2,4,6,8,10-*pentaenal* **4**.—(2*E*,4*E*,6*E*,8*E*,10*E*/2*E*,4*E*,6*E*,8*E*,10*Z*: 65/35); *red solid* (0.66 g, 68%), mp 156 °C; ν_{max} 1681 and 1611 cm^{-1}; λ_{max} 373 nm (ε 46 650); 2*E*,4*E*,6*E*,8*E*,10*E*: 65% δ_H 6.13 (dd, *J* 7.9 and 15.1, 2-H), 6.25 (dd, *J* 9.5 and 15.0, 9-H), 6.28 (dd, *J* 15.0 and 9.5, 8-H), 6.41 (m, 6-H), 6.43 (d, *J* 13.5, 11-H), 6.46 (m, 7-H), 6.49 (dd, *J* 14.5 and 11.4, 4-H), 6.65 (dd, *J* 14.5 and 10.1, 5-H), 6.76 (dd, *J* 13.5 and 10.4, 10-H), 7.10 (dd, *J* 15.1 and 11.4, 3-H) and 9.59 (d, *J* 7.9, 1-H); δ_C 111.05 (C-11), 130.56 (C-4), 131.26 (C-10), 132.67 (C-2), 132.76 (C-9), 132.91 (C-6), 137.25 (C-8), 137.64 (C-7), 142.05 (C-5), 151.33 (C-3) and 193.37 (C-1); 2*E*,4*E*,6*E*,8*E*,10*Z*: 35% δ_H 6.16 (dd, *J* 8.0 and 15.2, 2-H), 6.28 (d, *J* 6.3, 11-H), 6.42 (dd, *J* 10.8 and 14.2, 6-H), 6.46 (dd, *J* 10.7 and 13.9, 8-H), 6.50 (dd, *J* 11.2 and 14.2, 4-H), 6.56 (dd, *J* 14.2 and 10.7, 7-H), 6.68 (dd, *J* 6.3 and 10.4, 10-H), 6.70 (dd, *J* 13.9 and 10.4, 9-H), 6.72 (dd, *J* 14.2 and 10.8, 5-H), 7.12 (dd, *J* 15.2 and 11.2, 3-H) and 9.60 (d, *J* 8.0, 1-H); δ_C 110.51 (C-11), 130.82 (C-4), 131.08 (C-10), 131.31 (C-2), 132.28 (C-9), 133.41 (C-6), 135.41 (C-8), 137.96 (C-7), 142.06 (C-5), 151.41 (C-3) and 193.39 (C-1); *m*/*z* 240–238 ($M^{\cdot+}$, 40%) and 159 ($M^{\cdot+}$ − Br, 35) (Found: M^+, 239.9998–237.9976; C, 55.30; H, 4.70%. $C_{11}H_{11}BrO$ requires M, 239.9974–237.9993; C, 55.23; H, 4.60%).

Using ylides 13, 14. To a solution of a phosphonodioxolane[12] precursor of an ylide **13** or **14** (2.0 mmol) in THF (70 ml) at −70 °C was slowly added Bu^{t}OK (0.24 g, 2.14 mmol). The mixture was stirred for 90 min to allow the formation of the ylide and then 5-bromopenta-2,4-dienal **1b** 4*E*/4*Z*: 75/25 (0.24 g, 1.5 mmol) was added as a solution in 1 ml of THF. The mixture was warmed to 0 °C for 1 h and then was stirred for 90 min. After hydrolysis by water, extraction with pentane (5 × 20 ml) and the usual treatment, the crude product was chromatographed on silica gel [light petroleum (distilled 50–65 °C)–Et_2O (75/25 v/v)].

9-*Bromonona*-2,4,6,8-*tetraenal* **3**.—(2*E*,4*E*,6*E*,8*E*/2*E*,4*E*,6*E*,8*Z*: 80/20), brown solid (yield 70%), mp 76 °C.

11-*Bromoundeca*-2,4,6,8,10-*pentaenal* **4**.—(2*E*,4*E*,6*E*,8*E*,10*E*/2*E*,4*E*,6*E*,8*E*,10*Z*: 88/12), red solid (yield 68%), mp 154 °C.

ω-Halogeno polyenol ethers 5–7

General procedure. To a solution of methoxymethyl(triphenyl)phosphonium chloride or benzyloxymethyl(triphenyl)phosphonium chloride (2.3 mmol) in anhydrous THF (10 ml) at −50 °C was added Bu^{t}OK (0.26 g, 2.35 mmol). The mixture was stirred for 1 h and a halogeno polyenal **1**–**3** (2 mmol) was added as a solution in anhydrous THF (1 ml). The mixture was warmed to room temperature and stirred for 1 h. After treatment with aq. $NaHCO_3$ (5% w/v; 5 ml), the aqueous

layer was extracted with pentane (3 × 10 ml). After the usual treatment, the crude product was chromatographed over silica gel (deactivated by triethylamine) (pentane as eluent). The percentage of each stereoisomer and the NMR data of 1-halogeno-6-methoxyhexa-1,3,5-trienes **5a–c** are mentioned in Table 3.

1-*Chloro*-6-*methoxyhexa*-1,3,5-*triene* **5a**.—Yellow oil (0.22 g, 75%); ν_{max} 1615 cm^{-1}; *m*/*z* 147–145 [$(M + H)^+$, 100%].

1-*Bromo*-6-*methoxyhexa*-1,3,5-*triene* **5b**.—Yellow oil (0.31 g, 86%); ν_{max} 1625 cm^{-1}; *m*/*z* 190–188 ($M^{\bullet+}$, 34%) and 109 ($M^{\bullet+} - Br$, 100).

1-*Iodo*-6-*methoxyhexa*-1,3,5-*triene* **5c**.—Yellow oil (0.32 g, 73%); ν_{max} 1618 cm^{-1}; *m*/*z* 236 ($M^{\bullet+}$, 15%) and 109 ($M^{\bullet+} - I$, 30).

1-*Benzyloxy*-6-*bromohexa*-1,3,5-*triene* **5d**.—Yellow oil (0.42 g, 76%); mixture of four isomers: 1*Z*,3*E*,5*Z*, 1*E*,3*E*,5*Z*, 1*E*,3*E*,5*E* plus 1*Z*,3*E*,5*E* (indeterminable percentage); ν_{max} 1620 cm^{-1}; $\delta_H(C_6D_6)$ 4.32–4.40 (2 H, 4 s, OCH_2Ph), 4.98–5.60 (1 H, m, 2-H) and 5.70–7.70 (11 H, m); *m*/*z* 267–265 [$(M + H)^+$, 100%] and 185 [$(M + H - HBr)^+$, 24%].

8-*Bromo*-1-*methoxyocta*-1,3,5,7-*tetraene* **6** (non-systematic numbering).—Yellow oil (1.65 g, 76%); mixture of four isomers: 1*Z*,3*E*,7*Z*, 1*Z*,3*E*,7*E*/1*E*,3*E*,7*Z* plus 1*E*,3*E*,7*E*: 30 (or 40)/40 (or 30)/15/15; $\delta_H(C_6D_6)$ 3.05–3.15 (3 H, 4 s, OCH_3), 5.04 [1 H (30%), dd, *J* 6.1 and 11.2, 2-H], 5.06 [1 H (40%), dd, *J* 6.2 and 11.6, 2-H], 5.41 [1 H (15%), dd, *J* 12.5 and 9.7, 2-H], 5.46 [1 H (15%), dd, *J* 12.3 and 10.1, 2-H] and 5.55–6.90 (7 H, m); *m*/*z* 217–215 [$(M + H)^+$, 100%] and 135 [$(M + H - HBr)^+$, 30%].

1-*Bromo*-10-*methoxydeca*-1,3,5,7,9-*pentene* **7** (non-systematic numbering).—Unstable yellow oil (1.45 g, 61%); $\delta_H(C_6D_6)$ 3.05–3.06 (3 H, 3 s, OCH_3), 5.12 (1 H, m, 2-H) and 5.44–6.96 (9 H, m); *m*/*z* 243–241 [$(M + H)^+$, 100%] and 161 [$(M + H - HBr)^+$, 22%].

Polyenic aldehydes 17–20

General procedure. To a solution of halogeno polyenol ether **5**, **6** or **7** (1 mmol) in dry Et_2O (4 ml) cooled to −70 °C under argon was added a solution of Bu^tLi (1.6 M in pentane; 1.8 mmol) (or 1.8 mmol BuLi in pentane for **5c**) slowly with a syringe. The reaction mixture was stirred for 90 min and a solution of the carbonyl compound (0.8 mmol) in Et_2O (1 ml) was introduced. The reaction mixture was warmed to 0 °C and was stirred for 2 h before treatment at −50 °C with aq. HCl (1.5 M; 3 ml). The mixture was warmed to 10 °C and was stirred for 30 min. After return to room temperature, the organic layer was separated, washed with water and dried ($MgSO_4$). After evaporation, the crude product **17**–**20** was chromatographed over silica gel [light petroleum (distilled 50–60 °C)–Et_2O (70/30 v/v)].

7-*Phenylhepta*-2,4,6-*trienal* **17$_3$**.—2*E*,4*E*,6*E*. *Orange solid* (62% from bromo trienol ether **5b**, 68% from iodo trienol ether **5c**, 64% from bromo trienol ether **5d**), mp 115 °C; ν_{max} 3020 and 1640 cm^{-1}; δ_H 6.19 (dd, *J* 8.0 and 15.1, 2-H), 6.56 (dd, *J* 11.2 and 14.1, 4-H), 6.80 (d, *J* 14.8, 7-H), 6.83 (dd, *J* 10.1 and 14.1, 5-H), 6.90 (dd, *J* 10.1 and 14.8, 6-H), 7.19 (dd, *J* 15.1 and 11.2, 3-H), 7.25–7.50 (m, ArH) and 9.59 (d, *J* 7.9, 1-H); δ_C 126.77 (C-2′ and -6′), 127.49 (C-6), 128.50 (C-3′ and -5′), 128.60 (C-4′), 129.89 (C-4), 130.86 (C-2), 136.04 (C-1′), 138.09 (C-7), 142.54 (C-5), 151.58 (C-3) and 193.29 (C-1); *m*/*z* 184 ($M^{\bullet+}$, 100%) and 155 ($M^{\bullet+} - CHO$, 75) (Found: C, 84.52; H, 6.49. $C_{13}H_{12}O$ requires C, 84.78; H, 6.52%).

9-*Phenylnona*-2,4,6,8-*tetraenal* **17$_4$**.—2*E*,4*E*,6*E*,8*E*. *Orange solid* (130 mg, 59%), mp 134 °C; ν_{max} 2980, 1640 and 1600 cm^{-1}; λ_{max} 373 nm (ε 46 650); δ_H 6.17 (dd, *J* 7.9 and 15.2, 2-H), 6.45 (dd, *J* 14.7 and 11.0, 6-H), 6.48 (dd, *J* 11.3 and 14.7, 4-H), 6.65 (dd, *J* 14.7 and 10.7, 7-H), 6.71 (d, *J* 15.8, 9-H), 6.76 (dd, *J* 11.1 and 14.8, 5-H), 6.90 (dd, *J* 10.7 and 15.4, 8-H), 7.16 (dd, *J* 15.2 and 11.3, 3-H), 7.25–7.47 (m, ArH) and 9.57 (d, *J* 8.1, 1-H); δ_C 126.64 (C-2′ and -6′), 128.22 (C-4′ and -8), 128.64 (C-3′ and -5′), 129.84 (C-4), 130.89 (C-2), 131.72 (C-6), 135.86 (C-9), 136.58 (C-1′), 138.81 (C-7), 142.51 (C-5), 151.67 (C-3) and 193.38 (C-1); *m*/*z* 210 ($M^{\bullet+}$, 100%) and 181 ($M^{\bullet+} - CHO$, 60) (Found: C, 85.52; H, 6.49. $C_{15}H_{14}O$ requires C, 85.71; H, 6.67%).

10-*Methylundeca*-2,4,6,8-*tetraenal* **18$_4$**.—2*E*,4*E*,6*E*,8*E*. *Yellow oil* (80 mg, 56%); ν_{max} 2970, 1660 and 1580 cm^{-1}; δ_H 2.05 (d, *J* 6.7, 10-Me and 11-H_3), 2.39 (m, 10-H), 5.87 (dd, *J* 15.2 and 6.8, 9-H), 6.10 (dd, *J* 10.4 and 15.5, 8-H), 6.12 (dd, *J* 15.2 and 7.9, 2-H), 6.24 (dd, *J* 11.0 and 14.8, 6-H), 6.40 (dd, *J* 15.4 and 11.3, 4-H), 6.44 (dd, *J* 10.1 and 15.4, 7-H), 6.68 (dd, *J* 11.0 and 14.8, 5-H), 7.12 (dd, *J* 15.1 and 11.2, 3-H) and 9.54 (d, *J* 8.0, 1-H); δ_C 21.92 (C-11 and 10-Me), 31.35 (C-10), 127.09 (C-8), 128.83 (C-4), 129.37 (C-6), 130.40 (C-2), 139.43 (C-7), 143.01 (C-5), 146.59 (C-9), 152.06 (C-3) and 193.40 (C-1); *m*/*z* 176 ($M^{\bullet+}$, 100%) and 147 ($M^{\bullet+} - CHO$, 58) (Found: C, 81.80; H, 8.98. $C_{12}H_{16}O$ requires C, 81.82; H, 9.09%).

8-*Cyclohexylideneocta*-2,4,6-*trienal* **19$_4$**.—2*E*,4*E*,6*E*. *Yellow solid* (90 mg, 56%), mp 48 °C; ν_{max} 2934, 1672 and 1587 cm^{-1}; δ_H 1.55–1.65 (6 H, m, cyclohexylidene 3-, 4- and 5-H_2), 2.15–2.35 (m, cyclohexylidene 2- and 6-H_2), 5.90 (d, *J* 11.4, 8-H), 6.12 (dd, *J* 8.0 and 15.1, 2-H), 6.24 (dd, *J* 11.2 and 14.8, 6-H), 6.39 (dd, *J* 14.8 and 11.2, 4-H), 6.72 (dd, *J* 14.8 and 11.2, 5-H), 6.75 (dd, *J* 11.4 and 14.8, 7-H), 7.11 (dd, *J* 15.1 and 11.2, 3-H) and 9.53 (d, *J* 8.0, 1-H); δ_C 26.59, 27.87, 28.56, 29.68, 37.68 (C^{cyclo}), 122.35 (C-8), 128.37 (C-4), 129.26 (C-6), 130.21 (C-2), 134.98 (C-7), 143.71 (C-5), 149.69 (C-9), 152.35 (C-3) and 193.35 (C-1); *m*/*z* 202 ($M^{\bullet+}$, 100%) and 173 ($M^{\bullet+} - CHO$, 55) (Found: C, 83.35; H, 9.02. $C_{14}H_{18}O$ requires C, 83.17; H, 8.91%).

9-*Phenyldeca*-2,4,6,8-*tetraenal* **20$_4$**.—2*E*,4*E*,6*E*,8*E*/2*E*,4*E*,6*E*,8*Z*: 80/20. *Orange solid* (120 mg, 54%), mp 76 °C; ν_{max} 3010, 1660 and 1600 cm^{-1}; λ_{max}(EtOH)/nm 380 (ε 49 940), 324 (ε 44 300) and 276 (ε 38 750); δ_H 2.25 (s, CH_3), 6.17 (dd, *J* 7.9 and 15.1, 2-H), 6.45 (dd, *J* 14.6 and 11.1, 6-H), 6.49 (dd, *J* 11.1 and 14.6, 4-H), 6.60 (d, *J* 11.6, 8-H), 6.82 (dd, *J* 11.2 and 14.8, 5-H), 6.90 (dd, *J* 14.6 and 11.5, 7-H), 7.16 (dd, *J* 15.1 and 11.3, 3-H), 7.28–7.48 (m, ArH) and 9.57 (d, *J* 7.9, 1-H); δ_C 15.12 (CH_3), 125.56 (C-8), 126.60 (C-2′ and -6′), 127.67 (C-4′), 128.28 (C-3′ and -5′), 129.44 (C-4), 130.62 (C-2), 131.84 (C-6), 135.31 (C-7), 140.41 (C-1′), 142.12 (C-9), 142.94 (C-5), 151.78 (C-3) and 193.34 (C-1); *m*/*z* 224 ($M^{\bullet+}$, 100%) and 195 ($M^{\bullet+} - CHO$, 65) (Found: C, 85.51; H, 7.45. $C_{16}H_{16}O$ requires C, 85.71; H, 7.14%).

11-*Phenylundeca*-2,4,6,8,10-*pentaenal* **17$_5$**.—2*E*,4*E*,6*E*,8*E*,10*E*. Orange solid (130 mg, 69%), mp 223 °C; ν_{max} 1674 and 1573 cm^{-1}; λ_{max}(EtOH)/nm 406 (ε 14 370), 296 (ε 2932) and 243 (ε 2838); δ_H 6.14 (dd, *J* 8.0 and 15.1, 2-H), 6.37 (dd, *J* 14.7 and 11.1, 6-H), 6.41 (dd, *J* 11.1 and 14.5, 8-H), 6.45 (dd, *J* 11.2 and 14.7, 4-H), 6.53 (dd, *J* 14.5 and 10.6, 9-H), 6.59 (dd, *J* 11.1 and 14.6, 7-H), 6.64 (d, *J* 15.5, 11-H), 6.72 (dd, *J* 11.1 and 14.7, 5-H), 6.86 (dd, *J* 10.6 and 15.5, 10-H), 7.12 (dd, *J* 15.1 and 11.2, 3-H), 7.23–7.45 (m, ArH) and 9.57 (d, *J* 8.0, 1-H); δ_C 126.60 (C-2′ and -6′), 128.05 (C-4′), 128.72 (C-3′ and -5′), 128.74 (C-10), 129.92 (C-4), 130.90 (C-2), 131.75 (C-6), 132.63 (C-8), 134.76 (C-11), 136.76 (C-9), 136.97 (C-1′), 138.83 (C-7), 142.67 (C-5), 151.75 (C-3) and 193.45 (C-1); *m*/*z* 236 ($M^{\bullet+}$, 100%) and 207 ($M^{\bullet+} - CHO$, 65) (Found: C, 86.20; H, 6.79. $C_{17}H_{16}O$ requires C, 86.44; H, 6.78%).

12-*Methyltrideca*-2,4,6,8,10-*pentaenal* **18$_5$**.—2*E*,4*E*,6*E*,8*E*,10*E*. *Yellow solid* (90 mg, 59%), mp 95 °C; ν_{max} 2968, 1684 and 1579 cm^{-1}; λ_{max}(EtOH)/nm 368 (ε 3843), 271 (ε 2785) and 232 (ε 2643); δ_H 1.02 (d, *J* 6.8, $CHMe_2$), 2.37 (m, 12-H), 5.80 (dd, *J* 6.9 and 15.2, 11-H), 6.08 (dd, *J* 15.2 and 10.4, 10-H), 6.11 (dd, *J* 11.2 and 14.8, 2-H), 6.33 (dd, *J* 10.4 and 14.8, 9-H), 6.41 (dd, *J* 11.2 and 14.7, 4-H), 6.48 (dd, *J* 14.8 and 10.8, 7-H), 6.69 (dd, *J* 14.7 and 11.2, 5-H), 7.10 (dd, *J* 15.1 and 11.2, 3-H) and 9.53 (d, *J* 7.9, 1-H); δ_C 22.11 ($HCMe_2$), 31.42 (C-12), 127.40 (C-10), 129.25 (C-4), 130.14 (C-8), 130.60 (C-2), 130.62 (C-6), 137.27 (C-9), 139.23 (C-7), 142.94 (C-5), 145.33 (C-11), 151.97 (C-3) and 193.46 (C-1); *m*/*z* 202 ($M^{\bullet+}$, 100%) and 173 ($M^{\bullet+} - CHO$, 45) (Found: C, 83.48; H, 9.10. $C_{14}H_{18}O$ requires C, 83.17; H, 8.91%).

10-*Cyclohexylidenedeca*-2,4,6,8-*tetraenal* **19$_5$**.—2*E*,4*E*,6*E*,8*E*. *Yellow solid* (110 mg, 60%), mp 185 °C; ν_{max} 2943, 1671 and 1570 cm^{-1}; λ_{max}(EtOH)/nm 320 (ε 14 097), 292 (ε 11 750) and 242 (ε 8433); δ_H 1.52–1.60 (6 H, m, cyclohexylidene 3-, 4- and 5-H$_2$), 2.13–2.35 (m, cyclohexylidene 2- and 6-H$_2$), 5.87 (d, *J* 11.5, 10-H), 6.12 (dd, *J* 8.0 and 15.1, 2-H), 6.21 (dd, *J* 14.7 and 11.0, 8-H), 6.29 (dd, *J* 11.1 and 14.5, 6-H), 6.40 (dd, *J* 11.4 and 14.7, 4-H), 6.53 (dd, *J* 14.5 and 11.0, 7-H), 6.64 (dd, *J* 14.7 and 11.5, 9-H), 6.69 (dd, *J* 14.7 and 11.1, 5-H), 7.12 (dd, *J* 15.1 and 11.4, 3-H) and 9.53 (d, *J* 8.0, 1-H); δ_C 26.58, 27.80, 28.52, 29.56 and 37.58 (C^{cyclo}), 122.42 (C-10), 128.88 (C-8), 129.85 (C-4), 130.01 (C-6), 130.31 (C-2), 132.71 (C-9), 139.77 (C-7), 143.11 (C-5), 148.07 (C-11), 152.10 (C-3) and 193.44 (C-1); *m*/*z* 228 (M$^{\bullet+}$, 100%) and 199 (M$^{\bullet+}$ − CHO, 75) (Found: C, 84.65; H, 8.98. $C_{16}H_{20}O$ requires C, 84.21; H, 8.77%).

11-*Phenyldodeca*-2,4,6,8,10-*pentaenal* **20$_5$**.—2*E*,4*E*,6*E*,8*E*,10*E*/2*E*,4*E*,6*E*,8*E*,10*Z*: 90/10. *Orange solid* (100 mg, 50%), mp 204 °C; ν_{max} 2926, 1672 and 1566 cm^{-1}; λ_{max}(EtOH) 404 (ε 27 760), 292 (ε 10 750) and 243 (ε 14 040); δ_H 2.21 (s, CH$_3$), 6.13 (dd, *J* 8.0 and 15.1, 2-H), 6.37 (dd, *J* 14.7 and 11.4, 6-H), 6.41 (dd, *J* 11.2 and 14.7, 8-H), 6.45 (dd, *J* 11.3 and 14.2, 4-H), 6.58 (d, *J* 11.2, 10-H), 6.60 (dd, *J* 14.7 and 11.2, 7-H), 6.72 (dd, *J* 14.7 and 11.2, 9-H), 6.77 (dd, *J* 14.2 and 11.4, 5-H), 7.12 (dd, *J* 15.1 and 11.3, 3-H), 7.23–7.50 (m, ArH) and 9.55 (d, *J* 8.0, 1-H); δ_C 15.19 (CH$_3$), 125.74 (C-10), 126.75 (C-2′ and C-6′), 127.75 (C-4′), 128.37 (C-3′ and C-5′), 129.59 (C-4), 129.96 (C-8), 130.65 (C-2), 131.92 (C-6), 133.62 (C-9), 135.35 (C-7), 140.69 (C-1′), 142.05 (C-11), 143.24 (C-5), 151.83 (C-3), 193.57 (C-1); *m*/*z* 250 (M$^{\bullet+}$, 100%) and 221 (M$^{\bullet+}$ − CHO, 75) (Found: C, 86.23; H, 7.20. $C_{18}H_{18}O$ requires C, 86.40; H, 7.20%).

6-*tert*-Butyl-7-phenylhepta-2,4,6-trienal 22

To a solution of chloro polyenol ether **5a** (1 mmol) in dry Et$_2$O (4 ml) cooled to −70 °C under argon was added a solution of Bu^{t}Li (1.6 M in pentane; 1.8 mmol) slowly with a syringe. The reaction mixture was stirred for 90 min and a solution of the carbonyl compound (0.8 mmol) in Et$_2$O (1 ml) was introduced. The reaction mixture was warmed to 0 °C and stirred for 2 h before treatment at −50 °C with aq. HCl (1.5 M, 3 ml). The mixture was warmed to 10 °C and stirred for 30 min. After return to room temperature, the organic layer was separated, washed with water and dried (MgSO$_4$). After evaporation, the crude product was chromatographed over silica gel [light petroleum (distilled 50–60 °C)–Et$_2$O (70/30 v/v)].

2*E*,4*E*,6*E*. *Yellow oil* (32 mg, 38%); ν_{max} 2960, 1678 and 1608 cm^{-1}; δ_H(200 MHz) 1.25 (9 H, 2, Bu^t), 6.00 (dd, *J* 8.0 and 15.4, 2-H), 6.40 (dd, *J* 11.2 and 15.8, 4-H), 6.56 (s, 7-H), 6.64 (d, *J* 15.8, 5-H), 7.05 (dd, *J* 15.4 and 11.2, 3-H), 7.20–7.50 (m, ArH) and 9.50 (d, *J* 8.0, 1-H); δ_C(50 MHz) 29.86 (CH$_3$), 36.35 (*C*Me$_3$), 126.79, 128.06, 129.48 and 138.10 (C^{arom}), 147.04 (C-6), 128.60, 130.84, 131.33, 141.14 and 152.62 (C=C) and 193.51 (C-1); *m*/*z* 240 (M$^{\bullet+}$, 12%) (Found: C, 85.11; H, 8.10. $C_{17}H_{20}O$ requires C, 85.00; H, 8.33%).

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