8. N. Ya. Grigor'eva, O. N. Yudina, O. A. Pinsker, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 97 (1990).
9. E. P. Prokof'ev, N. Ya. Grigor'eva, and A. V. Semenovskii, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 834 (1980).
10. A. S. Shashkov, N. Ya. Grigor'eva, I. M. Avrutov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 388 (1979).
11. V. N. Odinokov, W. R. Achunova, R. I. Haleeva, et al., Tetrahedron Lett., 657 (1977).
12. H. R. Snyder and D. S. Matteson, J. Am. Chem. Soc., 79, 2217 (1957).
13. G. Buchi and H. Wüest, J. Org. Chem., 34, 1122 (1969).
14. L. Palfray and S. Sabetay, Bull. Soc. Chim. Fr., 4, 950 (1937).
15. E. E. Gilbert and H. R. Nychka, US Patent No. 2,928,836; Chem. Abstr., 54, 12165a (1960).
16. R. M. Coates and M. W. Johnson, J. Org. Chem., 45, 2685 (1980).

SYNTHESIS OF Z,Z-TRISHOMOFARNESAL TERT-BUTYLIMINE

N. Ya. Grigor'eva, O. N. Yudina, O. A. Pinsker, E. D. Daeva, and A. M. Moiseenkov

UDC 542.91:547.447.5

A highly stereoselective method was developed for the preparation of Z,Z-trishomofarnesal tert-butylimine, a key block synthone required for the construction of polyprenols with a nonnatural configuration of the "head" end of the chain, using as a basis the controlled condensation of aldehydes with aldimines. It was shown that introduction into the condensation of aldehydes containing an acetal grouping at the ω-position results in the formation of considerable amounts of aldols. The use of α-trimethylsilyl derivatives of aldimines makes it possible to dispense with this process and to direct the reaction toward the desired E-acroleins.

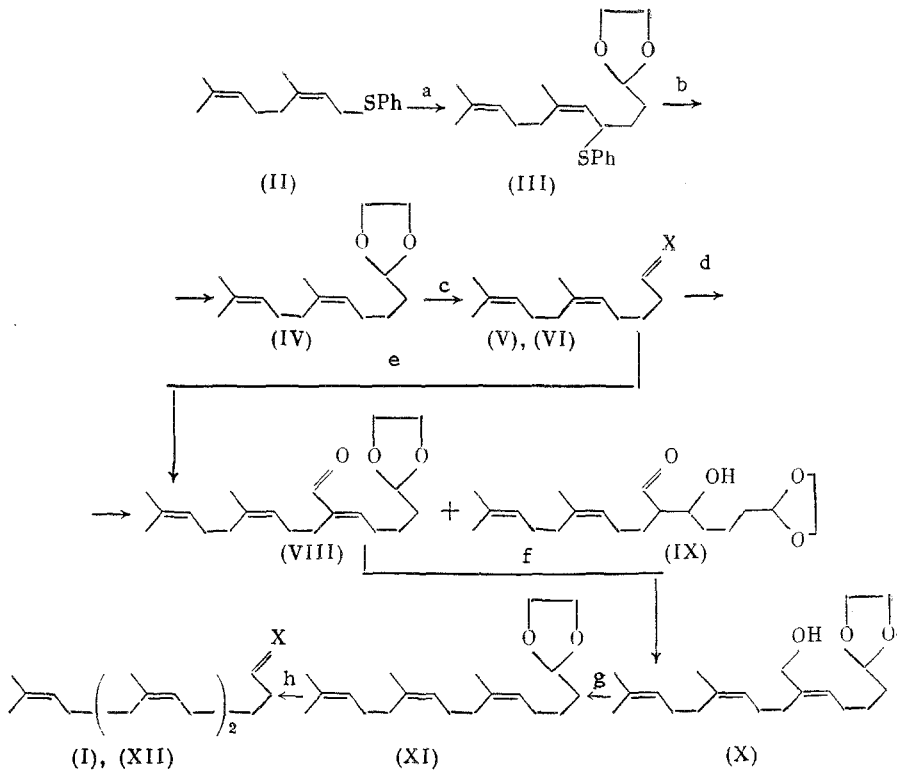
The use of the "block" scheme we have proposed for constructing linear isoprenoids [1], as applied to fully cisoid analogs of polyprenols, for example to hexaprenol WC_5OH [2], required development of a reliable method of synthesis of the aldimine (I) indicated in the heading. The limited availability of Z,Z-farnesol, an obvious precursor of (I), prompted us to study the possibility of obtaining this block-synthone starting from the substantially more readily available nerol, using for the Z-C_5-propagation of the "tail" fragment of its chain the glutaraldehyde monoacetal, similarly as tert-butylimine of this aldehyde was used by us for the Z-C_5-elongation of the "head" end of the isoprene chain in the synthesis of the above-mentioned hexaprenol [2]. The results thereby obtained are presented in the present article.

The alkylation of neryl sulfide (II) with β-bromopropanal ethyleneacetal gives sulfide (III), the reductive desulfuration of the latter gives acetal (IV), the hydrolytic splitting of this gives aldehyde (V), and finally, treatment of (V) with t-$BuNH_2$ gives aldimine (VI) (Scheme 1). The cross-combination of (VI), deprotonated by means of lithium diisopropylamide (LDA), with glutaraldehyde monoacetal (VII) [2] gives a mixture of the expected E-acrolein (VIII) in a good yield with an approximately fivefold amount of much more polar product which is readily separated by chromatography. The presence of absorption bands of the OH (3600 cm^{-1}) and CHO groups (1720 cm^{-1}) in the latter's IR spectrum, conforms well with the structure of aldol (IX). Confirming this structure, there are in the ^1H and ^{13}C NMR spectra of this compound the CHO signals in particular at δ ~ 9.7 and 205 ppm, respectively, doubled because of diastereomerism, together with signals at 2.4 and 55 ppm, corresponding to the HCCHO fragment.

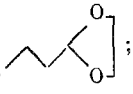
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 97-107, January, 1990. Original article submitted March 6, 1989.

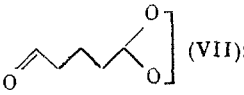
 0568-5230/90/3901-0084$12.50

Scheme 1



X = O (V), (XII), NBu-*t* (I), (VI).

a: 1. BuLi; 2. Br  ;

b: Li/NH_3; c: $H_3O^{\oplus}$; d: 1 LDA; 2.  (VII);

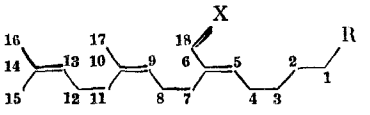
3. $H_3O^{\oplus}$ (pH4—4,5); e: 1. LDA; 2. Me_3SiCl; 3. LDA; 4 (VII); 5. pH4—4,5;

f: $NaBH_4$/EtOH; g: 1. $Py \cdot SO_3$; 2. $LiAlH_4$; 3: 1. $H_3O^{\oplus}$; 2. *t*-$BuNH_2$.

Attempts were unsuccessful to convert aldol (IX) into a disubstituted acrolein (VIII) under the conditions (pH ≥ 4, ~20°C) to ensure the later retention of the acetal protecting group required in subsequent operations. Therefore, aldehyde (VII) was subjected to olefinization according to Peterson, which made it possible to avoid (cf. [3]) the formation of ballast products of type (IX). The trimethylsilyl (TMS) component required for this, which is readily obtained by treating aldimine (VI), deprotonated by means of LDA, with Me_3SiCl, was found to be fairly unstable, and was used subsequently without isolation. The controlled cross-combination of TMS-(VI) with (VII) under the previously found conditions [1] gave a mixture of acroleins (VIII) in an overall yield of 45%, in a ratio of E/Z ≈ 5:1, as found by comparison in the PMR spectrum of the total product of the integral intensities of the singlet CHO signals for the main (δ ~ 9.3 ppm) and admixed (δ ~ 10 ppm) stereoisomers, cf. [1, 4]. The content of the undesired, thermodynamically less suitable Z-isomer (cf. [5]) could be reduced to ~3% (PMR) by holding the obtained sample of (VIII) in a $CHCl_3$ solution (Ar) at ~20°C for a week, or for 6 h at 140-150°C in a sealed ampul.

The E-acrolein (VIII) which was found to be on the whole preparatively available was further stereospecifically transformed without any difficulties (cf. [1, 2]) into the Z,Z-trishomofarnesal (XII), and then into the desired aldimine (I), via the intermediate stages of allyl alcohol (X), its O-sulfate (not isolated) and acetal (XI) in an overall yield of ~10% in the nine above-discussed stages (Scheme 1). The structure of the previously unknown compounds was confirmed spectrally.

TABLE 1. ^{13}C NMR Spectra of Compounds (VIII)-(XIII), (XVIII)-(XX), (XXII)-(XXIV) ($CDCl_3$, δ, ppm)



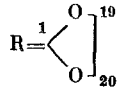
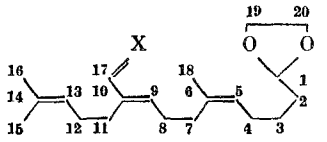
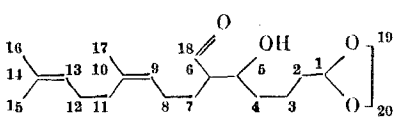
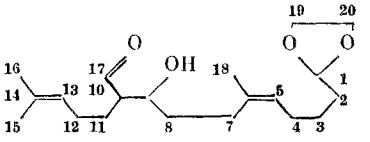
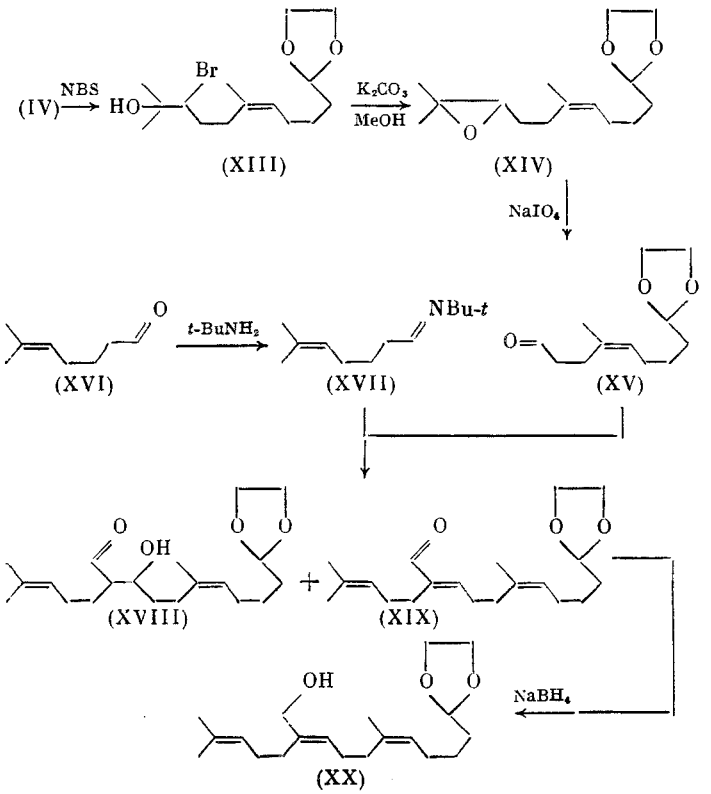
Atom				R=O	 [a]	
	X=O (VIII)	X=H, OH (X)	X=H, H (XI)	X=H, H (XII)	X=O (XXII)	X=H, OH (XXIV)
C^1	104,15	104,65	104,66	202,68	69,69	69,91
C^2	33,46	33,64	33,55	43,46	29,35	29,12
C^3	23,06	24,16	24,43	22,49	25,33	26,10
C^4	28,80	27,42 [c]	27,64	27,15	28,61	26,99
C^5	154,35	126,88	125,06	124,13 [c]	154,64	125,95
C^6	143,58	139,41	135,21 [c]	136,49 [d]	143,16	138,65
C^7	24,53 [c]	28,61	31,96 [d]	32,00	24,30 [c]	28,09
C^8	26,44 [c]	26,97 [c]	26,40	26,37 [c]	26,50	26,37 [d]
C^9	124,30	124,91	125,06 [c]	124,91 [c]	124,19	124,70 [c]
C^{10}	136,04	135,81	135,45 [c]	136,49 [d]	135,75	134,92
C^{11}	31,88 [c]	32,05	32,27 [d]	32,26 [d]	31,68 [c]	31,61
C^{12}	26,70 [c]	26,74 [c]	26,69	26,70	26,66 [c]	26,57 [c]
C^{13}	124,30	124,42	124,39	124,33	124,19	124,04 [d]
C^{14}	131,45	131,50	131,41	131,50	131,22	130,99
C^{15}	17,63	17,71	17,62	17,67	17,47	17,33
C^{16}	25,82	25,74	25,70	27,76	25,53	25,42
C^{17}	23,34	23,42	23,39	23,44	23,21	23,08
C^{18}	194,89	67,35	23,39	23,44	194,72	66,20
C^{19}	64,94	64,96	64,82	–	72,77	72,48
C^{20}	64,94	64,96	64,82	–	–	–

TABLE 1 (continued)

Atom				
	X=O (XIX)	X=H, OH (XX)	(IX) [b]	(XVIII) [b]
C^1	104,40	104,62	104,29	104,47
C^2	33,40	33,50	33,49	33,23 [c]
C^3	23,88 [c]	24,43	25,91	25,47
C^4	27,31	27,21 [c]	33,3[c]	27,45
C^5	125,52 [d]	125,40 [d]	74,23	125,79 [d]
C^6	133,71	134,98	55,32	134,75
C^7	30,56	31,75	21,68	27,77
C^8	27,64	25,76	33,4[c]	32,43 [c]
C^9	154,51	126,21	124,83	71,24
C^{10}	143,22	139,08	135,50	56,89
C^{11}	24,24	28,19	31,76	24,32
C^{12}	27,04	27,66[c]	26,39	33,10 [c]
C^{13}	123,52 [d]	124,17 [d]	124,12	123,23 [d]
C^{14}	132,20	131,80	131,50	134,75
C^{15}	17,58	17,68	17,45	17,68
C^{16}	25,63	25,77	25,47	25,63
C^{17}	195,05	66,94	23,14	205,48
C^{18}	23,14 [c]	23,28	205,17	23,22
C^{19}	64,79	64,84	64,59	64,77
C^{20}	64,79	64,84	64,59	64,77

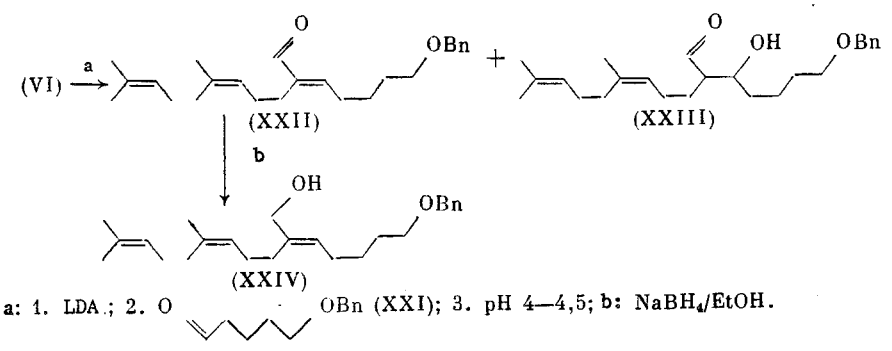
Notes. a) Phenyl group signals are also present in the spectra. b) Signals of the predominating diastereomer are given. c, d) The assignment of the noted signals is not unequivocal.

Scheme 2



The above-noted formation of a considerable amount of aldol product of type (IX) in a cross-condensation with the participation of ω-ethylenedioxy-substituted components is probably general in character. Thus, we have previously observed the formation of a considerable amount of an aldol during the condensation of tert-butylimino derivative of aldehyde (VII) with benzyloxyacetaldehyde [2]. The same also takes place in the reaction of aldehyde (XV) with aldimine (XVII), investigated as an alternative path for the synthesis of (I) (Scheme 2). Thus, the controlled cross-combination of (XVII), deprotonated by LDA, obtained from tris-homoprenal (XVI), with aldehyde (XV), prepared by a regioselective transformation of acetal (IV) by the modified van Tamelen method [6], via the stages of bromohydrin (XIII) and epoxide (XIV), gives under the above-described conditions a mixture of aldol (XVIII) and the disubstituted acrolein (XIX) in a 55% yield (≥95% E, NMR data) in a ~6:5 ratio. Compared with this, the combination under the same conditions of the above-described aldimine (VI) with the known aldehyde (XXI) carrying an ω-benzyloxy group results in a mixture of acrolein (XXII) (E ≥ 95%, NMR data) and aldol, (XXIII) in a 61% yield, with a clear (~4:1) predominance of the former (Scheme 3).

Scheme 3



a: 1. LDA; 2. O OBn (XXI); 3. pH 4—4,5; b: $NaBH_4$/EtOH.

It should be noted that despite the possibility of a smooth transition of E-acroleins (XIX) and (XXII) into their corresponding allyl alcohols (XX) and (XXIV), the subsequent transformation of the latter into trishomofarnesal (XII) was not carried out because of the discovered preference of its synthesis according to Peterson (Scheme 1).

As in the above-discussed cases, the structure of the previously unknown compounds given in Schemes 2 and 3 was confirmed spectrally, in particular by means of ^{13}C NMR spectra (Table 1), interpreted on the basis of data available for related compounds [1, 4, 7, 8].

EXPERIMENTAL

The IR spectra were run on a Perkin–Elmer 577 spectrophotometer in a thin layer and (for alcohols) in CCl_4 solutions, and the UV spectra of the alcoholic solutions – on a Specord UV-Vis spectrophotometer. The mass spectra were recorded at an ionizing voltage of 70 eV on a Varian MAT CH-6 spectrometer. The NMR spectra were measured in $CDCl_3$ relative to TMS on a Bruker WM-250 spectrometer, and the ^{13}C NMR spectra on a Bruker AM-300 spectrometer with a working frequency of 75.5 MHz, and for compounds (VIII)-(XII), (XVIII)-(XX), (XXII) and (XXIV) are given in Table 1. The preparative chromatography was carried out in a flash variant on silica gel L (40-100 mμ) from the firm Chemapol (Kavalier, CSSR), and the TLC on the Silufol plates from the same firm in systems A (ether–hexane, 1:1), or B (ether–hexane, 2:1). All the experiments were carried out in an Ar atmosphere, using freshly distilled solvents.

6,10-Dimethyl-4-phenylthioundeca-5Z,9-dien-1-al Ethyleneacetal (III). A solution of 16.97 g (69 mmoles) of (II) [9] in 300 ml of THF, stirred at −70°C, was successively treated in the course of 30 min with 50 ml of a 1.5 M solution of BuLi in hexane (75 mmoles) and after 3.5 h, with a solution of 19.9 g (110 mmoles) of 3-bromopropionaldehyde ethyleneacetal in 50 ml of THF. After 1.5 h, the reaction mixture was decomposed with 20 ml of a MeOH–ether (1:1) mixture at −70°C, and after raising the temperature to −10°C, was poured into 200 ml of an ice water–ether (1:1) mixture. The mixture was stirred for 15 min, and then the aqueous layer was separated and extracted with ether. After the standard treatment of the combined extract, the excess of bromoacetal was distilled under vacuum, and the residue (22.7 g) was chromatographed on 250 g of SiO_2. Gradient elution from hexane to ether (up to 15% of the latter), gave 19.92 g (83%) of (III) in the form of a colorless oil; bp (bath) 142-143°C (0.03 mm).

IR spectrum (ν, cm^{-1}): 3030, 2960, 2930, 2880, 1660, 1585, 1480, 1450, 1440, 1410, 1380, 1300, 1260, 1230, 1215, 1140, 1090, 1025, 940, 885, 750, 690. PMR spectrum (δ, ppm, J, Hz): 1.58 s (3H, cis-CH_3), 1.61 m (2H, CH_2), 1.69 s (6H, trans-CH_3), 1.8 m (6H, CH_2), 3.9 m (5H, CH_2O, CHS), 4.83 t (1H, OCHO, J = 4.3), 5.02 m (2H, HC=C), 7.35 m (5H, Ph). ^{13}C NMR spectrum (δ, ppm): 17.65 (cis-CH_3), 23.12 ($\underline{C}H_3C^6$), 25.64 (trans-CH_3), 26.32 (C^8), 29.80 (C^3), 31.60 (C^7), 32.11 (C^2), 46.78 (C^4), 64.87 (CH_2O), 104.23 (C^1), 124.10 (C^9), 126.08 (C^5), 127.21, 128.54, 133.71, 144.65 (Ph), 131.50 (C^{10}), 138.47 (C^6). Mass spectrum, m/z: 346 (M^+), 250, 238, 237, 236, 219, 218, 210, 176, 175, 149, 133, 123, 121, 119, 109, 107, 105, 100, 99, 95, 93, 91, 81, 79, 77, 73, 70, 69, 67, 65, 55, 53, 45, 43, 41, 39. Found, %: C 72.83, H 8.81, S 9.32. $C_{21}H_{30}O_2$. Calculated, %: C 72.79, H 8.73, S 9.25; mol. wt. 346.5.

6,10-Dimethyl-5Z,9-dien-1-al Ethyleneacetal (IV). A solution of 8.5 g (24.5 mmoles) of (III) in 15 ml of ether was added in the course of 10 min to a solution of 0.8 g (114 g-atom) of Li in 150 ml of NH_3, stirred at −40°C. The reaction mixture was allowed to stand for 4 h at −40°C, and then was decomposed by excess of NH_4Cl, and NH_3 was evaporated. The subsequent standard treatment gave 6 g of a product, which was chromatographed on 100 g of SiO_2. Gradient elution from hexane to ether (up to 10% of the latter) gave 5.20 g (89%) of (IV) in the form of a colorless oil; bp 110.5°C (2 mm). IR spectrum (ν, cm^{-1}): 2965, 2935, 2890, 2870, 1680, 1460, 1410, 1380, 1140, 1050, 950, 830, 790. PMR spectrum (δ, ppm, J, Hz): 1.46 m (2H, CH_2), 1.60 s (3H, cis-CH_3), 1.64 m (2H, CH_2), 1.68 s (6H, trans-CH_3), 2.03 m (6H, CH_2C=C), 3.9 m (4H, CH_2O), 4.83 t (1H, OCHO, J = 4.7), 5.10 t (2H, HC=C, J = 6.5). ^{13}C NMR spectrum (δ, ppm): 17.61 (cis-CH_3), 23.37 ($\underline{C}H_3$–C^6), 24.45 (C^3), 25.66 (trans-CH_3), 26.66, 27.64 ($C^{4,8}$), 32.01 (C^7), 33.59 (C^2), 64.84 (CH_2O), 104.69 (C^1), 124.40, 125.01 ($C^{5,9}$), 131.41 (C^{10}), 135.49 (C^6). Mass spectrum, m/z: 238 (M^+), 169, 156, 135, 133, 125, 107, 99, 93, 91, 86, 82, 81, 79, 73, 69, 67, 55, 44, 41. Found, %: C 75.85, H 11.07. $C_{15}H_{26}O_2$. Calculated, %: C 75.58, H 10.99; mol. wt. 238.4.

6,10-Dimethylundeca-5Z,9-dien-1-al (V). A solution of 5.2 g (21.8 mmoles) of (IV) and 0.1 ml of 96% H_2SO_4 in a 0.5 ml of an acetone–water (4:1) mixture was boiled for 4 h. The mixture was then neutralized at ~20°C with $NaHCO_3$, acetone was evaporated under vacuum, and the aqueous layer was extracted with ether. The standard treatment of the extract gave an oily product, which was distilled under vacuum. Yield 4.88 g (68%) of (V), bp 91-92°C (1.5

mm). IR spectrum (ν, cm^{-1}): 2970, 2940, 2860, 2720, 1730, 1455, 1415, 1380, 1240, 1140, 1115, 1070, 985, 835, 670. PMR spectrum (δ, ppm, J, Hz): 1.52 m (2H, CH_2), 1.60 s (3H, cis-CH_3), 1.68 s (6H, trans-CH_3), 2.0 m, (6H, $CH_2C{=}C$), 2.4 d.t (2H, $CH_2C{=}O$, J = 2.0 and 7.5), 5.07 m (2H, HC=C), 9.70 t (1H, CHO, J = 2.0). ^{13}C NMR spectrum (δ, ppm): 17.66 (cis-CH_3), 22.56 (C^3), 23.40 ($\underline{CH_3}$–C^6), 25.85 (trans-CH_3), 26.61, 27.18 (C^4, C^8), 32.03 (C^7), 43.48 (C^2), 124.13, 124.26 (C^5, C^9), 131.63 (C^{10}), 136.53 (C^6), 202.58 (C^1). Mass spectrum, m/z: 194 (M^+), 176, 169, 161, 151, 149, 133, 107, 99, 82, 81, 73, 69, 67, 55, 43, 41, 28.

6,10-Dimethylundeca-5Z,9-dien-1-al tert-Butylimine (VI). A solution of 5.4 g (73 mmoles) of t-$BuNH_2$ in 10 ml of ether was added in the course of 20 min to a solution of 2.72 g (14 mmoles) of (V) in 70 ml of ether, stirred at −10 to −5°C. The reaction mixture was stirred for 1.5 h at ~20°C, was then treated with 1 g of fused KOH, and after 20 min the organic layer was separated, dried over K_2CO_3, and evaporated to yield 3.38 g (97%) of (VI) in the form of a colorless oil. The oil was dried for 6 h at 20°C at 1 mm Hg, was then dissolved in 7 ml of ether, the solution was held for 12 h over molecular sieves (4 Å) at 2°C, and used further without additional purification. PMR spectrum (δ, ppm, J, Hz): 1.15 s (9H, CMe_3), 1.5 m (2H, CH_2), 1.57 s (3H, cis-CH_3), 1.67 s (6H, trans-CH_3), 2.0 m (6H, $CH_2C{=}C$), 2.22 d.t (2H, $CH_2C{=}N$, J = 4.8 and 7), 5.10 m (2H, HC=C), 7.50 t (1H, HC=N, J = 4.8).

10,14-Dimethyl-6-formylpentadeca-5E,9Z,13-trien-1-al Ethyleneacetal (VIII) and 10,14-Dimethyl-5-hydroxy-6-formylpentadeca-9Z,13-dien-1-al Ethyleneacetal (IX). A solution of 3.38 g (13.6 mmoles) of (VI) in 7 ml of ether was added in the course of 10 min with stirring at −10°C to a solution of LDA, freshly prepared at −15 to 0°C from 11 ml of a 1.5 M hexane solution of BuLi (16.5 mmoles) and 1.51 g (15 mmoles) of diisopropylamine in 70 ml of ether. The reaction mixture was allowed to stand for 40 min at −10°C, was then treated for 10 min at −70°C with a solution of 1.58 g (11 mmoles) of (VII) [2] in 5 ml of ether, stirred at this temperature for 2.5 h, and after raising the temperature to −5°C in the course of 1.5 h, it was cautiously transferred to a solution of 5.7 g (45 mmoles) of $(COOH)_2 \cdot 2H_2O$ in 88 ml of H_2O, cooled at 5°C. After stirring for 2 h at ~20°C, the aqueous layer was separated and extracted with ether. The standard treatment of the extract gave ~3 g of an oily product, which was chromatographed on 100 g of SiO_2. Gradient elution from hexane to ether (up to 50% of the latter) gave 0.35 g (10% of (VIII) containing 13% of its Z-isomer (PMR data) and 1.86 g (50%) of (IX). The solution of (VIII) in 5 ml of $CHCl_3$ was allowed to stand (Ar) for a week at ~20°C and was then evaporated under vacuum. Yield 0.35 g of (VIII) containing ≤3% of its Z-isomer (PMR data) in the form of a colorless oil; R_f 0.40 (A), bp (bath) 153-154°C (0.02 mm). IR spectrum (ν, cm^{-1}): 2960, 2920, 2870, 2710, 1690, 1640, 1450, 1410, 1380, 1135, 1045, 1030, 940, 830, 760, 710. UV spectrum: λ_{max} 230 nm (log ε 4.21). PMR spectrum (δ, ppm, J, Hz): 1.59 s (3H, cis-CH_3), 1.63 m (4H, CH_2), 1.68 s (6H, trans-CH_3), 2.0 m (6H, $CH_2C{=}C$), 2.25 t (2H, HC^7, J = 7.5), 2.40 d.t (2H, HC^4, J = 7.5 and 7.5), 3.9 m (4H, CH_2O), 4.87 t (1H, OCHO, J = 4.8), 5.08 t (2H, HC=C, J = 7.5), 6.43 t (1H, HC^5, J = 7.5), 9.34 s (1H, CHO). Mass spectrum, m/z: 320 (M^+), 302, 291, 251, 249, 205, 189, 187, 183, 171, 161, 149, 137, 135, 123, 121, 119, 109, 107, 105, 99, 95, 93, 91, 83, 82, 81, 73, 69, 68, 57, 55, 53, 46, 45, 44, 43, 41, 32, 31, 28. Found, %: C 75.45, H 10.04. $C_{20}H_{32}O_3$. Calculated, %: C 74.96, H 10.10; mol. wt. 320.4.

Aldol (IX) – colorless oil; R_f 0.10 (A), 0.44 (B), IR spectrum (ν, cm^{-1}): 3600, 2970, 2930, 2880, 2720, 1720, 1690, 1520, 1450, 1440, 1410, 1380, 1240, 1210, 1140, 1030, 1000, 970, 945, 890, 720. PMR spectrum (δ, ppm, J, Hz): 1.5 m (8H, CH_2), 1.57 s (3H, cis-CH_3), 1.68 s (6H, trans-CH_3), 2.0 m (6H, $CH_2C{=}C$), 2.4 m (1H, CHC=O), 3.9 m (5H, CH_2O, CHOH), 4.82 t (1H, OCHO, J = 5), 5.1 m (2H, HC=C), 9.70 d and 9.75 d (1H, CHO, J ≈ 3.5 and 2).

A solution of 3.44 g (13.8 mmoles) of (VI) in 7 ml of THF was added in the course of 10 min to a solution of LDA (15 mmoles) in 10 ml of hexane and 40 ml of THF, stirred at −10 °C, and after 40 min, a solution of 1.50 g (13.8 mmoles) of Me_3SiCl in 12 ml of THF was added at −50°C in the course of 20 min. The reaction mixture was stirred for 4 h at −50°C, and then was transferred to a dropping funnel cooled at −60°C, the contents of which were added in the course of 30 min to a solution of LDA (16 mmoles) in a mixture of 12 ml of hexane and 60 ml ether, stirred at −50°C. The mixture was allowed to stand for 40 min at −50°C and 15 min at −30°C, and was then treated at −70°C for 10 min with a solution of 1.58 g (11 mmoles) of (VII) in 5 ml of ether. The reaction mixture was stirred for 2.5 h at −70°C, was heated in the course of 1.5 h to −20°C, and was then decomposed at −70°C by a solution of 0.96 g (16 mmoles) of AcOH in 3 ml of ether, and after 15 min was poured into a solution of 6.05 g (48 mmoles) of $(COOH)_2 \cdot 2H_2O$ in 100 ml of H_2O cooled at 5°C. The subsequent treat-

ment, as described in the preceding experiment, gave 1.6 g (46%), containing ~3% of its Z-isomer (PMR data).

10,14-Dimethyl-6-hydroxymethylpentadeca-5E,9Z,13-trien-1-al Ethyleneacetal (X). A 0.98-g portion (25.6 mmoles) of $NaBH_4$ was added in the course of 20 min to a solution of 6.05 g (18.9 mmoles) of (VIII) in 0.2 liter EtOH, stirred at 0°C. The reaction mixture was stirred for 1.5 h at ~20°C, and it was then decomposed with 0.9 g (15 mmoles) of AcOH at 0°C. The oily product (~6 g) which was isolated by the subsequent standard treatment, was chromatographed on 100 g of SiO_2. Gradient elution from hexane to ether (up to 30% of the latter) gave 5.45 g (90%) of (X), bp (bath) 165-170°C (0.02 mm). IR spectrum (ν, cm^{-1}): 3620, 2960, 2920, 2880, 2860, 1670, 1450, 1410, 1380, 1195, 1140, 1030, 945, 890, 840, 705. PMR spectrum (δ, ppm, J, Hz): 1.52 m (2H, CH_2), 1.61 s (3H, cis-CH_3), 1.65 m (2H, CH_2), 1.68 s (6H, trans-CH_3), 2.1 m (10H, $CH_2C{=}C$), 3.9 m (4H, CH_2O), 4.03 s (2H, $\underline{CH_2}OH$), 4.85 t (1H, OCHO, J = 4.8), 5.13 m (2H, $HC{=}C$), 5.43 t (1H, HC^5, J = 6.8). Mass spectrum, m/z: 322 (M^+), 304, 291, 279, 277, 261, 254, 253, 240, 227, 222, 199, 185, 173, 172, 137, 135, 131, 125, 123, 121, 119, 109, 107, 105, 99, 95, 93, 91, 86, 82, 81, 80, 79, 73, 70, 69, 67, 57, 55, 45, 43, 41, 32, 29, 28.

6,10,14-Trimethylpentadeca-5Z,9Z,13-trien-1-al Ethyleneacetal (XI). A solution of 5.45 g (16.9 mmoles) of (X) in 0.2 liter of THF, stirred at 0°C, was treated for 15 min with 4.48 g (28.4 mmoles) of pyridine sulfotrioxide. The reaction mixture was allowed to stand at this temperature for 1.5 h, and was then treated for 40 min at −30°C with 135 ml of a 1 M solution of $LiAlH_4$ in THF (135 mmoles), then stirred for 4 days at ~20°C, and was then subjected to a treatment as previously described in [1]. Thus, 4.2 g of an oily product was obtained, which was chromatographed on 150 g of SiO_2. Gradient elution from hexane to ether (up to 30% of the latter) gave 3.76 g (72%) of (XI); bp (bath) 135-138°C (0.037 mm). IR spectrum (ν, cm^{-1}): 2960, 2920, 2880, 2860, 1730, 1660, 1450, 1410, 1375, 1310, 1140, 1040, 940, 875, 835, 735, 710. PMR spectrum (δ, ppm, J, Hz): 1.46 m (2H, CH_2), 1.60 s (3H, cis-CH_3), 1.64 m (2H, CH_2), 1.68 s (9H, trans-CH_3), 2.16 m (10H, $CH_2C{=}C$), 3.9 m (4H, CH_2O), 4.83 t (1H, OCHO, J = 4.5), 5.1 m (3H, $HC{=}C$). Mass spectrum, m/z: 306 (M^+), 238, 175, 169, 156, 149, 137, 133, 125, 122, 121, 119, 109, 107, 99, 95, 93, 81, 79, 77, 73, 69, 68, 67, 55, 41, 32, 18. Found, %: C 78.52, H 11.16. $C_{20}H_{34}O_2$. Calculated, %: C 78.38, H 11.18; mol. wt. 306.5.

6,10,14-Trimethylpentadeca-5Z,9Z,13-trien-1-al (XII). As described above for (IV), 2.16 g (67%) of (XII) was obtained by hydrolysis of 3.76 g of (XI), bp (bath) 126-130°C (0.04 mm). IR spectrum (ν, cm^{-1}): 2970, 2930, 2860, 2720, 1730, 1670, 1450, 1410, 1380, 1110, 1070, 835, 740. PMR spectrum (δ, ppm, J, Hz): 1.61 s (3H, cis-CH_3), 1.65 m (2H, CH_2), 1.68 s (9H, trans-CH_3), 2.0 m (10H, $CH_2C{=}C$), 2.41 d.t (2H, $CH_2C{=}O$, J = 2.0 and 7.5), 5.1 m (3H, $HC{=}C$), 9.75 t (1H, CHO, J = 2.0). Mass spectrum, m/z: 262 (M^+), 247, 244, 234, 218, 193, 191, 177, 175, 151, 149, 138, 137, 136, 133, 123, 121, 109, 107, 105, 95, 93, 82, 81, 79, 77, 69, 68, 67, 55, 53, 43, 41, 29, 18. Found, %: C 82.67, H 11.54. $C_{18}H_{30}O$. Calculated, %: C 82.38, H 11.52; mol. wt. 262.4.

6,10,14-Trimethylpentadeca-5Z,9Z,13-trien-1-al tert-Butylimine (I). As described above for (VI), 2.54 g (98%) of (I) was obtained from 2.15 g of (XII) in the form of a colorless oil. IR spectrum (ν, cm^{-1}): 2960, 2920, 2860, 2720, 1730, 1665, 1560, 1450, 1380, 1230, 1215, 1110, 1070, 985, 835, 740. PMR spectrum (δ, ppm, J, Hz): 1.16 s (9H, CMe_3), 1.53 m (2H, CH_2), 1.60 s (3H, cis-CH_3), 1.68 s (9H, trans-CH_3), 2.0 m (10H, $CH_2C{=}C$), 2.2 m (2H, $CH_2C{=}N$), 5.11 m (3H, $HC{=}C$), 7.58 t (1H, $HC{=}N$, J = 5.0).

6,10-Dimethyl-9-bromo-10-hydroxyundec-5Z-en-1-al Ethyleneacetal (XIII). A 4.5-g portion (25 mmoles) of N-bromosuccinimide was added in the course of 15 min to a solution of 5 g (21 mmoles) of (IV) in 85 ml of a t-BuOH–H_2O (5:4) mixture, stirred at 0-5°C. The reaction mixture was allowed to stand at this temperature for 5.5 h, was then concentrated in vacuo, and the residue was extracted with ether. The standard treatment of the extract gave 6.6 g of an oily product, which was chromatographed on 100 g of SiO_2. Gradient elution from hexane to ether (up to 30% of the latter) resulted in the isolation of 1.5 g of the initial (IV) (a 70% conversion) and 2.55 g (52%) of bromohydrin (XIII) in the form of a light-yellow oil; R_f 0.18 (A). IR spectrum (ν, cm^{-1}): 3625, 3570, 2980, 2960, 2930, 2880, 2250, 1730, 1500, 1410, 1390, 1370, 1330, 1215, 1140, 1040, 940, 910, 725. PMR spectrum (δ, ppm, J, Hz): 1.35 br. s (6H, CH_3), 1.5 m (4H, CH_2), 1.68 s (3H, CH_3), 2.06 m (4H, $CH_2C{=}C$), 2.22 m (2H, HC^8), 3.9 m (5H, CH_2O, HCBr), 4.85 t (1H, OCHO, J = 4.6), 5.20 (1H, $HC{=}C$, J = 7.3). ^{13}C NMR spectrum (δ, ppm): 23.24 ($\underline{C}H_3{-}C^6$), 24.37 (C^2), 26.02 and 26.44 ($\underline{C}H_3{-}C^{10}$ and C^{11}), 27.64 (C^4),

30.55 (C^7), 32.30 (C^8), 33.40 (C^3), 64.83 (CH_2O), 70.69 (C^9), 72.50 (C^{10}), 104.57 (C^1), 126.70 (C^5), 133.80 (C^6). Mass spectrum, m/z: 317, 254, 253, 240, 239, 211, 209, 195, 192, 183, 181, 169, 166, 155, 153, 152, 150, 149, 148, 137, 136, 135, 134, 133, 125, 123, 121, 119, 109, 108, 107, 106, 99, 95, 93, 91, 86, 85, 81, 79, 73, 71, 69, 68, 67, 59, 57, 56, 55, 45, 43, 41, 28, 18, 17, 16.

6,10-Dimethyl-9,10-epoxyundec-5Z-en-1-al Ethyleneacetal (XIV). A suspension of 2.3 g (6.9 mmoles) of (XIII) and 5.5 g of K_2CO_3 in 35 ml of MeOH was stirred for 30 min at ~20°C, the precipitate was filtered and washed with MeOH. The residue after vacuum distillation of the filtrate was dissolved in ether, and the solution was washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, and evaporated under vacuum. Yield 1.7 g (96%) of (XIV) in the form of a colorless oil, R_f 0.35 (A). IR spectrum (ν, cm^{-1}): 3450, 2960, 2920, 2870, 2250, 1730, 1505, 1410, 1380, 1250, 1130, 1030, 970, 910, 870, 735. PMR spectrum (δ, ppm, J, Hz): 1.21 s and 1.24 s (3H, CH_3 in each case), 1.42 m (2H, CH_2), 1.58 m (4H, CH_2), 1.64 s (3H, CH_3–C^6), 2.03 m (4H, $CH_2C{=}C$), 2.65 t (1H, HC(O)C, J = 6.5), 3.84 m (4H, CH_2O), 4.78 t (1H, OCHO, J = 5), 5.1 t (1H, HC=C, J = 7.5). ^{13}C NMR spectrum (δ, ppm): 18.65 and 24.86 ($\underline{C}H_3$–C^{10}), 23.27 ($\underline{C}H_3$–C^6), 24.27 (C^2), 27.35 (C^4), 27.54 (C^7), 28.45 (C^8), 33.40 (C^3), 58.50 ($\underline{C}^{10}$), 64.04 (C^9), 64.80 (CH_2O), 104.54 (C^1), 125.61 (C^5), 134.5 (C^6). Mass spectrum, m/z: 255 $(M + 1)^+$, 239, 211, 183, 169, 155, 149, 125, 123, 121, 119, 109, 108, 107, 106, 105, 101, 100, 99, 95, 94, 93, 86, 85, 81, 79, 73, 71, 69, 68, 67, 59, 57, 55, 45, 44, 43, 41, 32, 28, 18, 17, 16.

4-Methyl-9,9-ethylenedioxynon-4Z-en-1-al (XV). A solution of 2.44 g (11.4 mmoles) of $NaIO_4$ in 35 ml of H_2O was added to a solution of 1.7 g (6.7 mmoles) of (XIV) in 25 ml of THF, stirred at ~20°C. The reaction mixture was allowed to stand for 20 h at ~20°C, and then was poured into a saturated aqueous solution of Na_2SO_4, and extracted with ether. The standard treatment of the extract and distillation of the residue under vacuum gave 1.2 g (85%) of (XV) in the form of a colorless oil; bp (bath) 122°C (1 mm). IR spectrum (ν, cm^{-1}): 2950, 2930, 2880, 2860, 2720, 1730, 1450, 1410, 1390, 1380, 1360, 1220, 1145, 1050, 1030, 940, 890. PMR spectrum (δ, ppm, J, Hz): 1.35 m and 1.52 m (2H, CH_2 in each case), 1.55 s (3H, CH_3), 1.92 d.t (2H, HC^6, $J_1 = J_2 = 7.5$), 2.22 t (2H, HC^3, J = 7.5), 2.38 d.t (2H, HC^2, J = 2 and 7.5), 3.78 m (4H, CH_2O), 4.71 t (1H, OCHO, J = 5), 5.06 t (1H, HC=C, J = 7.5), 9.67 t (1H, CHO, J = 2). ^{13}C NMR spectrum (δ, ppm): 22.90 ($\underline{C}H_3$–C^4), 24.10 (C^3, C^8), 27.43 (C^6), 33.24 (C^7), 42.13 (C^2), 64.68 (CH_2O), 104.34 (C^9), 126.24 (C^5), 133.17 (C^4), 201.94 (C^1). Mass spectrum, m/z: 212 (M^+), 211, 185, 184, 183, 170, 169, 155, 150, 149, 135, 125, 124, 121, 119, 113, 109, 108, 107, 106, 100, 99, 95, 93, 86, 83, 82, 81, 79, 73, 69, 67, 57, 55, 45, 44, 43, 41, 32, 31, 29, 28, 27, 18, 17, 16. Found, %: C 67.69, H 9.51. $C_{12}H_{20}O_3$. Calculated, %: C 67.94, H 9.44; mol. wt. 212.1.

6-Methylhept-5-en-1-al tert-Butylimine (XVII). As described above for (VI), 1.63 g (~100%) of compound (XVII) was obtained from 1.15 g of aldehyde (XVI) [10], in the form of a colorless oil. PMR spectrum (δ, ppm, J, Hz): 1.03 (9H, CMe_3), 1.42 m (2H, HC^3), 1.44 s (3H, cis-CH_3), 1.52 s (3H, trans-CH_3), 1.87 d.t (2H, HC^4, J = 7.8 and 7.0), 2.09 d.t (2H, HC^2, J = 5.5 and 6.4), 4.96 t (1H, HC^5, J = 7.8), 7.46 t (1H, HC^1, J = 5.5).

6,14-Dimethyl-9-hydroxy-10-formylpentadeca-5,13-dien-1-al Ethyleneacetal (XVIII) and 6,14-Dimethyl-10-formylpentadeca-5Z,9E,13-trien-1-al Ethyleneacetal (XIX). As described above for (VIII) and (IX), 0.32 g (24%) of (XIX) (E ≥ 95%, PMR data) and 0.44 g (31%) of (XVIII) were obtained from 10 mmoles of DLA, 1.36 g (7.5 mmoles) of (XVII) and 0.9 g (4.2 mmoles) of (XV), and were separated by chromatography on SiO_2 with a gradient elution from hexane to ether (up to 50% of the latter).

Acrolein (XIX) – colorless oil, R_f 0.43 (B). IR spectrum (ν, cm^{-1}): 2960, 2930, 2710, 1690, 1640, 1450, 1400, 1380, 1260, 1230, 1140, 1035, 940, 890, 740. UV spectrum: λ_{max} 228 nm ($\log \varepsilon$ 4.09). PMR spectrum (δ, ppm, J, Hz): 1.36 m (2H, HC^3), 1.45 s (3H, cis-CH_3), 1.54 m (2H, HC^2), 1.53 s (3H, trans-CH_3), 1.62 s (3H, CH_3C^6), 1.92 m (4H, HC^4, HC^{12}), 2.12 m (4H, HC^7, HC^{11}), 2.33 d.t (2H, HC^8, J = 7.0), 3.78 m (4H, CH_2O), 4.82 t (1H, OCHO, J = 4.5), 5.0 t (1H, HC^5, J = 7.0), 5.1 t (1H, HC^{13}, J = 7.0), 6.35 t (1H, HC^9, J = 7.3), 9.25 s (1H, CHO). Mass spectrum, m/z: 319 $(M - 1)^+$, 302, 258, 251, 189, 181, 169, 150, 135, 121, 109, 107, 99, 95, 93, 82, 81, 79, 73, 69, 67, 57, 55, 53, 45, 44, 43, 41, 32, 29, 28, 18, 17.

Aldol (XVIII) – a colorless oil, R_f 0.36 (B). IR spectrum (ν, cm^{-1}): 3485, 2960, 2920, 2870, 2730, 1720, 1630, 1450, 1410, 1380, 1130, 1050, 1030, 940, 910, 830, 730, 650. PMR spectrum (δ, ppm, J, Hz): 1.40 m (2H, HC^3), 1.50 s (3H, cis-CH_3), 1.55 m (2H, HC^2), 1.60 s (6H, trans-CH_3), 2.02 m (6H, $CH_2C{=}C$), 2.28 m (1H, HC^{10}), 3.83 m (5H, CH_2O, CHOH), 4.79 t (1H, OCHO, J = 5.0), 5.08 m (2H, HC=C), 9.66 d (0.6H, CHO, J = 3.5), 9.69 d (0.4H, CHO, J = 3.3). Mass spectrum, m/z: 338 (M^+), 320, 310, 292, 269, 251, 241, 213, 189, 184, 183, 169, 155, 151, 150, 137, 135, 133, 125, 124, 123, 122, 121, 119, 111, 109, 107, 99, 95, 93, 86, 83, 82, 81, 79, 73, 69, 67, 57, 55, 45, 43, 41, 39, 28, 18.

6,14-Dimethyl-10-hydroxymethylpentadeca-5Z,9E,13-trien-1-al Ethyleneacetal (XX). As described above for (VIII), from 0.23 g of (XIX), 0.21 g (90%) of (XX) was obtained in the form of a colorless oil. R_f 0.2 (B). IR spectrum (ν, cm^{-1}): 3620, 2960, 2920, 2860, 1670, 1460, 1410, 1380, 1230, 1140, 1060, 1040, 940, 910, 730, 650. PMR spectrum (δ, ppm, J, Hz): 1.43 m (2H, HC^3), 1.56 s (3H, cis-CH_3), 1.62 m (2H, HC^2), 1.65 s (6H, trans-CH_3), 2.06 m (10H, $CH_2C{=}C$), 3.87 m (4H, CH_2O), 3.98 s (2H, CH_2OH), 4.80 t (1H, OCHO, J = 4.7), 5.10 m (2H, HC=C), 5.37 t (1H, HC^9, J = 7). Mass spectrum, m/z: 322 (M^+), 304, 279, 261, 253, 169, 156, 135, 125, 122, 121, 109, 108. 107, 99, 97, 95, 94, 93, 91, 86, 85, 83, 82, 81, 79, 77, 73, 71, 70, 69, 67, 57, 55, 53, 45, 44, 43, 41, 32, 31, 29, 28, 27, 18, 17.

Benzyl Ether of 10,14-Dimethyl-6-formylpentadeca-5E,9Z,13-trien-1-ol (XXII) and Benzyl Ether of 10,14-Dimethyl-5-hydroxy-6-formylpentadeca-9Z,13-dien-1-ol (XXIII). As described above for (VIII) and (IX), 1.25 g (49%) of (XXII) and 0.35 g (12%) of (XXIII) were obtained by condensation of 2.3 g (9 mmoles) of (VI) with 1 g (7 mmoles) of (XXI) [11], followed by chromatography on SiO_2. Acrolein (XXII) – colorless oil, R_f 0.48 (A), IR spectrum (ν, cm^{-1}): 3090, 3060, 3030, 2960, 2930, 2830, 2710, 1690, 1640, 1490, 1450, 1400, 1380, 1360, 1200, 1110, 1045, 1030, 730, 700. UV spectrum: λ_{max} 230 nm (log ε 4.06). PMR spectrum (δ, ppm, J, Hz): 1.61 s (3H, cis-CH_3), 1.65 m (4H, CH_2), 1.68 s (6H, trans-CH_3), 2.04 m (6H, $CH_2C{=}C$), 2.27 t (2H, HC^7, J = 7.5), 2.38 d.t (2H, HC^4, J = 7.7 and 7.0), 3.49 t (2H, CH_2OBn, J = 5.7), 4.50 s (2H, CH_2Ph), 5.10 m (2H, HC=C), 6.43 t (1H, HC^5, J = 7.7), 7.35 m (5H, Ph), 9.36 s (1H, CHO). Mass spectrum, m/z: 368 (M^+), 350, 325, 277, 261, 177, 149, 147, 145, 137, 135, 133, 131, 123, 121, 109, 95, 91, 89, 83, 82, 81, 80, 79, 71, 69, 68, 67, 66, 65, 55, 53, 43, 41, 39, 27.

Aldol (XXIII) – colorless oil, R_f 0.12 (A). PMR spectrum (δ, ppm, J, Hz): 1.35 m (8H, CH_2), 1.62 s (3H, cis-CH_3), 1.71 s (6H, trans-CH_3), 2.06 m (6H, $CH_2C{=}C$), 2.32 m (1H, CHC=O), 3.49 m (2H, CH_2OBn), 3.80 m (1H, CHOH), 4.50 s (2H, CH_2Ph), 5.13 m (HC=C), 7.3 m (5H, Ph), 9.71 m (1H, CHO).

Benzyl Ether of 10,14-Dimethyl-6-hydroxymethylpentadeca-5E,9Z,13-trien-1-ol (XXIV). As described for (VIII), 1.13 g (90%) of (XXIV) was obtained from 1.25 g of (XXII). IR spectrum (ν, cm^{-1}): 3620, 3100, 3080, 3030, 2980, 2960, 2930, 2860, 1500, 1455, 1420, 1380, 1370, 1320, 1210, 1190, 1110, 1050, 1040, 1020, 1010, 850, 740, 705. PMR spectrum (δ, ppm, J, Hz): 1.48 m (4H, CH_2), 1.63 s (3H, cis-CH_3), 1.72 s (6H, trans-CH_3), 2.08 m (10H, $CH_2C{=}C$), 3.48 t (2H, CH_2OBn, J = 6.2), 4.0 s (2H, CH_2OH), 4.5 s (2H, CH_2Ph), 5.15 m (2H, HC=C), 5.42 t (1H, HC^5, J = 7), 7.34 m (5H, Ph). Mass spectrum, m/z: 370 (M^+), 352, 288, 279, 262, 261, 246, 233, 203, 179, 175, 161, 149, 137, 135, 133, 123, 121, 119, 111, 109, 108, 107, 105, 95, 94, 93, 92, 91, 85, 83, 82, 81, 79, 77, 71, 70, 69, 68, 67, 65, 57, 55, 53, 43, 41, 39, 29, 28.

LITERATURE CITED

1. N. Ya. Grigorieva, I. M. Avrutov, and A. M. Semenovsky, Tetrahedron Lett., 24, 5531 (1983); A. V. Semenovskii, N. Ya. Grigor'eva, I. M. Avrutov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 152 (1984); N. Ya. Grigor'eva, I. M. Avrutov, O. M. Pinsker, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1824 (1984).
2. N. Ya. Grigor'eva, O. N. Yudina, E. D. Daeva, and A. M. Moiseenkov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 89 (1990).
3. T. N. Chan, Acc. Chem. Res., 10, 442 (1977).
4. E. P. Prokof'ev, N. Ya. Grigor'eva, and A. V. Semenovskii, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 834 (1980).
5. N. Ya. Grigor'eva, E. P. Prokof'ev, and A. V. Semenovskii, Dokl. Akad. Nauk SSSR, 245, 366 (1979); K. Ya. Burshtein and N. Ya. Grigor'eva, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 449 (1982).

6. E. E. Van Tamelen and T. J. Curphey, Tetrahedron Lett., 121 (1962).
7. A. S. Shashkov, N. Ya. Grigor'eva, I. M. Avrutov, et al., Izv. Akad. Nauk SSSR, No. 2, 388 (1979).
8. I. M. Avrutov, N. Ya. Grigor'eva, V. S. Bogdanov, and A. M. Moiseenkov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2194 (1987).
9. E. M. Burgess and M. C. Pulcrano, J. Am. Chem. Soc., 100, 6538 (1978).
10. J. E. Bielman and J. B. Ducep, Tetrahedron, 27, 5861 (1971).
11. T. D. Perrine, J. Org. Chem., 18, 1356 (1953).

EFFICIENT [4 + 2]CYCLOADDITION DURING ADSORPTION ON CHROMATOGRAPHIC SOLVENTS*

V. V. Veselovskii, A. S. Gybin, A. V. Lozanova, A. M. Moiseenkov, and V. A. Smit

UDC 542.955+66.095.252.7:547.592.2:541.183.5:546.284-31

An essentially new method was developed for carrying out [4 + 2]cycloaddition on the surface of chromatographic adsorbents in the absence of solvent. This method permits the use of much milder reaction conditions and to increase the reaction's selectivity.

Earlier it was shown that carrying out intramolecular reactions such as the Khand—Pauson reaction ([2 + 2 + 1]cycloaddition) [2] and the Carroll rearrangement ([3,3]sigmatropic rearrangement) [3] on the surface of chromatographic adsorbents in the absence of solvent permits a significant moderation of the reaction conditions and increases the efficiency of the processes. The aim of the present work was to study the effect of experimental conditions on the course of intermolecular [4 + 2]cycloaddition (primarily on the Diels—Alder reaction).

We studied the addition of dienophiles such as methyl vinyl ketone (IIa), acrolein (IIb), methacrolein (IIc), and (E)-crotonaldehyde (IId) to butadiene (Ia), isoprene (Ib), 2,3-dimethylbutadiene (Ic), myrcene (Id), and cyclohexadiene (Ie). Diene condensation of these reagents in the liquid phase in the absence of catalysts usually requires drastic conditions (120-160°C, 3-6 h [4]).

By reacting substrates (I) and (II) on the surface of chromatographic adsorbents† in the absence of solvent, we were able to decrease the reaction temperature significantly (by 50-100°C) and, in many cases, to achieve higher yields of diene synthesis products (III)-(XIII) (Table 1) compared with the standard liquid-phase procedure.

The best results were obtained when the reactions were carried out using different brands of silica gel as the "dry medium" (Chemapol, Czechoslovakia, 40/100 μ, 100/160 μ, Silperl; Woelm, FRG, 5/20 μ; Mallincrodt, FRG, <150 μ; Silokhrom C-120, USSR, 100/200 μ; all of comparable activity). The activity of the silica gel depended on its H_2O content. Thus, the use of SiO_2 containing 10-12% H_2O (equilibrium content at 25°C and average atmospheric humidity) required a higher temperature (by 70-80°C) than when the SiO_2 was dried at 200°C to a constant mass.

Magnesium silicate (Florisil, Merck, FRG, 75/150 μ) proved to be a less-effective medium for carrying out these reactions. To obtain an effect comparable to that obtained with SiO_2, the reaction temperature had to be raised by 30-50°C. Al_2O_3 (Reanal, Hungary, neutral or acid) was ineffective, because the reagents underwent significant tarring on its surface.

*For previous communication, see [1].
†This effect is also observed on the surface of zeolites [5].

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 107-113, January, 1990. Original article submitted December 29, 1988.

 0568-5230/90/3901-0094$12.50