

Base-Induced Decarboxylation of Polyunsaturated α -Cyano Acids Derived from Malonic Acid: Synthesis of Sesquiterpene Nitriles and Aldehydes with β -, φ -, and ψ -End Groups

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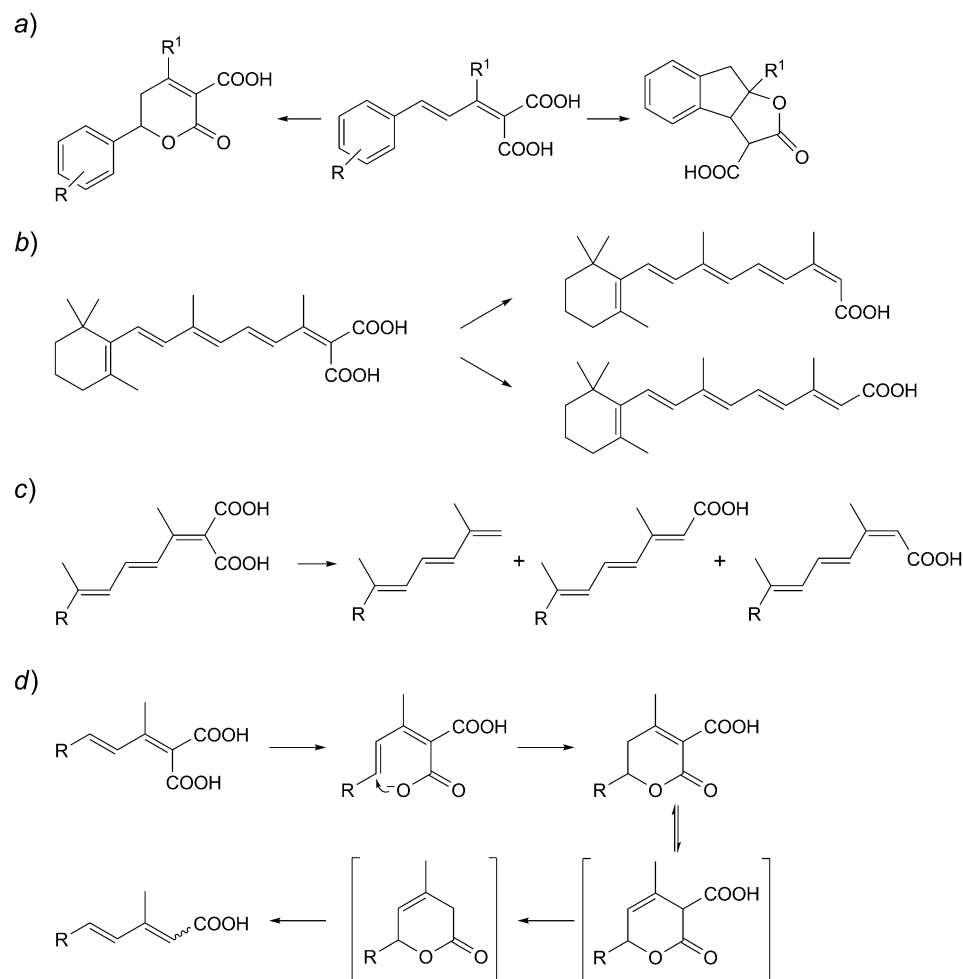
Catalytic base-induced decarboxylation of polyunsaturated α -cyano- β -methyl acids derived from malonic acid led to the corresponding nitriles **3** (Schemes 2 and 3), **6** (Scheme 5), and **9** (Scheme 6). This decarboxylation occurred with previous deconjugation of the α,β -alkene moiety of the α -cyano- β -methyl acid, leading to an α -cyano- β -methylene propanoic acid which was easily decarboxylated (see Scheme 2). β -Methylene intermediates, in some cases, could be isolated; mechanistic pathways are proposed. The nitriles **3**, **6**, and **9** were reduced to the sesquiterpene aldehydes **4** (β -end group), **7** (φ -end group), and **10** (ψ -end group), respectively.

Introduction. – Decarboxylations are important in biological systems and occur frequently in primary and secondary metabolisms: glycolysis, gluconeogenesis, glycogenolysis, and glycogenesis, degradation and synthesis of fatty acids, *Krebs* citric acid cycle (including pyruvate to acetyl-CoA, oxalosuccinate to α -ketoglutarate, α -ketoglutarate to succinyl-CoA). Other decarboxylations are important, such as formation of significant amines from amino acids, 5-HTP to serotonin, L-DOPA to dopamine.

We have worked on the base/acid-induced decarboxylation of polyunsaturated malonic acid derivatives for many years. Thus, in a strong acidic medium and depending on the substitution pattern of the side chain, we have found that γ -lactones or δ -lactones could be obtained [1] (Scheme 1,a).

In another study related to new syntheses of retinoids and carotenoids [2], we have demonstrated that stereospecific/stereoselective monodecarboxylations were possible, depending on the base used [3][4] (Scheme 1,b). In a recent work, we have revealed that bis-decarboxylation of some malonic acid derivatives could occur easily, and that this reaction is accompanied by formation of (*E*)- and (*Z*)-configured mono-acids [5] (Scheme 1,c). According to Corey and Fraenkel [6], these decarboxylations of malonic acid derivatives require a previous isomerization to an intermediary β -unsaturated δ -lactone (Scheme 1,d). In the series of corresponding cyanoacetic acid derivatives with β -, φ -, and ψ -end groups, different mechanistic pathways were proposed, which may explain the process of decarboxylation.

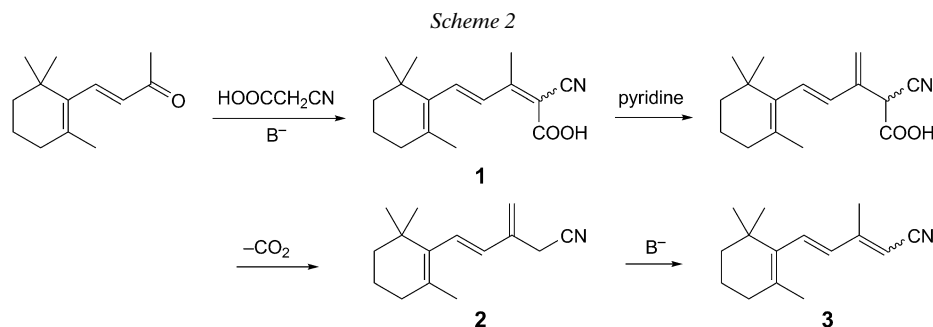
Scheme 1



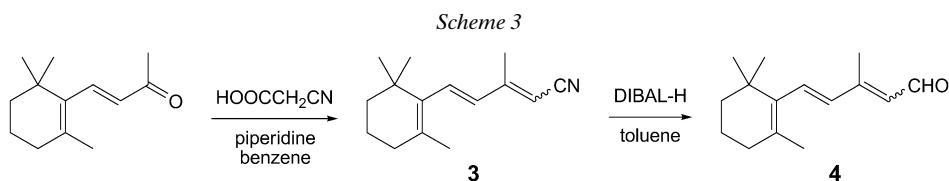
Sesquiterpenes are usually found as natural products [7] and could also be of interest in chemical synthesis. C_{15} -Sesquiterpene aldehydes are commonly used for the syntheses of diterpenes (especially related to retinoic acids, retinals, and retinols), and numerous references show them to be exceptional intermediates [8]. This paper reports on new syntheses of some β -, φ -, and ψ -sesquiterpene aldehydes as useful synthons for retinoid syntheses.

Results and Discussion. – β -End Group. *Knoevenagel* condensation of β -ionone with cyanoacetic acid led to the α -cyano- β -methyl acid **1** [9], which, after decarboxylation in pyridine furnished the β,γ -unsaturated nitrile **2** (Scheme 2). In a previous report, *Smit* [10] considered this step as an abnormal decarboxylation. Nitrile **2** was isomerized to the α,β -unsaturated isomers **3** ((*2E,4E*)/(*2Z,4E*) 4:1) by heating in

KOH/MeOH. In this case, we think that the decarboxylation occurred in a regular manner, due to the presence of the stronger electron-withdrawing effect of the nitrile group, which could induce the suggested process, *i.e.*, abstraction of a H-atom from Me–C(3) by the base prior to loss of CO₂ (Scheme 2).

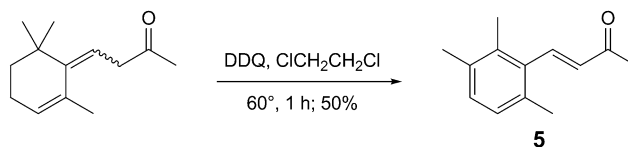


We now developed an improved process which allowed the formation of nitrile **3** in a ‘one-pot’ procedure, with a good regioselectivity. Thus, condensation of β -ionone with cyanoacetic acid in piperidine/benzene under reflux (*Dean–Stark*; 6.5 h) led to **3** nearly quantitatively ((*2E,4E*)/(*2Z,4E*) 95:5 to 98:2; Scheme 3). Piperidine (8 equiv.) and benzene (as solvent) seemed to be indispensable because other bases and solvents led to a mixture of nitriles with poor regioselectivity. Under these experimental conditions, the initially formed cyanoacetic acids were concomitantly decarboxylated in the reaction mixture. The (*2E,4E*)-nitrile **3** was easily purified by column chromatography (SiO₂, CH₂Cl₂). Thus, the crude C₁₅-nitrile **3** was reduced by diisobutylaluminium hydride (DIBAL-H) in toluene at 0° (30 min) to yield the sesquiterpenene aldehyde **4** ((*2E,4E*)/(*2Z,4E*) 95:5 to 98:2). The crude aldehyde was purified by column chromatography (SiO₂, CH₂Cl₂) to provide (*2E,4E*)-**4** as a yellow oil in 82% yield from **3** [10].



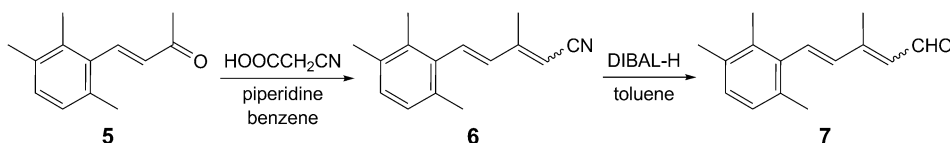
φ -End Group. We have also recently reported that oxidation of β -ionone and α -ionone having the respective β - and ε -end group of carotenoids led to the corresponding C₁₃ aromatic ketone **5**. By an improved procedure, under particularly mild conditions, ketone **5** could be obtained from *retro*-ionone, an isomer of β - and α -ionones (Scheme 4). Hence *retro*-ionone was heated at 60° for 1 h with 3 equiv. of 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) in 1,2-dichloroethane to produce the aromatic ketone **5** in 50% yield [11]. In this rapid process, extraction and purification were easier. This reaction could be integrated into a new biomimetic aromatization of a β -end group to a φ -end group, with regiospecific migration of one of the Me groups [2].

Scheme 4



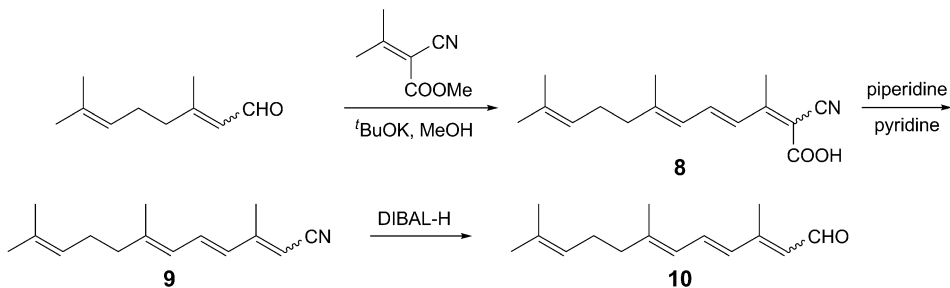
As described above (Scheme 3), a *Knoevenagel* condensation of aromatic ionone **5** with cyanoacetic acid in piperidine/benzene under reflux (*Dean–Stark*) led to the sesquiterpene nitrile **6** ((*2E,4E*)/(*2Z,4E*) 95:5) (Scheme 5). The (*E,E*)-nitrile was easily purified by recrystallization from pentane/ Et_2O 70:30 and was further reduced by DIBAL-H in toluene at 0° (30 min) to the corresponding aldehyde **7** (85%).

Scheme 5



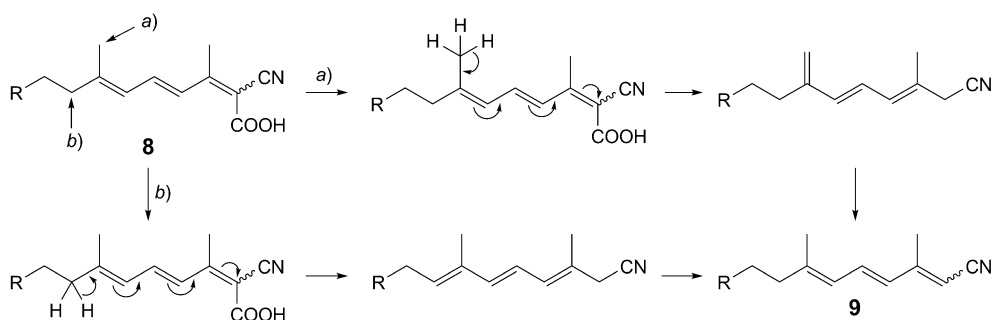
ψ -End Group. Condensation of citral with methyl cyano(isopropylidene)acetate, under *Stobbe's* conditions ($t\text{BuOK}$, MeOH, 0° , then 24 h r.t.) led to cyano acid **8** ((*E*)/(*Z*)-isomer *ca.* 4:1), which was further decarboxylated in pyridine/piperidine under reflux (2–3 h) to provide nitrile **9** as a 7:3 mixture of (*E*)- and (*Z*)-isomers (Scheme 6). After reduction with DIBAL-H at 0° (30 min), aldehyde **10** was obtained as a 7:3 mixture of (*E*)- and (*Z*)-isomers which were separated by chromatography.

Scheme 6



Taking into account the results of the above series (Scheme 6), two routes, *a*) and *b*), can be competing in the acyclic series as shown in Scheme 7, and two nitriles may be predicted as intermediates (unfortunately not detected under our experimental conditions in the decarboxylation process).

Scheme 7



Conclusion. – This work and previous ones reported elsewhere showed that decarboxylation of malonic acid derivatives or analogs can be dependent on many factors, such as base effect, steric hindrance, electron-withdrawing effect of the malonic acid derived moiety, and others.

Experimental Part

General. Starting materials and solvents were obtained from *Aldrich* (Germany) and were used without further purification. All reactions were carried out under Ar. M.p.: *Leitz-350*-microscope heating stage; not corrected. IR Spectra: *Bruker-IF-55* spectrometer; $\tilde{\nu}$ in cm^{-1} . ^1H - and ^{13}C -NMR Spectra: *Bruker-Avance-DPX-400* spectrometer; at 400 (^1H) and 100 MHz (^{13}C); in CDCl_3 ; δ in ppm rel. to Me_4Si as internal standard, J in Hz.

(2*E*,4*E*)- and (2*Z*,4*E*)-2-Cyano-3-methyl-5-(2,6,6-trimethylcyclohex-1-en-1-yl)penta-2,4-dienoic Acid (**1**). Its synthesis is reported in [9][10][12]: (2*E*,4*E*)-**1** was obtained as orange crystals after recrystallization from benzene, m.p. 174°. The mother liquor (benzene) was diluted with petroleum ether to furnish (2*Z*,4*E*)-**1** as orange crystals, m.p. 124°.

(4*E*)-3-Methylene-5-(2,6,6-trimethylcyclohex-1-en-1-yl)pent-4-enenitrile (**2**). The crude α -cyano acids **1** were refluxed in pyridine for 2 h, the pyridine was distilled off under reduced pressure, and the oily mixture was acidified with 1*N* HCl and extracted with Et_2O . The extract was purified by filtration through SiO_2 , the filtrate evaporated, and the residue distilled *in vacuo* to give **2**. Colorless oil (90%). IR (film): 2212. ^1H -NMR¹⁾: 6.11 (s, H-C(7), H-C(8)); 5.37, 5.33 (2s, CH_2 -C(9)); 3.33 (s, CH_2 (10)); 2.02 (m, CH_2 (4)); 1.70 (s, Me-C(5)); 1.63 (m, CH_2 (3)); 1.47 (m, CH_2 (2)); 1.02 (s, 2 Me-C(1)). ^{13}C -NMR : 132.7; 129.3; 117.9; 39.8; 33.3; 29.2; 22.0; 21.6; 19.6.

(2*E*,4*E*)- and (2*Z*,4*E*)-3-Methyl-5-(2,6,6-trimethylcyclohex-1-en-1-yl)penta-2,4-dienenitrile (**3**). *a*) Nitrile **2** (5 g) was isomerized in 2*M* NaOH (100 ml) at r.t. overnight: (2*E*,4*E*)/(2*Z*,4*E*)-**3** 4:1. This mixture was separated by CC (SiO_2 , CH_2Cl_2).

(2*E*,4*E*)-**3**: IR (film): 2210, 1610. ^1H -NMR¹⁾: 6.50 (d, $J = 16$, H-C(7)); 6.08 (d, $J = 16$, H-C(8)); 5.10 (s, H-C(10)); 2.20 (s, Me-C(5)); 2.00 (m, CH_2 (4)); 1.70 (s, Me-C(9)); 1.60 (m, CH_2 (3)); 1.40 (m, CH_2 (2)); 0.92 (s, 2 Me-C(1)). ^{13}C -NMR (CDCl_3): 156.9; 136.5; 135.3; 132.5; 132.2; 128.1; 96.2; 39.3; 34.0; 33.0; 26.7; 21.5; 16.3.

(2*Z*,4*E*)-**3**: IR (film): 2210, 1610. ^1H -NMR¹⁾: 6.60 (d, $J = 16$, H-C(8)); 6.50 (d, $J = 16$, H-C(7)); 5.00 (s, H-C(10)); 2.00 (s, Me-C(5) and m, CH_2 (4)); 1.70 (s, Me-C(9)); 1.60 (m, CH_2 (3)); 1.50 (m, CH_2 (2)); 1.02 (s, 2 Me-C(1)).

¹⁾ Trivial atom numbering.

b) β -Iodone (6 g) was condensed with cyanoacetic acid (1.1 equiv.) in piperidine (20 ml) and benzene (20 ml) under reflux (*Dean-Stark* apparatus): (2*E*,4*E*)/(2*Z*,4*E*)-**3** 4:1 (nearly quant.). This mixture was separated by CC (SiO₂, CH₂Cl₂).

(2*E*,4*E*)- and (2*Z*,4*E*)-3-Methyl-5-(2,6,6-trimethylcyclohex-1-en-1-yl)penta-2,4-dienal (**4**). At 0°, 1,2M DIBAL-H in toluene (23.5 ml, 28.2 mmol, 1.1 equiv.) was added slowly to **3** (5.06 g) in toluene (20 ml). After 30 min, the reaction was quenched with 1M H₂SO₄. The salts were filtered off, and Et₂O (40 ml) and H₂O (20 ml) were added. The org. layer was washed twice with brine, dried (MgSO₄), and concentrated. The crude (2*E*,4*E*)/(2*Z*,4*E*)-**4** 49:1 was separated by CC (SiO₂, CH₂Cl₂): (2*E*,4*E*)-**4** (82%). Yellow oil. IR: 1668. ¹H-NMR¹: 10.11 (*d*, *J* = 8.16, H–C(11)); 6.73 (*d*, *J* = 16.2, H–C(7)); 6.20 (*d*, *J* = 16.2, H–C(8)); 5.92 (*d*, *J* = 8.16, H–C(10)); 2.3 (*s*, Me–C(9)); 2.03 (*m*, CH₂(4)); 1.71 (*s*, Me–C(5)); 1.6 (*m*, CH₂(3)); 1.47 (*m*, CH₂(2)); 1.03 (*s*, 2 Me–C(1)). ¹³C-NMR: 135.7 (CH); 135.4 (CH); 128.7 (CH); 39.7 (CH₂); 33.4 (CH₂); 19.4 (CH₂); 28.9 (Me); 21.6 (Me); 12.9 (Me).

(3*E*)-4-(2,3,6-Trimethylphenyl)but-3-en-2-one (**5**). *retro-α*-Ionone (9.62 g; 50 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 34 g, 3 equiv.) in 1,2-dichloroethane (100 ml) were heated for 1 h at 65°. The mixture was filtered, the filtrate concentrated, and the crude product purified by CC (SiO₂, pentane/1,2-dichloroethane 1:1): **5** (50%). Yellow oil. IR (film): 1680. ¹H-NMR¹: 7.72 (*d*, *J* = 16, H–C(7)); 7.05, 6.95 (2*d*, *J* = 7, H–C(3), H–C(4)); 6.25 (*d*, *J* = 16, H–C(8)); 2.40, 2.35, 2.30, 2.25 (4*s*, 4 Me). ¹³C-NMR (CDCl₃): 188.0 (C=O); 134.6 (C); 134.5 (C); 133.5 (C); 143.1 (CH); 133.4 (CH); 129.8 (CH); 127.5 (CH); 27.4 (Me); 20.8 (Me); 16.9 (Me).

(4*E*)-3-Methyl-5-(2,3,6-trimethylphenyl)penta-2,4-dienitrile (**6**). In a *Dean-Stark* apparatus, a soln. of **5** (6 g) and cyanoacetic acid (8.21 g, 3 equiv.) in benzene (30 ml) was cooled to 0°, and piperidine (25.43 ml, 8 equiv.) was slowly added. Then, the mixture was refluxed for 4 h. The benzene was evaporated, the crude product extracted with Et₂O, the org. layer washed with brine and H₂O, dried (MgSO₄), and concentrated, the crude product extracted with CH₂Cl₂, and this extract quickly filtered over a mixture of basic alumina and SiO₂ 40:60: (2*E*,4*E*)/(2*Z*,4*E*)-**6** 95:5 (96%; ratio determined by ¹H-NMR). Yellow ochre crystals which were purified by recrystallization from Et₂O/pentane 30:70: major isomer (2*E*,4*E*)-**6**. M.p. 62°. IR (film): 2206. ¹H-NMR¹: 7.02 (*d*, *J* = 16.3, H–C(7)); 6.98 (*d*, *J* = 7.5, H–C(3)); 6.96 (*d*, *J* = 7.5, H–C(4)); 6.28 (*d*, *J* = 16.3, H–C(8)); 5.25 (*s*, H–C(10)); 2.32 (*s*, Me–C(2)); 2.26 (*s*, Me–C(9)); 2.25 (*s*, Me–C(5)); 2.2 (*s*, Me–C(1)). ¹³C-NMR (CN): 118.0; 157.1 (C); 136.0 (C); 134.9 (C); 134.7 (C); 133.8 (C); 135.9 (CH); 134.5 (CH); 129.7 (CH); 127.8 (CH); 98.3 (CH); 21.2 (Me); 20.7 (Me); 17.4 (Me); 16.9 (Me).

(4*E*)-(2,3,6-Trimethylphenyl)penta-2,4-dienal (**7**). At 0°, 1,2M DIBAL-H in toluene (24 ml, 1.2 equiv.) was slowly added under vigorous stirring to **6** (5 g) in toluene. The mixture was stirred for 2 h and then hydrolyzed by 2M H₂SO₄. After filtration of the aluminium salts, Et₂O (50 ml) and H₂O (50 ml) were added. The org. layer was washed with brine and H₂O, dried (MgSO₄), and concentrated and the crude product purified by CC (SiO₂, CH₂Cl₂): major isomer (2*E*,4*E*)-**7** (85%). Yellow oil. IR (film): 1659. ¹H-NMR¹: 10.20 (*d*, *J* = 8.1, H–C(11)); 7.18 (*d*, *J* = 16.4, H–C(7)); 7.01 (2*d*, *J* = 7.6, H–C(3), H–C(4)); 6.36 (*d*, *J* = 16.4, H–C(8)); 6.14 (*d*, *J* = 8.1, H–C(10)); 2.44 (*s*, Me–C(9)); 2.26 (*s*, Me–C(1), Me–C(2)); 2.23 (*s*, Me–C(5)). ¹³C-NMR: 191.3 (C=O); 154.1 (C); 135.9 (C); 134.5 (C); 134.4 (C); 133.5 (C); 137.2 (CH); 135.2 (CH); 129.7 (CH); 129.2 (CH); 127.5 (CH); 20.8 (Me); 20.4 (Me); 13.0 (Me); 9.7 (Me).

(2*E*,4*E*,6*E*)- and (2*Z*,4*E*,6*E*)-2-Cyano-3,7,11-trimethyldodeca-2,4,6,10-tetraenoic Acid (**8**) and (2*E*,4*E*,6*E*)- and (2*Z*,4*E*,6*E*)-3,7,11-Trimethyldodeca-2,4,6,10-tetraenenitrile (**9**). At 0°, a mixture of citral (1.52 g) and methyl cyano(isopropylidene)acetate (= methyl 2-cyano-3-methylbut-2-enoate; **3**; 2.325 g, 1.5 equiv.) was added to ^tBuOK (1.12 g, 1 equiv.) in MeOH (25 ml). The soln. was allowed to stay at r.t. for 24 h. The MeOH was evaporated and ice (100 g) was added. The mixture was extracted with Et₂O, the aq. layer acidified and extracted with Et₂O, and this extract washed with H₂O, dried (MgSO₄), and concentrated: crude **8** as a mixture of isomers.

A soln. of crude **8** (1 g) in piperidine (50 ml) and pyridine (50 ml) was refluxed until the flow of CO₂ ceased (2–3 h). The bases were evaporated and the crude product was extracted with Et₂O. The extract was washed successively with a 1M HCl and H₂O, dried (MgSO₄) and concentrated: (2*E*,4*E*,6*E*)/(2*Z*,4*E*,6*E*)-**9** 7:3. This mixture was separated by CC (SiO₂, CH₂Cl₂).

(2E,4E,6E)-**9**: (85%): IR(film): 2213. ¹H-NMR¹: 1.60 (s, Me_a-C(1)); 1.68 (s, Me_b-C(1)); 1.87 (s, Me-C(5)); 2.17 (m, CH₂(3), CH₂(4)); 2.21 (s, Me-C(9)); 5.17 (m, H-C(2)); 5.29 (s, H-C(10)); 5.93 (d, J = 11.0, H-C(6)); 6.19 (d, J = 15.2, H-C(8)); 6.76 (dd, J = 15.2, 11.0, H-C(7)). ¹³C-NMR: 133.0 (CH); 130.2 (CH); 127.6 (CH); 123.8 (CH); 96.4 (CH); 40.7 (CH₂); 26.8 (CH₂); 26.1 (Me); 18.1 (Me); 17.0 (Me). (2Z,4E,6E)-**9**: ¹H-NMR¹: 1.56 (s, Me_a-C(1)); 1.64 (s, Me_b-C(1)); 1.86 (s, Me-C(5)); 2.10 (m, CH₂(3), CH₂(4)); 2.18 (s, Me-C(9)); 5.11 (m, H-C(2), H-C(10)); 6.04 (d, H-C(6)); 6.70 (d, J = 15.0, H-C(8)); 6.76 (dd, J = 15.0, 11.0, H-C(7)). ¹³C-NMR: 133.5 (CH); 129.9 (CH); 125.7 (CH); 124.8 (CH); 95.0 (CH); 33.3 (CH₂); 27.2 (CH₂); 24.8 (Me); 19.8 (Me); 18.1 (Me).

(2E,4E,6E)- and (2Z,4E,6E)-3,7-Trimethyldodeca-4,6-trienal (**10**). As described for **7**, with **9** (0.645 g) in toluene and DIBAL-H (1.1 equiv.) in toluene. After 30 min, the reaction was quenched with 1M H₂SO₄. After filtration and usual workup, the org. layer was rapidly filtered over Al₂O₃: (2E,4E,6E)/(2Z,4E,6E)-**10** 7:3 (65%). This mixture was separated by CC (SiO₂, CH₂Cl₂).

(2E,4E,6E)-**10**: ¹H-NMR¹: 1.60 (s, Me_a-C(1)); 1.70 (s, Me_b-C(1)); 1.89 (s, Me-C(5)); 2.05 (m, CH₂(3), CH₂(4)); 2.36 (s, Me-C(9)); 5.11 (m, H-C(2)); 5.96 (d, J = 8.1, H-C(10)); 6.24 (m, H-C(3), H-C(4)); 10.09 (d, J = 8.0, H-C(11)). ¹³C-NMR: 191.6 (C=O); 133.1 (CH); 129.1 (CH); 126.3 (CH); 125.3 (CH); 123.8 (CH); 40.7 (CH₂); 26.8 (CH₂); 26.1 (Me); 17.7 (Me); 13.5 (Me).

(2Z,4E,6E)-**10**: ¹H-NMR¹: 1.61 (s, Me_a-C(1)); 1.68 (s, Me_b-C(1)); 1.87 (s, Me-C(5)); 2.15 (m, CH₂(3), CH₂(4)); 2.3 (s, Me-C(9)); 5.08 (m, H-C(2)); 5.85 (d, J = 8.0, H-C(10)); 5.95 (d, J = 15.0, H-C(6)); 6.98 (m, J = 15.0, H-C(8)); 7.37 (m, H-C(7)); 10.18 (d, J = 7.5, H-C(11)). ¹³C-NMR: 190.4 (C=O); 134.0 (CH); 133.3 (CH); 127.9 (CH); 125.4 (CH); 125.1 (CH); 33.4 (CH₂); 27.2 (CH₂); 24.9 (Me); 21.6 (Me); 18.1 (Me).

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