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σ-COMPLEXES OF TRANSITION METALS IN ORGANIC SYNTHESIS. 8.* COUPLED ADDITION OF ALLYL Mn(II)-ORGANIC COMPOUNDS TO ESTERS AND NITRILES OF α,β-UNSATURATED CARBOXYLIC ACIDS

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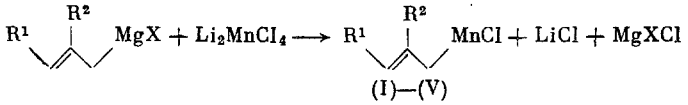
Allyl Mn(II)-organic compounds $R^1CH{=}C(R^2){\cdot}CH_2MnCl$ (R^1 = H, Me; R^2 = H, Me, Bu, $PhCH_2$) react with esters and nitriles of crotonic, trans-2-hexenoic, sorbic, cinnamic, maleic, fumaric, heptylidenemalonic, and trans-(2-butenylidene)malonic acids in THF at –78 to –60°C giving 1,4-addition products. A single diastereoisomer is formed in the case of $MeCH{=}CHCO_2Me$ and $PrCH{=}CHCO_2Me$.

Coupled addition of organometallic derivatives to α,β-unsaturated carbonyl substrates is the most important method of forming a new carbon–carbon bond [2-4].

Previously we have described the use of allyl derivatives of Mn(II) in carrying out chemo-, regio-, and stereoselective crosslinking with allyl halides [1, 5, 6].

In this work we studied reactions of allyl derivatives of Mn(II) with esters and nitriles of α,β-unsaturated carboxylic acids. The initial organomanganese compounds (I)-(V) were produced in situ from Li_2MnCl_4 and the corresponding Grignard reagents in THF at –78°C [7]:



$R^1, R^2 = H$ (I); $R^1 = Me, R^2 = H$ (II); $R^1, R^2 = Me$ (III); $R^1 = Me, R^2 = Bu$ (IV); $R^1 = Me, R^2 = CH_2Ph$ (V); X = Cl, Br.

*For previous communication, see [1].

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TABLE 1. Reactions of MeCH=C(Me)CH_2MnCl (III) with Esters and Nitriles of α,β-Unsaturated Carboxylic Acids (THF, –78 to –60°C, 2 h, (III):substrate = 2:1)

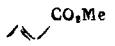
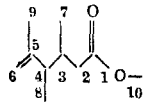
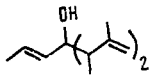
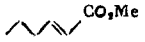
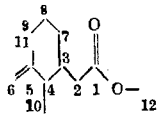
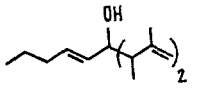
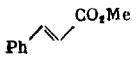
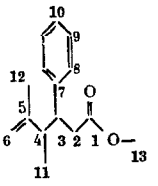
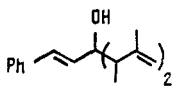
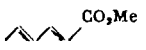
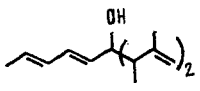
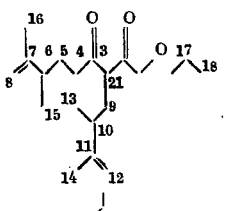
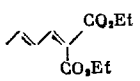
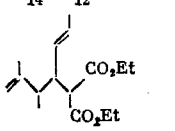
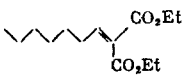
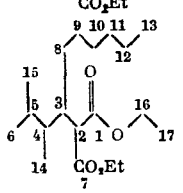
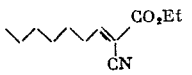
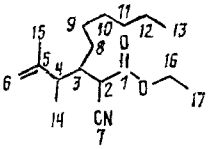
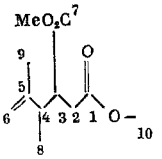
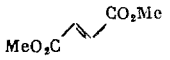
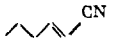
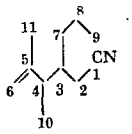
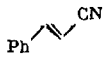
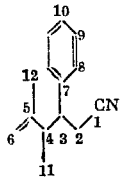
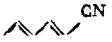
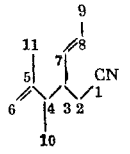
Substrate	Reaction product*		Yield, %
		(VIa)	69
		(VIIa)	18
		(VIb)	45
		(VIIb)	39
		(VIc)	27
		(VIIc)	36
		(VIId)	56
		(VIII)	62
		(XIa)	69
		(XIb)	63

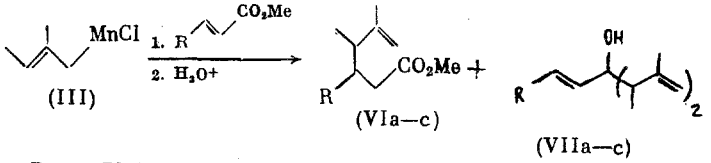
TABLE 1 (continued)

Substrate	Reaction product*	Yield, %
	 (XIc)	90
	 (XId)	67
	(XId)	43
	 (XIIa)	55
	 (XIIb)	73
	 (XIIc)	31

*Compounds (VIa and b) are a single stereoisomer; compounds (VIc), (XIa-d), and (XIIa-c) are a mixture of diastereoisomers.

Data on the reactions of 2-methyl-2-butenylmanganese chloride (III)* with a number of unsaturated substrates containing a complex ester group are given in Table 1.

Interaction of reagent (III) with the methyl esters of crotonic, trans-2-hexenoic, and cinnamic acids gives in each case a mixture of 1,4-addition products (VI) and tertiary alcohols (VII):



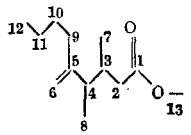
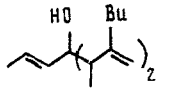
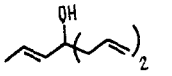
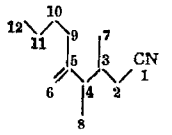
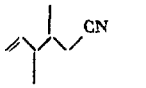
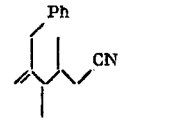
(III) (VIa–c) (VIIa–c)

R = Me (a), Pr (b), Ph (c).

The reaction with methyl cinnamate, in addition, is complicated by the formation of significant amounts of polymeric products. Unlike these listed substrates, methyl sorbate gives only the tertiary alcohol (VIId) on reaction with reagent (III).

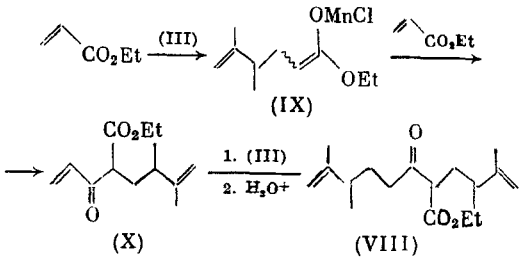
*Not less than a two-fold excess of reagent (III) is necessary owing to the relatively low stability of allyl derivatives of Mn(II) [1, 5, 6].

TABLE 2. Reactions of Allyl Organomanganese Reagents with the Methyl Ester and Nitrile of Crotonic Acid

Substrate	Reagent	Reaction product*	Yield, %
Methyl crotonate	(IV)	 (XIII)	37
		 (XIVa)	58
Methyl crotonate	(I)	 (XIVb)	78
Crotononitrile	(IV)	 (XV)	72
Crotononitrile	(II)	 (XVI)	96
Crotononitrile	(V)	 (XVII)	42

*Compound (XIII) is a single diastereoisomer; compounds (XV)-(XVII) are a mixture of diastereoisomers.

Condensation of (III) with ethyl acrylate yields the β-ketoester (VIII). It is evidently formed as a result of three successive stages: coupled addition of (III) to CH_2=$CHCO_2Et$, interaction of the manganese enolate (IX) with CH_2=$CHCO_2Et$ in a complex-ester condensation, and further 1,4-addition of reagent (III) to the enone (X):



Compounds containing a double bond activated by two electron-acceptor groups are extremely active substrates in coupled-addition reactions [2, 8]. Trans-diethyl-2-butenylidene malonate, in contrast to methyl sorbate, reacts with (III) exclusively at the β-carbon atom to give the complex ester (XIa). Condensation of (III) with heptylidenemalonic and E-heptylidenecyanoacetic esters also leads to formation of similar products (XIb and c) with no trace of tertiary alcohols.

There is practically no side process of 1,2-addition when (III) reacts with the dimethyl esters of maleic and fumaric acids. The yield of the substituted dimethyl succinate (XId) depends on the configuration of the double bond in the substrate and decreases on going from dimethyl maleate to dimethyl fumarate. In the second case, along with the diester (XId), a complex mixture of compounds is produced, the structure of which was not determined.

Compared with trans-methyl 2-hexenoate, methyl cinnamate, and methyl sorbate (Table 1), the corresponding nitriles react with (III) to produce substantially larger yields of 1,4-addition products (XIIa-c).

The effect of structure of the initial organomanganese compound on the ratio of condensation products was studied using reactions of the allyl derivatives (I)-(V) with the methyl ester and nitrile of crotonic acid (Table 2).

On interaction of methyl crotonate with 2-butyl-2-butenylmanganese chloride (IV), the ester (XIII) is formed in lower yield and the tertiary alcohol (XIVa), on the other hand, in higher yield than the ester (VIa) and the alcohol (VIIa) produced using reagent (III) (Table 1). Condensation of $MeCH{=}CHCO_2Me$ with allylmanganese chloride (I) gives only the diallylpropenylcarbinol (XIVb) (Table 2). Treatment of reagents (IV) and (II) with the nitrile of crotonic acid yields the 1,4-addition products (XV) and (XVI) respectively. In the analogous reaction of MeCH=CHCN with 2-benzyl-2-butenylmanganese chloride (V) the yield of nitrile (XVII) is substantially lower owing to appreciable resinification.

According to PMR and ^{13}C-NMR data, coupled addition of reagents (III) and (IV) to methyl esters of crotonic and trans-2-hexenoic acids is accompanied by formation of only a single diastereoisomer in each case. In contrast to these substrates, nitriles of the same acids, and also $PhCH{=}CHCO_2Me$, PhCH=CHCN, MeCH=CHCH=CHCN, and compounds with a double bond activated by two electron–acceptor groups (Table 1), do not react stereoselectively.

Thus, interaction of allyl derivatives of Mn(II) with esters and nitriles of α,β-unsaturated carboxylic acids provides a convenient method for synthesis of a variety of unsaturated products containing a complex-ester or CN-group.

EXPERIMENTAL

Chromatographic analysis was carried out using a Chrom-5 chromatograph with a flame-ionization detector in a current of He (50 ml/min); column 1.2 mm × 3 mm, 5% SE-30 on inerton-super. The PMR spectra in CCl_4 were recorded on a Tesla BS-467 (60 MHz) spectrometer and ^{13}C-NMR spectra in $CDCl_3$ on a JEOL FX-90 Q spectrometer; TMS was used as the internal standard. The IR spectra were recorded on a UR-20 apparatus using a thin layer of the substance. Mass spectra were recorded on an MX-1300 spectrometer with an input temperature of 100°C and electron-ionization energies of 70 and 12 eV.

2-Methyl, 2-Butyl-, and 2-Benzyl-2-butenylmagnesium bromides were prepared by hydromagnesation of isoprene, 2-butyl-, and 2-benzylbutadiene in the presence of Cp_2TiCl_2 [9]. Crotylmagnesium bromide [10], Li_2MnCl_4 (as a 0.8 M solution in THF) [7], heptylidenemalonic and heptylidenecyanoacetic esters [11], and 2-butenylidenemalonic ester [12] were prepared by known procedures. All reactions were carried out in an atmosphere of dry Ar. Immediately before use THF was redistilled over $LiAlH_4$.

Reactions of Allyl Organomanganese Compounds with Esters and Nitriles of α,β-Unsaturated Carboxylic Acids. To a flask fitted with a stirrer were added 8 ml THF and 6 ml (6 mmoles) 1 M 2-methyl-2-butenylmagnesium bromide in ether solution. With mixing and cooling to –78°C, 7.5 ml (6 mmoles) 0.8 M Li_2MnCl_4 in THF were run in and stirred for 40 min at –78°C. To the resulting red-brown solution of compound (III) were added 0.3 g (3 mmoles) of methyl crotonate. The reaction mixture was warmed to –60°C for 2 h, then hydrolyzed with 40 ml 2 N HCl, and extracted with ether (3 × 15 ml). The ether layer was washed with water, dried with $MgSO_4$, and concentrated. Column chromatography (silica gel L 40/100; 5:1 hexane–ether) yielded 0.112 g (18%) alcohol (VIIa) and 0.352 g (69%) ester (VIa).

Similar procedures were used for the reactions of organomanganese compounds (I)-(V) with other esters and nitriles of α,β-unsaturated carboxylic acids. The results are shown in Tables 1 and 2.

Methyl Ester of 3,4,5-Trimethyl-5-hexenoic Acid (VIa). IR spectrum (ν, cm^{-1}): 3080, 1730, 1640, 1430, 1380, 1250, 895. PMR spectrum (δ, ppm): 0.90 d (3H, Me, J = 7 Hz), 0.95 d (3H, Me, J = 7 Hz), 1.63 s (3H, MeC=), 1.43-2.46 m (4H, CH, CHC=, CH_2CO), 3.53 s (3H, MeO), 4.6 m (2H, CH_2=). ^{13}C NMR spectrum (δ, ppm): 174.13 s (C^1), 38.17 t (C^2), 37.78 d (C^3), 46.21 d (C^4), 148.56 s (C^5), 110.85 t (C^6), 18.69 q (C^7), 15.87 q (C^8), 19.88 q (C^9), 51.36 q (C^{10}). Mass spectrum, m/z: 170 [M]+.

1,1-Bis(1,2-dimethyl-2-propenyl)-2-butenol (VIIa). IR spectrum (ν, cm^{-1}): 3550, 3080, 3040, 1670, 1640, 1460, 1380, 1175, 990, 905. PMR spectrum (δ, ppm): 0.94 d and 0.98 d (6H, Me, J = 7 Hz), 1.23-1.83 m (10H, MeC=, OH), 2.29 q (2H, CHC=, J = 7 Hz), 4.53 m and 4.68 m (4H, CH_2=), 5.27-5.55 m (2H, CH=). Mass spectrum, m/z: 208 [M]+.

Methyl Ester of 3-Propyl-4,5-dimethyl-5-hexenoic Acid (VIb). IR spectrum (ν, cm^{-1}): 3090, 1740, 1650, 1460, 1385, 1180, 905. PMR spectrum (δ, ppm): 0.90 t (3H, Me, J = 7 Hz), 0.93 d (3H, Me, J = 7 Hz), 1.10-1.50 m (4H, CH_2), 1.68 s (3H, MeC=), 1.83-2.53 m (4H, CH, CH_2CO, CHC=), 3.54 s (3H, MeO), 4.47-4.88 m (2H, CH_2=),

^{13}C NMR spectrum (δ, ppm): 174.35 s (C^1), 35.22 t (C^2), 36.52 d (C^3), 42.59 d (C^4), 148.73 s (C^5), 110.69 t (C^6), 35.00 t (C^7), 19.99 t (C^8), 14.14 q (C^9), 14.25 q (C^{10}), 20.97 q (C^{11}), 51.31 q (C^{12}). Mass spectrum, m/z: 198 [M]+.

1,1-Bis(1,2-dimethyl-2-propenyl)-2-hexenol (VIIb). IR spectrum (ν, cm^{-1}): 3550, 3080, 3035, 1640, 1460, 1385, 1175, 995, 905. PMR spectrum (δ, ppm): 0.87 t (3H, Me, J = 7 Hz), 0.95 d and 0.99 d (6H, Me, J = 7 Hz), 1.13-1.47 m (2H, CH_2), 1.67 s (6H, MeC=), 1.75-2.12 m (3H, CH_2C=, OH), 2.34 q (2H, CHC=, J = 7 Hz), 4.47-4.9 m (4H, CH_2=), 5.28-5.58 m (2H, CH=). Mass spectrum, m/z: 236 [M]+.

Methyl Ester of 3-Phenyl-4,5-dimethyl-5-hexenoic Acid (VIc). IR spectrum (ν, cm^{-1}): 3080, 3040, 1750, 1650, 1620, 1500, 1480, 1255, 1170, 900, 760. PMR spectrum (δ, ppm): 0.97 d and 1.00 d (3H, Me, J = 7 Hz), 1.57 s and 1.65 s (3H, MeC=), 2.2-2.75 m (3H, CH_2CO, CHC=), 2.85-3.27 m (1H, CHPh), 3.38 s (MeO), 4.5 m and 4.73 m (2H, CH_2=), 7.06 m (5H, arom.). ^{13}C NMR spectrum (δ, ppm): 173.11 s (C^1), 37.01 t (C^2), 46.28 d, 47.20 d (C^3), 45.04 d (C^4), 147.79 s, 148.05 s (C^5), 111.62 t, 113.32 t (C^6), 143.02 s (C^7), 128.01 d, 128.36 d, 128.66 d (C^8, C^9), 126.24 d (C^{10}), 16.19 q, 14.10 q (C^{11}), 22.26 q, 20.24 q (C^{12}), 51.37 q (C^{13}). Mass spectrum, m/z: 232 [M]+.

1,1-Bis(1,2-dimethyl-2-propenyl)-3-phenyl-2-propenol (VIIc). IR spectrum (ν, cm^{-1}): 3540, 3085, 3040, 1640, 1605, 1500, 1460, 1390, 1170, 990, 910, 780, 765, 710. PMR spectrum (δ, ppm): 1.03 d and 1.06 d (6H, Me, J = 6.5 Hz), 1.60 s and 1.68 s (6H, MeC=), 1.9 s (1H, OH), 2.28-2.7 m (2H, CHC=), 4.58 m and 4.75 m (4H, CH_2=), 6.11 d and 6.15 d (1H, CH=, J_{AB} = 16 Hz), 6.3 d and 6.48 d (1H, PhCH=, J_{AB} = 16 Hz), 7.14 m (5H, arom.). Mass spectrum, m/z: 270 [M]+.

1,1-Bis(1,2-dimethyl-2-propenyl)-2,4-hexadienol (VIId). IR spectrum (ν, cm^{-1}): 3550, 3085, 3030, 1645, 1460, 1390, 1110, 990, 910, 810. PMR spectrum (δ, ppm): 0.94 d and 0.99 d (6H, Me, J = 7 Hz), 1.45-1.83 m (9H, MeC=), 2.37 q (2H, CHC=, J = 7 Hz), 4.45-4.9 m (4H, CH_2=), 5.08-6.2 m (4H, CH=). Mass spectrum, m/z: 234 [M]+.

Ethyl Ester of 2-(2,3-Dimethyl-3-butenyl)-3-oxo-6,7-dimethyl-7-octenoic Acid (VIII). IR spectrum (ν, cm^{-1}): 3085, 1740, 1720, 1650, 1460, 1380, 1270, 1180, 910. PMR spectrum (δ, ppm): 0.95 d and 1.00 d (6H, Me, J = 6.5 Hz), 1.13-1.9 m (7H, Me, CH_2), 1.59 s (6H, MeC=), 1.95-2.5 m (4H, CHC=, CH_2CO), 3.0-3.53 m (1H, CHCO), 3.83-4.27 m (2H, CH_2O), 4.58 m (4H, CH_2=). ^{13}C NMR spectrum (δ, ppm): 167.90 s (C^1), 55.59 d, 54.83 d (C^2), 203.29 s (C^3), 38.62 t (C^4), 26.17 t (C^5), 37.38 d (C^6), 146.83 s (C^7), 108.47 t (C^8), 30.88 t (C^9), 37.71 d, 38.52 d (C^{10}), 146.45 s, 146.12 s (C^{11}), 109.17 t, 109.34 (C^{12}), 16.25 q, 16.63 q, 17.72 q, 17.99 q (C^{13}, C^{14}, C^{15}, C^{16}), 59.22 t (C^{17}), 12.19 q (C^{18}). Mass spectrum, m/z: 294 [M]+.

Ethyl Ester of 2-Ethoxycarbonyl-3-(1-propenyl)-4,5-dimethyl-5-hexenoic Acid (XIa). IR spectrum (ν, cm^{-1}): 3085, 3040, 1750, 1735, 1670, 1650, 1460, 1380, 1170, 990, 910. PMR spectrum (δ, ppm): 0.88 d and 0.93 d (3H, Me, J = 7 Hz), 1.19 t and 1.21 t (6H, Me, J = 7 Hz), 1.59 s and 1.61 s (6H, MeC=), 2.08-2.72 m (2H, CHC=), 3.15-3.42 m (1H, CHCO), 4.05 q and 4.10 q (4H, CH_2O, J = 7 Hz), 4.62 m (2H, CH_2=), 5.2-5.6 m (2H, CH=). Mass spectrum, m/z: 282 [M]+.

Ethyl Ester of 2-Ethoxycarbonyl-3-hexyl-4,5-dimethyl-5-hexenoic Acid (XIb). IR spectrum (ν, cm^{-1}): 3090, 1750, 1735, 1650, 1460, 1380, 1170, 930, 750. PMR spectrum (δ, ppm): 0.83 t (3H, Me, J = 7 Hz), 0.91 d (3H, Me, J = 7 Hz) 1.05-1.4 m (16H, Me, CH_2), 1.62 s (3H, MeC=), 1.88-2.3 m (2H, CH, CHC=), 3.17-3.35 m (1H, COCHCO), 4.03 q and 4.05 q (4H, CH_2O, J = 7 Hz), 4.66 m (2H, CH_2=). ^{13}C NMR spectrum (δ, ppm): 169.26 s, 169.15 s, 168.93 s, 168.50 s (C^1, C^7), 52.39 d, 54.67 d (C^2), 39.99 d, 40.53 d (C^3), 42.37 d, 43.34 d (C^4), 147.91 s, 148.13 s (C^5), 111.07 t, 111.23 t (C^6), 30.18 t, 31.53 t (C^8), 28.77 t, 27.85 t (C^9), 29.20 t, 29.58 t (C^{10}), 31.53 t (C^{11}), 22.38 t (C^{12}), 13.76 q (C^{13}), 14.80 q, 15.50 q (C^{14}), 20.43 q, 19.51 q (C^{15}), 60.68 t, 60.57 t (C^{16}), 13.76 q (C^{17}). Mass spectrum, m/z: 326 [M]+.

Ethyl Ester of 2-Cyano-3-hexyl-4,5-dimethyl-5-hexenoic Acid (XIc). IR spectrum (ν, cm^{-1}): 3090, 2270, 1745, 1650, 1470, 1260, 1150, 925, 755. PMR spectrum (δ, ppm): 0.82 t (3H, Me, J = 7 Hz), 0.99 d (3H, Me, J = 7.5 Hz), 1.10-1.50 m (13H, Me, CH_2), 1.55-1.78 m (3H, MeC=), 1.87-2.45 m (2H, CH, CHC=), 3.35-3.57 m (1H, COCHCN), 3.93-4.43 m (2H, CH_2O), 4.80 m (2H, CH_2=). ^{13}C NMR spectrum (δ, ppm): 167.09 s, 166.23 s (C^1), 40.58 d, 41.56 d, 41.72 d, 42.64 d, 42.80 d, 45.08 d (C^2-C^4), 147.42 s, 147.26 s (C^5), 112.37 t, 113.02 t, 113.46 t (C^6), 115.41 s (C^7), 27.63 t, 27.09 t, 29.75 t, 29.37 t, 30.07 t, 30.50 t, 31.59 t, 31.26 t (C^8-C^{11}), 22.59 t (C^{12}), 14.03 q, 15.87 q (C^{13}, C^{17}), 16.20 q, 17.23 q, 17.77 q, 18.85 q, 19.67 q, 20.86 q (C^{14}, C^{15}), 62.58 t, 62.74 t, 62.42 t (C^{16}). Mass spectrum, m/z: 279 [M]+.

Methyl Ester of 3-Methoxycarbonyl-4,5-dimethyl-5-hexenoic Acid (XId). IR spectrum (ν, cm^{-1}): 3090, 3030, 1740, 1650, 1450, 1180, 910. PMR spectrum (δ, ppm): 0.89 d and 0.94 d (3H, Me, J = 7 Hz), 1.58 s and 1.8 s

(3H, MeC=), 2.15-3.28 m (4H, CHC=, CHCO, CH_2CO), 3.57 s and 3.6 s (6H, MeO), 4.63 m and 4.7 m (2H, CH_2=). ^{13}C NMR spectrum (δ, ppm): 172.89 s (C^1), 31.70 t, 35.38 t (C^2), 41.99 d, 43.89 d (C^3), 44.10 d, 44.97 d (C^4), 146.61 s, 146.29 s (C^5), 111.83 t, 112.91 t (C^6), 174.62 s, 175.17 s (C^7), 14.90 q, 17.61 q (C^8), 20.53 q, 18.31 q (C^9), 51.69 (C^{10}). Mass spectrum, m/z: 214 [M]+.

Nitrile of 3-Propyl-4,5-dimethyl-5-hexenoic Acid (XIIa). IR spectrum (ν, cm^{-1}): 3085, 2260, 1650, 1435, 910. PMR spectrum (δ, ppm): 0.89 t (3H, Me, J = 7 Hz), 0.94 d (3H, Me, J = 6.5 Hz), 1.1-1.58 m (5H, CH_2, CH), 1.62 s (3H, MeC=), 1.88-2.38 m (3H, CH_2CN, CHC=), 4.72 m (2H, CH_2=). ^{13}C NMR spectrum (δ, ppm): 119.03 s, 118.70 s (C^1), 18.26 d, 19.83 d (C^2), 37.06 d (C^3), 44.27 d, 43.02 d (C^4), 147.48 s (C^5), 112.32 t, 111.83 t (C^6), 37.06 t, 35.75 t (C^7), 19.83 t (C^8), 14.25 q, 14.03 q (C^9), 15.33 q, 16.53 q (C^{10}), 19.99 q, 18.58 q (C^{11}). Mass spectrum, m/z: 165 [M]+.

Nitrile of 3-Phenyl-4,5-dimethyl-5-hexenoic Acid (XIIb). IR spectrum (ν, cm^{-1}): 3080, 2265, 1650, 1610, 1505, 1460, 1435, 1130, 1085, 910, 770, 750, 720. PMR spectrum (δ, ppm): 1.06 d (3H, Me, J = 6.5 Hz), 1.48 s and 1.67 s (3H, MeC=), 2.27-3.0 m (4H, CH_2CN, CH, CHC=), 4.55 m and 4.68-4.95 m (2H, CH_2=), 6.93-7.33 m (5H, arom.). ^{13}C NMR spectrum (δ, ppm): 118.49 s (C^1), 21.46 t (C^2), 45.30 d (C^3), 44.75 d, 45.89 d (C^4), 146.56 s (C^5), 112.32 t, 113.13 t (C^6), 140.92 s (C^7), 128.24 d (C^8), 127.00 d, 127.07 d (C^9), 127.54 d (C^{10}), 16.85 q, 17.61 q (C^{11}), 19.51 q, 17.88 q (C^{12}). Mass spectrum, m/z: 199 [M]+.

Nitrile of 3-(1-Propenyl)-4,5-dimethyl-5-hexenoic Acid (XIIc). IR spectrum (ν, cm^{-1}): 3085, 3035, 2260, 1460, 1385, 985, 910. PMR spectrum (δ, ppm): 0.93 d and 0.99 d (3H, Me, J = 7 Hz), 1.62 s and 1.63 s (6H, MeC=), 1.9-2.25 m (4H, CHC=, CH_2CN), 4.68 m and 4.76 m (2H, CH_2=), 5.08-5.96 m (2H, CH=). Mass spectrum, m/z: 163 [M]+.

Methyl Ester of 3,4-Dimethyl-5-butyl-5-hexenoic Acid (XIII). IR spectrum (ν, cm^{-1}): 3090, 1740, 1640, 1460, 1385, 1185, 905. PMR spectrum (δ, ppm): 0.90 t (3H, Me, J = 7 Hz), 0.94 d (6H, Me, J = 6.5 Hz), 1.07-1.57 m (5H, CH_2, CH), 1.68-2.18 m (5H, CH_2C=, CHC=, CH_2CO), 3.55 s (3H, MeO), 4.58-4.8 m (2H, CH_2=). ^{13}C NMR spectrum (δ, ppm): 174.19 s (C^1), 37.71 t (C^2), 33.00 d (C^3), 44.86 d (C^4), 153.00 s (C^5), 108.85 t (C^6), 18.80 q (C^7), 15.71 q (C^8), 34.19 t (C^9), 30.23 t (C^{10}), 22.65 t (C^{11}), 14.03 q (C^{12}), 51.31 q (C^{13}). Mass spectrum, m/z: 212 [M]+.

1,1-Bis(1-methyl-2-butyl-2-propenyl)-2-butenol (XIVa). IR spectrum (ν, cm^{-1}): 3550, 3090, 3040, 1670, 1640, 1470, 1385, 1170, 990, 910, 805. PMR spectrum (δ, ppm): 0.89 t (6H, Me, J = 7 Hz), 0.93 d (6H, Me, J = 7 Hz), 1.3-1.52 m (8H, CH_2), 1.57 d (3H, MeC=, J = 6 Hz), 1.68 s (1H, OH), 1.75-2.13 m (4H, CH_2C=), 2.34 q (2H, CHC=, J = 7 Hz), 4.77 m (4H, CH_2=), 5.3-5.6 m (2H, CH=). Mass spectrum, m/z: 292 [M]+.

Nitrile of 3,4-Dimethyl-5-butyl-5-hexenoic Acid (XV). IR spectrum (ν, cm^{-1}): 3090, 2260, 1640, 1460, 1380, 910. PMR spectrum (δ, ppm): 0.89 t (3H, Me, J = 7 Hz), 0.95 d and 1.00 d (6H, Me, J = 6 Hz), 1.16-1.60 m (4H, CH_2), 1.72-2.38 m (5H, CH, CH_2C=, CH_2CN), 4.73 m (2H, CH_2=). ^{13}C NMR spectrum (δ, ppm): 119.02 s (C^1), 21.41 t, 23.45 t (C^2), 33.64 d (C^3), 44.39 d, 44.99 d (C^4), 152.10 s, 152.31 s (C^5), 109.62 t, 109.74 t (C^6), 18.46 q, 16.95 q, 16.69 q, 16.38 q (C^7, C^8), 34.07 t, 33.29 t (C^9), 30.17 t (C^{10}), 22.67 t (C^{11}), 14.04 q (C^{12}). Mass spectrum, m/z: 173 [M]+.

Nitrile of 3,4-Dimethyl-5-hexenoic Acid (XVI). IR spectrum (ν, cm^{-1}): 3090, 2260, 1640, 1460, 1435, 1385, 1015, 935. PMR spectrum (δ, ppm): 1.00 d and 1.05 d (6H, Me, J = 6 Hz), 1.45-1.90 m (1H, CH), 1.97-2.45 m (3H, CHC=, CH_2CN), 4.79-5.87 m (3H, CH_2=, CH=). Mass spectrum, m/z: 123 [M]+.

Nitrile of 3,4-Dimethyl-5-benzyl-5-hexenoic Acid (XVII). IR spectrum (ν, cm^{-1}): 3075, 3040, 2220, 1645, 1610, 1490, 1460, 1125, 1090, 920, 750, 720. PMR spectrum (δ, ppm): 0.94 d (3H, Me, J = 6.5 Hz), 0.97 d (3H, Me, J = 6 Hz), 1.65-2.32 m (4H, CH, CH_2CN, CHC=), 3.23 s (2H, CH_2Ph), 4.68 m and 4.79 m (2H, CH_2=), 7.11 m (5H, arom.). Mass spectrum, m/z: 213 [M]+.

Diallyl-(1-propenyl)carbinol (XIVb). IR spectrum (ν, cm^{-1}): 4330, 3070, 3020, 1635, 1110, 990, 975, 905. PMR spectrum (δ, ppm): 1.5 s (1H, OH), 1.62 d (3H, MeC=), J = 6 Hz), 2.13 d (4H, CH_2C=, J = 7 Hz), 4.66-5.16 m (4H, CH_2=), 5.33-6.04 m (4H, CH=). Mass spectrum, m/z: 152 [M]+.

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