FORMATION OF DERIVATIVES OF 1,3-CYCLOHEXADIENECARBOXYLIC ACID FROM ACYCLIC ISOPRENOID α,β-ENALS AND MONOETHYL MALONATE BY THE KNOEVENAGEL REACTION

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UDC 542.953:547.381.4:547.461.3'262:547.595.4

In the presence of piperidine in toluene (110°C, 40 min) the reaction of 3-methyl-2-butenal, citral, or farnesal with monoethyl malonate gives, along with the esters of the respective alkenylideneacetic acids, the ethyl esters of 6-alkenyl-4-methyl-, 5,6-dialkenyl-4-methyl-, and 4,6-dialkenyl-substituted 1,3-cyclohexadienecarboxylic acids. At 2:1 aldehyde–monoethyl malonate molar ratio the second reaction goes almost exclusively (64-90% yield). From the composition of the mixture of substituted 1,3-cyclohexadienes that is formed by the reaction of citral and monoethyl malonate the course of the reaction was determined.

In [1] we described the condensation of 3-methyl-2-butenal (I), citral (II), or farnesal (III) with monoethyl malonate (MEM). When equimolar amounts of aldehydes (I)-(III) and MEM are heated in the presence of 10 mole % of piperidine in benzene the yields of ethyl esters of "prenylideneacetic" acids (IV), "citrylideneacetic" (V), and "farnesylideneacetic" acids (VI) under standard conditions were 23, 34, and 48%, respectively (see [1]). Along with (IV)-(VI) were obtained more volatile and less polar liquid products with typical UV absorption at 300-309 nm.

The reaction of citral (II) with MEM in the presence of pyridine has been known since 1899, but the formation of products other than (V) has not been noticed previously. On the other hand, the formation of anomalous 1:1 products when (II) or (III) was condensed with malonic acid was well known (see [2, 3] and references there). However, the latter products are tricyclic dilactones with a high degree of saturation which is inconsistent with the strong UV absorption that we obtained for unknown compounds at 300-309 nm.

Increasing the reaction temperature to ~110°C (boiling in toluene) reduces the yield of esters (IV)-(VI) and increases the yield of "anomalous" products with λ_{max} ~ 300 nm. The product of the reaction of (I) and MEM was isolated by vacuum distillation and on the basis of its spectral and chemical properties was identified as ethyl 6-(2'-methyl-1'-propenyl)-4-methyl-1,3-cyclohexadienecarboxylate (VII). When (II) or (III) was condensed with MEM similar "anomalous" products were separated by chromatography on silica gel of the blue residues from the distillation of esters (V) and (VI). Although according to TLC these compounds are homogeneous, they are actually difficultly separable mixtures of structural isomers, respectively (VIII) and (IX) in the case of citral and (X) and (XI) in the case of farnesal; each isomer is a set of E/Z stereoismers (VIIIa, b) and (IXa, b). The nonuniformity is disclosed by GLC, by GLC-mass spectrometry (MS), and by consideration of the PMR spectra of (VIII), (IX) and (X), (XI) mixtures. The molecular weights of compounds (VII)-(XI) showed that according to the stoichiometry of their formation they correspond to a condensation of two molecules of (I), (II), or (III) with one MEM, accompanied by splitting off one CO_2 and two H_2O molecules. Indeed when the molar ratio of aldehydes (I)-(III) to MEM is changed from 1:1 to 2:1 their reaction in toluene gives a preparative yield (64-90%) of (VII)-(XI), while (IV)-(VI) are not formed at all. At the same time (VII)-(XI) are not formed when equimolar amounts of ethers (IV)-(VI) and aldehydes (I)-(III) are heated in the presence of 10 mole % of piperidine. Thus under the conditions of the Knoevenagel reaction two competing processes take place between the isoprenoid aldehydes (I)-(III) and MEM:

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 605-612, March, 1990. Original article submitted February 7, 1989.

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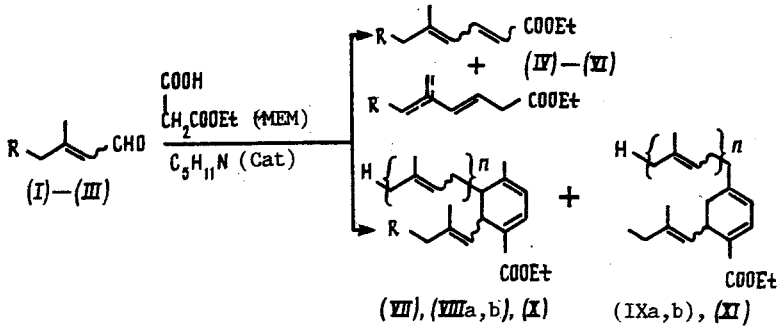
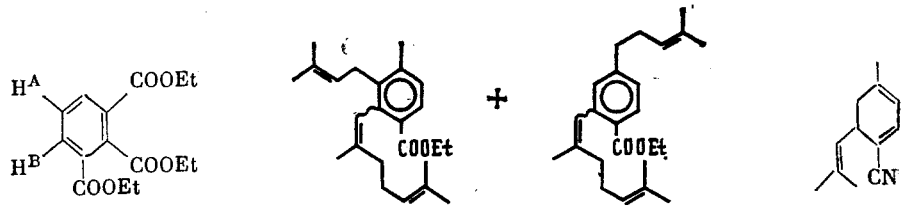


R = H, $n = 0$ (I), (IV), (VII); R = $Me_2C{=}CHCH_2$, $n = 1$ (II), (V), (VIIIa,b), (IXa,b), *E*-(a), Z-isomer (b);

R=H—[—$CH_2C{=}CHCH_2$—]$_n$ (CH$_3$), $n = 2$ (*E*/*Z* ~ 2 : 1) (III), (VI), (X), (XI).

The structures of compounds (VII)-(XI) as derivatives of 1,3-cyclohexadienecarboxylic acid follow from the totality of their spectral properties (Tables 1 and 2), the formation of their derivatives (XII)-(XIV) and the spectral properties of (XV):



(XII)
E- (a), Z-isomer (b)

(XIIIa,b) (XIVa,b) (XV)

In its general appearance and in its values for δ and SSCC the PMR spectrum of ester (VII) recalls that of ethyl 4,6-dimethyl-1,3-cyclohexadienecarboxylate [4] and other similar derivatives of 1,3-cyclohexadienecarboxylic acid [4-7]. The IR spectra of all three "anomalous" products contain intense absorption bands at 1705-1708, 1640-1650, and 1580-1590 cm^{-1} that are typical of the bond system of C=C–C=C–COOEt in derivatives of 1,3-cyclohexadienecarboxylic acid [4-7]. In the UV spectra of (VII), (VIIIa) + (VIIIb), and (IXa) + (IXb) the λ_{max} values are quite consistent with the 1,4 location of the alkyl and ethoxycarbonyl groups; they are 5-15 nm greater than for the isomers with 1,3 or 1,2 locations of those substituents in the diene system (see [4, 8]).

When (VII) was heated with diethyl acetylenedicarboxylate (DEAC) for 3 h at 180°C triethyl 4-methylbenzene-1,2,3-tricarboxylate (XII) was separated in 60% yield. Its formation involves the elimination of the "ethane" bridge of C_6H_{10} from the thermolabile [4 + 2]-cycloadduct that is obtained in the reaction of (VII) with DEAC. Although theoretically triester (XII) might also be obtained from the cycloadduct of DEAC with the isomeric diene (VII'), the formation of (VII') from (I) and MEM under Knoevenagel conditions is impossible.

The product (VIII), (IX) that was obtained from citral that was homogeneous according to TLC, turned out by GLC-MS to be composed of six isomers in a ~7:19:7:22:15:30 ratio (in order of increasing R_t). The first four components that issue from the chromatograph show practically identical fragmentation in their mass spectra; the fifth and sixth components have similar fragmentation but differ in the first decomposition route:

Component peaks (GLC)	Relative intensity (%) of ions in m/z range from 356 (M^+) to 200									
	356	341	313	311	299	287	271	241	233	223
1–4	1	–	–	~1	–	10–28	–	11–23	–	8–11
5–6	~6	~1.5	~6.5	~6.5	9–11	~3.5	~26	27–30	12	–

TABLE 1. PMR Spectra (250 MHz) of Derivatives of Substituted 1,3-Cyclohexadienecarboxylic Acids[a] ($CDCl_3$, δ, ppm)

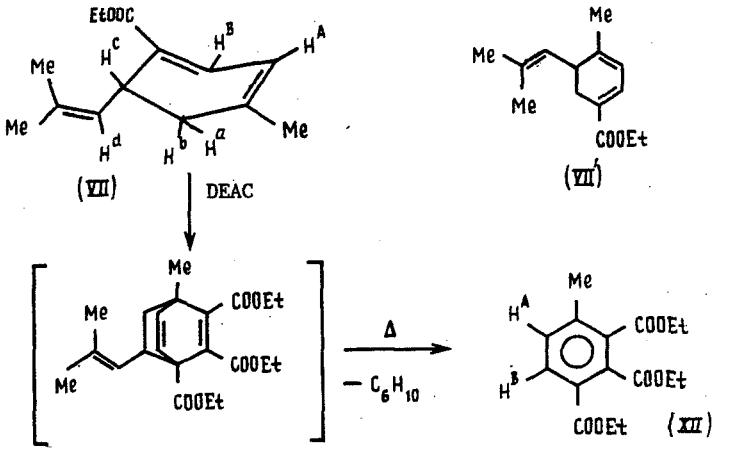
Compound	2-H [b]	3-H[c]	4-CH_3	5-H(a)[d]	5-H(b)[e]	6-H(c) [f]	CH_3—C=C [g]	H—C=C[h]	H_2C—C=C
(VII)	6,90 d	5,75 m	1,78 br.s	1,93 d.d	2,50 m	3,48 m	1,57 d (3H) 1,67 d (3H)	5,12 m (1H)	–
(VIII), (IX)	6,92 d (0,7H) 6,82 d (0,3H)	5,75 m	1,80<1,83 two br.s (~2H)	2,45–2,55 m[i] (0,7H) 2,20–2,35 m (0,3H)		3,50 m	1,50–1,70 m (~16H) (six peaks)	5,02 m (3H)	1,85–2,15 m (6H)
(X), (XI)	6,8 d	5,75 m	1,80–1,85 m (~3H)	2,30–2,60 m (2H)		3,50 m	1,50–1,70 m (21H)	5,06 m (5H)	1,75–2,2 m (14H)
(XV)	6,54 d	5,73 m	1,82 br.s	2,03 m	2,33 m	3,27 m	1,55 d (3H) 1,67d (3H)	5,14 m (1H)	–

[a] Typical OEt signals for esters (VII)-(XI) at δ 1.22t (3H) and 4.07-4.10m (2H).
[b] $J_{2,3}$ = 5.5-6.0 Hz (AB quartet).
[c] $J_{2,3}$ = 5.5-6.0 Hz; J_{allyl} = 1.4-2.0 Hz.
[d] J_{ab} = 18; J_{ac} = 1.8 Hz.
[e] J_{ab} = 18; J_{bc} = 8.7-9.0; J_{allyl} = 1.4-2.0 Hz.
[f] J_{ac} = 1.8; J_{bc} = 8.7-9.0; J_{cd} = 10 Hz.
[g] J_{allyl} ~ 1.5 Hz.
[h] J_{cd} = 10, J_{allyl} = 1.5 Hz.
[i] J_{bc} ~ 9, J_{allyl} ~ 2 Hz.

TABLE 2. IR, UV, and Mass Spectral Data for Derivatives of Substituted 1,3-Cyclohexadiene Carboxylic Acids*

Compound	ν, cm^{-1} (CCl_4)	λ, nm (EtOH) (ε)	m/z
(VII)	1705, 1650, 1590 (C=C–C=C–COOEt), 1445, 1375, 830	300 (11700)	220 (M^+), 205 (M–CH_3), 191 (M–C_2H_5), 175 (M–OEt), 173 (M–OEt–2H), 165 (M–C_4H_7), 147 (M–COOEt), 136, 129
(VIII), (IX)	1708, 1645, 1580 (C=C–C=C–COOEt), 1445, 1380, 830	306 (10600)	356 (M^+), 311 (M–OEt), 299 (M–C_4H_7), 287 (M–C_5H_9), 271, 241 (M–C_5H_9–EtOH), 213 (M–C_5H_9–COOEt), 185, 173, 159, 145, 119
(X), (XI)	1706, 1640, 1586 (C=C–C=C–COOEt), 1446, 1375, 840	309 (5400)	493 (M+H), 447 (M–OEt), 423 (M–C_5H_9), 370 (M–C_9H_{14}), 355 (M–$C_{10}H_{17}$), 341, 301, 299, 219, 191, 177, 165, 137, 123, 109
(XV)	2210, 1645, 1580 (C=C–C=C–C≡N), 1450, 1380, 830	300 (10400)	173 (M^+), 158 (M–CH_3), 143, 131 (M–CH_3–HCN), 116, 105

*Compounds (VII) and (XV) are individual substances, the mixture of (VIII) and (IX) contains six components, the (X)-(XI) mixture contains at least ten components (according to GLC).



(VII) (VII′) (XII)

In the m/z region from 200 to 70, for both components 1-4 and 5, 6 the ions with m/z 185, 173, 145 (principle in spectra of 1-4), 123, 119, 109, 105, and 91 (principle in spectra of 5, 6) are typical.

The fragmentation of components 1-4 is in good agreement with the structures of (VIII) and (IX); the successive detachment of a C_6H_9 prenyl radical, an EtOH molecule, and a C_9H_{14} fragment causes stabilization by delocalizing the charges on the ions with m/z of 287, 241, and 119. From the presence in the mass spectra of components 5 and 6 of ions corresponding to the unlikely [for (VIII) and (IX)] detachment of CH_3, C_3H_7, and C_4H_7 fragments (m/z of 341, 313, and 299), we can assume that two of the six components undergo rearrangement under electron impact that gives an isomeric molecular ion, where detachment of CH_3, C_3H_7, and C_4H_7 is more likely.*

*An alternative assumption is that components 5 and 6 are formed from components 1-4 by thermolysis under conditions of GLC. But this assumption does not agree with the uncertainty in the ratio of the peak areas of 1-6 when evaporator temperature is varied from 110 to 260°C. Furthermore the PMR spectra of (VIII) + (IX) purified by chromatography on silica gel or by distillation at 136-137°C (0.03 mm Hg) and 170-190°C bath temperature are practically indistinguishable.

From the ratio of the integrated intensities of the single type proton signals at positions 2 and 5 of the cyclohexadiene system and from the ratio of the intensities of the 4-CH_3 signals, at δ ~ 1.8 (~2H instead of 3H) and the other allyl CH_3 groups at δ ~ 1.5-1.7 (~16H), we can conclude that in the (VIII), (IX) mixture about two thirds of the mass is due to the sum of the (VIII) stereoisomers and about one third to the (IX) stereoisomers. This conclusion is in agreement with the ratio of components 1-6 as determined by GLC-MS.

The (X), (XI) mixture has even more components; theoretically 16 stereoisomers are possible for (X) and eight for (XI). GLC analysis at 235-240°C column temperature shows that at least ten components overlap, according to exit time.

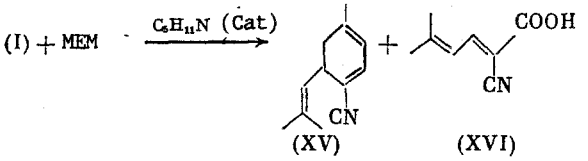
For chemical confirmation of the structures of the components of the (VIII), (IX) mixture, they were subjected to dehydrogenation by sulfur at 190°C. A mixture of four products was obtained with typical UV absorption of styrene at ~290 nm and an isomer ratio of ~21:8:22:49 (in order of increasing R_t in GLC analysis). In the PMR spectrum of the mixture of aromatization products (XIIIa, b) and (XIVa, b) the proton signals for positions 5 and 6 of the benzene ring (δ 7.75 and 6.95 ppm, J_o = 8 Hz) and that of position 3 (δ 6.90 ppm, J_m ~ 0.9 Hz) are in a ratio of ~3:3:1. It follows that two thirds of the weight of aromatization product is due to the 1,2,3,4-tetrasubstituted isomers (XIIIa, b) and one third to the 1,2,4-trisubstituted isomers (XIVa, b). Further evidence is the lowered intensity of the $ArCH_3$ singlets (for δ 2.43 rather than 2.49, overall ~2H instead of 3H) and the increased intensity, relative to (XIII) of the allyl CH_3 signals at δ 1.45-1.8 ppm (~16H). Judging from the integrated intensity of the "styrene" proton signals at δ 6.45 and 6.58 ppm, the ratio of E- and Z-isomers in the side chains of (XIII) and (XIV), i.e., the (XIIIa):(XIIIb) and (XIVa):(XIVb) ratios, is close to 2.3. From all these data it follows that when the (VIII), (IX) mixture is dehydrogenated by sulfur a mixture of (XIIIa), (XIIIb), (XIVa), and (XIVb) isomers is formed in ~49:21:22:8 proportion. This confirms the correctness of the estimation of the ratio of all (VIII) stereoisomers to all (IX) stereoisomers in the initial (VIII), (IX) mixture as determined by GLC-MS and PMR. Thus when citral reacts with MEM in the presence of piperidine the formation of the isomeric derivatives of 1,3-cyclohexadienecarboxylic acid is characterized by a (VIII):(IX) ratio of ≈7:3.

From the qualitative resemblance of the PMR spectrum of the (VIII), (IX) mixture to that of the (X), (XI) mixture we can ssume a similar structural trend in the farnesal–MEM reaction:

$$((\text{VIII}) + (\text{IX})) \xrightarrow[190^\circ]{S} (\text{XIII}_{a,b}) + (\text{XIV}_{a,b})$$

To evaluate the general character of this reaction we studied the reaction of prenal (I) with cyanoacetic acid at 2:1 molar ratio.

The nitrile of 6-(2'-methyl-1'propenyl)-4-methyl-1,3-cyclohexadienecarboxylic acid (XV) was separated by chromatography from the oil that was left after the removal of the principle reaction products, crystalline prenylidenecyanoacetic acid (XVI). Nitrile (XV) was characterized by its spectral data (see Tables 1 and 2); its yield was only 13%.



(XV) (XVI)

Compounds (VII), (XV), (VIII), (IX), and (X), (XI) are formed apparently by two routes: via an aldol adduct formed by two aldehyde molecules with MEM or by the reaction of [4 + 2]-cyclo compound that is formed from the reaction of the dienamine of aldehydes (I)-(III) with the corresponding ylidenemalonic monoester, followed by regeneration of piperidine upon decarboxylation (see [9]). The elucidation of this mechanism will be the subject of a subsequent communication.

EXPERIMENTAL

Boiling points of synthesized compounds were not corrected. Chemical purity and ratio of geometrical isomers were monitored by GLC on a LKhM-8-MD instrument with stainless steel column 2.0 m × 3 mm and DIP; stationary phase was 5% XE-60 on Chromatone N-AW-DMCS, add-

itionally silanized with hexamethyldisilazane; mobile phase N_2 (P_{exc} 0.5 atm). Reaction mixture was analyzed qualitatively on Silufol plates (Czech. SSR) with 9:1 hexane–AcOEt. PMR spectra were obtained with Tesla BS-467 (60 MHz) and Bruker WM-250 (250 MHz) instruments. IR spectra were recorded with a UR-20 instrument in CCl_4; mass spectra with an MX-1303; UV spectra with a Specord UV-VIS in EtOH. The (VIII), (IX) mixture was analyzed by GLC-MS with an MOT-111 instrument with a glass column (ℓ = 1.5 m, i.d. = 3 mm, 3% SE-30 on Chromatone N-AW-DMCS, N_2 carrier gas, evaporator temperature 220°C, thermostat program 200-260°C, heating rate 4°C/min). Aldehydes (I) and (III) were obtained by isomerization of the respective acetylenic carbinols according to [10]; the ratio of 6E/6Z stereoisomers in (III), as in the initial dehydronerolidol, was ~2:1 according to GLC and PMR. The 2E/2Z ratio in (II) and (III) was ~2:1 according to GLC and PMR.

Ethyl 6-(2'methyl-1'-propenyl)-4-methyl-1,3-cyclohexadienecarboxylate (VII). A mixture of 1.7 g (0.02 mole) of (I), 1.32 g (0.01 mole) of MEM, and 0.2 ml (172 mg, 2 mmoles) of piperidine in 10 ml of dry toluene was boiled for 40 min; the water azeotrope was removed by means of a Dean-Stark attachment. By that time the initial (I) had reacted completely (as shown by GLC). Toluene was removed in a rotary evaporator; vacuum distillation of the residue gave pure ester (VII), bp 138°C (10 mm Hg), n_D^{17} 1.5141. ^{13}C NMR spectrum (250 MHz, δ, $CDCl_3$, ppm): 13.85 ($\underline{CH_3}CH_2O$), 17.54 (2'-CH_3), 23.37 (4-CH_3), 25.34 ($C^{3'}$), 30.28 (C^6), 35.51 (C^5), 59.37 ($\underline{OCH_2}CH_3$), 118.40 (C^3), 124.35 ($C^{1'}$), 127.65 (C^1), 131.04 ($C^{2'}$), 132.28 (C^2), 141.62 (C^4), 166.44 (COOEt). For other spectral data see Tables 1 and 2. Yield of (VII): 1.40 g (64%).

Ethyl 6-(2',6'-dimethyl-1',5'-heptadienyl)-5-(3'-methyl-2'-butenyl)-4-methyl-1,3-cyclohexadienecarboxylate (VIII), and Ethyl 6-(2',6'-dimethyl-1',5'-heptadienyl)-4-(4'-methyl-3'-pentenyl)-1,3-cyclohexadienylcarboxylate (IX). The six-component mixture containing four stereoisomers with the structure of (VIII) and two with the structure of (IX) in ~7:3 ratio was obtained from 3.04 g (0.02 mole) of citral, 1.32 g (0.01 mole) of MEM and 0.2 ml of piperidine in toluene by the procedure described above for (VII). Yield: 3.05 g (85%), bp 136-137°C (0.03 mm Hg), n_D^{21} 1.5175. For spectral properties see Tables 1 and 2.

Ethyl 6-(2',6',10'-trimethyl-1',5',9'-undecatrienyl)-5-(3',7'-dimethyl-2',6'-octadienyl)-4-methyl-1,3-cyclohexadienylcarboxylate (X) and Ethyl 6-(2',6',10'-trimethyl-1',5',9'-undecatrienyl)-4-(4',8'-dimethyl-3',7'-nonadienyl)-1,3-cyclohexadienylcarboxylate (XI). The mixture of stereoisomeric esters of general formula (X) and (XI) was obtained by the procedure described for (VII), with the following difference: after the solvent was removed the residue was placed on a column of 15 g of silica gel which was then eluted first with pure hexane, then with 95:5 hexane–Et_2O; purity was monitored by TLC. From 4.40 g (0.02 mole) of farnesal there was obtained 4.42 g (90% yield) of bright yellow oil, uniform by TLC, n_D^{19} 1.5190. For spectral properties see Tables 1 and 2.

1-Cyano-6-(2'-methyl-1'-propenyl)-1,3-cyclohexadiene (XV) was obtained from 1.72 g (0.02 mole) of aldehyde (I) and 0.85 g (0.01 mole) of cyanoacetic acid by the procedure for the synthesis of (VII). After the reaction mixture was cooled, the crystals were filtered off and washed on a porous No. 2 filter with hexane. There was obtained 1.1 g of pure 2-cyano-5-methyl-2,4-hexadienoic acid (XVI), mp 168-170°C (according to [11], 168-171°C). IR spectrum ($CHCl_3$, ν, cm^{-1}): 3300-3200, 2230, 1695, 1617, 1576. UV spectrum (EtOH, λ, nm): 295 (ε 20,600). Mass spectrum: M^+ 151. After separation of (XVI) the filtrate was evaporated. The residue was chromatographed on a column of 8 g of silica gel and eluted with 97:3 hexane–Et_2O to give 0.225 g (13%) of nitrile (XV) as a colorless oil. For spectral properties, see Tables 1 and 2.

Triester (XII). A mixture of 1.1 g (5 mmoles) of ester (VII) and 0.85 g (5 mmoles) of DEAC was heated in an oil bath at 180°C for 3 h with a reflex condenser and an argon closure. The reaction product was vacuum distilled to give pure (XII), bp 138°C (0.2 mm Hg), n_D^{20} 1.5022. Yield: 0.92 g (60%). PMR spectrum (CCl_4, δ, ppm): 1.30 br.s (9H, $\underline{CH_3}CH_2O$), 2.37s (3H, 4-CH_3), 4.25q (6H, $CH_3\underline{CH_2}O$), 7.20d (1H, J = 8 Hz), 7.70d (1H, J = 8 Hz). IR spectrum (CCl_4, ν, cm^{-1}): 1737, 1600, 1586, 1518, 1450, 1220, 1160, 840. UV spectrum: λ 238 (ε 7200) and 275 nm (ε 2000). Mass spectrum, m/z: 308 (M^+), 263 (M – EtO), 235 (M – COOEt), 220, 189 (parent ion), 163, 149, 105, 91.

Dehydrogenation of mixture of (VIII) and (IX). A mixture of (VIII) and (IX), 3.56 g (0.01 mole) was treated with 0.32 g (0.01 g·atom) of sulfur, then heated in an oil bath at 185-195°C for 2 h under a reflex condenser and an argon closure. The mixture was distilled

in vacuum and the fraction boiling at 155-157°C (0.05 mm Hg) was collected, n_D^{24} 1.5266. Yield: 1.2 g (33%). PMR spectrum (CCl_4, δ, ppm): 1.30-1.33m (3H), 1.45-1.80m (~16H), 1.8-2.8m (8H), 2.43 > 2.49s (~2H), 4.10 (2H), 5.1m (2H), 6.45 and 6.58m (total 1H), 6.9 br.s (0.35 H), 6.95 br.d (1H, J = 8 Hz), 7.75 (1H, J = 8 Hz). IR spectrum (CCl_4, ν, cm^{-1}): 3027, 1722, 1654, 1610, 1595, 1520, 1450, 1220, 1140, 840. UV spectrum: λ 234 (ε 15,000) and 290 nm (ε 2700). Mass spectrum, m/z: 354 (M^+), 265, 215, 197, 171, 167, 157, 145, 143, 128, 109, 105, 91.

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