CODIMERIZATION OF MYRCENE WITH METHYL ACRYLATE CATALYZED BY IRON AND COBALT COMPLEXES

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The cooligomerization of 1,3-dienes with methyl acrylate in the presence of complexes of the transition metals is a simple and convenient route for the synthesis of rare unsaturated acids [1].

We were the first to show that the codimerization of myrcene with methyl acrylate on a catalyst composed of iron acetylacetonate, electron-donor additives, and an organoaluminum reducing agent gives the methyl esters of the 6,10-dimethyl-2-trans-5,9-undecatriene- and 6,10-dimethyl-2-cis-5,9-undecatrienecarboxylic acids (I) and (II). The linear oligomerization is accompanied by diene synthesis, which leads to cyclic esters (III)-(IV). The total yield and the ratio of the linear and cyclic codimers are quite dependent on the reaction conditions and type of modifier. In view of this we studied the effect of the structure of the electron-donor modifiers and the solvent on the yield and composition of the codimerization products of myrcene with methyl acrylate.

As can be seen from Table 1, the highest yield of linear codimers can be obtained when a mixture of Ph_3P, $Fe(acac)_3$, and $AlEt_3$ in THF is used as the catalyst. The total yield of linear and cyclic codimers ≥ 38 or 75-80%, when based on reacted myrcene. Up to 8-10% of higher oligomers is formed here, the identification of which has been difficult up to now. The unreacted myrcene is recovered completely. The yield of cyclic esters (III) and (IV) represents 17% of the total yield of codimers. When Ph_3Sb, tricyclohexylphosphine, triphenylantimonite, or Ph_3P is used as the modifier the amount of esters (III) and (IV) in the mixture reaches 36-43%.

The ratio of the linear cis, trans-codimers (II) and (I) is usually 1 : 2 and remains practically constant in the experiments. It is interesting to mention that the amount of cyclic dimers (III) and (IV) increases up to 50% when a total of 1% of cobalt acetylacetonate is added to the $Fe(acac)_3—Ph_3P—AlEt_3$ catalyst system. Here the total yield of codimers (I)-(IV) rises to 70%. Replacing the $Fe(acac)_3$ by $Co(acac)_3$ makes it possible to run the codimerization selectively to give the practically pure cyclic dimer (III). As a result, catalysts based on cobalt direct the reaction toward the formation of the cyclic dimer, while iron complexes give mainly linear codimers.

Solvents exert a noticeable effect on the direction of the codimerization reaction. From the data in Table 1 it follows that the total yield of codimers (I)-(IV) decreases when going from ether solvents to aromatic hydrocarbons, but the fraction of cyclic dimers (III) and (IV), and of higher oligomers, increases.

Variation of the codimerization temperature also affects the yield and ratio of the linear and cyclic dimers in the mixture. Thus, the reaction of myrcene with methyl acrylate at 25°C for 100 h gives a mixture of (I) + (II) and (III) + (IV) in a total yield of 9% and an 82 : 18 ratio. Codimers (I)-(IV) can be obtained in a higher yield of 38% at 50° and a reaction time of 10 h. A further increase in the reaction temperature and time fails to lead to a noticeable increase in the yield of dimers (I)-(IV).

The isomerization of linear esters (I) and (II) was studied. Quantitative isomerization to trans-isomer (I) results when ester (II) is heated with iodine. Treatment of a mixture of esters (I) + (II) with methanolic KOH solution at 40° facilitates a shift of the double bond to give the methyl ester of the 6,10-dimethyl-trans-3,5,9-undecatriene acid (VII). The reaction of a mixture of (I) + (II) with t-BuOK in hexametapol at 100°

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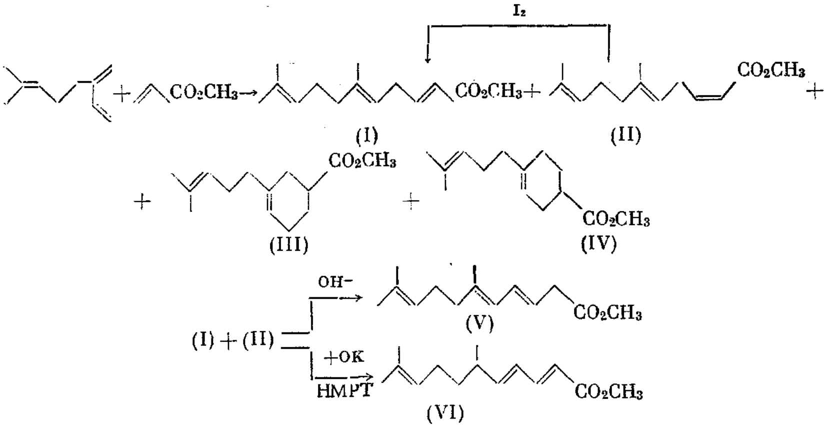
TABLE 1. Codimerization of Myrcene with Methyl Acrylate

Solvent	Electron-donor additive	Time, h	T., °C	Myrcene conversion, %	Total yield of (I)-(IV), g	Yield of higher oligomers, g	Composition of codimers		
							(I)	(II)	(III)+(IV)
Benzene	$P(C_6H_5)_3$	10	50	57,0	14,7	8,6	49	25	26
»	$Sb(C_6H_5)_3$	10	50	57,8	13,5	9,8	43	21	36
»	$P(C_6H_{11})_3$	10	50	58,1	12,4	7,2	39	23	38
»	$Sb(OC_6H_5)_3$	10	50	59,2	11,6	11,9	37	21	42
»	$P(OC_6H_5)_3$	10	50	59,2	11,6	11,8	37	20	43
Ether	$P(C_6H_5)_3$	10	50	51,5	16,0	5,5	53	24	23
»	$Sb(C_6H_5)_3$	10	50	50,7	13,9	6,9	45	22	33
»	$P(C_6H_{11})_3$	10	50	51,8	12,9	8,2	42	21	37
THF	$P(C_6H_5)_3$	100	25	11,0	4,0	0,7	55	27	18
»	The same	10	50	49,5	16,9	4,1	53	30	17
»	»	5	50	25,8	8,9	2,1	51	32	17
»	»	16	50	59,9	19,0	6,1	54	22	24
»	»	5	80	37,8	10,4	5,2	54	25	21
»	»	10	80	57,7	17,5	6,5	55	22	23
»	»	16	80	67,9	19,8	8,3	53	20	27
»	»*	10	50	27,3	7,6	3,6	28	14	58
»	$Sb(C_6H_5)_3$	10	50	48,5	15,1	5,2	57	23	20
»	$P(C_6H_{11})_3$	10	50	48,0	13,8	6,0	50	24	26
»		10	50	34,6	9,8	4,5	26	14	60

*Two moles of $P(C_6H_5)_3$.

gives the methyl ester of the 6,10-dimethyl-2,4,9-undecatriene acid in good yield. The obtained conjugated esters do not react with maleic anhydride when refluxed in xylene.



EXPERIMENTAL

The monomers used in the study were at least 99.8% pure. The NMR spectra were recorded on a Tesla BS-480B instrument (CCl_4 or $CDCl_3$, internal standard = HMDS). The IR and UV spectra were recorded on UR-20 (film or Nujol mull) and Specord UV-Vis (alcohol) spectrophotometers. The chromatographic analysis was run on a Tswett-102 chromatograph, using a flame-ionization detector, a 1 m × 3 mm column packed with 15% Apiezon L deposited on Chromatone, a temperature of 150°, nitrogen as the carrier gas, and a flow rate of 40 ml/min. The preparative separation was run on a Chrom-31 chromatograph, using a flame-ionization detector, a 1 m × 10 mm column packed with 15% Silicone Elastomer deposited on Celite-545, a temperature of 160°, and nitrogen as the carrier gas.

General Procedure for Codimerization of Myrcene with Methyl Acrylate. To a solution of 3 mmoles of $Fe(acac)_3$, 4 mmoles of the modifier, and 2.5 ml of myrcene in 25 ml of the solvent, cooled to −5°, was added 16 mmoles of $AlEt_3$ in an argon atmosphere. The mixture was stirred at −5° for 1.5 h and then transferred to an autoclave, where 17.2 g of methyl acrylate and 25.2 g of myrcene were added. The experiments were run under various conditions. To isolate the reaction products the catalyzate was diluted with benzene, washed with 5% HCl solution, then with water, dried over $MgSO_4$, the solvent was removed, and the products were vacuum-distilled. The undistillable residue represents higher oligomers.

The results of the experiments are given in Table 1. Preparative GLC was used to isolate the methyl esters of the 6,10-dimethyl-2-trans-5,9- and 6,10-dimethyl-2-cis-5,9-undecatriene acids (I) and (II). Compound (I): bp 110° (1 mm); n_D^{20} 1.4800. Ultraviolet spectrum: λ_{max} (alcohol) 202 nm, ε 20,200. Infrared spectrum (ν, cm^{-1}): 840 [$(CH_3)_2C=CH-$], 980 (trans-$CH=CH-$), 1725 ($=\underset{|}{C}-CO_2CH_3$). NMR spectrum (δ, ppm): 1.50 [6H, $(CH_3)_2C=C-$], 1.51 (3H, $CH_3-\underset{|}{C}=\underset{|}{C}-$), 1.92 (4H, $-CH_2-\underset{|}{C}$), 2.80 d (2H, $=\underset{|}{C}-CH_2-\underset{|}{C}=$, J = 6 Hz), 3.56 (3H, $-OCH_3$), 5.0-6.90 (4H, vinyl protons). Found: C 75.30; H 9.64%. $C_{14}H_{22}O_2$. Calculated: C 75.60; H 9.90%.

Compound (II): bp 108° (1 mm); n_D^{20} 1.4777. Ultraviolet spectrum: λ_{max} (alcohol) 203 nm, ε 22,000. Infrared spectrum (ν, cm^{-1}): 720 (cis-$CH=CH-$), 840 [$(CH_3)_2C=CH-$], 1722 ($=C-CO_2CH_3$). NMR spectrum (δ, ppm): 1.50 [6H, $(CH_3)_2C=C-$], 1.51 (3H, $CH_3-\underset{|}{C}=$), 1.92 (4H, $-CH_2-\underset{|}{C}=$), 3.40 d (2H, $=\underset{|}{C}-CH_2-\underset{|}{C}=$, J = 6.5 Hz), 3.60 (3H, $-OCH_3$), 4.96–6.10 (4H, vinyl protons). Found: C 75.22; H 9.60%. $C_{14}H_{22}O_2$. Calculated: C 75.60; H 9.90%.

The codimerization of 25.2 g of myrcene with 17.2 g of methyl acrylate in the presence of a catalyst, prepared from 3.96 mmoles of $Fe(acac)_3$, 0.04 mmole of $Co(acac)_2$, 4 mmoles of Ph_3P, 16 mmoles of $AlEt_3$, and 2 g of myrcene, at 50°, for 10 h gave a 70% yield of a mixture of (I), (II), (III), and (IV) in a 15:3.5:0.5:4.5 ratio.

Under the same conditions, from 27.2 g of myrcene and 17.2 g of methyl methacrylate in the presence of a system composed of 4 mmoles of $Co(acac)_2$, 4 mmoles of Ph_3P, and 16 mmoles of $AlEt_3$ was obtained ester (IV) in 70% yield, bp 118° (1 mm); n_D^{20} 1.4848. Saponification with 5% methanolic caustic solution gave the acid, mp 54-55°, which was identical with the compound obtained by the diene synthesis from myrcene and acrylic acid [2].

Methyl Ester of 6,10-Dimethyl-3,5,9-trans-undecatriene Acid (V). A mixture of esters (I) + (II) (0.5 g) was treated with 10 ml of a 0.1% KOH solution in absolute methanol at 40° for 3 h. The mixture was poured into water and then extracted with CH_2Cl_2. After the usual workup and vacuum-distillation we isolated 0.43 g of (V), bp 102° (1 mm), n_D^{20} 1.4836. Ultraviolet spectrum: λ_{max} (alcohol) 235 nm, ε 13,500. Infrared spectrum (ν, cm^{-1}): 840 [$(CH_3)_2C=CH-$], 975 (trans-$CH=CH-$), 645 ($-CH=CH-CH=CH-$), 1745 ($-CO_2CH_3$).

Methyl Ester of 6,10-Dimethyl-2,4,9-trans-undecatriene Acid (VI). To a solution of 0.152 g of t-BuOK in 10 ml of hexametapol was added in drops, at 100°, in an inert atmosphere, 1 g of a mixture of esters (I) + (II). The reaction was ended in 5 min. The mixture was diluted with 10 ml of water, extracted repeatedly with light petroleum ether, the extract was washed with water, dried over $MgSO_4$, the petroleum ether was evaporated, and the residue was vacuum-distilled. We obtained 0.55 g of (VI), bp 86° (1mm); purity 95%; n_D^{20} 1.4900. Ultraviolet spectrum: λ_{max} (alcohol) 283 nm, ε 13,800. Infrared spectrum (ν, cm^{-1}): 840 [$(CH_3)_2C=CH-$], 992 (trans-$CH=CH-$), 1610, 1640 ($-\underset{|}{C}H=CH-CH=CH-$), 1720 ($=\underset{|}{C}-CO_2CH_3$). NMR spectrum (δ, ppm): 0.90 (3H, $CH_3-\underset{|}{C}-$), 1.48 (2H, $-CH_2-$), 1.57 [6H, $(CH_3)_2C=\underset{|}{C}-$], 2.00 (2H, $-CH_2-\underset{|}{C}=$), 2.57 (1H, $-\overset{|}{C}H-$), 3.55 (3H, $-OCH_3$), 4.7-6.2 (5H, vinyl protons). Found: C 75.4; H 9.8%. $C_{14}H_{22}O_2$. Calculated: C 75.6; H 9.9%.

Isomerization of (II) with Iodine. A mixture of 0.5 g of (II) and 0.01 g of I_2 was kept at 120° for 12 h, after which it was cooled, diluted with petroleum ether, filtered through Al_2O_3, the ether was evaporated, and the residue was distilled. We obtained 0.38 g of (I), n_D^{20} 1.4800. Infrared spectrum (ν, cm^{-1}); 840 [$(CH_3)_2C=CH-$], 980 (trans-$CH=CH-$), 1725 ($=C-CO_2CH_3$).

CONCLUSIONS

1. We were the first to study the codimerization of myrcene with methyl acrylate in the presence of catalysts based on iron and cobalt complexes, which leads to the methyl esters of the 6,10-dimethyl-2-trans-3,9-undecatriene- and 6,10-dimethyl-2-cis-5,9-undecatrienecarboxylic acids. A study was made of the effect of electron-donor modifiers and of solvents on the yield and composition of the codimers.

2. Conditions were found for the preparation of the esters of the 6,10-dimethyl-2,5,9- and 6,10-dimethyl-3,5,9-undecatriene acids in high yields.

LITERATURE CITED

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