SYNTHESIS AND TRANSFORMATIONS OF 2,5,10-UNDECATRIENOIC ACID

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UDC 542.91:541.64:
547.39:547.315.2

The cooligomerization of 1,3-dienes with methyl acrylate, catalyzed by nickel complexes, is a promising method for the preparation of polyenoic acids. However, the existing data testify to the fact that the routes for a practical realization of the theoretical schemes are beset by a number of difficulties. For example, in the cooligomerization of butadiene with methyl acrylate the yield of the methyl ester of 2,5,10-undecatrienoic acid (I) is 15-38% due to an inadequate selectivity of the catalysts [1, 2]. In a search for the optimum conditions of preparing (I) we investigated the effect of the structure of electron-donor modifiers and organoaluminum reducing agents, and also of the type of solvent, on the yield of (I). The effect of temperature, ratio of monomers, and of the catalyst components, was studied at the same time.

It was shown that operation under the conditions given in [2] (catalyst = $Ni(acac)_2 + P(C_6H_5)_3 + Al(C_2H_5)_3 = 1:1:5$, 160°C) gives a mixture of 4-vinylcyclohexene (II), 1,5-cyclooctadiene (III), trans, trans, trans-1,5,9-cyclododecatriene (IV), methyl tetrahydrobenzoate (V), ester (I), and the esters of the 4-vinyl-2,7- and 4-vinyl-7,10-dodecadienedicarboxylic acids (VI)-(VII). The esters of the tetradecatrienedicarboxylic acids described in [2] were not found. The yield of (I) ranged from 15 to 25%.

We established that the highest yield of (I) (75%) can be obtained at an optimum temperature of 120° on a catalyst that is composed of $Ni(acac)_2$, triphenylphosphine, and tris(3-methyl-4,6-heptadienyl)aluminum (VIII), taken in a 1:2:4 ratio. The mixture of oligomers included (I), (II), (III), (V), and the methyl ester of 3,4-divinylcyclohexanecarboxylic acid (IX). The latter is the isomerization product of the initially

TABLE 1. Cooligomerization of Butadiene with Methyl Acrylate

Solvent	Modifier	Yield of mixed oligomers, %	Composition of oligomers, %						
			(I)	(II)	(III)	(IV)	(V)	(IX)	(VI–VII)
Toluene	$(Ph)_3P$	95	75,0	4,5	7	—	10	3,5	—
»	$(Ph)_3P$ (1*M*)	95	42,5	5,5	3,5	1,5	14	4	29
»	$(Ph)_3P$ (3*M*)	25	—	—	—	—	100	—	—
»	$(Ph)_3P$ (4*M*)	15	—	—	—	—	100	—	—
»	$(C_6H_{11}O)_3P$	97	58,5	10	14	—	6,5	5	6,0
»	$(C_6H_5O)_3P$	98	48,0	7,0	20,0	1,0	9,0	9	6,0
»	$(C_2H_5O)_3P$	98	33,5	10,0	24,0	3,5	12,0	5	12,0
»	$(C_2H_5)_3N$	80	27,5	13,0	8,0	—	25,0	2	24,5
»	$(C_6H_{11})_3P$	94	22,5	8,0	2,0	4,5	52,5	10,5	—
»	$O{=}P[N(CH_3)_2]_3$	95	16	15	1,0	1,0	62	1	—
»	PCl_3	90	—	—	—	—	100	—	—
THF	$(Ph)_3P$	95	21,5	6,0	2,0	1,0	14	4,0	50,5
Hexafluorobenzene	Ph_3P	85	13,0	10,0	1,5	0,5	40,0	4,0	31,0
Acetone	Ph_3P	80	11,0	15,0	—	3,5	71	—	Traces
Sulfolane	Ph_3P	78,5	34,0	10,0	4,0	3,0	18,0	6,0	25
Hexane	Ph_3P	93,0	40,5	4,0	7,5	4,0	18,5	1,0	24,5
Toluene*	Ph_3P	78	52	6,0	15,0	3,5	20,0	3,5	—
" †	Ph_3P	70	30	8,0	10	6,5	15	7,5	23

*Reducing agent $(C_2H_5)_2Al_2O$.

†Reducing agent (XI).

Institute of Chemistry, Bashkir Branch of Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2018-2023, September, 1975. Original article submitted November 10, 1974.

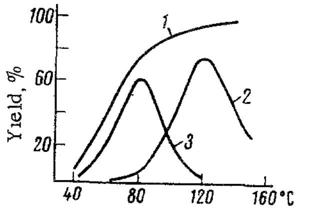


Fig. 1

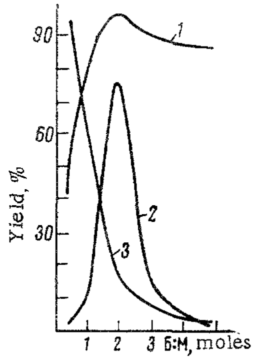


Fig. 2

Fig. 1. Effect of temperature on yield and composition of butadiene—methyl acrylate cooligomers: 1) total yield of cooligomers; 2) yield of (I); 3) yield of (VI)-(VII). Reaction conditions: $Ni(acac)_2$: Ph_3P : (VIII) = 1 : 2 : 4; butadiene—methyl acrylate = 2 : 1, toluene, 5 h.

Fig. 2. Effect of butadiene (B) and methyl methacrylate (M) ratios on yield of methyl esters (I) and (V): 1) total yield; 2) yield of (I); 3) yield of (V). Reaction conditions: $Ni(acac)_2$: Ph_3P : (VIII) = 1 : 2 : 4, toluene, 120°, 5 h.

formed 4-carbomethoxy-1,7-cyclodecadiene (X). The structure of (IX) was proved by dehydrogenation on Pd/C and subsequent oxidation with HNO_3 to trimellitic acid [3]. It should be mentioned that the formation of (IX) on a catalytic system containing Ph_3P was observed for the first time. The structure of (I) was confirmed by the spectral data, and also by the formation of oxalic, malonic, and glutaric acids on ozonization.

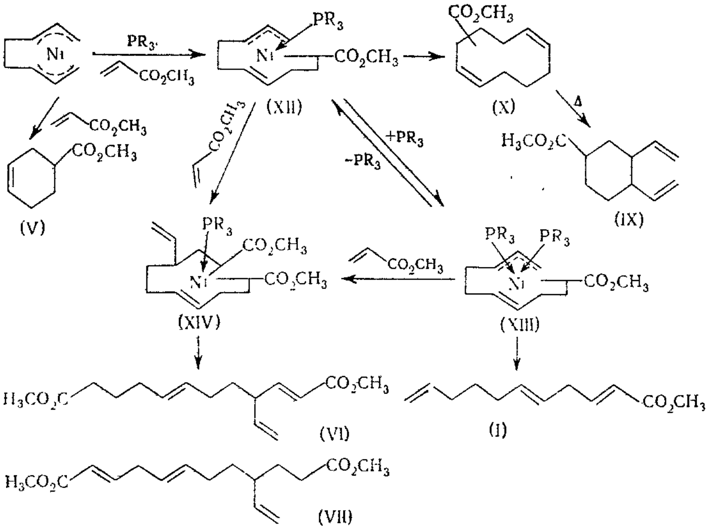
A change in the Ni : P ratio from 1 : 2 to 1 : 1 leads to a decrease in the yield of ester (I) to 40%, and increase in the yield of cyclooctadiene, and the appearance of the esters of dicarboxylic acids (VI)-(VII). The total yield of the oligomers is close to 100%. At a Ni : P ratio = 1 : 3-4 the yield of the oligomers drops to 15%, in which connection the sole reaction product is ester (V). As a result, a phosphine, which occupies three or four coordination sites on the Ni atom, prevents a coordination of the monomers. In view of this, all of the subsequent experiments on studying the effect of electron-donor additives were run at the optimum Ni : P ratio = 1 : 2. As can be seen from Table 1, the amount of ester (I) in the mixture of oligomers decreases in the series: $P(C_6H_5)_3$, $P(OC_6H_{11})_3$, $P(OC_6H_5)_3$, $P(OC_2H_5)_3$, $N(C_2H_5)_3$, although the total yield of oligomers is at least 95% in all of the experiments. Even lower yields of ester (I) were obtained when ($P(C_6H_{11})_3$ and $O = P[N(CH_3)_2]_3$ were used. Ester (I) is completely absent in the mixture of oligomers that are obtained on the catalysts involving PCl_3.

The structure of the organoaluminum reducing agent has an important effect on the total yield of oligomers and the amount of (I) in them. The best results were obtained in the experiments with $Al(C_2H_5)_3$, $(C_2H_5)_2AlOAl(C_2H_5)_2$, and (VIII). The use of perhydro-9b-aluminophenolene (XI) [4] leads to a decrease in the yield of (I) and an increase in the amount of the esters of dicarboxylic acids (VI) and (VII).

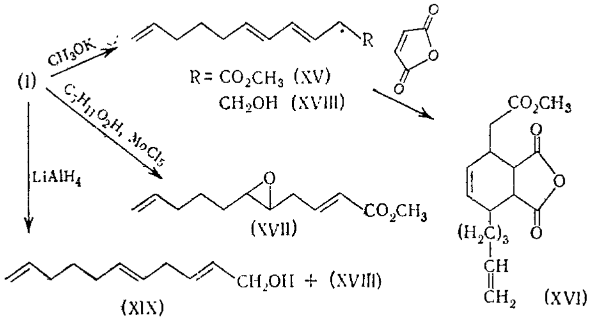
The best solvents are hydrocarbons. The use of THF, C_6H_6, acetone, or sulfolane facilitates an increase in the yield of (V), (VI), and (VIII); in these cases the amount of (I) in the mixed oligomers does not exceed 35%. The composition and yield of the oligomers as functions of the reaction temperature and ratio of monomers are plotted in Figs. 1 and 2.

The esters of dicarboxylic acids (VI)-(VII) were isolated by vacuum distillation as a mixture that could not be separated. The cleavage of the mixed esters by ozonolysis gave glutaric, malonic, oxalic, 2-carboxyglutaric, and 4-carboxypimelic acids, which were identified as the methyl esters by GLC. The (VI) : (VII) ratio changes somewhat from experiment to experiment as a function of the type of modifier and reaction conditions, and on the average is 6 : 4. Their yield increases with decrease in the temperature and reaches a maximum (75%) at 80°.

Starting with the obtained data, the following cooligomerization scheme can be depicted. Depending on the conditions, the coordination-unsaturated nickel σ,π-complex (XII) [5] can give two 18-electron complexes (XIII) and (XIV), the equilibrium between which is regulated by the temperature. The more stable complex at elevated temperature is (XIII), and it leads to trienoic ester (I). The insertion of methyl acrylate at the π-allyl-Ni bond leads to the irreversible conversion of complex (XIII) to the σ,σ-complex (XIV). This process proceeds at a lower temperature.



Some transformations of (I) were examined. Treatment with NaOH or MeOK in methanol gives the methyl ester of 3,5,10-undecatrienoic acid (XV), which with maleic anhydride gives adduct (XVI). The epoxidation of (I) by treatment with tert-amyl hydroperoxide in the presence of $MoCl_5$ gives methyl 5,6-epoxy-2,10-undecadienoate (XVII) in quantitative yield. The reduction of (XVI) with $LiAlH_4$ gave 3,5,10-undecatrienol. It is characteristic that (I) under reduction conditions gives a mixture of 2,5,10-undecatrienol (XIX) and (XVIII) (7 : 3). The latter is formed via isomerization by the $LiAlH_4$.



EXPERIMENTAL METHOD

The butadiene and methyl acrylate used in the study were at least 99.8% pure. The mixture of hydrocarbons was analyzed on a Tsvett-102 chromatograph, using a flame-ionization detector, a 2-m-long column packed with 15% Apiezon L deposited on Celite 545, and nitrogen as the carrier gas. The preparative separation was carried out 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.

The NMR spectra were recorded on a Tesla-480B instrument in CCl_4 solution, using HMDS as the internal standard. The IR spectra were recorded on a UR-20 spectrophotometer (as a film). The mass spectra were recorded on an MKh-13-06 instrument, using an electron ionizing energy of 50 eV and a chamber temperature of 200°.

Cooligomerization of Butadiene with Methyl Acrylate. With stirring, 0.06 mole of (VIII) was added at 0-5°, in a nitrogen stream, to 0.015 mole of $Ni(acac)_2$, 0.015 mole of the activator, and 5 ml of butadiene in 20 ml of the solvent. The catalyst solution was loaded into a 300-ml stainless-steel autoclave, followed by the addition of 56 g of butadiene and 45 g of methyl acrylate, and the stirred mixture was heated.

After cooling, the mixture was treated with 5 ml of alcohol to decompose the catalyst, after which the product was vacuum distilled. The experimental results and their dependence on the temperature and ratio of monomers are given in Table 1 and plotted in Figs. 1 and 2. The oligomers, which were separated by fractional distillation through a column, had the following constants.

Methyl ester of 2,5,10-trans-undecatrienoic acid (I) [2]: bp 85-86° (0.4 mm), n_D^{20} 1.4730. Infrared spectrum (ν, cm^{-1}): 920, 1000, 3090 ($-HC=CH_2$), 975,3030 (trans-$CH=CH-$), 1720($=C-CO_2CH_3$). NMR spectrum (δ, ppm): 1.5 m (2H, CH_2); 2.04 m (4H, $-CH_2C$); 2.88 (2H, $=CCH_2C=$); 3.63 (3H, OCH_3); 4.96(2H, $>C=CH_2$); 5,62(4H, $-CH=CH-$); 6.7 (1H, $-CH=CH_2$); m/e 194. Ultraviolet spectrum (in alcohol): λ_{max} 205 nm, ε 15000.

Methyl ester of 3,4-divinylcyclohexanecarboxylic acid (IX) [5]: bp 90° (2 mm); n_D^{20} 1.4780. Infrared spectrum (ν, cm^{-1}): 920, 1000, 3085 ($-HC=CH_2$), 1740 ($-CO_2CH_3$). NMR spectrum (δ, ppm): 1.72 (6H, CH_2); 2.36 (2H, CH); 3.60 (3H, OCH_3); 5.04 (4H, $>C=CH_2$); 5.76 (2H, $-CH=CH_2$); m/e 197.

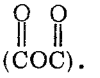
Dimethyl esters of 4-vinyl-2,7- and 4-vinyl-7,10-dodecadienedicarboxylic acids (VI) and (VII): bp 230-233° (1mm); n_D^{20} 1.4861. Infrared spectrum (ν, cm^{-1}): 915, 995, 3090 ($-HC=CH_2$), 975, 3030 (trans- $CH=CH-$), 1720 ($=C-CO_2CH_3$), 1735($-CO_2CH_3$). NMR spectra (δ, ppm): 1.5 (4H, CH_2); 1.98(3H, $=CCH_2$); 2.22(2H,CH_2C-); 2.84(2H, $=CCH_2C=$); 3.54(3H, OCH_3); 3.61(3H, OCH_3); 5.04(2H, $>C=CH_2$); 5.46(3H, $CH=CH$); 5.79(1H, $=CCHC$); 6.93(1H, $CH=CHC$); m/e 280. Found: C 68.9; H 8.8%. $C_{16}H_{24}O_4$. Calculated: C 68.57; H 8.57%. The constants of oligomers (II), (III), (IV), and (V) coincide with the literature data.

Ozonolysis of Esters (I)and (VI)-(VII). a) A solution of 5 g of (I) in 20 ml of AcOH was ozonized at 5-10° until 3.6 g of ozone was absorbed, after which the mixture was treated with 10-15 ml of 30% H_2O_2 solution and kept at 50° for 10 h. The solvent was evaporated, while the residue was methylated with an ether solution of CH_2N_2. After removal of the solvent we obtained 7.5 g of mixed esters, which, based on the GLC, was a mixture of the methyl esters of oxalic, malonic, and glutaric acids.

b) The ozonolysis of (VI) + (VII), after methylation with CH_2N_2, under the same conditions gave a mixture of esters, which, based on the GLC data, contains the methyl esters of the 2-carboxyglutaric, 4-carboxypimelic, glutaric, malonic and oxalic acids. The structure of the first two compounds was confirmed by comparing with compounds that had been synthesized by known methods [6, 7].

Methyl Ester of trans-3,5,10-Undecatrienoic Acid (XV). a) To a refluxing solution of 0.5 g of MeOK in 30 ml of abs. methanol was added dropwise 10 g of (I) in 20 min and the mixture was kept at this temperature for another 15 min. Then the mixture was cooled, poured into 40 ml of water, and extracted with hexane. The extracts were combined, dried over $MgSO_4$, and after removal of the solvent the residue was vacuum distilled. We obtained 8.5 g of (XV), bp 108-110° (1 mm); n_D^{20} 1.4752. Ultraviolet spectrum (in alcohol): λ_{max} 232 nm, ε 16000. Infrared spectrum (ν, cm^{-1}): 920, 1000, 3090($-HC=CH_2$), 980, 3030 (trans-$CH=CH$), 1735 (CO_2CH_3). NMR spectra (δ, ppm): 1.57 m (2H, CH_2); 1.98 m (4H, $=C-CH_2CH_2C=$); 2.96 t (2H, $=CCH_2CO_2R$); 3.52(OCH_3); 4.89(2H, $>C=CH_2$); 5.52(4H, $CH=CH$); 6.02(1H, $CH=C$). Found: C 74.0; H 9.41%. $C_{12}H_{18}O_2$. Calculated: C 74.23; H 9.28%.

A mixture of (XV) and maleic anhydride in toluene was refluxed for 3 h to give adduct (XVI) in ~100% yield, mp 176-178°. Infrared spectrum (ν, cm^{-1}): 720, 3030 (cis- $CH=CH$), 920, 1000, 3090($HC=CH_2$); 1735(CO_2CH_3), 1780, 1850



$(\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C})$. Found: C 62.48; H 6.54%. $C_{15}H_{22}O_5$. Calculated: C 64.3; H 6.43%.

b) To a solution of 0.3 g of NaOH in 50 ml of methanol was added 10 g of (I) and the mixture was stirred at 40° for 3 h. After the above-described workup we obtained 8.3 g of (XV).

Reduction of (I) and (XV). a) With stirring and cooling, 5 g of (XV) was added to a suspension of 0.8 g of $LiAlH_4$ in 50 ml of abs. ether and the mixture was kept at ~20° for another 0.5 h. The excess $LiAlH_4$ was decomposed with water, the obtained precipitate was filtered and washed with hot $CHCl_3$, and the filtrate was dried over $MgSO_4$. The solvent was evaporated, while the residue was vacuum distilled. We obtained 4.1 g of (XVIII) with bp 93-94° (1 mm); n_D^{20} 1.4252. Ultraviolet spectrum (in alcohol): λ_{max} 232 nm, ε 22,000. Infrared spectrum (ν, cm^{-1}): 920, 1000, 3090 ($HC=CH_2$), 990, 3030 (trans-$CH=CH-$), 1150, 3600 (OH). Found: C 78.82; H 11.05%, $C_{11}H_{18}O$. Calculated: C 79.6; H 10.8%. Acetate (XX), bp 97° (1 mm); n_D^{20} 1.4811. Ultraviolet spectrum (in alcohol): λ_{max} 232 nm, ε 22,000. Infrared spectrum

(ν, cm^{-1}): 920, 1000, 3090($HC=CH_2$), 990, 3030 (trans-$CH=CH$), 1735 ($OCCH_3$); m/e 208. NMR spectrum (δ, ppm): 1.87 (3H, $\overset{\overset{O}{\|}}{C}CH_3$); 3.94 (2H, CH_2O); 1.98 (4H, $=CCH_2CH_2C=$); 4.89 (2H, $>C=CH_2$); 5.52 (4H, $CH=CH_2$); 6.02 (1H, $CH=C<$). Found: C 75.26; H 8.9%. $C_{13}H_{18}O_2$. Calculated: C 75.73; H 8.74%.

b) The reduction of 10 g of (I) under analogous conditions gave 8.5 g of a mixture of alcohols, which, based on the GLC data, contained 70% of (XIX) and 30% of (XVIII). Fractional distillation of the mixture in vacuo gave 4.5 g of (XIX), bp 93-94° (1 mm); n_D^{20} 1.4811. Ultraviolet spectrum (in alcohol): λ_{max} 205, ε 13,400. Infrared spectrum (ν, cm^{-1}): 920, 1000, 3090 ($HC=CH_2$), 985, 3030 (trans-$CH=CH-$), 3600 (OH). Found: C 79.11; H 10.45%. $C_{11}H_{18}O$. Calculated: C 79.6; H 10.8%. Acetate (XXI), bp 90° (1 mm); n_D^{20} 1.4626. Ultraviolet spectrum (in alcohol): λ_{max} 205, ε 13,400. Infrared spectrum (ν, cm^{-1}): 920, 1000, 3095 ($HC=CH_2$), 980, 3030 (trans-$CH=CH-$), 1730 ($O\overset{\overset{O}{\|}}{C}CH_3$); m/e 208. NMR spectrum (δ, ppm): 1.5 (2H, CH_2-); 1.87 (3H, $\overset{\overset{O}{\|}}{C}CH_3$); 2.02(4H, CH_2); 2.74 (2H, $=CCH_2C=$); 3.93 (2H, CH_2O); 4.96 (2H, $>C=CH_2$); 5.6 (4H, $CH=CH$); 6.1 (1H, $CH=C<$). Found: C 76.0; H 8.50%. $C_{13}H_{18}O_2$. Calculated: C 75.73; H 8.74%.

Methyl 5,6-Epoxy-2,10-Undecadienoate (XVII). To 10 g of (I) in 50 ml of abs. benzene at ~20° was added an equimolar amount of tert-amyl hydroperoxide and 10 mg of $MoCl_5$ in 10 ml of benzene. The mixture was heated at 70° for 1 h, cooled, and filtered through 30 g of Al_2O_3. The solvent was evaporated, and the residue was vacuum distilled. We obtained 9.5 g of (XVII), bp 110-112° (1 mm); n_D^{20} 1.4732. Ultraviolet spectrum (in alcohol): λ_{max} 205, ε 13,400. Infrared spectrum (ν, cm^{-1}): 920, 1000, 3090 ($HC=CH_2$), 985 (trans-$CH=CH$). 1725 (CO_2CH_3). Found: C 68.5; H 8.7%. $C_{12}H_{18}O_3$. Calculated: C 68.57; H 8.57%.

CONCLUSIONS

1. The conditions were found for obtaining methyl trans-2,5,10-undecatrienoate and the methyl esters of the 4-vinyl-2,7- and 7,10-dodecadienecarboxylic acids in high yields by the cooligomerization of butadiene with methyl acrylate on nickel-containing catalysts.

2. The transformations of methyl trans-2,5,10-undecatrienoate were studied.

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