LINEAR COOLIGOMERIZATION OF BUTADIENE WITH ACRYLATES HAVING VARIOUS STRUCTURES IN THE PRESENCE OF NICKEL COMPLEXES

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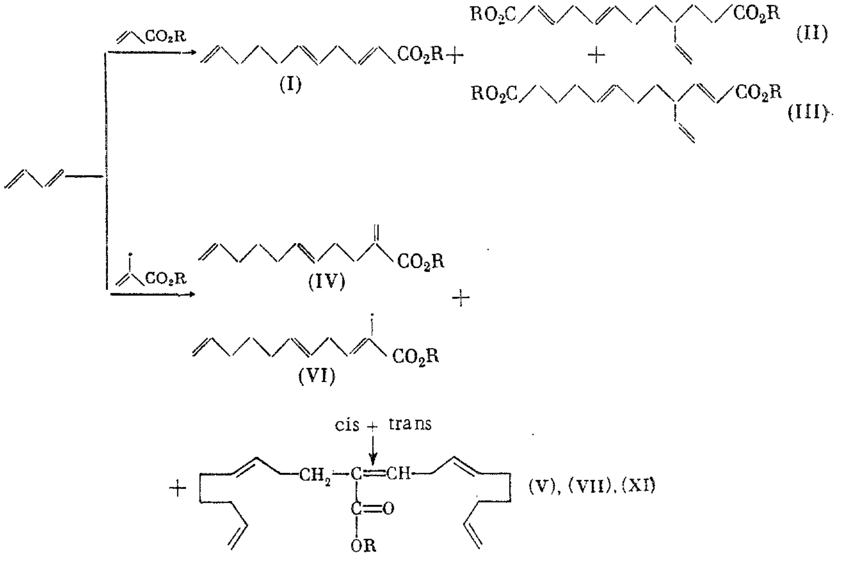
The linear cooligomerization of methyl acrylate with butadiene (BD) under the influence of nickel complexes leads to methyl 2, 5, 10-undecatrienoate (I) and dicarboxylic esters (II, III), depending on the conditions [1]. Methyl 2-methylene-5, 10-undecadienoate (IV) and the pentaenoic ester (V) are formed during the linear cooligomerization of methyl methacrylate with BD. The yields of the esters are low, since the reaction is complicated by the formation of oligomers of BD and diene synthesis adducts.



R = CH_3 (I)—(V), $C_2H_5O(CH_2)_2$ (VI), (VII), cholesteryl (XI)

To study the effect of the structure of the ester radical of the acrylates on the direction and structural selectivity of their cooligomerization with 1, 3-dienes [2-5] we investigated the reactions of 2-ethoxyethyl acrylate (EA), 2-ethoxyethyl methacrylate (EMA), phenyl acrylate, phenyl methacrylate, ethylene glycol diacrylate and dimethacrylate, cholesteryl methacrylate, and phenyl α-fluoroacrylate in solutions of nickel-containing catalysts and organoaluminum reducing agents.

The reaction of BD with EMA gives a mixture of 2-methyl-trans-2, 5, 10-undecatrienoic (VI) and 1-trans-6, 9, 13, 18-nonadecapentaene-10-carboxylic (VII) esters in addition to the butadiene cyclic oligomers 4-vinylcyclohexene (VCH), 1, 5-cyclooctadiene (COD), and all-trans-1, 5, 9-cyclododecatriene (CDT). The total conversion of the monomers amounts to 95%. The ratio of the obtained products depends on the type of activator, the ratio of the monomers, and the temperature. The structure of the organoaluminum reducing agent does not have a significant effect.

Thus, the content of the ester (VII) in the catalysis product increases with increase in the electron-donating capacity of the activator in the following order: $[(CH_3)_2N]_3PO$(HMPTA) > C_6H_5N > $P(C_4H_9)_3$ > $Sb(C_6H_5)_3$ > $P(C_6H_5)_3$ > morpholine > $(C_2H_5O)_3P$ > $(C_2H_5O{-}CH_2{-}CH_2{-}O)_3P$. For instance, with a BD : EA ratio of 1 : 1 the

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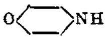
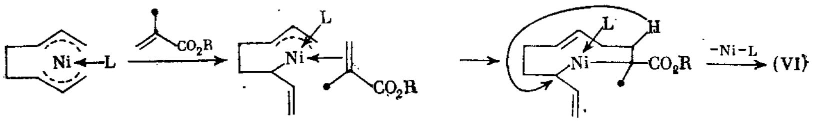
TABLE 1. Cooligomerization of Butadiene with 2-Ethoxyethyl Methacrylate [80°C, 8 h, $Ni(acac)_2$—TEA—L = 1 : 4 : 1, butadiene—methacrylate ratio 4 : 1, toluene]

Activator	Total yield of cooligomers, %	Composition of oligomer mixture, %			
		CDT	(VII)	(VI)	other oligomers
$[(CH_3)_2{-}N]_3P{=}O$	93	12	69	18	1 (VCH)
$(C_4H_9)_3P$	85	22	59	19	–
C_6H_5N	86	22	66	12	–
$(C_6H_5)_3Sb$	96	21	59	20	–
$(C_6H_5)_3P$	78	30	52	12	6 (COD)
	98	6	46	44	4 (VCH)
$(C_2H_5O)_3P$	91	38	42	20	–
$[C_2H_5O(CH_2)_2O]_3P$	79	15	38	47	–
$(C_6H_5O)_3P$	79	60	21	19	–
Without activator	28	66	6	28	–

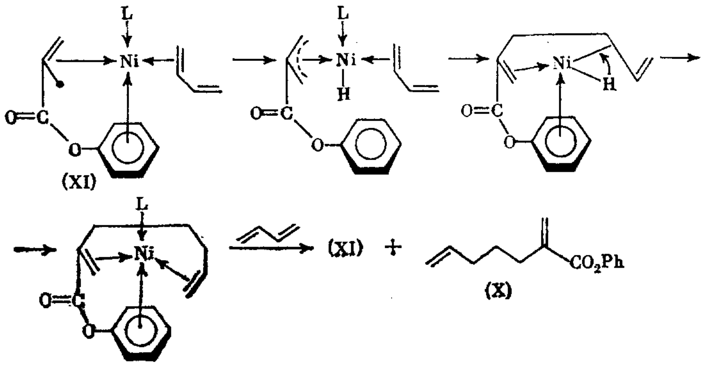
yield of (VII) amounts to 69% on the catalyst with HMPTA and ≤ 6% in the absence of HMPTA. Conversely, the content of the ester (VI) increases with decrease in the electron-donating capacity of the activator, reaching 66% on nickel in the absence of the activator (Table 1). The overall yield of the oligomers is appreciably higher in solvents of the aromatic and ester type than in hexane. With the optimum catalyst the yield of the ester (VII) increases with increase in the proportion of BD in the initial mixture, reaching a maximum (70%) with a BD : EMA ratio of 4 : 1. The yield of (VII) decreases somewhat with increase in temperature; at the same time the yield of (VI) and CDT increase. Transesterification of (VII) by methanol in the presence of potassium methoxide gave the ester (VIII), which was synthesized by the isomerization of (V) with potassium methoxide in boiling methanol.

Thus, by replacement of methyl methacrylate by EMA it is possible not only to increase the yield of the cooligomers and regulate their ratio as a function of the nature of the activator but also to direct the reaction towards the formation of the thermodynamically more stable trienoic ester (VI):

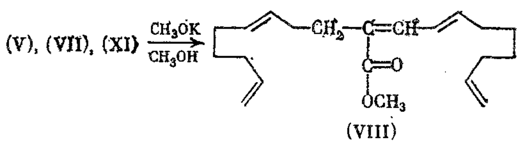


The reaction of phenyl methacrylate with BD in the presence of the $Ni(acac)_2$—PPh_3—$Al(C_2H_5)_3$ system led unexpectedly to the previously undescribed phenyl 2-methylene-6-heptenoate (X) in addition to CDT.

The new direction of the cooligomerization of BD with acrylates can be explained by the fact that the C_6H_5 group, being a "reservoir" of electrons, takes part in the creation of the coordination sphere of the nickel, preventing coordination of subsequent BD molecules and their addition. Compound (X) is probably formed according to the following scheme:



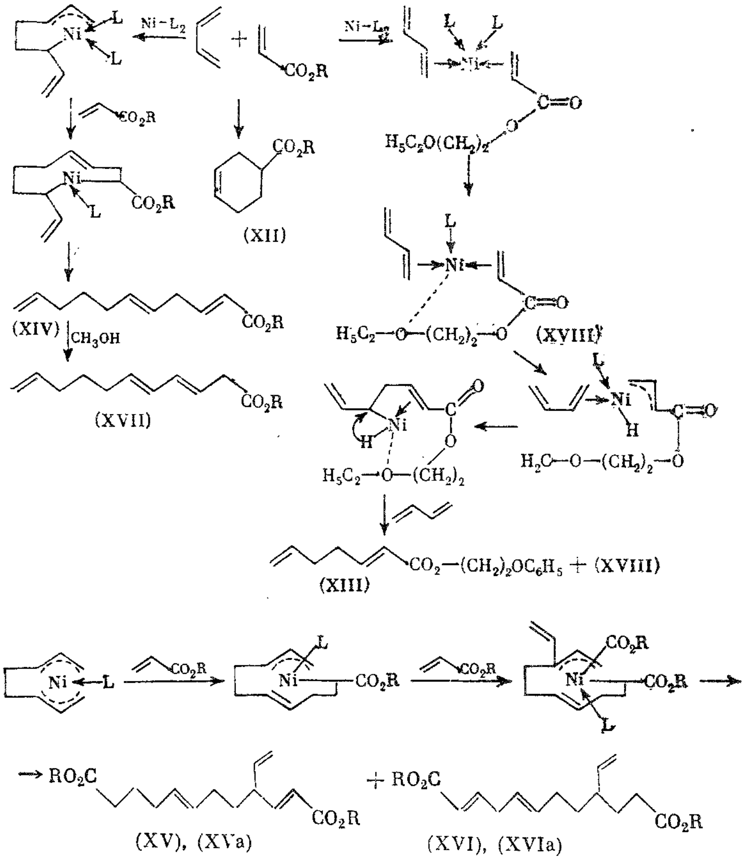
The introduction of the cholesterol residue into the methacrylate substantially affected the composition of the catalysis product. Although the conversion of cholesteryl methacrylate does not exceed 10%, it is all consumed in the exclusive formation of the ester (IX). Its transesterification with methanol in the presence of potassium methoxide is accompanied by a shift of one of the double bonds, giving (VIII). As seen, the polycyclic substituent creates conditions for selective cooligomerization, although steric hindrances lead to a decrease in the yield of the oligomer.



(VIII)

In experiments on the cooligomerization of EA with BD it was established that catalysts based on $P(C_6H_5)_3$ have the highest activity. The composition of the product depends strongly on the ratio of the monomers. Thus, a mixture of tetrahydrobenzoic (XII), trans-2, 6-heptadienoic (XIII), and trans-2, 5, 10-undecatrienoic (XIV) esters in a ratio of 40: 35: 25 respectively is formed with an EA : BD ratio of 1: 2 on the $Ni(acac)_2—PPh_3—Al(C_2H_5)_3$ catalyst. The formation of BD oligomers is not observed. The cooligomerization of BD with EA (1: 1) at the $Ni(acac)_2—PPh_3—Al(C_2H_5)_3$ catalyst led to the production of a mixture of esters (XIII) and (XIV) and dicarboxylic esters (XV) and (XVI), and 75% of the catalysis product corresponds to the last two compounds. The yield of (XIV) does not exceed 5%. Transesterification of the ester (XIV) with methanol gave the known [5] methyl 3, 5, 10-undecatrienoate (XVII).

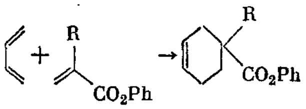
Consequently, the introduction of a substituent capable of complex formation with nickel into the ester group makes it possible to control the composition of the cooligomers. However, the tendency toward the formation of the codimer (XIII) is not so clearly defined as in the experiments with phenyl methacrylate. The overall scheme of the transformations can be represented as follows:



R = $C_2H_5O(CH_2)_2$ (XII)–(XVI), CH_3(XVa), (XVIa), (XVII)

All attempts to bring ethylene glycol diacrylate and dimethacrylate into the reaction with BD were unsuccessful. These esters not only do not enter into reaction but block the oligomerization of BD like maleates and fumarates [1].

Irrespective to the nature of the activator and the reaction conditions, the reaction of phenyl acrylate and phenyl α-fluoroacrylate with BD leads only to diene synthesis adducts (XIX) and (XX). The outcome of the experiments with phenyl acrylate was somewhat unexpected, although the effect of C_6H_5 results in the exclusive formation of the codimer of BD and phenyl acrylate:



R = H(XIX), F(XX)

EXPERIMENTAL

Monomers of ≥ 99.5% purity were used. The mixtures of hydrocarbons were analyzed on a Tsvet-102 chromatograph with a flame-ionization detector, a 2-m column, 15% Apiezon L on Celite-545, and nitrogen as carrier gas. The PMR spectra were recorded on a Tesla-480B instrument in carbon tetrachloride with HMDS as internal standard. The IR and UV spectra were recorded on UR-20 (film) and Spekord UV-VIS instruments (in alcohol). The mass spectra were recorded on an MKh-13-06 instrument with 50-eV ionizing electrons and with the ionization chamber at 200°C.

General Method for the Cooligomerization of 2-Ethoxyethyl Methacrylate with Butadiene. To a solution of 0.38 g (0.0015 mole) of $Ni(acac)_2$, 0.0015 mole of the activator, and 1 ml of butadiene in 10 ml of absolute toluene in an argon atmosphere at −5°C we added 0.006 mole of the organoaluminum reducing agent. The mixture was stirred for a further 30 min at the same temperature. The solution of the catalyst was placed in a stainless-steel autoclave (100 ml) in a stream of argon, 31 ml (0.4 mole) of BD and 15.8 g (0.1 mole) of 2-ethoxyethyl methacrylate were added, and the mixture was heated at the given temperature for 8 h. The autoclave was cooled, the catalysts was decomposed with 5 ml of alcohol, and the reaction mass was submitted to fractional distillation. The results are given in Table 1.

The cooligomers isolated by fractional distillation have the following constants. 2-Ethoxyethyl 2-methyl-2, 5, 10-undecatrienoate, bp 160°C (1 mm Hg), n_D^{20} 1.4821. UV spectrum (λ, nm): 220, ε 15000. IR spectrum (ν, cm^{-1}): 830, 3030 (trans-CH= CH), 915, 1000, 3090 ($CH=CH_2$), 980, 3030 (trans-CH=CH), 1725 ($=CCO_2R$). PMR spectrum (δ, ppm): 1.06 (3H, OC_2H_5, CH_3); 3.45 (4H, OCH_2); 4.1 (2H, $COOCH_2$); 2.04 (4H, $=CCH_2$); 1.8 (3H, $CH_3C=C$); 2.88 (2H, $=CCH_2C=$); 4.8 (2H, $C=CH_2$); 5.2 (1H, $HC=CCO_2R$); 5.3 (2H, CH= CH); 6.0 (1H, CH=C). m/e 278.

2-Ethoxyethyl 1, 6, 9, 13, 18-nonadecapentaen-10-oate (VIII), bp 200°C (1 mm Hg); n_D^{20} 1.4906. UV spectrum (λ, nm): 206, ε 14000. IR spectrum (ν, cm^{-1}): 920, 1000, 3085 ($CH=CH_2$), 980, 3030 (trans-CH= CH), 1720 ($=CCO_2R$). PMR spectrum (δ, ppm): 1.06 (3H, $OC_2H_5CH_3$); 1.42 (4H, CH_2); 2.04 (10H, $=CCH_2$); 2.9 (2H, $=CCH_2C=$); 3.45 (4H, OCH_2); 4.01 (2H, $COOCH_2$); 4.89 (4H, $C=CH_2$); 5.6 (4H, CH= CH); 5.91 (2H, CH=C); 6.71 (2H, $HC=CCO_2R$). m/e 386. The structure of the BD oligomers was confirmed by GLC by comparison with the authentic compounds.

Cooligomerization of 2-Ethoxyethyl Acrylate with Butadiene. A solution of the catalyst prepared from 0.51 g (0.2 mole) of $Ni(acac)_2$, 1 g (0.04 mole) of Ph_3P, and 0.8 mole of R_3Al was transferred to a stainless-steel autoclave (100 ml) at −5°C in a stream of argon, 13 ml of BD and 14.2 g (0.1 mole) of EA were added, and the mixture was heated at 120°C for 10 h. After the usual treatment 20 g of a mixture of oligomers was obtained. According to GLC, it consisted of 40% of 2-ethoxyethyl tetrahydrobenzoate (XII), 35% of 2-ethoxyethyl 1, 5-hexadienoate (XIII), and 25% of 2-ethoxyethyl 2, 5, 10-undecatrienoate (XIV).

The esters, isolated by fractional distillation on a column, have the following constants. 2-Ethoxyethyl tetrahydrobenzoate (XII), bp 52°C (1 mm Hg), n_D^{20} 1.4821. IR spectrum (ν, cm^{-1}): 720, 3030 (cis-CH=CH), 1735 (CO_2R). m/e 198.

2-Ethoxyethyl 1, 5-heptadienoate (XIII), bp 81°C (1 mm Hg); n_D^{20} 1.4580. UV spectrum (λ, nm): 204, ε 12000. IR spectrum (ν, cm^{-1}): 920, 1000, 3080 ($CH=CH_2$), 975, 3030 (trans-CH= CH), 1720 ($=CCO_2R$). PMR spectrum (δ, ppm): 1.1 (3H, OC_2H_5); 2.04 (4H, $=CCH_2$); 3.40 (4H, OCH_2); 4.1 (2H, $COOCH_2$); 4.96 (2H, $C=CH_2$); 5.62 (2H, CH= CH); 6.7 (1H, CH= C).

2-Ethoxyethyl 2, 5, 10-undecatrienoate (XIV), bp 190°C (1 mm Hg); n_D^{20} 1.4801. UV spectrum (λ, nm): 205, ε 18000. IR spectrum (ν, cm^{-1}): 920, 1000, 3085 ($CH-CH_2$), 975, 3030 (trans-CH= CH), 1720 ($=CCO_2R$). PMR spectrum (δ, ppm): 1.08 (3H, OC_2H_5, CH_3); 2.0 (4H, $=CCH_2$); 2.8 (2H, $=CCH_2C=$); 3.45 (4H, OCH_2); 4.1 (2H, $COCH_2$); 4.9 (2H, $C=CH_2$); 5.62 (4H, CH= CH); 6.7 (1H, CH= C). m/e 252.

During the cooligomerization of 12 g of BD with 32 g of EA (1 : 1) in a solution of 0.5 g of $Ni(acac)_2$, 0.51 g of $Ph(OPh)_3$, and 0.91 g of $Al(C_2H_5)_3$ at 80°C for 10 h we obtained 39.6 g of a mixture of oligomers. According to GLC, it consisted of 75% of 4-vinyl-2, 7- and 4-vinyl-7, 10-dodecadienecarboxylic esters (XV, XVI), 21% of 2-ethoxyethyl 1, 5-heptadienoate (XIII), and 4% of 2-ethoxyethyl tetrahydrobenzoate (XII). The formation of BD oligomers was not observed.

Mixture of bis(2-ethoxyethyl) 4-vinyl-2, 7- and 4-vinyl-7, 10-dodecadienecarboxylates (XV) and (XVI), bp 136°C (0.05 mm Hg); n_D^{20} 1.4810. UV spectrum (λ, nm): 206, ε 16000. IR spectrum (ν, cm^{-1}): 920, 1000, 3090 ($CH=CH_2$), 975, 3030 (trans-CH= CH), 1720 ($=CCO_2R$), 1735 (CO_2R). PMR spectrum (δ, ppm): 1.07 (5H, OC_2H_5, CH_3); 1.5 (4H, CH_2); 1.98 (3H, CCH_2); 2.22 (2H, $CH_2C=O$); 2.84 (2H, $=CCH_2C=$) ; 3.45 (8H, OCH_2); 4.1 (4H, $COOCH_2$); 5.04 (2H, $C=CH_2$); 5.46 (3H, CH=CH); 5.79 (1H, OCOCH= C); 6.93 (1H, CH= C), m/e 420.

Cooligomerization of Phenyl Methacrylate with Butadiene. A solution of the catalyst prepared from 0.38 g of $Ni(acac)_2$, 0.39 g of $P(Ph)_3$, and 0.68 g of $Al(C_3H_5)_3$ in 10 ml of toluene by the method described above was transferred to an autoclave (100 ml), 15 g of PMA and 5.4 g of BD were added, and the mixture was heated at 80°C for 8 h. After the usual treatment 14.3 g of the oligomers was obtained. According to GLC data, the mixture contained 71% of (X) and 29% of cyclododecatriene. The above-mentioned compounds were isolated by vacuum distillation. Phenyl 2-methylene-6-heptenoate (X), bp 150°C (1 mm Hg); n_D^{20} 1.5100. PMR spectrum (δ, ppm): 1.33 (2H, CH_2); 1.93 (2H, = CCH_2); 2.26 (2H, $=CCH_2$); 4.85 (2H, $C=CH_2$); 5.15 (4H, CH=); 5.5 (1H, methylene); 6.2 (1H, methylene) and 6.98 (5H, C_6H_5), m/e 216.

The IR spectrum contains frequencies characteristic of a conjugated ester (1650, 1720 cm^{-1}), methylene (1895, 3080 cm^{-1}), and vinyl (920, 1000, 3090 cm^{-1}) groups.

Cooligomerization of Cholesteryl Methacrylate with Butadiene. In a 300-ml steel autoclave we placed the catalytic system prepared from 0.38 g of $Ni(acac)_2$, 0.39 g of $P(Ph)_3$, and 0.8 g of $Al(C_2H_5)_3$. We added 4.7 g of BD and 10 g of CMA in 120 ml of toluene and heated the mixture at 80°C for 8 h. The autoclave was then cooled, 5 ml of alcohol was added, and the solvent was removed under vacuum. The residue was chromatographed on aluminum oxide (III activity) with benzene. The eluates were combined and evaporated. From 4 g of the mixture of oligomers by preparative TLC we obtained 0.4 g of (IV) and 3.6 g of the unreacted initial ester. The cooligomer (IX) was a colorless gelatinous mass. IR spectrum (ν, cm^{-1}): 760, 3030 (cis-CH=CH), 920, 1000, 3085 ($C=CH_2$), 950, 980 (trans-CH=CH), 1650, 1720 ($=CCO_2R$). Found %: C 82.4; H 10.5. $C_{47}H_{74}O_2$. Calculated %: C 82.2; H 10.7.

Transesterification of 0.3 g of the ester (IX) with methanol in the presence of catalytic amounts of potassium methoxide by the method in [5] led to the production of methyl 1, 7, 9, 13, 18-nonadecapentaene-10-carboxylate (VIII) and cholesterol, which were separated by column chromatography on aluminum oxide.

Cooligomerization of Phenyl α-Fluoroacrylate and Phenyl Acrylate with Butadiene. Six-membered codimers were obtained during the reaction of the above-mentioned monomers in a solution of $Ni(acac)_2$ and $Al(C_2H_5)_3$, irrespective of the nature of the activator and the reaction conditions. In particular phenyl 1-fluorotetrahydrobenzoate (XIX) was obtained with a yield of 30% from BD and phenyl α-fluoroacrylate, and phenyl acrylate with BD gave phenyl tetrahydrobenzoate (XX) with a 70% yield.

Phenyl 1-fluorotetrahydrobenzoate (XIX), bp 125°C (1 mm Hg), n_D^{20} 1.5110. IR spectrum (ν, cm^{-1}): 690, 700, 1500, 1600 (in C_6H_5), 740, 3030 (cis-CH= CH), 1735 (CO_2P). PMR spectrum (δ, ppm): 2.11 m (6H, CH_2); 5.5 (2H, CH= CH); 7.12 (5H, CH in C_6H_5). m/e 220. The constants of (XX) coincide with the constants of the authentic compound.

Isomerization of Methyl 1, 6, 9, 13, 18-Nonadecapentaene-10-carboxylate with KOH. To a solution of 1 g of compound (V), obtained by the method in [1] in 5 ml of absolute methanol, we added 0.05 g of potassium methoxide in 5 ml of methanol. The mixture was boiled for 0.5 h, decomposed with an equal volume of cold water, and extracted repeatedly with methylene chloride. The extracts were dried over magnesium sulfate, the methylene chloride was distilled, and the residue was distilled under vacuum. A 0.8-g yield of the ester (VIII) was obtained; bp 208°C (0.5 mm Hg); n_D^{20} 1.4893. UV spectrum (λ, nm): 260, ε 20000. IR spectrum (ν, cm^{-1}): 920, 1000, 3085 ($HC=CH_2$), 980, 3030 (trans-CH=CH), 1725 ($=CCO_2CH_3$). PMR spectrum (δ, ppm): 1.57 (6H, CH_2); 2.04 (12H, $=CCH_2$); 3.52 (2H, OCH_3); 4.89 (4H, $C=CH_2$); 5.52 (5H, CH= CH); 6.0 (2H, CH= C). m/e 316.

The isomerization of 5 g of 2-ethoxyethyl 1, 6, 9, 13, 18-nonadecapentaene-10-oate (VII) under the above-mentioned conditions gives the ester (VIII), fully identical with the product obtained by the method described above.

Under analogous conditions 2-ethoxyethyl 2, 5, 10-undecatrienoate (XIV) is converted into methyl 3, 5, 10-undecatrienoate (XVII) [5].

Transesterification of the Esters (XV) and (XVI) by Methanol. To a solution of 1 g of the mixture of (XV) and (XVI) in 10 ml of absolute methanol we added 0.2 g of sodium methoxide. The mixture was stirred at ~20°C for 2 h and then diluted with 30 ml of cold water and extracted repeatedly with methylene chloride. The extracts were combined and dried over magnesium sulfate. After removal of the solvent the residue was distilled under vacuum. A 0.9-g yield of a mixture of dimethyl 4-vinyl-2, 7- and 4-vinyl-7, 10-dodecadienoates was obtained [5].

CONCLUSIONS

1. Aliphatic linear and cyclic radicals affect the selectivity of the cooligomerization of butadiene with acrylic and methacrylic esters in the presence of nickel complexes and in a number of cases make it possible to obtain previously unknown codimers.

2. The cooligomerization of phenyl methacrylate with butadiene leads to the production of the previously unknown phenyl 2-methylene-6-heptenoate with a high yield. Under analogous conditions phenyl α-fluoroacrylate and phenyl acrylate with butadiene give diene synthesis products exclusively.

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OXIDATION OF 1-METHYL- AND 1-ETHYLCYCLOHEXANOL WITH CERIUM AMMONIUM NITRATE

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and E. P. Kaplan

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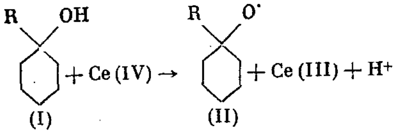
Tertiary cyclic alcohols (1-alkylcyclopropanols and 1-alkylcyclobutanols) are oxidized by Ce(IV) compounds to form alkoxyl radicals, which isomerize with ring opening (β-decomposition) [1, 2]. The oxoalkyl radicals which form recombine with each other, abstract hydrogen from the medium, and are oxidized. Nitrates or unsaturated compounds respectively can form during the oxidation of alkyl and cycloalkyl radicals by cerium ammonium nitrate (CAN) [2, 3]. In contrast to three- and four-membered cyclic alcohols 1-alkylcyclopentanols do not enter into reaction with Ce(IV) [1]. Concerning six-membered cyclic alcohols it is known only that cyclohexanol is converted into cyclohexanone under the influence of CAN [4].

We investigated the oxidation of 1-methyl- and 1-ethylcyclohexanol (Ia, b) by CAN in aqueous and anhydrous acetonitrile. The composition and amounts of the obtained products are given in Table 1. The reaction in aqueous acetonitrile takes place according to the following scheme:



(1)

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