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Synthesis, Film-Forming, and Light-Sensitivity Properties of Allyl and Propargyl Maleopimarates and Cytraconopimarates

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Abstract—Previously unknown allyl and propargyl esters of maleopimaric and citraconopimaric acids were synthesized. The film-forming and light-sensitivity properties of these compounds were studierd.

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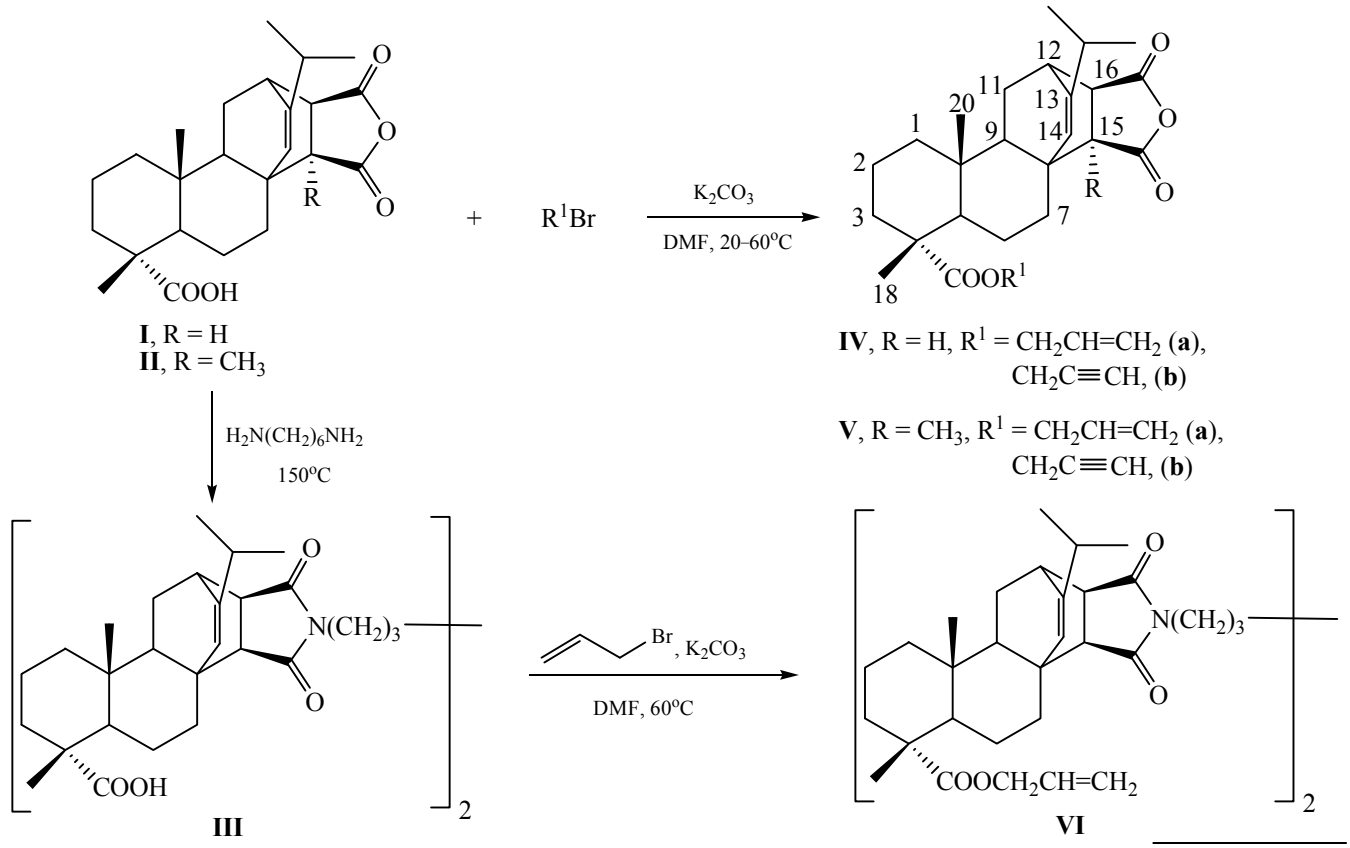
Recently an interest increased in the synthesis of thin film materials based on the derivatives of resin acids. On the basis of these compounds protective coatings were obtained for steel [1, 2], negative photoresists [3], and photoactive materials [4].

Among the unsaturated esters of maleopimaric acid vinyl [5] and diallyl [6, 7] esters have been described and esters on the basis of epoxy-derivatives of maleopimaric acid as well as of acrylic and methacrylic acids [1, 3]. Diallyl maleopimarate has been synthesized by the reaction of diallyl maleate with gum rosin at 165–180°C followed by extraction of the adduct formed from the reaction mixture [6, 7]. This communication describes the synthesis and physicochemical, including film-forming and photosensitivity properties of new derivatives of unsaturated resin acids, the allyl and propargyl esters of maleopimaric (**I**) and citraconopimaric acids (**II**), and of diallyl ester of the imidodiacid (**III**).

Methods of synthesis of the esters was tested by the example of the synthesis of allyl maleopimarate (**IVa**). Initial maleopimaric acid (**I**) contains a carboxylic and an anhydride groups, and therefore it is difficult to carry out esterification with allyl alcohol only of the carboxylic group. We studied a possibility of obtaining the target ester (**IVa**) by the reaction of maleopimaroyl chloride with allyl alcohol in the presence of triethylamine. We found that treatment of the acid **I** chloride with equimolar amount of allyl alcohol and triethylamine in tetrahydrofuran and maintaining the reaction mixture for 72 h at 20–22°C led to the formation of no more than 30% of the allyl ester **IVa** (by the data of ^{1}H NMR spectroscopy). Adding to the reaction mixture excess reactants leads to the formation of a complex mixture containing products of the anhydride group cleavage, as evidenced by the disappearance of absorption bands at 1790 and 1850 cm^{-1} in the IR spectrum of the obtained product.

The traget allyl ester **IVa** was synthesized in a high yield (98–99%) by the reaction of maleopimaric acid **I** with allyl bromide in dimethylformamide in the presence of potassium carbonate, therewith the anhydride ring remained intact. By similar technique we prepared earlier unknown propargyl maleopimarate **IVb**, as well as allyl and propargyl esters of citraconopimaric acid **Va, Vb**, and diallyl ester of imidodicarboxylic acid **VI**.

Unsaturated esters **IVa, IVb, Va, Vb,** and **VI** are colorless crystalline substances, soluble in chloroform, methylene chloride, acetone, and poorly soluble in hexane. Target products do not require additional treatment and contain no admixtures of the initial reagents. The structures of esters **IV–VI** are proved by the data of elemental analysis, IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, and by mass-spectrometric determination of molecular weight. According to the ^{1}H NMR spectroscopy, the purity of the compounds obtained was 98 ± 1%. In the ^{13}C NMR spectra of these compounds the number of signals corresponds to the number of carbon atoms in the unsaturated esters



I, R = H
II, R = CH_3

IV, R = H, R^1 = $CH_2CH{=}CH_2$ (**a**), $CH_2C{\equiv}CH$, (**b**)

V, R = CH_3, R^1 = $CH_2CH{=}CH_2$ (**a**), $CH_2C{\equiv}CH$, (**b**)

III **VI**

IV–VI. In the IR and ^{1}H NMR spectra there are the absorption bands and the signals of protons confirming the presence of the structural fragments of ester groups.

In the IR spectra of esters **IV–VI** a group of bands of stretching vibrations of O–H bonds at 2850–2500 cm^{-1} was not observed. The presence of the $CH{=}CH_2$ in compounds **IVa, Va**, and **VI** is confirmed by the presence of absorption band at 3100 cm^{-1}, C≡CH group in the spectra of compounds **IVb** and **Vb** gives rise to absorption bands at 3290–3320 and 2130 cm^{-1}.

In the ^{1}H NMR spectra of esters **IVa, Va,** and **VI** the signals of $=CH_2$ groups appear as doublets in the region of 5.31–5.34 ppm (H-*cis*, $=CH_2$), 5.24–5.26 ppm (H-*trans*, $=CH_2$), the signal of C*H*$=CH_2$ proton as a multiplet in the range of 5.88–5.96 ppm. In the ^{1}H NMR spectra of compounds **IVb, Vb** the signal of ≡CH proton appears as a triplet at 2.48 ppm, and of OCH_2 protons, as a quartet in the range of 4.63–4.72 ppm.

The derivatives **IV, V** of maleopimaric acid are optically active compounds, with $[\alpha]_D^{20}$, deg: –31.8° (**IVa**), –28.9° (**IVb**), –25.3° (**Va**), and –23.8° (**Vb**).

Weighed samples (0.1 mmol, 0.040–0.090 g) of the synthesized esters **IVa, IVb, Va, Vb,** and **VI** and of the source acids **I, II** were used for thermal vacuum deposition (TVD) to obtain colorless transparent glossy films of thickness 0.9–1.4 μm with good adhesion to the surface of various substrates (silicon monocrystal, quartz, polymer layers, etc.). The samples evaporated completely, without forming residues. In the process of vacuum evaporation the compounds **I, II, IV–VI** did not undergo significant chemical transformations that confirms the identity of IR spectra in KBr pellets of starting powders and thin-film material with IR spectra of TVD films on the single crystal substrates.

Glossy surface and the transparency of deposited films of the compounds **I, IVa, IVb,** and **Vb** remain unchanged for a long time (more than 10 days). In the films obtained from compounds **II** and **Va** after 1–2 h formed the centers of crystallization that then turned to frosting. The glossy surface of the films of compounds **I, II, IVa, IVb, Va,** and **Vb** remained unchanged after keeping them for 15–20 min in 15–20% hydrochloric acid.

The TVD-films from compounds **I, IVa, IVb, Va,** and **Vb** are sensitive to UV radiation (3.6–7.1 J cm^{-2}).

Thus, at the exposure through a mask to filtered radiation of the lamp DRT-1000 for 10–20 min in the film formed a latent image which appeared at heating in a vacuum up to temperatures close to the temperature of evaporation of the initial compound. The unexposed areas removed from the film and a negative type relief with the minimum element size 2.0–2.5 μm is formed.

The TVD-films from compounds **I, II, IV–VI** may be of practical interest for the manufacture of photomask for wet etching of topology in the transparent conductive layer of indium–tin oxide (ITO).

EXPERIMENTAL

IR spectra of the compounds were recorded on a Specord IR-75 spectrometer in KBr tablets. ^{1}H and ^{13}C NMR spectra of solutions in $CDCl_3$ were recorded on a spectrometer AVANCE 500 (500 MHz for ^{1}H and 125 MHz for ^{13}C). Chemical shifts were determined relative to the signal of solvent (7.27 ppm ^{1}H, 77.70 ppm ^{13}C). Mass spectra were obtained on the mass spectrometer Accela with mass detector LCQ Fleet in the mode of chemical ionization (APCI) with the detection of positive ions. Angles of rotation of the polarization plane were determined on a Polamat A (Carl Zeiss) device.

Individuality of compounds was monitored by TLC on Silufol UV-254 plates in the hexane–acetone 5:2 system.

The TVD-films were deposited using the installation VUP-4 acoording to the procedure described in [8, 9] from the gas phase onto silicon substrate. The process of forming the films was controlled with a quartz crystal resonator, and the film thickness was measured on a Linnik interferometer MII-4. The IR spectra of the films deposited on silicon substrates were recorded on a Protege-460 spectrophotometer.

The initial maleopimaric acid **I** was purified by double crystallization from acetic acid of the adduct obtained by the reaction of rosin with maleic anhydride at 180°C for 6 h [10]. To remove the acetic acid from the maleopimaric acid – CH_3COOH solvate the latter was kept for 30 minutes at 140°C. The acid **I** with mp 229–230°C, $[\alpha]_D^{20}$ –25.0° (*c* 3.08, chloroform) was obtained, which corresponds to published data [10].

Maleopimaric acid chloride was obtained by the method [11].

Citraconopimaric acid **II** was obtained from the product of reaction of rosin and itaconic acid at 200°C in 8 h [12]. Individual isomer (C^{15}–CH_3) of citraconopimaric acid was used, isolated from a mixture of two isomers of citraconopimaric acid by crystallization from benzene [12]; mp 198–199°C, $[\alpha]_D^{20}$ –13.5° (*c* 1.76, acetone).

The initial imidoacid **III** [13] was obtained by the method developed by us from maleopimaric acid and hexamethylenediamine: a mixture of 10.00 g (0.025 mol) of maleopimaric acid and 1.45 g (0.012 mol) of hexamethylenediamine was heated in 50 ml of *o*-dichlorobenzene at 150°C in a flask with a reflux condenser and a Dean–Stark trap for 6 h. Then the solvent was distilled off from the reaction mixture in a vacuum (90–100°C, 10 mm Hg). To the residue 30 ml of ethyl alcohol was added, the mixture was stirred for 5 min, the solution was decanted and left for 1.5 h at 18°C for crystallization. The precipitated crystals were filtered off, dried at 70°C for 1 h, and recrystallized from 40 ml of benzene. 5.58 g (50.6%) of compound **III** was obtained, mp 212–214°C (benzene). ^{1}H NMR spectrum (δ, ppm): 0.51 s (6H, $C^{20}H_3$), 0.87 m (2H), 0.84 d, 0.88 d (12H, (CH_3CH), 1.08–1.77 m (38H), 2.08 sextet [2H, $(CH_3)_2CH$], 2.33 d (2H, $C^{21}H$), 2.44 m (2H, $C^{7}H$), 2.68 d.d (2H, 16H), 2.96 br.s (2H, $C^{12}H$), 3.20 m (4H, N–CH_2), 5.31 s (2H, $C^{14}H$). IR spectrum, ν, cm^{-1}: 3460, 2670 (O–H), 1780, 1740 [(C=O)N], 1700 [(C=O)OH], 1370, 1350 (C–N), 1180, 1150 [$CH(CH_3)_2$]. Mass spectrum, *m/z*: 882 $[M + 1]^+$. Found, %: C 73.24, H 8.96; N 3.36. Calculated, %: C 73.60; H 8.69; N 3.18.

Unsaturated maleopimaric and citraconopimaric esters (IVa, IVb, Va, and Vb). A mixture of 0.01 mol of acid, 0.012 mol of allyl or propargyl bromide, and 0.012 mol of potassium carbonate in 30 ml of dimethylformamide was stirred for 12–16 h at 20ºC. The progress of reaction was monitored by TLC on Silufol UV-254 plates (20 cm) (hexane–acetone, 3:1). The reaction mixture was filtered through a glass filter, the solvent was distilled off in a vacuum (60–70°C, 10 mm Hg). To the resulting residue 30 ml of $CHCl_3$ was added, the solution was filtered through a glass filter. The solvent was removed, the residue was kept in vacuum (1 mm Hg, 50°C) for 1 h.

Allyl maleopimarate (IVa). Yield 99% (4.37 g), mp 142–144°C (benzene), $[\alpha]_D^{20}$ –31.8º (*c* 3.64, $CHCl_3$). ^{1}H NMR spectrum (δ, ppm): 0.59 s (3H, $C^{20}H_3$), 0.94 m (1H), 0.98 d, 0.99 d [6H, $(CH_3)_2CH$], 1.17 s (3H, $C^{18}H_3$), 1.25 m (2H), 1.37–1.80 m (11H),

2.25 sextet [1H, $(CH_3)_2CH$, 2.51 m (1H, C^7H), 3.11 m (2H, $C^{12}H$, $C^{16}H$), 4.59 m (2H, OCH_2), 5.24 d (1H, $=CH_2$, H-*trans*), 5.32 (1H, $=CH_2$, H-*cis*), 5.53 s (1H, $C^{14}H$), 5.92 m (1H, $CH=CH_2$). IR spectrum, ν, cm^{-1}: 3100 (=C–H), 1840, 1790 [$(C=O)_2O$], 1730 [(C=O)OR], 1250 (C–OCH_2), 1200, 1170 [$CH(CH_3)_2$]. Mass spectrum, *m/z*: 442 $[M + 1]^+$. Found, %: C 73.14, H 8.75. $C_{27}H_{36}O_5$. Calculated, %: C 73.61; H 8.24.

Propargyl maleopimarate (IVb). Yield 98% (4.29 g), mp 152–153°C (ester), $[\alpha]_D^{20}$ –28.9° (*c* 1.4, $CHCl_3$). ^1H NMR spectrum (δ, ppm): 0.59 s (3H, $C^{20}H_3$), 0.95 m (1H), 0.98 d, 0.99 d [6H, $(CH_3)_2CH$], 1.18 s (3H, $C^{18}H_3$), 1.26 m (1H), 1.37–1.80 m (11H), 2.26 sextet [1H, $(CH_3)_2CH$], 2.48 m (1H, ≡CH), 2.51 m (1H, C^7H), 2.74 d (1H, $C^{15}H$), 3.11 m (2H, $C^{12}H$, $C^{16}H$), 4.67 m (2H, OCH_2), 5.53 s (1H, $C^{14}H$). IR spectrum, ν, cm^{-1}: 3290 (≡C–H), 2130 (C≡C), 1850, 1790 [$(C=O)_2O$], 1745 [(C=O)OR], 1240 (C–OCH_2), 1190, 1170 [CH $(CH_3)_2$]. Mass spectrum, *m/z*: 440 $[M + 1]^+$. Found, %: C 73.80, H 8.29. $C_{27}H_{34}O_5$. Calculated, %: C 73.94, H 7.81.

Allyl citraconopimarate (Va). Yield 95% (4.33 g), mp 150–152°C (ester), $[\alpha]_D^{20}$ –25.3° (*c* 2.0, $CHCl_3$). ^1H NMR spectrum (δ, ppm): 0.62 s (3H, $C^{20}H_3$), 0.97 m (1H), 0.98 d, 0.99 d [6H, $(CH_3)_2CH$], 1.18 s (3H, $C^{18}H_3$), 1.27 m (1H), 1.43 s (3H, $C^{15}Me$), 1.44–1.80 m (11H), 2.24 sextet [1H, $(CH_3)_2CH$], 2.29 m (1H , C^7H), 2.59 d (1H, $C^{16}H$), 3.03 br.s (1H, $C^{12}H$), 4.60 m (2H, OCH_2), 5.25 d (1H, $=CH_2$, H-*trans*), 5.35 d (1H, $=CH_2$, H-*cis*), 5.59 s (1H, $C^{14}H$), 5.93 m (1H, $CH=CH_2$). IR spectrum, ν, cm^{-1}: 3100 (=C–H) 1840, 1780 [$(C=O)_2O$], 1720 [(C=O)OR], 1250 (C–OCH_2), 1180, 1150 [CH $(CH_3)_2$]. Mass spectrum, *m/z*: 456 $[M + 1]^+$. Found, %: C 74.31, H 8.65. $C_{28}H_{38}O_5$. Calculated, %: C 73.98; H 8.43.

Propargyl citraconopimarate (Vb). Yield 98% (4.43 g), mp 168–170°C (ester), $[\alpha]_D^{20}$ –23.8° (*c* 1.2, $CHCl_3$). ^1H NMR spectrum (δ, ppm): 0.61 s (3H, $C^{20}H_3$), 0.97 m (1H), 0.98 d, 1.00 d [6H, $(CH_3)_2CH$], 1.18 s (3H, $C^{18}H_3$), 1.30 m (2H), 1.43 s (3H, $C^{15}Me$), 1.44–1.77 m (10H), 2.25 sextet [1H, $(CH_3)_2CH$], 2.29 m (1H , C^7H), 2.48 m (1H, ≡CH), 2.59 d (1H, $C^{16}H$), 3.03 br.s (1H, $C^{12}H$), 4.69 m (2H, OCH_2), 5.58 s (1H , $C^{14}H$). IR spectrum, ν, cm^{-1}: 3320 (≡C–H), 2130 (C≡C), 1840, 1780 [$(C=O)_2O$], 1730 [(C=O)OR], 1250 (C–OCH_2), 1190, 1170 [$CH(CH_3)_2$]. Mass spectrum, *m/z*: 454 $[M + 1]^+$. Found, %: C 74.10, H 8.63. $C_{28}H_{36}O_5$. Calculated, %: C 74.31; H 8.02.

Diallyl ester of imidodicarboxylic acid (VI). A mixture of 0.88 g (0.001 mol) of imidodicarboxylic acid (**III**), 0.26 ml of allyl bromide (0.003 mol) and 0.41 g (0.003 mol) of potassium carbonate in 3 ml of dimethylformamide was stirred for 12 hours at 60ºC. The progress of reaction was monitored by TLC on Silufol UV-254 plates (20 cm) (hexane–acetone, 3:1). After the reaction completing the mixture was treated like in the synthesis of esters **IV** and **V**. Compound **VI**, 0.78 g (82%), was obtained, mp 75–77ºC. ^1H NMR spectrum (δ, ppm): 0.59 s (6H, $C^{20}H_3$), 0.93 m (2H), 0.91 d, 0.95 d [12H, $(CH_3)_2CH$], 1.17 s (6H, $C^{18}H_3$), 1.17–1.80 m (32H), 2.16 sextet [2H, $(CH_3)_2CH$], 2.40 d (2H, $C^{21}H$), 2.49 m (2H, C^7H), 2.76 d.d (2H, $C^{16}H$), 3.04 br.s (2H, $C^{12}H$), 3.28 m (4H, N–CH_2), 4.58 m (4H, OCH_2), 5.32 m (4H, $=CH_2$), 5.37 s (2H, $C^{14}H$), 5.92 m (2H, $CH=CH_2$). IR spectrum, ν, cm^{-1}: 3100 (=C–H), 1780, 1740 [(C=O)N], 1700 [(C=O)OH], 1385, 1360 (C–N), 1250 (P–OCH_2), 1160, 1130 [$CH(CH_3)_2$]. Mass spectrum, *m/z*: 962 $[M + 1]^+$. Found, %: C 75.43, H 8.96; N 3.16. $C_{60}H_{84}N_2O_8$. Calculated, %: C 74.96; H 8.81; N 2.91.

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