

INTERACTION OF ALLYL ESTERS OF ALCOHOLS-TELOMERES

($n = 1, 2, 3$) WITH MALEOPIMARIC ACID

L.M. Popova¹, A.S. Tsyrunnikova¹, S.V. Vershilov², I.U. Butko¹

¹Saint Petersburg State University of Industrial Technologies and Design, Higher School of Technology and Energetics
Ivan Chernykh Street, 4, St. Petersburg, 198095 (Russia)
e-mail: lorapopova@mail.ru

²Federal State Unitary Enterprise Scientific And Research Institute of Synthetic Rubber named after Academic S. V. Lebedev
Gapsalskaya street, 1, St. Petersburg, 198035 (Russia)

The synthesis of esters was carried out by the reaction of maleopimaric acid with 6,6,7,7-tetrafluoro-4-oxahept-1-ene, 6,6,7,7,8,8,9,9-octafluoro-4-oxanon-1-ene and 6,6,7,7,8,8,9,9-dodecafluoro-4-oxaundec-1-ene under conditions of acid catalysis.

Key words: alkylation, allyl ethers of telomeres ($n = 1, 2, 3$), maleopimaric acid.

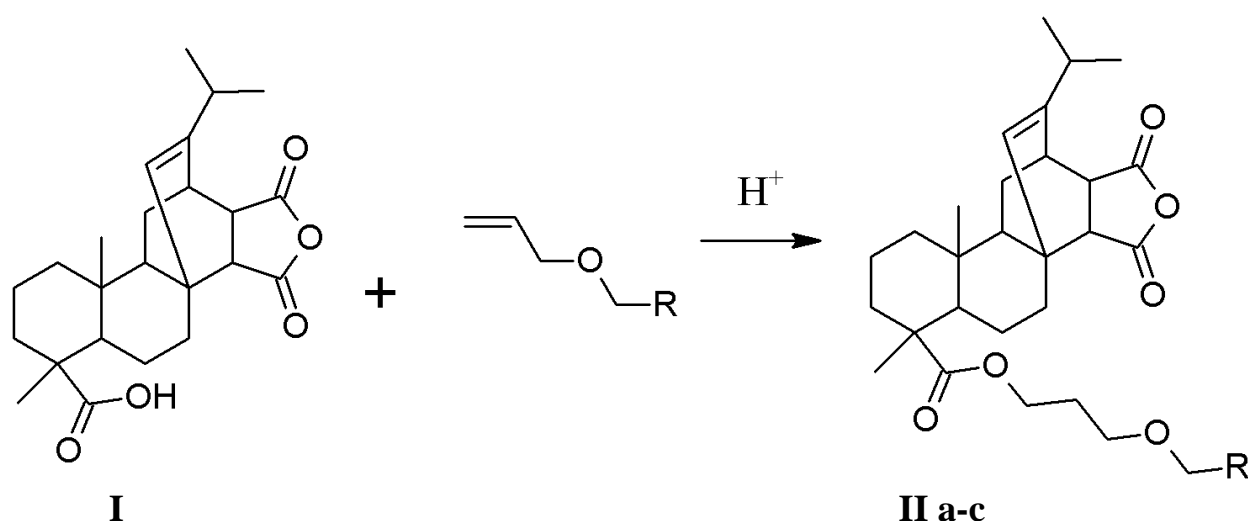
Rosin and the products of its chemical transformations such as derivatives of maleopimaric acid are actively studied and used in various fields for decades [1-4]. Thus, rosin-based compounds are used as adhesives in the paint and varnish industry for the production of artificial rubbers in electrical engineering and other fields.

It is known that the introduction of fluorine atoms into an organic molecule significantly affects the physicomechanical properties of substances: it increases chemical and heat resistance, resistance to light, and mechanical treatments. The introduction of fluorine atoms affects the electrical conductivity, foaming and emulsification ability.

This research is derived to acylation of allyl ethers of alcohol-telomeres investigation when resin acids derivatives applied [8].

The interaction of maleopimaric acid with (polyfluoroalkoxy) allyl ethers (a-b) was carried out under acid catalysis for 20 h without any solvent (IIa-c) and in presence of toluene as a solvent (IIb) at heating (104-158 °C) (Sch.1). The reaction was monitored by TLC. At the end of the process, the stock was dissolved in diethyl ether and washed with distilled water until neutral pH and was dried with anhydrous sodium sulfate. The crystalline substances (IIa-b) of a light brown color (yields 40-89%) were obtained after removal of the solvent and dried under vacuum over P₂O₅.

Scheme 1



R = $-(\text{CF}_2\text{CF}_2)\text{H}$ (a), $-(\text{CF}_2\text{CF}_2)_2\text{H}$ (b); $-(\text{CF}_2\text{CF}_2)_3\text{H}$ (c).

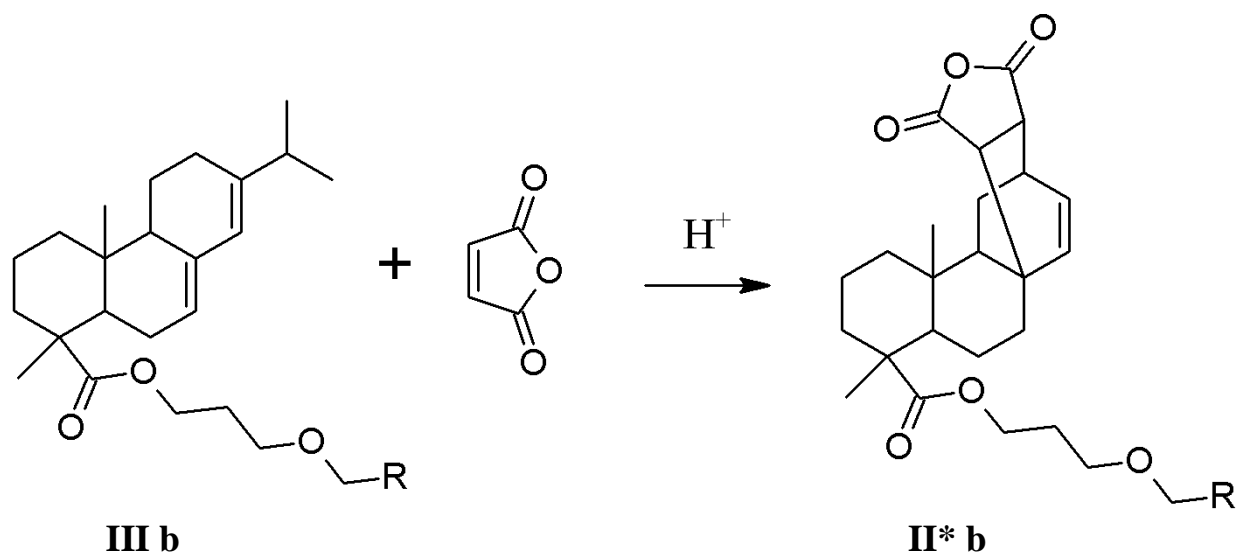
The NMR ^1H spectra of products (II a-c) contain proton signals of $-\text{CF}_2\text{H}$ -group in the form of triplet of triplets with a chemical shift 5.96 ppm (for II a), 6.08 (for II b), and 6.09 ppm ($^3J_{\text{H-F}}=52$ Hz, $^2J_{\text{H-F}}=4$ Hz) (for II c). The proton signals in the form of triplet of ester groups $-\text{C}^1\text{H}_2\text{O}$ at 3.83 (for II a) at 3.94 ppm (for II c), 3.95 ppm (for II b) indicate the undergoing of the reactions. The protons' resonance signals of other (polyfluoroalkoxy) allyl fragments are also present. They correspond to the structure of the ether by their chemical shifts, multiplicity and integral intensities. The analysis of the NMR ^1H spectra indicates that the reaction also proceeds against the Markovnikov's rule [8].

In the NMR ^{19}F spectra of products (II a-c), the following resonant signals of fluorine atoms of difluoromethylene groups of the alkyl fragment are observed: for the product (II a) at -125.40 ppm and -140.01 ppm. in the form of doublet ($J=51$ Hz); for the product (II b) $-\text{C}^6\text{F}_2$, C^7F_2 , C^8F_2 in the form of singlets with chemical shifts, respectively, 119.54, -125.17 and -129.85 ppm, and C^9F_2 as doublets at -133.14 ppm. ($J=50.8$ Hz), for the product (II c): C^6F_2 and C^7F_2 – singlets with chemical shifts - 119.35. and 122.16 ppm, C^8F_2 and C^9F_2 - doublet with $\delta_{\text{F}} = 123.35$ ppm ($J=46.9$ Hz), C^{10}F_2 – singlet with $\delta_{\text{F}} = 129.35$ ppm and $\text{C}^{11}\text{F}_2\text{H}$ as a doublet with $\delta_{\text{F}} - 137.08$ ppm. ($J=46.98$ Hz). The signals correspond to the ascribed structures by the chemical shifts and integrated intensities.

There are bands of stretching vibrations of C-H bonds in the range of 3028-2872 cm^{-1} , bands of stretching vibrations of carbonyl group C=O at 1778 cm^{-1} , stretching vibrations of double bond C=C at 1693 cm^{-1} , stretching vibrations of ether C-O-C bond in the range of 1250-1249 cm^{-1} and stretching vibrations of C-F in the interval 1130-1084 cm^{-1} in the IR spectrum of products (II).

The counter synthesis of the product (II* b) was carried out by the reaction of diene synthesis of 3-(1,1,2,2,3,3,4,4-octafluoropentoxy) propylabietate (III b) with maleic anhydride without any solvent at a temperature of 147-152 $^{\circ}\text{C}$ for 2 h (sch. 2).

Scheme 2



R= $-(CF_2CF_2)_2H$ (6).

The reaction was monitored by TLC. At the end of the process, the stock was dissolved in diethyl ether, washed with distilled water and dried with anhydrous sodium sulfate. The crystalline product of a dark brown color (II *b) was obtained (raw yield 89%) after removal of the solvent and drying under vacuum over P_2O_5 .

In the NMR 1H spectrum of the products (II* b) there are multiplet signals of the polyfluoroalkyl fragment in the form of triplet triplets with chemical shifts at 6.09 ppm corresponding to the protons of CF_2H group. The proton signals of ester groups $-CH_2O-$ are observed at 3.94 ppm. The formation of the diene synthesis product is indicated by the signal with a chemical shift at 5.56 ppm.

In NMR ^{19}F spectrum of the product (II* b), there are resonant signals corresponding to the polyfluoroalkyl fragment by the chemical shifts, multiplicities and integrated intensities in the range of $137.14 \div 119.54$ ppm.

In the UV spectrum of the ether (II * b) the absorption maxima corresponding to the $\pi \rightarrow \pi^*$ transition in the 210 nm intervals ($\lg \epsilon$ 5.26) and 260 nm ($\lg \epsilon$ 5.18) appear in alcohol solution.

Experimental

The UV spectra of alcohol solutions of compounds were obtained using spectrophotometer SF-2000 at the concentration of 10^{-4} mol/l, the thickness of the absorbing layer is 1 cm.

The NMR 1H and ^{19}F spectra were registered using Bruker 500 with the operating frequency of 500 MHz for 1H (470 MHz for ^{19}F), in solutions of $CDCl_3$ and $DMSO-d_6$. The internal standard is TMS, the external is CCl_3F .

The IR spectra were recorded by Shimadzu IRPrestige-2. The measurements were analyzed on KBr glasses (the solutions in $CHCl_3$ and CCl_4).

The process of these reactions and the purity of starting and resulted compounds were carried out by TLC on Sorbfil plates, the eluent: hexane-methylene chloride-acetone (1: 1: 0.5) or hexane-methylene chloride (1:1).

The freshly distilled allyl ethers were used at this research – 6,6,7,7-tetrafluoro-4-oxahept-1-ene (a) (b.p. 110-112°C), 6,6,7,7,8, 8,9,9-octafluoro-4-oxanone-1-ene (b) (b.p. 141°C) and 6,6,7,7,8,8,9,9,10,10,11, 11-dodecafluoro-4-oxaundec-1-ene (c) (b.p. 171.8°C), synthesized according to the method [9], and also maleopimaric acid (I) (mp 218°C), received likewise [10], maleic anhydride (mp 52.8°C) and 3-(1,1,2,2,3,3,4,4-octafluoropentoxy) propylabietate (IIIb) synthesized by the method [8].

6,6,7,7-Tetrafluoro-4-oxaheptyl ester of maleopimaric acid (IIa). 0.8 g (6.0 mmol) of 6,6,7,7-tetrafluoro-4-oxahept-1-ene (a) and 2 drops of concentrated H₂SO₄ were added to 2.0 g (5.0 mmol) of maleopimaric acid (I), and was heated at 104-110 °C for 20 h. At the end of the process, the stock was cooled, dissolved in diethyl ether, washed with distilled water until neutral pH. The organic layer was separated and dried with Na₂SO₄. The solvent was distilled off and the residue was dried in vacuum over P₂O₅. Yield: (IIa): 2.37 g (89%), light brown crystalline solid, mp 94-102 °C, R_f 0.45 (C₆H₁₂-CH₂Cl₂-CH₃COCH₃, 1:1:0.5). IR spectrum (CCl₄), Cm⁻¹: 3028–2871(ν_{C-H}).1777 ($\nu_{C=O}$, anhydride); 1730 ($\nu_{C=O}$, ester.); 1696 ($\nu_{C=C}$); 1204 (ν_{C-O-C}); 1126-1016 (ν_{CF}). UV spectrum (EtOH), nm (lg ϵ): 208 (4.71), 235 (4.53), 260 (5.73). NMR ¹H spectrum, δ , ppm: 1.02 (d, $J=6$ Hz); 1.26 (dd, $J_1=19$ Hz, $J_2=8$ Hz); 2.20 (s 1H C¹⁵H); 2.56 (d $J=13$ Hz, 2.75 d $J=8$ Hz); 3.83 (t 2H, OCH₂ ester., $J_1=12$ Hz); 4.11 (t 2H, CH₂O, $J=6$ Hz); 4.12 (t 2H, CH₂O, $J=6$ Hz); 5.57 (s 1H C¹⁴H); 5.96 (tt 1H, CF₂H, $J_1=53$ and $J_2=6$ Hz). NMR ¹⁹F spectrum, δ , ppm: - 140.01 (d 2F, C⁵F₂, $J=51$ Hz) -125.40 (s 2F, CF₂).

6,6,7,7,8,8,9,9-Octafluoro-4-oxanonyl ester of maleopimaric acid (IIb). The product (IIb) was obtained in a similar manner to the product (IIa) from 3.5 g (8.75 mmol) (I), 2.86 g (10.5 mmol) of 6,6,7,7,8,8,9,9-octafluoro-4-oxanone-1-ene), 3 drops of concentrated H₂SO₄, 20 ml of toluene, at 116-118°C for 20 h. Yield: (IIb): 2.37 g (40%), dark brown crystalline solid, mp 136-142 °C, R_f 0.56 (C₆H₁₂-CH₂Cl₂-CH₃COCH₃, 1:1:0.5). UV spectrum (EtOH), nm (lg ϵ): 212 (6.42), 247 (shoulder). NMR ¹H spectrum, δ , ppm: 0.63 (s 3H C²⁰H₃); 1.03 (d 6H, C¹⁶H₃ $J=6$ Hz); 1.26 (dd $J_1=20$ Hz, $J_2=7$ Hz); 2.20 (s 1H C¹⁵H); 3.95 (t 2H, OCH₂ ester, $J=14$ Hz); 4.11 (t 2H, OCH₂, $J=6$ Hz); 4.16 (t 2H, OCH₂, $J=6$ Hz); 5.56 (s 1H, C¹⁴H), 6.09 (tt 1H, CF₂H, $J_1=52$ Hz, $J_2 = 4$ Hz). NMR ¹⁹F spectrum, δ , ppm: - 137.14 (d 2F, C⁹F₂, $J=50.8$ Hz); - 129.85 (s 2F, C⁸F₂); - 125.17 (s 2F, C⁷F₂); - 119.54 (s 2F, C⁶F₂).

6,6,7,7,8,8,9,9,10,10,11,11-Dodecafluoro-4-oxaundecanyl ester of maleopimaric acid (IIc). The product (IIc) was obtained in a similar manner to the product (IIa) from 2.0 g (5.0 mmol) of (I), 2.06 g (5.5 mmol) of 6,6,7,7,8,8,9,9,10,10,11,11-dodecafluoro-4 -oxaundec-1-ene (c), 3 drops of concentrated H₂SO₄, at 155-158°C for 20 h. Yield: 1.93 g (50%), crystalline substance of dark brown color, mp 138-143 °C, R_f 0.61 (C₆H₁₂-CH₂Cl₂-CH₃COCH₃,

1:1:0.5). UV spectrum (EtOH), nm (lg ϵ): 214 (6.15), 256 (shoulder). NMR ^1H spectrum, δ , ppm: 0.89 (s 3H C^{20}H_3); 2.20 (s 1H C^{15}H); 3.94 (t 2H, OCH_2 ester, $J=14$ Hz); 4.15 (t 2H, OCH_2 , $J=6$ Hz); 4.16 (t 2H, OCH_2 , $J=6$ Hz); 5.57 (s 1H C^{14}H); 6.08 (tt 1H, CF_2H , $J_1=52$ Hz, $J_2=4$ Hz). NMR ^{19}F spectrum, δ , ppm: - 137.08 (d 2F, $\text{C}^{11}\text{F}_2\text{H}$, $J=46.98$ Hz); - 129.35 (s 2F, C^{10}F_2); - 123.35 (s 4F, $\text{C}^8\text{F}_2\text{C}^9\text{F}_2$); - 122.16 (s 2F, C^7F_2); - 119.35 (s 2F, C^6F_2).

The counter synthesis of 6,6,7,7,8,8,9,9-octafluoro-4-oxanonyl ester of maleopimaric acid (II*b). 0.51 g (5.2 mmol) of maleic anhydride, 3 drops of concentrated H_2SO_4 were added to 2.5 g (4.4 mmol) of 3-(1,1,2,2,3,3,4,4-octafluoropentoxy) propylabietate (IIIb) and was heated at 147-152°C for 2 h. The reaction was monitored by TLC. At the end of the process, the resulting product was cooled, dissolved in toluene, washed with distilled water until neutral pH. The organic layer was separated and dried with Na_2SO_4 . Toluene was distilled off, and the residue was dried in vacuum over P_2O_5 . Yield (II*b): 2.65 g (90%), crystalline sand-colored substance, mp 123-127°C, R_f 0.67 ($\text{C}_6\text{H}_{12}\text{-CH}_2\text{Cl}_2\text{-CH}_3\text{COCH}_3$, 1:1:0.4). IR spectrum, cm^{-1} : 3027-2651 ($\nu_{\text{C-H}}$); 1778 ($\nu_{\text{C=O}}$, anhydride); 1735 ($\nu_{\text{C=O}}$, ester); 1695 ($\nu_{\text{C=C}}$); 1229 ($\nu_{\text{C-O-C}}$); 1204; 1190-948 (ν_{CF}). UV spectrum (EtOH), nm (lg ϵ): 210 (5.26), 260 (5.18). NMR ^1H spectrum, δ , ppm: 0.65 (s, 3H, C^{20}H_3); 1.02 (d 6H, C^{16}H_3 , $J=6.88$ Hz); 1.19 (s 3H, C^{19}H_3); 1.81 ÷ 1.41 (12H, CH_2); 2.27 (m 1H, C^{15}H); 2.55 (d 2H, C^7H_2 , $J=13.6$ Hz); 2.76 (d 1H, C^{21}H , $J=8.56$ Hz); 3.94 (t 2H, OCH_2 ester, $J=14$ Hz); 4.11 (t 2H, OCH_2 , $J=6$ Hz); 4.16 (t 2H, OCH_2 , $J=6$ Hz); 5.56 (s 1H, C^{14}H); 6.09 (tt 1H, CF_2H , $J_1 = 52$ Hz, $J_2 = 4$ Hz). NMR ^{19}F spectrum, δ , ppm: - 137.14 (d 2F, C^9F_2 $J=50.8$ Hz); - 129.85 (s 2F, C^8F_2); - 125.17 (s 2F, C^7F_2); - 119.54 (s 2F, C^6F_2).

Conclusions

It was shown that the alkylation of maleopimaric acid with 6,6,7,7-tetrafluoro-4-oxahept-1-ene, 6,6,7,7,8,8,9,9-octafluoro-4-oxanon-1-ene and 6,6,7,7,8,8,9,9,10,10,11,11-dodecafluoro-4-oxaundec-1-ene without using any solvent (or in toluene) in the presence of conc. H_2SO_4 at 104-158 °C for 20 h. leads to formation of the corresponding esters

The similar result was obtained by the reaction of 3- (1,1,2,2,3,3,4,4-octafluoropentoxy) propylabietate (III b) with maleic anhydride without using any solvent in the presence of conc. H_2SO_4 at 147-152°C for 2 h (yield 89%).

References

1. Simonsen J. *The terpenes. Volume III. The sesquiterpenes, diterpenes and derivatives.* Cambridge: At the University press, 1952. 579 p.
2. Sandermann W. *Naturharze Terpentintallöl. Chemie und Technologie /* Springer Verlag: Berlin, 1960. 172 p.
3. Tolstikov G.A., Tolstikova T.G., Shul'c E.E., Tolstikov S.E., Hvostov M.V. *Smolyanye kisloty hvojnnyh Rossii.* Novosibirsk: Akadem. Izd-vo «Geo», 2011. 396 s.

4. *Rosin – based Chemicals and Polymers* / Ed. by Jinwen Zhang. Shawbury, Shrewsbury, Shropshire: Smithers Rapra Technology Ltd., 2012. 234 p.
5. Ishikawa N., Kobaeashi Y. *Fluorine compounds. Chemistry and application*. M.: Mir, 1982. 276 p.
6. *New of Technology of Fluorine Compounds* / Red. Ishikawa N. M.: Mir, 1984. 592 p.
7. *Soedineniya ftora: Sintez i primenenie: per.s yap. // pod red. N.Isikavy*. M.: Mir, 1990. 407 s.
8. Popova L.M., Vershilov S.V. *Acetoksilirovanie 6,6,7,7,8,8,9,9-oktaftorpentoksipropena-1 smolyanymi kislotami*. Fluorine Notes. 2015. N 2.
9. M. Hudlicky. *Chemistry of organic fluorine compounds*. M.: Goschimizdat, 1961. 373 p.
10. Kalninysh A.I., Dobelis Yu.Ya. *Dienovyj sintez v oblasti smolyanyh kislot. Primenenie katalizatorov pri poluchenii adduktov smolyanyh kislot s dienofilami*. Izv. AN Latv.SSR. 1969. №5. S. 54-57.