

Received: December, 2012

## ESTERIFICATION OF 5,9-DIMETHYL-16-ISOPROPYL-5,13OI, 14OI-TRIHYDROXYMETHYLTETRACYCLO[10.2.2.01.10.04.9]HEXADEC-15-ENE USING PERFLUORO(2-METHYL-3-OXAHEXANOYL)FLUORIDE

L. M. Popova<sup>1</sup>, S. V. Vershilov<sup>2</sup>, A. N. Gorbenko<sup>1</sup>

<sup>1</sup>*Saint-Petersburg State Technological University of Plant Polymers, Saint-Petersburg, Russia  
e-mail: lorapopova@mail.ru*

<sup>2</sup>*State Enterprise S.V.Lebedev Research Institute of Synthetic Rubber (NIISK), Saint-Petersburg, Russia*

**Abstract:** *New polyfluoroalkyl triester has been synthesized esterifying 5,9-dimethyl-16-isopropyl-5,13OI,14OI-trihydroxymethyltetracyclo[10.2.2.01.10.04.9]- hexadec-15-ene using perfluoro(2-methyl-3-oxahexanoyl)fluoride in 1,4-dioxane over triethylamine.B*

**Keywords:** *Abietic acid, Maleopimaric adduct, Reduction, Triol, Etherification, Polyfluoroalkyl-containing triesters.*

Syntheses based on diterpenoic acids are of big interest of researchers. The spectrum of practical tasks solving which they assume using of derived resin acids, particularly based on their dienoadducts is constantly widening. New fields of application for those classes of compounds are being discovered along with such traditional directions as developing of paints, coatings and polymers [1], emulsifiers [2] and corrosion inhibitors [3]. They suggested using of TVD (Thermal Vacuum Deposition)-films derivatives of maleopimaric and citraconic acids for the production of photomasks in microelectronics [4]. The opportunities of developing of stereoselective complex metallic catalysts [5], вЂњionic liquidsвЂќ [6] based on derivatives of abietic acid have been considered as well. In our opinion, the search for effective surfactants and biologically active compounds in the row of modified polyfluoroderivatives of diterpenoic alcohols has got no less potential [7].

In the present report you will find the information on the synthesis of new tri(polyfluoroalcoxyacylate)triol obtained using method of maleopimaric adductвЂќ™s reduction.

It is known, that obtaining of dienoadducts like maleopimaric acid increases the resistance of material to oxidation and also provides for carrying out further chemical modification of resin acids [8, 9]. However, only a few reports refer to the synthesis of polyols based on maleopimaric acid. Thus, the obtaining method of triol (m. p. 168 -170 yield app. 50%) by reduction of maleopimaric acid using lithiumaluminumhydride in ether at room temperature in 7 days has been patented [8]. In another report Mr. Zalkov with co-workers [9] have obtained polycyclic hydrocarbon containing four hydroxyl groups when reducing Oi-lactone tetracyclohexadecene of tricarboxylic acid by lithiumaluminumhydride in ether during 8 hour boiling.B B

We have synthesized the initial maleopimaric adduct out of tall oil rosin and maleic anhydride over concentrated sulphuric acid at 120B°C using known method described in the work [11]. The product yield (I) was 35%.

Diterpenoic triol (II) has been synthesized similarly to the procedure described in [9]: the solution of adduct (I) in tetrahydrofurane was added to the suspension of lithiumaluminumhydride in THF at room temperature and was kept for 24 hours. The process has been controlled using method of Thin Layer



The composition and structure of mixture obtained has been analyzed using analytical and spectral methods.

In the IR spectrum (III) there are stripes of stretching vibrations of C-H bonds in the range of 2950-2865  $\text{cm}^{-1}$ , and also stretching vibrations of carbonyl groups C=O at 1780  $\text{cm}^{-1}$  and C=C at 1690  $\text{cm}^{-1}$ .

In the UV spectrum (III) in the alcoholic solution three maximum values of absorption of corresponding  $\pi\pi^*$ -transitions showed themselves at 223 nm (lg 5.60), 242 nm (shoulder) and 257 nm (lg 5.78), confirming the presence of conjugated bonds in the products.

Multiplet signals of methylene groups connected with perfluorinated fragments are typical for tripolyfluoroacylate (III) in  $^1\text{H}$  NMR at 2.86 d (1H,  $\text{H}^{20}$ , 11.3), 3.18 d (1H,  $\text{H}^{20}$ ), 3.44 t (1H,  $\text{H}^{17}$ ,  $J_{17A,1} = J_{17A,17B}$  10 Hz), 3.70 m (1H,  $\text{H}^{16}$ ), 3.74 m (1H,  $\text{H}^{16}$ ), 4.19 dd (1H,  $\text{H}^{17}$ ), as in spectra of triesters described in the work [5], insignificant shifts into strong field for pointed signals are observed. Signal with chemical shift at 5.54 ppm with (1H,  $\text{H}^{11}$ ) corresponds to double bond of maleopimaric fragment. Also the signals of protons of diene system are in the spectrum of obtained mixture at 5.36 ppm ( $\text{C}^7\text{-H}$ )  $\delta$  5.75 ppm ( $\text{C}^{14}\text{-H}$ ) (ester of abietinol), besides that the signals of aromatic protons with  $\delta$  6.86 with ( $\text{C}^{14}\text{H}$ ), 6.98 d ( $\text{C}^{14}\text{H}$ ) and 7.14 d ( $\text{C}^{11}\text{H}$ ) ppm (the ester of dehydroabietinol). The rate of products in the mixture virtually hasn't changed (triester : ester of abietinol : ester of dehydroabietinol, 1 : 0.5 : 1 respectively).

In the  $^{19}\text{F}$  NMR spectrum of product (III) there are resonance signals of fluorine atoms, which according to chemical shifts, multipletness and integral intensities correspond to perfluorinated fragments in the range of  $\delta$  141.40  $\text{C}\ddagger$   $\delta$  71.70 ppm.

## Experimental Part

UV spectra of compounds  $\text{C}_n\text{F}_m$  ethanol solutions were obtained using SF-2000 spectrophotometer at concentration of compounds equal to  $10^{-4}$  mole/l the thickness of absorbing layer equals to 1cm.

$^1\text{H}$  and  $^{19}\text{F}$  NMR spectrum has been registered using Bruker 500 with operational frequency of 500 MHz (470 MHz - for  $^{19}\text{F}$ ), in  $\text{CDCl}_3$  exterior standard  $\delta$   $\text{CCl}_3\text{F}$ .

IR spectra were registered at Specord M-80 (Jena) with operational frequency within the range of 4000-900  $\text{cm}^{-1}$ . The measurements were carried out using  $\text{CaF}_2$  glasses with the cuvettes  $\text{C}_n\text{F}_m$ s thickness of 200  $\mu\text{m}$ .

The reaction path and purity of initial and obtained compounds have been carried out using TLC method at Sorbphil plates, eluent: hexane-methylenchloride (1-1) and hexane-methylenechloride-acetone (1-1-0.5).

The purification and dehydration of tolyol, tetrahydrofurane and 1,4-dioxane were carried out using the known methods [12].

Tall rosin and perfluoro(2-methyl-3-oxahexanoyl)fluoride (boiling point 54  $^\circ\text{C}$ ) have been used as initial compounds in the work process [13].

**Maleopimaric adduct of tall oil rosin (I).** 3.5 g (36 mmole) of maleic anhydride, 4-5 drops of concentrated  $\text{H}_2\text{SO}_4$  are added to 10 g (33 mmole) of tall oil rosin and kept for 1 hour at 120 $^\circ\text{C}$ . The reaction is controlled using method of TLC. The reaction mass is extracted using toluene (3 x 20ml) upon the end of the process and the extract itself is washed through with hot water till neutral reaction is obtained, dried with  $\text{Na}_2\text{SO}_4$ , the solvent is distilled and dried in vacuum over  $\text{P}_2\text{O}_5$ . The yield of product (I) amounted to 8 g (60%).

**Resedimentation of maleopimaric acid [11] (I).** 23 ml of diethyl ether are being added to 6.0 g (15 mmole) of maleopimaric adduct and heated up till total dissolving, afterwards the product (I) is precipitated using light petroleum ether, then it is cooled, filtered and lade-down crystals are dried in vacuum over  $\text{P}_2\text{O}_5$ . Yield amounted to 1.7 g (35%).

**5,9-Dimethyl-16-isopropyl-5,13OI,14OI-trihydroxymethyltetracyclo- [10.2.2.0<sup>1.10</sup>.0<sup>4.9</sup>]hexadec-15-ene (II).** The solution of 2.74 g (6.8 mmole) of maleopimaric acid in 20 ml of THF is being added drop by drop to the mixture of 0.8 g (21 mmole) of  $\text{LiAlH}_4$  in 13 ml of THF at room temperature, then mixed up and kept for 24 hours at room temperature, afterwards 43 ml of  $\text{H}_2\text{O}$  and 36 ml of 1M  $\text{H}_2\text{SO}_4$  are being added dropwise and mixed up for 3 hours. Upon ending of decomposition of  $\text{LiAlH}_4$  the reaction

mixture has been extracted using diethyl ether (3Г—30 ml), the organic phase has been washed through with distilled water, dried with Na<sub>2</sub>SO<sub>4</sub> and solvent has been distilled off. The yield of product (II) amounted to 2.35 g (95%).

**Tri[perfluoro(2-methyl-3-oxahexanoyl)] ester 5,9-dimethyl-16-isopropyl-5,13 -5,13OI,14OI-trihydroxymethyltetracyclo-[10.2.2.0<sup>1.10</sup>.0<sup>4.9</sup>]hexa-dec-15-ene (III).** The solution of 6.2 g (19 mmole) perfluoro(2-methyl-3-oxahexanoyl)fluoride in 10 ml of 1,4-dioxane was added dropwise to the mixture of 2,34 g (6.2 mmole) triol (II) and 1.89 g (19 mmole) triethylamine. The reaction mixture was kept for 2 hours at 50-55B°C, the reaction path was controlled using TLC method. Upon the reaction end the excess of perfluoro(2-methyl-3-oxahexanoil)fluoride, triethylamine and 1,4-dioxane was distilled off. Afterwards the residue was dissolved in diethyl ether, washed through with distilled water, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was distilled off. The yield (III) amounted to 2.8 g (35%).

## Conclusion

The processing of triol, the product of reduction of maleopimaric adduct using the equimolar quantity of perfluoro(2-methyl-3-oxahexanoyl)fluoride over acceptor of hydrogen fluoride (triethylamine) results in formation of polyfluorine containing complex triester.

## References

1. Maiti S., Sinha Ray S., Kundu A.K. // Prog. Polym. Sci. 1989. V.14, N 3-4. p. 297-338.
2. Nemtsov M.S., Shenderovich F.S. // Kauchuk i rezina. 1961. № 2. s. 4-11.
3. Pat. US 2008/0179570 A1, F.W.Hurd, G.D.Fultz, B.A.Neumann. Maleinated and Oxidized fatty acids. Publ. 31.07.2008, Int. Cl C23F 11/10.
4. Bei M.P., Azarko V.A., Yuvchenko A.P. // ZhOKh. 2010. T. 80, № 5. s. 770-773.
5. Tolstikov A.G., Karpyshev N.N., Tolstikova O.V. i dr. // ZHOrH. 2001. T. 37, № 8.s. 1193-1207.
6. Glushkoi V.A., Kotelev M.S., Rudovskij i dr. // ZhOrKh. 2009. T. 45, № 3. s. 416-418.
7. Isikava N., Kobayasi Y. Ftor. Khimiya i primenenie. M.: Mir, 1982. 276 s.
8. Pat. US 2,750,422; T.F.Sanderson, Triol of levopimaric anhydride adduct. Publ. 12.06.1956, Cl. 260-617.
9. Zalkow L.H., Ford R.A., Kutney J.P. // J.Org.Chem. 1962. V. 27, N 10.p. 3535-3539.
10. Kalnin'sh A.I., Dobelis Yu.Ya. // Izv. AN Latv.SSR. 1969. № 5. S. 54-57.
11. Arbuzov B.A. // ZhOrKh. 1932. T. 2, № 8.s. 806-813.
12. Gordon. A., Ford R. Sputnik khimika: Spravochnik. M.: Mir, 1976. 542 s.
13. Ponomarenko V.A., Krukovskij S.P., Alybina A.Yu. Ftorsoderzhashchie geterocepnye polimery. M.:Nauka. 1973. 304 s.

*Recommended for publication by V. Kornilov*