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Alicyclic and Cyclic Derivatives of Dicarboxylic Acids

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Abstract

A brief review of the results of studies in the area of obtaining linear and polycyclic derivatives of dicarboxylic acids is presented. Attention to the indicated compounds is due to the broad and diverse areas of their application in technology, in agrochemical and pharmaceutical industries, as biologically active agents, fragrances, additives to lubricating oils, plasticisers, stabilising and modifying agents for polymer materials, etc. Biologically active compounds – the derivatives of bisamides of dicarboxylic acids possessing antibacterial, antiviral, anticonvulsant, antitumour, analgesic, fungicide properties are used for prophylactics and treatment of cardiovascular, viral and oncological diseases. The high thermal and thermal-oxidative stability of the adamantine derivatives based on dicarboxylic acids is also of great interest. These compounds, due to their properties caused by the presence of the framework fragment, are used for the synthesis of high-molecular compounds, in the production of fuel and lubricants, or as additives to them. The rational use of more available, cheap raw material and the possibilities to use it for obtaining the derivatives of dicarboxylic acids in higher yields define the relevance of the studies aimed at the search for new promising methods to synthesise these compounds.

Keywords: dicarboxylic acids, esters, linear and cyclic derivatives of dicarboxylic acids, lubricating oils

INTRODUCTION

Esters of dicarboxylic acids and esters of polyhydric alcohols are known as good lubricating agents for various modern devices, apparatuses and mechanisms requiring special performance characteristics that cannot be provided by mineral lubricating oils and animal grease. These esters are also used as hydraulic brake fluids, white oils for the textile industry, components for various consistent lubricants, etc. In the pure form, they usually do not possess all those properties that are necessary for their application, namely a gently sloping curve of the dependence of viscosity on the temperature within the range −60 to +200 °C, relatively low viscosity at low temperatures, low chilling temperature, low evaporation ability, thermal stability, the ability to cause no corrosion of various metals, *etc*. To eliminate the listed shortcomings, special additives are used: viscosity-improving, antioxidant, and anticorrosive, which are to be added in small amounts to provide the possibility of making lubricating materials based on the esters of dicarboxylic esters to meet the above-listed requirements. The derivatives of dicarboxylic acids are also key reagents for the synthesis of polymer materials and broad-range biologically active preparations. Results of the studies into the synthesis, properties and application of some classes of the derivatives

of carboxylic acids, in particular diesters based on dicarboxylic esters and monohydric alcohols of linear and branched structure, cyclic derivatives of bisamides, bi- and tetracyclic esters, are considered in the review.

LUBRICATING OILS AND ADDITIVES

Lubricating oils based on the esters of dicarboxylic acids occupy one of the leading positions in the petrochemical industry. Permanent demand for the synthesis of new lubricating oils is due to the improvement of their lubricating ability and quality.

The synthesis of diesters of some dicarboxylic acids used as the component of lubricating oils was carried out by re-esterification of their dimethyl esters with 2-ethylhexanol and 3,5,5-trimethylhexanol according to Scheme 1 [1].

Their basic physicochemical properties and the compatibility with synthetic oils based on polyalphaolefins were determined, the stability against evaporation under the action of thermo-oxidative factors and against hydrolytic decomposition was evaluated. It was established that the linear adipinates and sebacates of 2-ethylhexanol and 3,5,5-trimethylhexanol, as well as oligomeric esters with the terminal 2-ethylhexyl group, may be used as the components of lubricating oils. The addition of these esters to synthetic polyalphaolefinic oils promotes a decrease in chilling temperature by 40 °C, improvement of viscosity index and lubricating properties in comparison with the basic oil. The results showed that the studied polyalphaolefin oils with the addition of dialkyl carbonates were characterised by too low boiling temperature, which is evidenced by the high concentration (19–22 %) of volatile components in the oil after mixing, while dialkyl adipinates and dialkyl sebacates containing methoxy groups in their structure turned out to be immiscible with the basic polyalphaolefin oil.

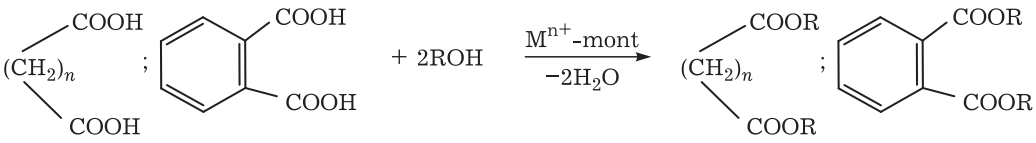
Esterification of glutaric acid with various alcohols of linear structure (octanol, decanol, dodecanol) in the presence of *p*-toluenesulphonic acid as a catalyst was used to synthesise the corresponding diesters; the stability against oxidation, the viscosity, flare temperature and chilling point of the synthesised compounds were determined [2]. It was established that didodecyl glutarate is a solid substance at room temperature, its flare point is 210 °C, while dioctyl glutarate and dodecyl glutarate are liquid. Diesters of glutaric acid are characterised by low chilling temperature and the temperature of oxidation stability above 187 °C, which has a positive effect on their properties.

In [3], the synthesis of some esters based on oleic alcohol and some dicarboxylic acids possessing good lubricating and viscosity-temperature characteristics is described. For instance, dioleyl pimelate, dioleyl adipinate, dioleyl glutarate and dioleyl succinate are characterised by low chilling points: −10, −12, −16 and −20 °C, respectively. It was determined that the flare point of dioleyldecanedionate is 305 °C, the temperature of oxidation stability is 183 °C, which confirms the good lubricating parameters of this compound. It was shown that with an increase in the amount of carbon in dicarboxylic acid, the flare point of its ester rises, while its oxidation stability is determined by the unsaturated oleyl alcohol. Tribological studies showed that the indicated diesters, except dioleyldodecanedionate, are non-Newtonian fluids. They have low friction coefficients and may be used as basic lubricating oils.

The interaction of norbornene with dicarboxylic acids – oxalic, malonic, cinnamic and maleic – was studied in the presence of boron trifluoride etherate as a catalyst with the formation of bicyclic monoesters of the listed acids at the first stage. The optimal conditions of the synthesis of monoesters were determined (temperature 90 °C; molar ratio 1 : 1, duration 4 h) in a yield within 80–90 mass %. At the second stage, the corresponding diesters of the listed acids were obtained through the interaction of the synthesised monoesters with saturated monohydric alcohols of C_2–C_7 series in the presence of KU-2-8 heterogeneous catalyst in the H-form. These diesters were considered as additives to synthetic oils for the purpose of improving their performance characteristics [4–6].

$$\begin{array}{l} CO(OCH_3)_2 \\ CH_3OOC(CH_2)_nCOOCH_3 + 4ROH \end{array} \longrightarrow \begin{array}{l} CO(OR)_2 \\ ROOC(CH_2)_nCOOR + 4CH_3OH \end{array}$$

Scheme 1. Synthesis of diesters of carbonic, adipinic, and sebacinic acids, where $n = 4$ – adipinic, $n = 8$ – sebacinic acids; R = 2-ethylhexanol, 3,5,5-trimethylhexanol.

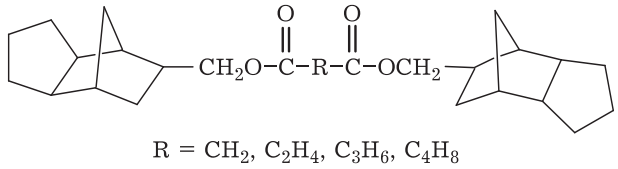


Scheme 2. Synthesis of diesters of malonic, maleic, succinic, adipinic and phthalic acids.

The synthesis of diesters of such dicarboxylic acids as malonic, maleic, succinic, adipinic and phthalic, with simple alcohols (ethanol, propanol, butanol, 2-methyl-2-propanol, phenol and *p*-cresol) was carried out in the presence of catalysts based on metal-modified montmorillonite clay (M^{n+}-mont; M^{n+} = Al^{3+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, Mn^{2+} and Ni^{2+}). The catalyst used by the authors was smectite-rich white montmorillonite GK-129 with the composition, %: SiO_2 67.2, Al_2O_3 15.2, Fe_2O_3 1.9, MgO 3.2, CaO 1.92, Na_2O 2.58, K_2O 0.09, with the cation-exchange capacity 0.8 mg-equiv/g. Relatively high activity of Al^{3+}-montmorillonite was detected: in its presence, the yield of esters was 94 % (Scheme 2). The use of the catalysts prepared from montmorillonite clay allows for the process to be carried out under mild conditions (ecological compatibility, low prime cost, high selectivity, the possibility to use them repeatedly and simplicity of operation, the absence of aggressive acid catalytic systems promoting corrosive side processes and the formation of acid wastes in the reaction). The reaction meets the requirements of green chemistry and has found practical application [7].

High-boiling esters of di(tricyclodecanemethylol) were also recommended as additives to oils. These esters were obtained in a yield of 50−60 % as a result of esterification of hydroxymethyltricyclo[5.2.1.$0^{2,6}$]decane with maleic, adipinic, malonic, phthalic, terephthalic, succinic and sebacinic acids (Scheme 3) [8−10].

The viscosity-temperature characteristics and thermooxidative stability of the synthesised esters of dimethyladamantandicarbinol with aliphatic alcohols and the esters of dimethyladamantandicarbinol with aliphatic acid were studied. The listed esters were considered potential components for high-temperature lubricating oils (Scheme 4) [11−12].

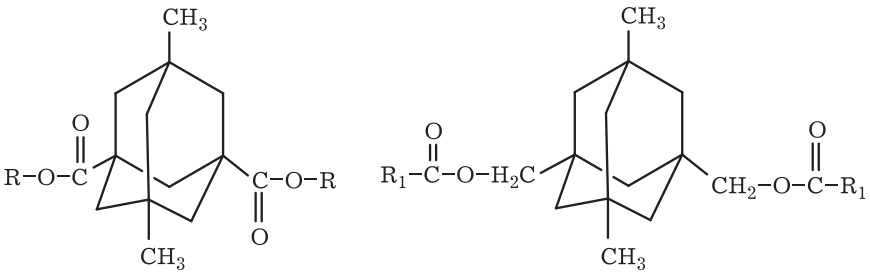


R = CH_2, C_2H_4, C_3H_6, C_4H_8

Scheme 3. Esters of di-(tricyclodecanmethylol).

Diesters were synthesised in a yield of 77−83 % from 1,3-adamantyldiacetic, 5-ethyl-1,3-adamantandicarboxylic and 5-ethyl-3-carboxy-1-adamantylacetic acids and aliphatic alcohols (*n*-propanol, *n*-butanol, *n*-pentanol and *n*-hexanol) in the presence of *p*-toluenesulphonic acid as a homogeneous catalyst [13]. The physicochemical characteristics (kinematic viscosity at a positive and negative temperature, viscosity index, chilling temperature, flare temperature, density) and thermooxidative properties of these diesters were studied. The properties of the synthesised esters were compared with the characteristics of the diesters of adamantancarboxylic acid and diesters of adipinic and sebacinic acids, which were used previously as synthetic oils and hydraulic fluids. It was established that, in comparison with diesters of adipinic and sebacinic acids of similar structure, all the studied adamantan derivatives containing diesters of a dicarboxylic acid are distinguished by the high thermal stability and better physicochemical characteristics.

The composition incorporating N-substituted bisamide or an ester of the amide of oxalic acid containing at least two hydrocarboxylic groups



Scheme 4. Esters of dimethyladamantancarbinol.

with 12–22 carbon atoms was proposed for use as a friction modifier for automatic transmission [14].

POLYMER MATERIALS

The esters of dicarboxylic acids containing functional groups are of interest as monomers for the synthesis of polymers and copolymers with different compositions and for different purposes, in particular for the synthesis of copolymers based on dimethyl esters of bicyclo[2.2.1] hept-5-ene-2,3-dicarboxylic acid (DME), which, in turn, are synthesised according to Diels–Alder reaction from the side product of petroleum pyrolysis – dicyclopentadiene and dimethyl maleate [15]. A mixture of *exo*,*exo*- and *endo*,*endo*-DME isomers is formed in this reaction in the amounts of 40 and 60 mass %, respectively (Scheme 5).

Copolymers of DME with a bifunctional monomer *exo*,*exo*-N,N′-hexylene-di(norbornene-2,3-dicarboxyimide) are characterised by increased strength, thermal stability and resistance to aggressive media. As a result of metathesis polymerisation, a material with a net structure is formed. The process was carried out with the Hoveyda–Grubbs catalyst of the II generation with the mass ratio of the catalyst/monomer equal to 1 : 15 000.

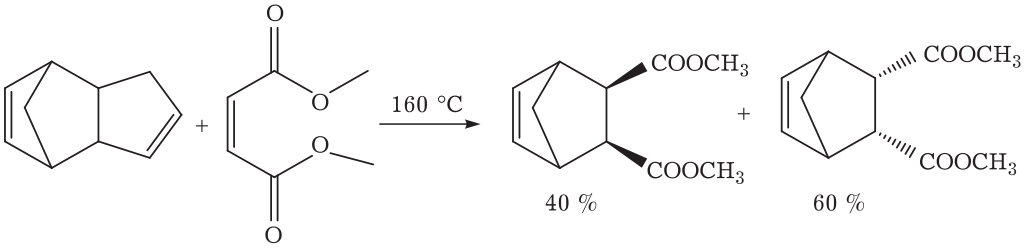
The possibility to synthesise hinge-ladder polyimides with the desirable spatial structure on the basis of the synthesised N-aminoimides of polychlorinated cyclic dicarboxylic acids was demonstrated [16]. Acylation of N-alkyl (aryl) aminoimides of 1,4,5,6,7,7-hexachlorobicyclo[2.2.1] hept-5-ene-2,3-dicarboxylic acid **1** and 1,2,3,4,11,11-hexachlorotricyclo[6.2.1.$0^{5,10}$]-undec-2-ene-7,8-dicarboxylic acid **2** with maleic anhydride at a temperature of 150 °C in dimethylformamide (DMF) leads to N,N'-maleinalkyl (aryl) substituted imides of 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid **3** and *endo*,*endo*-1,2,3,4,11,11-hexachlorotricyclo[6.2.1.$0^{5,10}$]undec-2-ene-7,8-dicarboxylic acid **4**. To obtain diene-dienophil bisimides of N,N'-maleinalkyl (aryl) substituted imide of 1,2,3,4-tetrachlorocyclohexa-1,3-diene-5,6-dicarboxylic acid **5** and *endo*,*exo*-2,3,4,5-tetrachlorobicyclo[4.4.0]deca-2,4-diene-8,9-dicarboxylic acid **6**, the synthesised bisimides **3** and **4** were brought into interaction with pyridine and acetic anhydride in DMF (Scheme 6).

The synthesis of N-adamantyl-*exo*-norbornene-5,6-dicarboxyimide (Scheme 7), identification and the synthesis of copolymers on its basis by means of ring-opening metathesis polymerisation under the action of ruthenium catalyst of Hoveyda–Grubbs type II were described in [17].

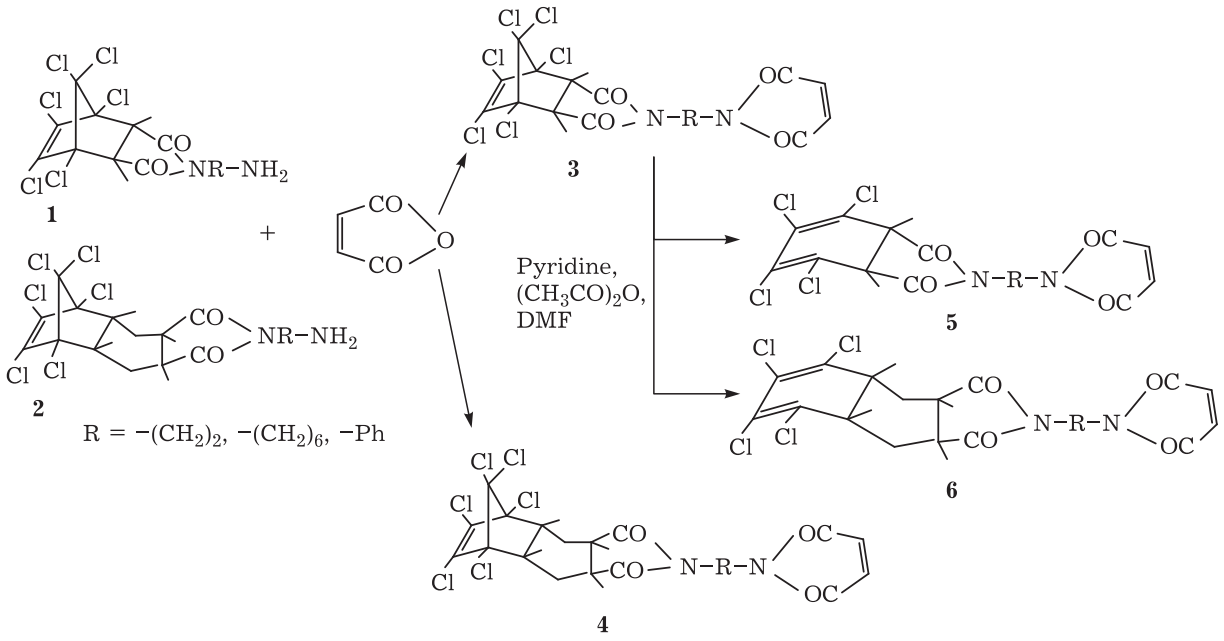
As described in [18], the use of a mixture of *endo*- and *exo*-dimethyl esters of norbornene-2,3-dicarboxylic acids at a ratio of 3 : 2 as the monomer material, and ethyleneglycoldinorbornene-5-carboxylate (EGDNC) as a linking agent in the presence of ruthenium[1,3-bis-(2,6-dimethylphenyl)-2-imidazolidinylidene]dichloro-(2-(N,N-dimethylaminomethyl)benzilidene) as a catalyst in the atmosphere of nitrogen, copolymers with the glass transition temperature within 80 to 86 °C were synthesised with EGDNC concentration equal to 10 %. The reaction mass was initially kept for 20 min at a temperature of 80 °C, and then 20 min at a temperature of 140 °C.

It was shown in the studies of photophysical and thermal characteristics of a series of polynorbornene-dicarboximides synthesised through ring-opening metathesis polymerisation that with binding of different electron-acceptor groups with the electron-donor group of tricarbazole in the side chain of polynorbornene, the resulting polymers exhibited different fluorescence emission colouring: purple-blue (418 nm), greenish-blue (489 nm), green (515 nm) and orange-yellow (594 nm). The synthesised polymers exhibit high thermal stability at a temperature above 400 °C [19].

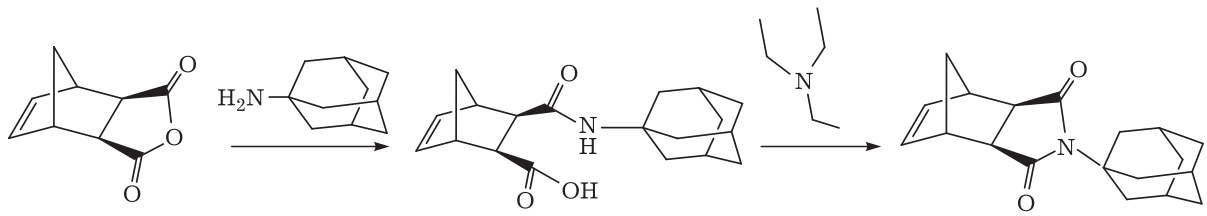
The authors of [20] describe the synthesis of 4-aminophenylcycloalkanedicarboxylic acids and



Scheme 5. Synthesis of dimethyl esters of bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid.



Scheme 6. Synthesis of N,N′-maleinalkyl aryl(imide) 1,2,3,4-tetrachlorocyclohexa-1,3-diene-5,6-dicarboxylic acid **5** and 2,3,4,5-tetrachlorobicyclo[4.4.0]deca-2,4-diene-8,9-dicarboxylic acid **6**.



Scheme 7. Synthesis of N-adamantyl-*exo*-norbornene-5,6-dicarboxyimide.

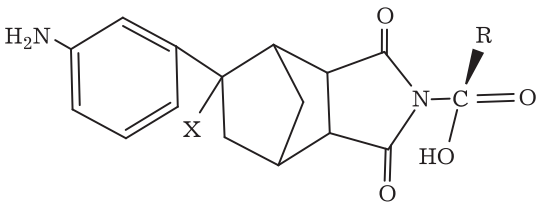
their derivatives that may be used as monomers to synthesise new polyimides.

The reaction of the monoester of norbornene-2,3-dicarboxylic acid with amino acid protected at the carboxyl group under the action of dicyclohexylcarbodiimide and then the alcohol solution of alkali was used to synthesise the corresponding imide [21].

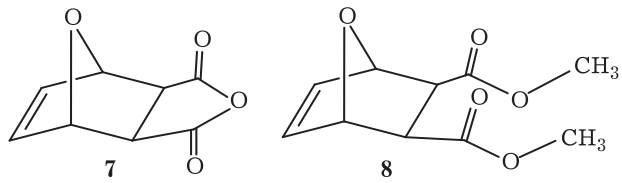
As a result of ring-opening metathesis polymerisation in the presence of chloroform using the Grubbs' initiator of the I generation and ethyl vinyl ether as a stopper, poly(N-adamantyl-*exo*-norbornene-5,6-dicarboximide) was obtained; its average molecular mass was 27 000 g/mol, polydispersity index 2.19, it was characterised by the high glass transition temperature 281 °C, and high temperature of thermal decomposition 385 °C (with the loss 10 %) [22].

Benzene alkylation with (1R, 2S, 3R, 4S)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, (1R,2S)/(1S,2R)-cyclohex-4-ene-1,2-dicarboxylic and (1R,2S)/(1S,2R)-4-methylcyclohex-4-ene-1,2-dicarboxylic acids in the presence of $AlCl_3$ was studied depending on the order of reagents addition; a method was developed for the synthesis of new optically active diastereomerically pure imides on the basis of the derivatives of phenylcycloalkanedicarboxylic and methylphenylcycloalkanedicarboxylic acids containing trifluoromethyl group [23]. On the basis of the indicated imides, chiral aminocarboxylic acids as monomers for the synthesis of optically active polyamidoimides were synthesised through catalytic reduction. The resulting polymers are characterised by high thermal durability and stability, good solubility in dipolar aprotic and protic solvents (Scheme 8).

According to Diels–Alder reaction, through the interaction of furan with maleic anhydride, *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride was obtained, and then Fischer esterification in boiling methanol was used to synthesise the dimethyl ester of 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (Scheme 9). Then metathesis polymerisation of the synthe-



Scheme 8. Chiral amino acid with X = H, CH_3; R = CH_3, *i*-Pr, *i*-Bu.



Scheme 9. *Exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride **7** and dimethyl ester of 7-oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic acid **8**.

sised ester with ring opening under the action of ruthenium catalyst $Ru(PPh_3)_2Cl_2(CHPh)$ was used to obtain polymers with different molecular masses depending on the molar ratio of monomer and catalyst [24].

Polyester resins of maleic acid are also of practical interest. A method of obtaining unsaturated polyester resin on the basis of maleic acid and ethylene glycol is described in the patent [25], the resin is used as a construction polymer material providing a decrease in the mass of construction units and structures, a decrease in labour consumption for their manufacture, an increase in the productivity of building and installation works, the durability of structures under the action of aggressive media, improvement of the quality and shortening of construction time. The recommended method of resin synthesis involves mixing of initial reagents at a molar ratio of 1 : 1, temperature 140–150 °C and reaction time 40–45 min. To solidify the synthesised polyester, 1 % dimethylaniline and benzoyl peroxide are used as initiators, in the presence of cobalt naphthenate as a promoter.

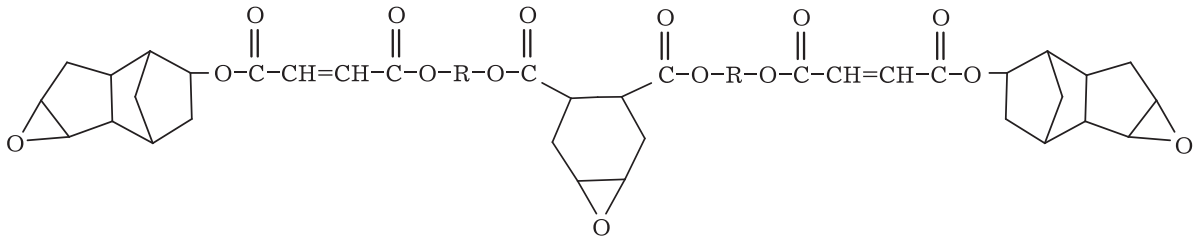
The synthesis of new polyesters based on epoxydicyclopentadiene with styrene was carried out in three stages, which included the addition of maleic acid to dicyclopentadiene (DCPD), polycondensation of the obtained acid ester of DCPD with the anhydride of cyclohex-4-ene-dicarboxylic acid, maleic anhydride and the corresponding glycol: ethylene, diethylene or triethylene glycol, and final epoxidation of polyesters [26]. The synthesised polyesters were successfully used as a component of copolymers with different styrene content (10–80 mass %) (Scheme 10).

Water-based coatings solidified thermally and/or under the action of high-energy radiation, as well as coatings with the high content of biologically active substances, are described in the patent [27]. The composition of the coating includes the fused polycondensate of a dicarboxylic acid and a diol with semi-ester of dicyclopentadiene-maleic acid, or semi-ester of endic-maleic acid, or semi-ester of methylendic and maleic acids (Scheme 11).

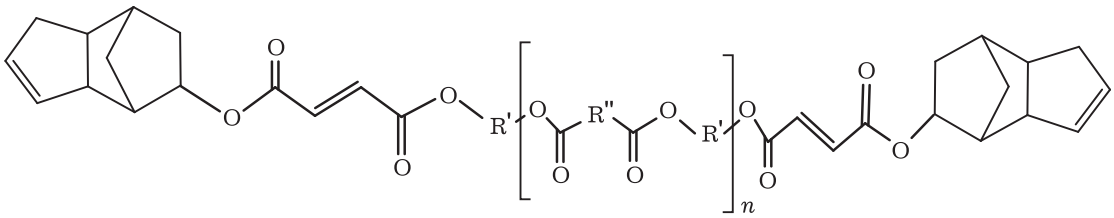
A series of diblock copolymers of norbornene (NOR) and deuterated 2-norbornene-5,6-dicarboxylic acid (NORCOOH) modified with ferric oxide was synthesised and characterised by means of X-ray photoelectron spectroscopy, small-angle neutron scattering and the data of experiments carried out using a superconducting quantum interference device. The nanoparticles of γ-Fe_2O_3 were prepared in the microdomains of diblock-copolymers with the volume ratios of NOR/NORCOOH equal to 0.64 : 0.36, 0.50 : 0.50 and 0.40 : 0.60. Block-copolymers containing γ-Fe_2O_3 nanoparticles were supermagnetic at room temperature (Scheme 12). The microdomains of the resulting block-copolymers were used as nanoreactors for the synthesis of magnetic nanoparticles, which are the subject of extensive investigation due to their interesting magnetic properties and technological applications, such as ferrofluids, recording tapes, flexible magnetic high-density data storage devices, biomedical materials and catalysts [28].

Re-esterification of various methyl esters of long-chain fatty acids (myristic, palmitic, stearic) with the glycerol ester of diacids (succinic or adipinic) was used to synthesise a number of new non-ionogenic surface-active substances (SAS) comparable in their characteristics with widely used non-ionogenic SAS – octylphenolethoxylate [29]. It should be stressed that the major effect of their surface-active characteristics is caused by the molecular structure and the length of the hydrophobic chain.

Mono- and diesterified derivatives of glycerol were synthesised through the interaction of glycerol with the esters of aliphatic dicarboxylic acids C_2–C_9 (Scheme 13). Among the synthesised compounds, 2,3-dihydroxypropylmethyl succinate, -ethyl glutarate, -methyl adipinate and -methyl azelate possess surface-active properties [30].



Scheme 10. Structure of copolymer of epoxydicyclopentadiene with styrene.

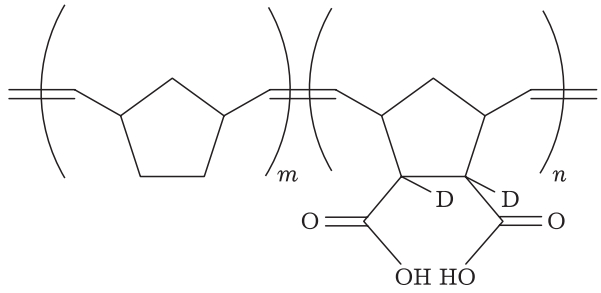


Scheme 11. Composition of coating with R′ and R″ designating aliphatic, cycloaliphatic, aromatic hydrocarbons C_1–C_{20}, n = 1–10.

Some esters of dicarboxylic acids found application as plasticisers of polymer products. For instance, the authors of [31] described a method to synthesise the esters of cyclohexenedicarboxylic acid by means of [4+2]-cycloaddition of butadiene-1,3 with maleic anhydride, followed by the interaction of the formed anhydride of cyclohexenedicarboxylic acid with various alcohols. The products of their hydrogenation to the corresponding derivative of cyclohexenedicarboxylic acid found application as plasticisers for PVC plastics or polyvinylbutirol.

Esterification of succinic, glutaric, adipinic acids by 2-ethylhexan-1-ol, catalysed by *p*-toluenesulphonic acid, is described in [32]. This catalyst exhibits higher activity in comparison with sulphuric acid, provides conversion higher than 98 % under the following reaction conditions: catalyst concentration $1.3 \cdot 10^{-2}$ mol/dm^3, reaction time 60 min, the molar ratio of dicarboxylic acids to 2-ethylhexan-1-ol = 2.65 : 1. The acid number of the mixture of diesters varies between 0.04 and 0.1 mg KOH/g, the kinematic viscosity is 13–17 mm^2/s. The indicates esters were proven to be competitive with the commercial plasticisers, such as dioctyl adipinate and dibutyl phthalate.

The composition containing at least one polymer ester of dicarboxylic acid and one diester of dicarboxylic acid, as well as the moulding material which is a thermoplastic polymer or elastomer, used as plasticiser, were described in [33].

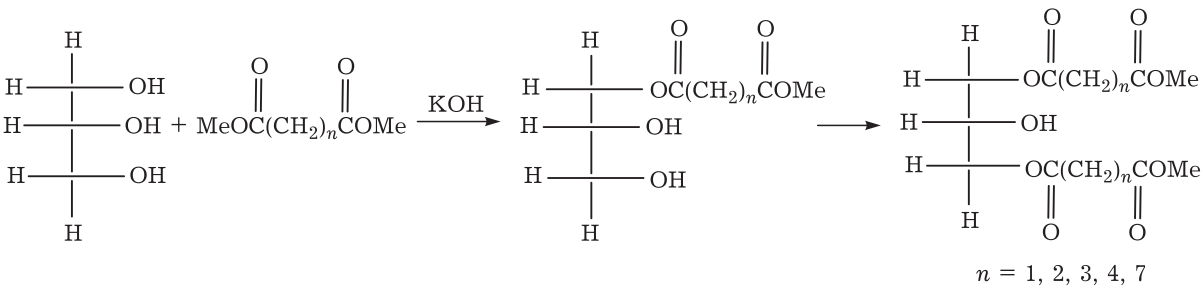


Scheme 12. Structure of copolymer of norbornene and 2-norbornene-5,6-dicarboxylic acid, m = 290–360 and n = 120–260..

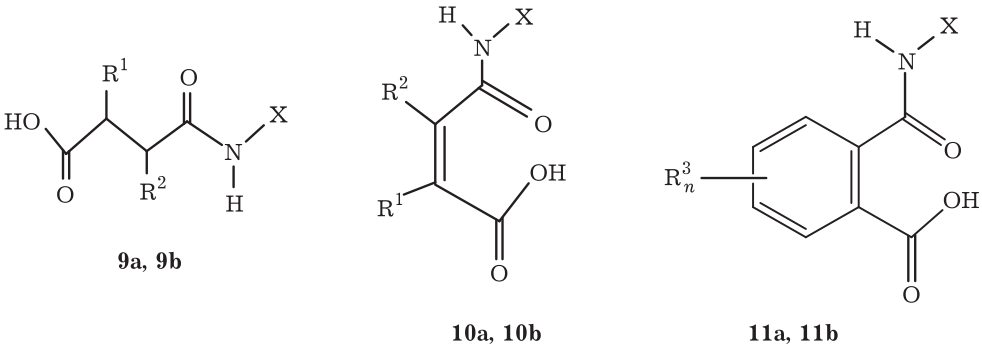
BIOLOGICALLY ACTIVE COMPOUNDS

The derivatives of dicarboxylic acids have also found broad application in the production of biologically active preparations. For instance, the methods of synthesis of substituted amides, ilyden- and acylhydrazides of 1,4-dicarboxylic acids (succinic, maleic, citraconic, fumaric and phthalic acids and their derivatives) used in the synthesis biologically active substances were considered in a review article [34]. The main method of obtaining substituted amides and hydrazides of succinic **9**, maleic **10** and phthalic **11** acids and their aryl derivatives is in acylation of amines, substituted hydrazines, hydrazides of carboxylic acids, or hydrazones of aldehydes and ketones by the corresponding anhydrides of dicarboxylic acids under mild conditions (Scheme 14).

The substituted amides and hydrazides of dicarboxylic acids and their linear derivatives –



Scheme 13. Synthesis of mono- and diesterified derivatives of glycerol.



Scheme 14. Substituted amides and hydroxides of succinic **9**, maleic **10** and phthalic acids **11**.

ethers, amides, hydrazides – are low-toxic and possess antibacterial, antihelminthic, antiviral, anticonvulsant, anti-inflammatory, antitumour, analgesic, fungicidal and other properties [35–40].

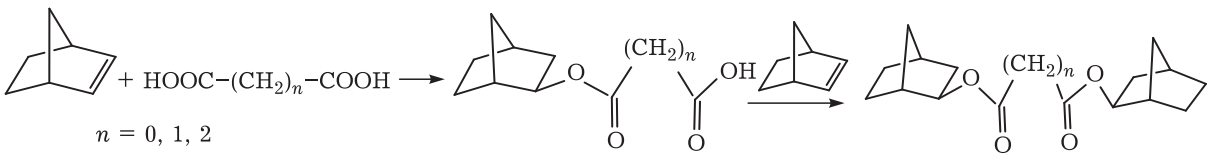
Monoamides of dicarboxylic acids, in particular cyclic imides of succinic, maleic, glutaric and phthalic acids, readily synthesised under mild conditions, form an important class of organic compounds with therapeutic properties [41, 42].

It is demonstrated in [43] that dicarboxylic acids (oxalic, malonic, succinic) add to norbornene selectively (up to 99 %) in the presence of an H-Beta zeolite catalyst giving rise to mono- and diesters of the listed acids (Scheme 15). The possibility and potential of the use of the indicated esters as biologically active preparations are evaluated. A noticeable growth-stimulating activity was demonstrated with the seedlings of dicotyledonous plants (pea).

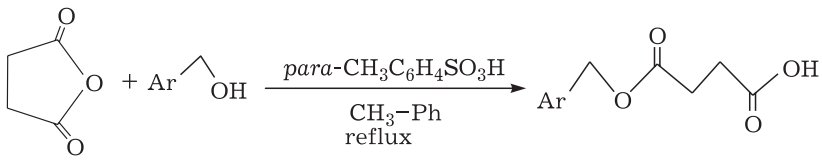
The monoesters of succinic acid were synthesised through the interaction of succinic anhydride with aryl alcohols and their derivatives, using *p*-toluenesulphonic acid as a catalyst and toluene as a solvent [44]. This method was used to synthesise monoesters of di- and trisubstituted aryl alcohols (yield 57–72 %), which are valuable products in the agrochemical and pharmaceutical industries (Scheme 16).

Stereo- and enantioselective synthesis of the esters of mono- (Scheme 17) and diesters (Scheme 18) of carboxylic acids of the cyclohexene series was carried out through thermal and catalytical asymmetrical Diels–Alder reaction in the presence of chiral catalysts ($AlCl_2OMent$, $[AlCl(OMent)_2$, $BBr_2OMent]$ [45].

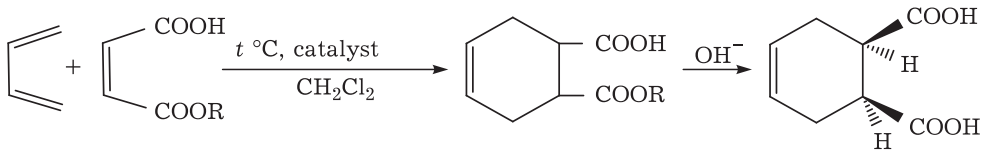
Under the conditions of thermal synthesis, the adducts with 1R,2R-(–)configuration are formed, while catalytic reactions result in the formation of the adducts with 1S,2S-(+)configuration. The



Scheme 15. Synthesis of mono- and diesters of norbornenedicarboxylic acids.

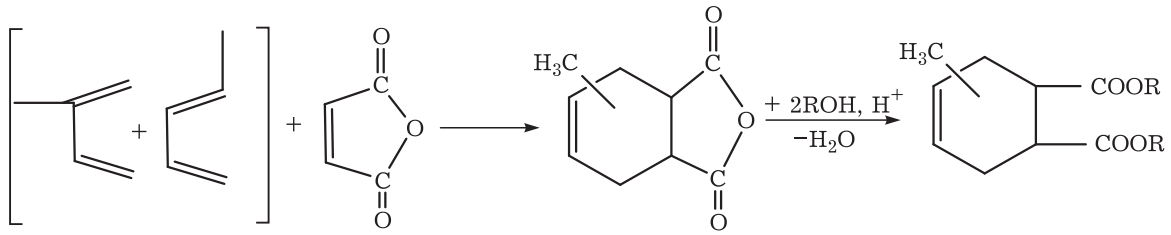


Scheme 16. Synthesis of monoesters of succinic acid with difluoro-, trifluoro-, chloro-, bromo-, nitro- and methyl-substituted aryl alcohols.



R = *n*-Pr, *iso*-Pr; *n*-Bu, *iso*-Bu, *tert*-Bu; cyclohexyl

Scheme 17. Synthesis of monoesters of 3(4)-methylcyclohex-4-ene-1,2-dicarboxylic acid.



R = *iso*-C_3H_7; *n*-C_4H_9; *n*-C_8H_{17}; cycloxehyl; *p*-methylcyclohexyl

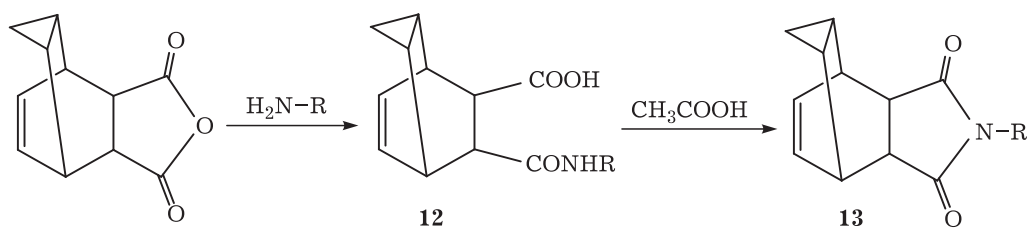
Scheme 18. Synthesis of diesters of 3(4)-methylcyclohex-4-ene-1,2-dicarboxylic acid.

antimicrobial properties of the synthesised stereoisomers and enantiomers against various microorganisms were tested by means of serial dilutions, and the possibility to use these compounds as local antiseptics was established.

Eicosanoidic and docodocosanoic acids were isolated from the colonial shell of marine microorganisms of the Polyclinidae family, and Diels–Alder cyclization was employed to synthesise six new bicyclic derivatives of α,ω-dicarboxylic acids. Thus synthesised compounds demonstrated selective cytotoxicity against human tumour cells [46].

Dicarboxylic acids and their derivatives – esters (vinyl and trifluoroethyl diesters) and anhydrides (succinic and glutaric) – were used as acylating agents in the reactions catalysed by lipase in organic solvents. As a result, dimer and hybrid derivatives of biologically active natural compounds (saccharide derivatives) were obtained, as well as the functionalised polyesters with increased solubility in water [47].

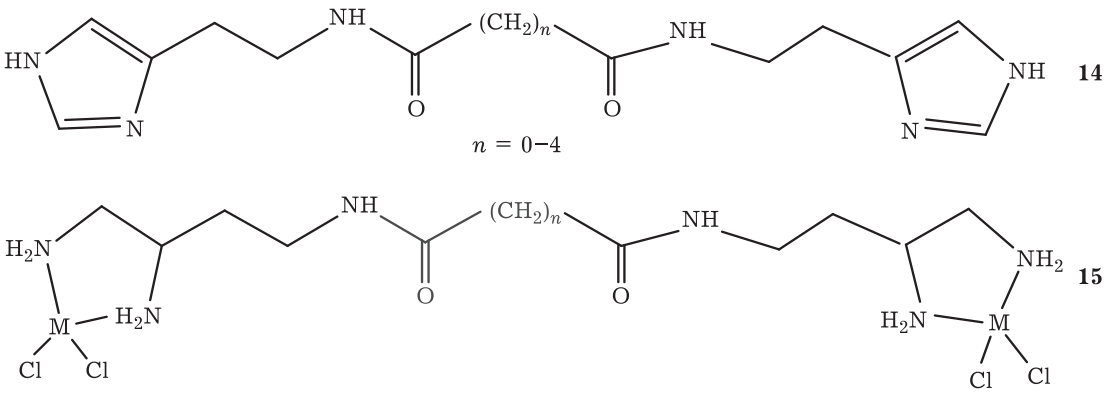
The conditions of the synthesis of monoamides **12** and imides **13** of tricyclo[3.2.2.$0^{2,4}$] non-8-ene-6,7-dicarboxylic acid from its anhydride, which are of interest for the development of new medicinal preparations, are described in [48] (Scheme 19).



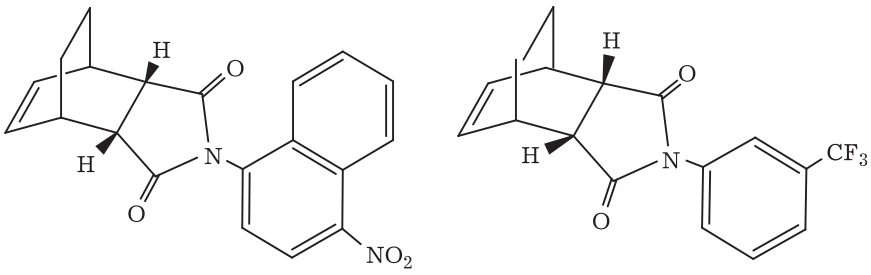
R = ethyl-, 2,5-dimethoxy-4-bromo-, 3,4-dimethoxy-, *o*-phenetidine-, *p*-phenoxy-, *p*-benzoxy-, *p*-iodo-, 4-(*p*-*tert*-butylphenoxy)-

Scheme 19. Synthesis of amides and imides of tricyclo[3.2.2.$0^{2,4}$]non-8-ene-6,7-dicarboxylic acid.

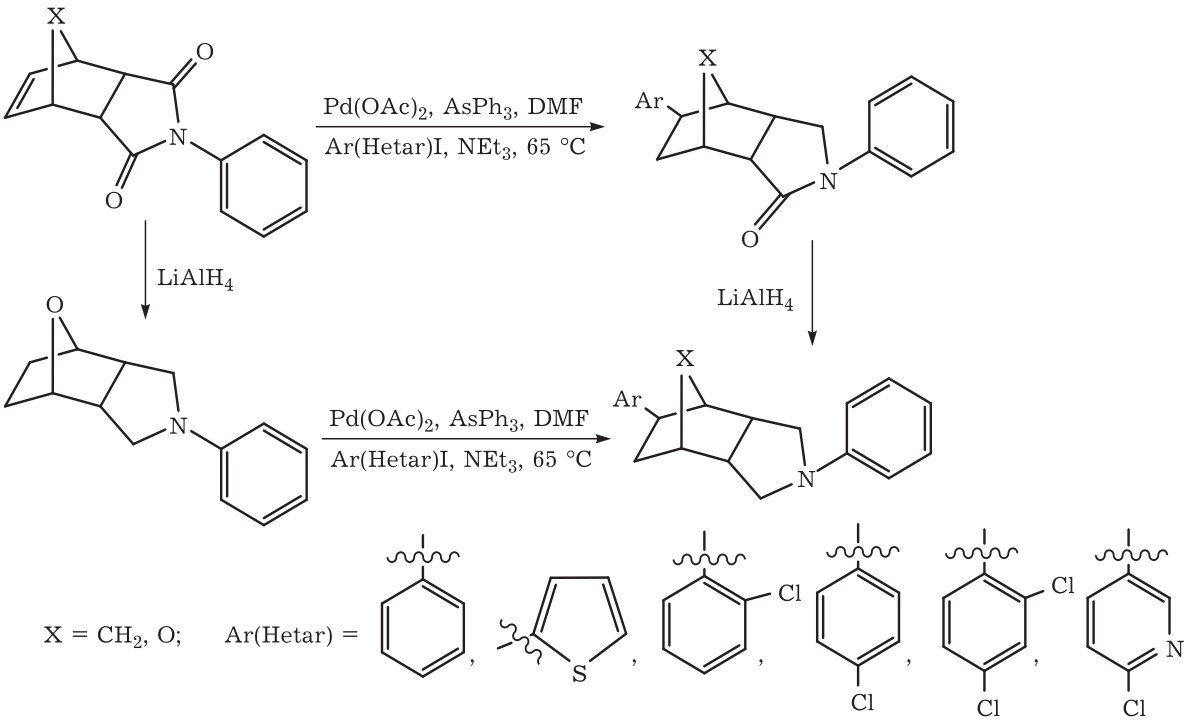
The synthesis of the derivatives of bisamides of dicarboxylic acids possessing the ability to complexing or chelating the ions of Zn, Cu, Fe, Mg and Ca (Scheme 20) was described in the patent [49]. The indicated derivatives of the bisamides of dicarboxylic acids found application as the means for the prophylactics and treatment of cardiovascular, viral, oncological diseases, diabetes, iron-deficient anemia, porphyria tarda, poisoning with the salts of transition metals, *etc.*



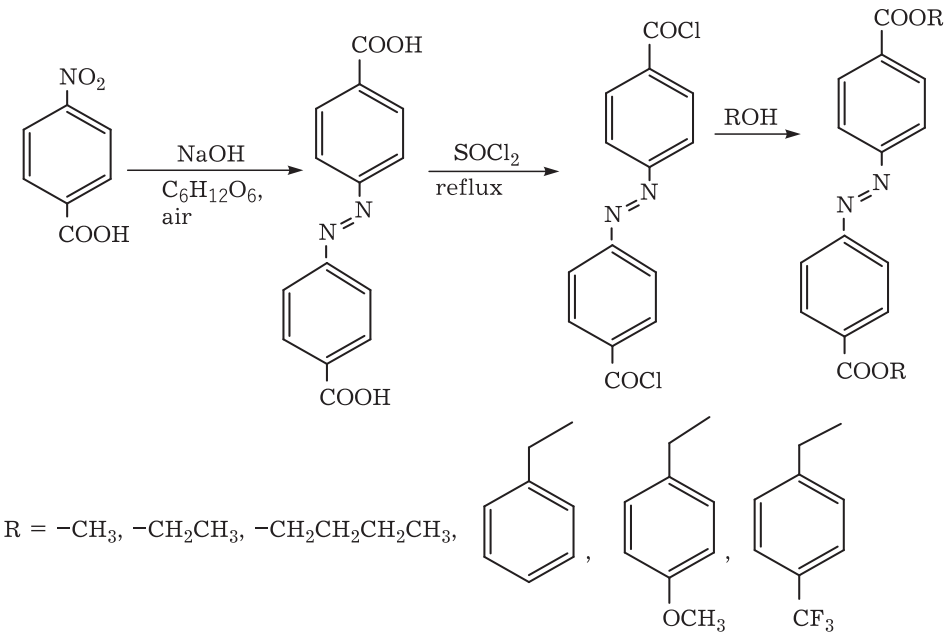
Scheme 20. Derivatives of bisamides of dicarboxylic acids **14** and chelates with metal ions (M) **15**.



Scheme 21. Derivatives of bicyclo[3.2.2]nonane.



Scheme 22. Synthesis of bridging derivatives of perhydroisoindole.



Scheme 23. Synthesis of the derivatives of dialkyl esters of azobenzene-4,4′-dicarboxylic acid.

The imides of bicyclo[3.2.2]nonane and the derivatives of trifluoromethylaniline (Scheme 21) exhibit anti-cancer properties [50].

Through the addition of two bicyclic unsaturated dicarboxyimides to aryl and heteroaryl halides as a result of the reductive Heck reaction, 5-substituted N-phenylbicyclo[2.2.1]heptane-2,3-di-carboxyimides were synthesised (Scheme 22). The reduction of the latter compounds opens a new direction, namely the synthesis of bridging derivatives of perhydroisoindole with clearly pronounced biological activity, which is of interest for pharmacology [51].

New electrochromic and photosensitive materials were synthesised from the dialkyl ester of azobenzene-4,4′-dicarboxylic acid (DEABD) (Scheme 23). The derivatives of DEABD exhibited substantial electrochromic action, as well as reversible properties in photoisomerisation. On the basis of the listed esters, electrochromic devices were manufactured and their characteristics were analysed; colour changes from colourless to purple between 0.0 V (colourless state) and ±3.0 V (coloured state) was demonstrated. It was shown that the new redox-active derivatives of azobenzene are promising for the manufacture of electronic devices with full-colour screens, electronic paper, intellectual windows, optical memory devices, the systems of delivery for several pharmaceutical components possessing double effect [52].

CONCLUSION

Synthesis methods and a set of physicochemical properties of the derivatives of the esters of dicarboxylic acids determining the versatility of their applications and the potential of expanding the studies aimed at the synthesis and revelation of the new application areas are described in the review.

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