

Fine Chemicals and New Hybrid Materials From Cardanol

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Abstract: Cardanol, a low-cost largely available renewable material obtained from distillation of CNSL (Cashew Nut Shell Liquid), has been used for the preparation of fine chemicals and hybrid materials. The long chain attached to the meta position of the phenolic ring of cardanol makes this compound a unique natural source because it confers to all derivatives, particular properties (good solubility, good processability, interesting physical properties and so on). New fine chemicals as well as new cardanol hybrid materials combined with porphyrins, phthalocyanines and fullerenes have been synthesized recently, developing at the same time new synthetic strategies for the preparation of new eco-friendly fine chemicals, composites and functional organic materials. The aim of this review is also to show that the chemistry of cardanol is becoming a stimulating area in academic and industrial research.

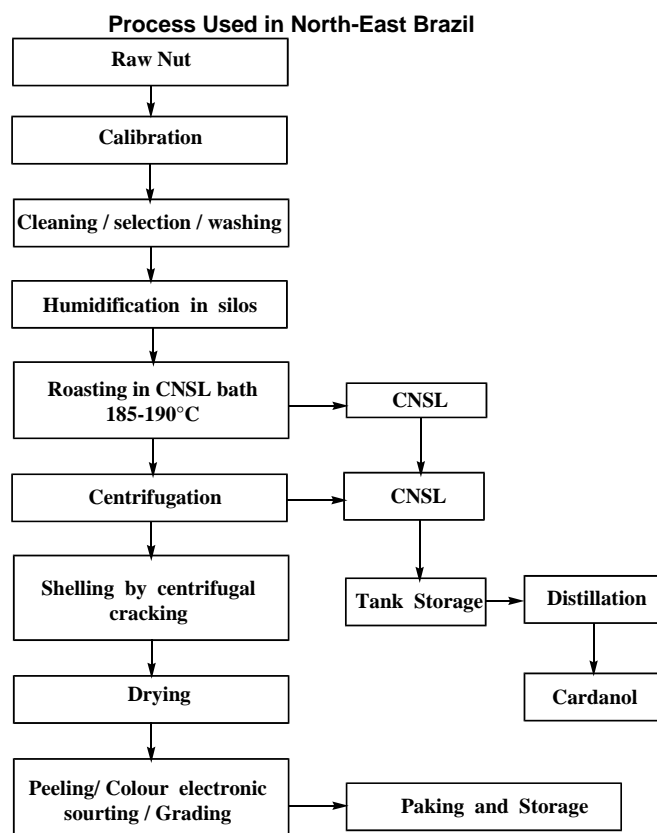
Keywords: Cardanol, CNSL, hybrid materials, fine chemicals.

INTRODUCTION

Cardanol, a by-product from the cashew industry obtained by vacuum distillation of the liquid of the shell of the cashew (CNSL) [1], is an organic and cheap material, which can be considered by now a useful natural renewable product. Recently CNSL, cardanol and its derivatives have been used for the preparation of composite materials having different practical applications [2]; however, the aim of this review is to show how it is possible to use waste, such as cardanol, as a starting material and building block for the preparation of fine chemicals and hybrid functional materials.

Obtaining fine chemicals from waste is a hold concept. In fact, it is a well known phrase “from waste to value”, which means making useful chemical products using the waste of industry. Using waste deriving from CNSL industry could represent in this way a good strategy to minimize the environmental impact of this low-cost natural material.

The preparation of fine chemicals from natural and renewable materials is however, an attractive topic of research especially when the purpose is to recycle huge amount of agro-industrial wastes to produce, possibly through environmentally sustainable processes, compounds that possess interesting chemical and physical properties and which have potential applications. Thus, cardanol, obtained from waste of the cashew industry, can be considered a good starting material and unique natural resource with unsaturated long-chain attached to the phenolic ring. In the Scheme 1 is shown the flow sheet of a typical process used in North-East Brasil [3]: the raw nuts, after cleaning, selection, washing, humidification in silos, and centrifugation of the roasted material produce a waste liquid, called CNSL. The composition of CNSL turns to be a mixture of anacardic acid, cardanol, and traces of cardol and 2-methylcardol (Fig. 1). The alkyl side chain (R) of each of them may be saturated, monolefinic (8), diolefinic (8, 11) and triolefinic (8, 11, 14) with an average of one/two double bonds per molecule.



Scheme 1.

As shown in Table 1, the chemical composition of the CNSL depends strongly on the temperature of the extraction-purification process.

It must be pointed out that: i) the decarboxylation reaction of the anacardic acid that occurs during high temperature extraction/distillation processes, gives cardanol enriched mixtures; ii) the yellow oil obtained by vacuum distillation of CNSL, which is called cardanol, is itself a mixture of different compounds **1**, **1a-1c** (see Fig. 2).

The average composition of cardanol is: 3-*n*-pentadecyl phenol (**1**) 20-30%, 3-(pentadeca-8-enyl) phenol (**1a**) 70-80%, 3-(pentadeca-8,11-dienyl) phenol (**1b**) nearly 5%, 3-(pentadeca-8,11,14-trienyl) phenol (**1c**) less than 5%. Obvi-

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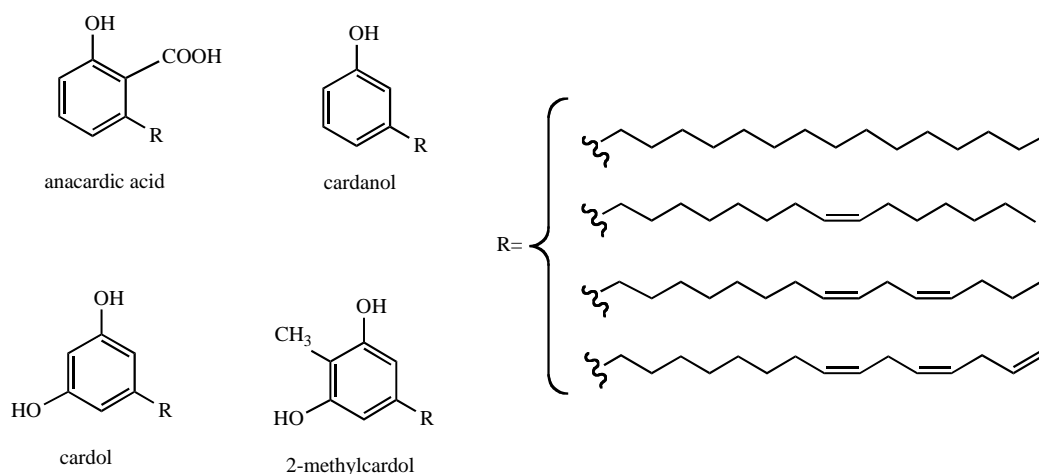


Fig. (1). Main components of CNSL.

Table 1.

Components	Low Temperature Extraction Process	High Temperature (80-200°C) Extraction Process
Anacardic acid	70 %	<5 %
Cardol	20 %	20 %
Cardanol	5 %	70 %
Methyl cardol	3 %	3 %
Unidentified products	2 %	2 %
Polymerized products	-	10 %

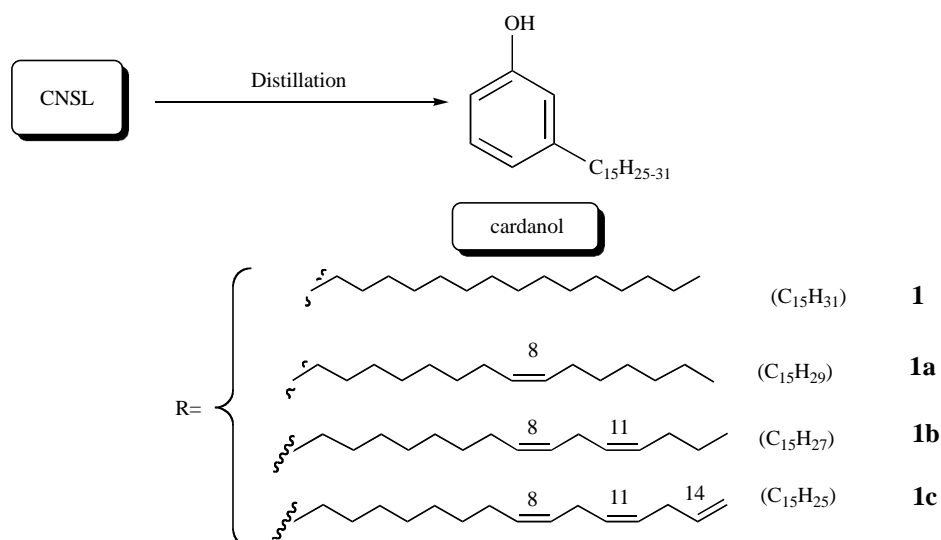
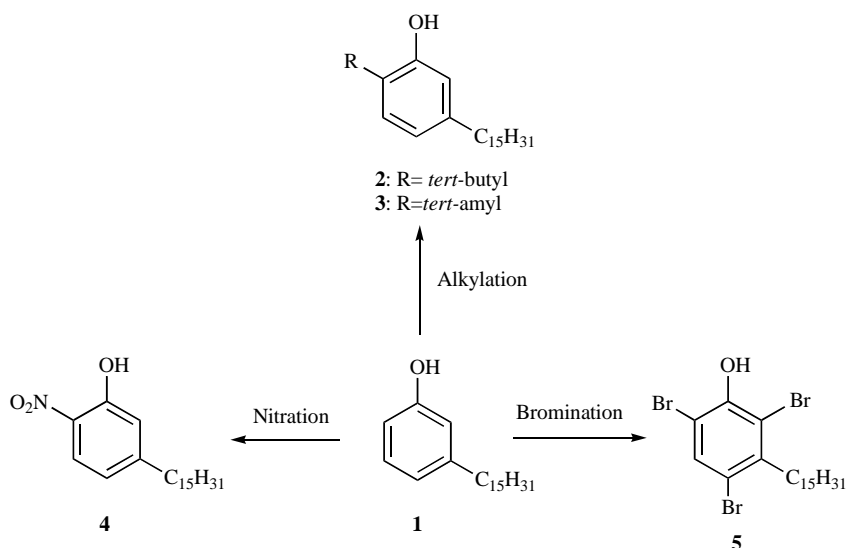


Fig. (2).

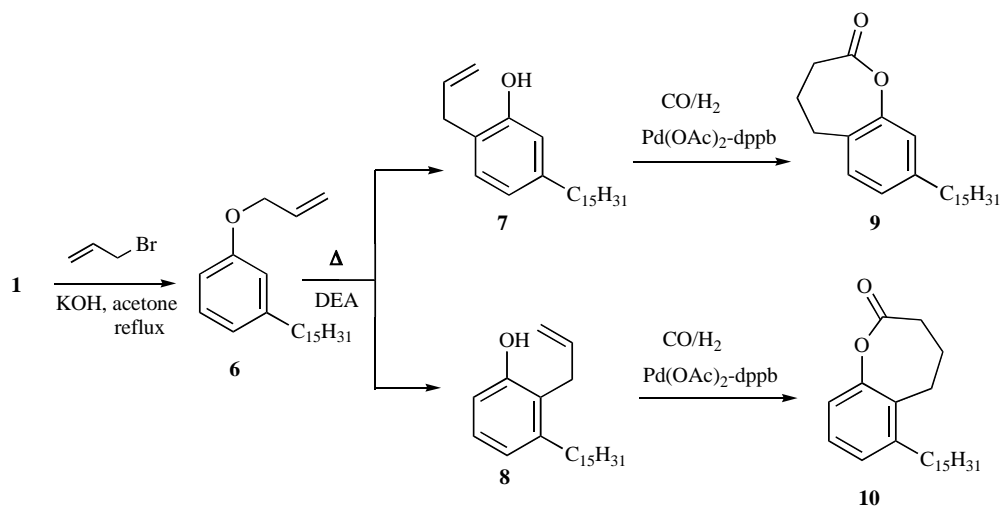
ously, cis and trans isomers of each components are present in the mixture; but usually the cis component is the major one. However, after opportune purification, it is possible to obtain a mixture that is rich (averagely 90 %,) in the monoolefinic component, 3-(pentadeca-8-enyl) phenol **1a**, together with minor amounts of the tri olefinic, diolefinic

and 3-*n*-pentadecyl phenol **1**; this latter can be obtained almost pure (> 98%), after catalytic hydrogenation of the cardanol mixture (**1**, **1a-1c**) [4].

Electrophilic aromatic substitution reactions are important class of reactions that allow the introduction of substituents onto the aromatic ring of cardanol. Various precursors



Scheme 2.



Scheme 3.

of the fine chemicals reported in this review, and other compounds having practical perspective in organic processes, have been prepared using alkylation [4], nitration [5], and bromination [6] reactions (see Scheme 2).

Synthesis of Lactones and Bis-Lactones

As well known, lactones are important compounds because of their utility as biologically active products with pharmacological activity (fungicidal, anti-tumoral and anti-inflammatory) as well as for the synthesis of polyesters *via* ring opening polymerization.

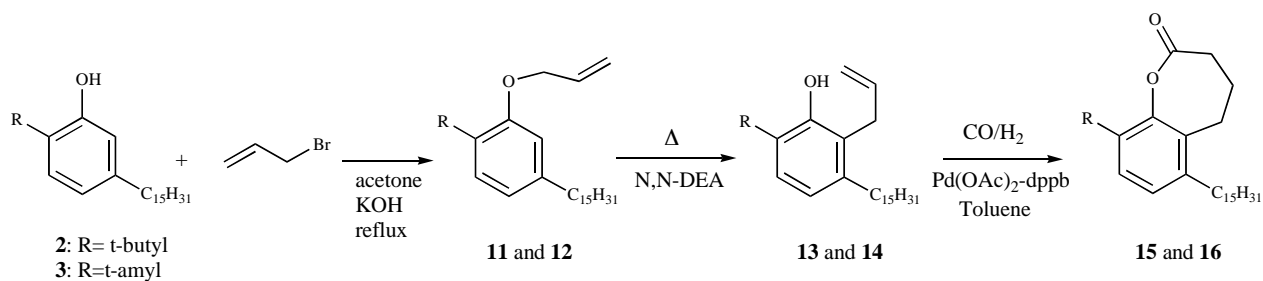
Structurally, lactones can contain saturated (or unsaturated) five or larger rings and during the past years, different strategies of synthesis have been developed depending on the ring size [7] and palladium based catalysts have proved to be the most efficient in the preparation of different ring sizes heterocycles compounds such as for example mono-, bis-lactones and lactams [8].

Lactones and bis-lactones have been prepared from cardanol using catalytic carbonylation reactions methods. In this way, cardanol derivatives have been transformed easily

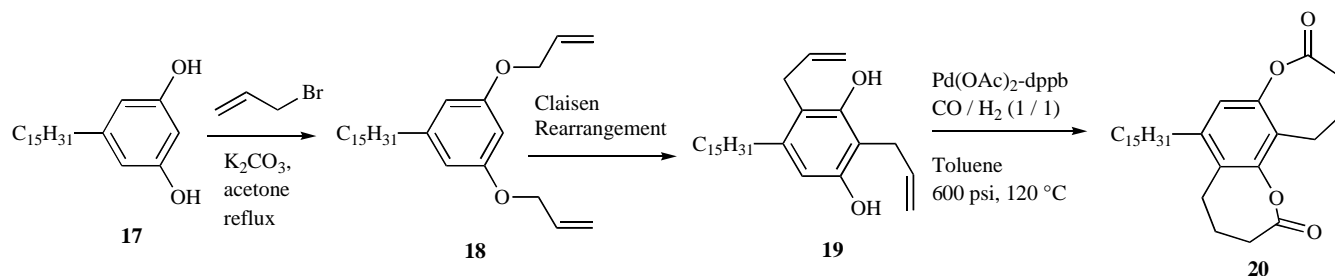
into the corresponding lactones through cyclocarbonylation reactions using palladium acetate and 1, 4-bis (diphenylphosphino)butane (dppb) as catalytic system. As shown in Scheme 3, 3-*n*-pentadecylphenol **1**, for example, was firstly allylated with allyl bromide, to give **6**. Successively, Claysen rearrangement of **2**, refluxed in *N,N* diethylaniline (DEA), produced two allyl derivative isomers **7** and **8**, which were then cyclo-carbonylated in the presence of $\text{Pd}(\text{OAc})_2$ and dppb as catalyst to give lactones **9** and **10**. In this Scheme only the reaction of pentadecyl phenol is reported; however, the cyclo-carbonylation can be carried out also with the cardanol mixture **1**, **1a-1c** [3-(pentadeca-8-enyl) phenol, 3-(pentadeca-8,11-dienyl) phenol, and 3-(pentadeca-8,11,14-trienyl) phenol] to produce the corresponding unsaturated cardanol lactones **9a-9c**; **10a-10c**.

The reaction has been carried out also on other derivatives of cardanol **13** and **14** to produce the corresponding lactone cardanol derivatives **15** and **16** as reported in Scheme 4 [9].

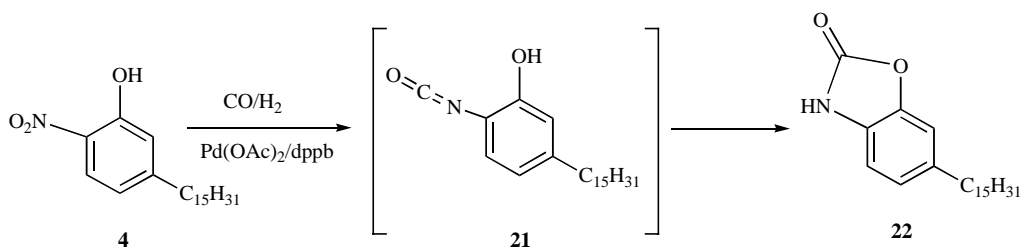
The homogeneous catalytic system $\text{Pd}(\text{OAc})_2\text{-dppb}$ was demonstrated to be an active catalyst also for double cyclo-carbonylation reactions of cardol, **17**, to produce the corre-



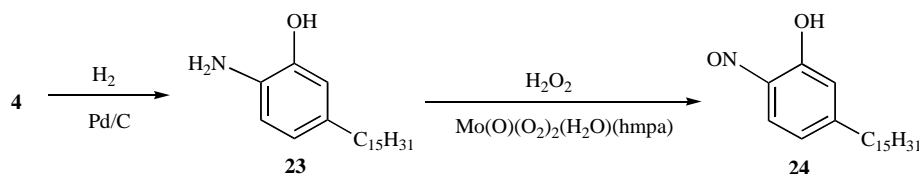
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

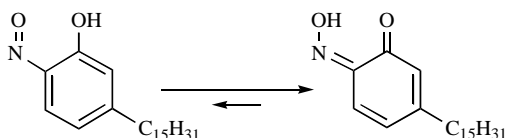
sponding of bis-lactones **20** [10]. Thus, (Scheme 5) cardol, firstly allylated with allyl bromide in acetone and successively double Claysen rearranged to produce the bis allyl compound, can be successively double carbonylated in the presence of Pd(OAc)₂-dppb catalyst to give the corresponding bis-lactone **20**.

Synthesis of Benzoxazol-2-One, Amino and Nitroso Compounds Cardanol Based

Cyclocarbonylation reaction of 5-n-pentadecyl-2-nitrophenol **4** was carried out under mild conditions in the presence of the homogeneous catalytic system Pd(OAc)₂/dppb and a 1:1 mixture of CO/H₂ to produce the benzoxazol-2-one derivative **22** in good yield (Scheme 6). This reaction presumed the formation of an isocyanate **21** as intermediate, which reacted further with the hydroxyl group to give the final product [5].

The nitro compound **4** was reduced to amino derivative by using palladium/carbon as the catalyst. Nitroso cardanol compounds have been also prepared and their preparation involves the reduction sequence RNO₂ → RNH₂ → RNO. In Scheme 7 not only the *ortho* nitroso isomer (**24**) is reported, but also the *para* isomer can be prepared starting from *para*-nitro isomer. From the chemical point of view, aromatic and aliphatic nitroso compounds are interesting due to their equilibrium monomer-dimer [11], as well as for their coordination properties to metals (through the oxygen or nitrogen atom or through the N=O double bond) [12]. Recently they have been found to present liquid crystalline properties when coordinated to metals. In connection to this, nitroso cardanol, when bonded to metals, because of the long chain, can give rise to compounds which usually have low melting points and which can possess liquid crystalline properties. All nitroso cardanol compounds have been characterized by spectroscopic techniques. So, for example, spectro-

scopic data of the *ortho* nitroso cardanol indicated that an equilibrium between nitroso-phenolic form and ketone mono oxime form occurred (Scheme 8) (the equilibrium is shifted towards carbonyl form), as reported in the literature for similar compounds. Also, FT-IR-spectrum revealed the presence of the signal at 1698 cm^{-1} , typical of carbonyl moiety. ^{13}C NMR spectrum also confirmed the existence of a ketone monooxime form (a peak at 192 ppm was present). The UV-Vis spectrum (10^{-3} M solution of **24** in CHCl_3 was analyzed) showed a maximum of absorption at 426 nm, indicating that no aromatic form was present in chloroform solution.



Scheme 8.

Synthesis of Hybrid Compounds from Cardanol Based Derivatives

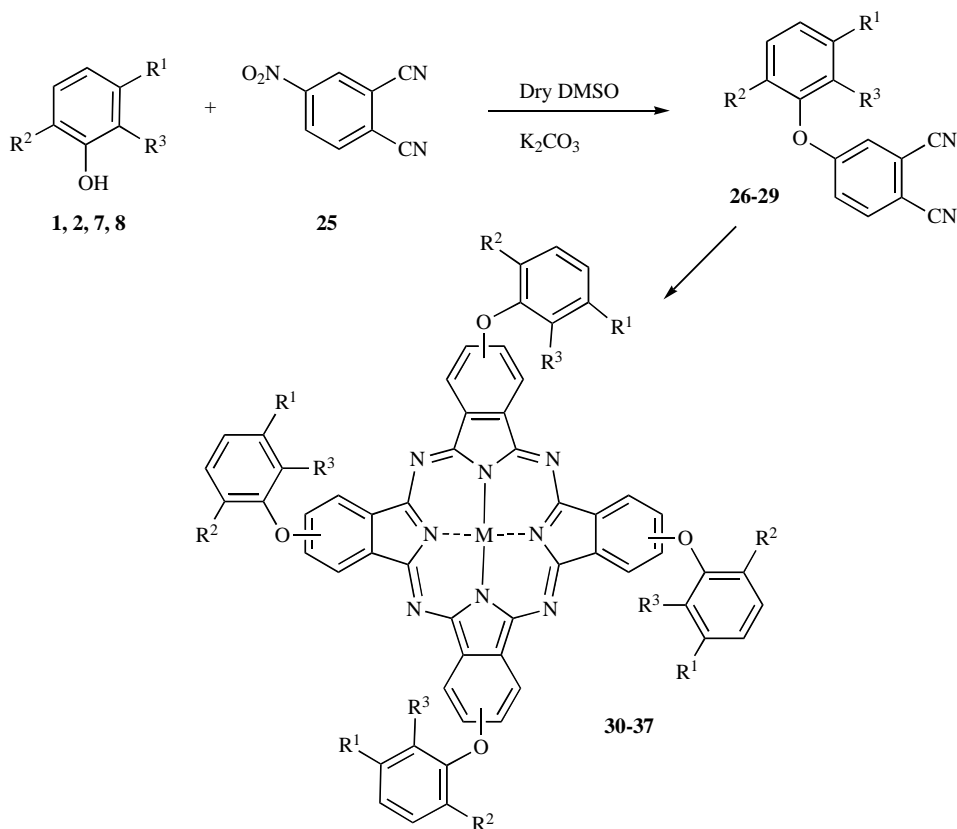
Cardanol based derivatives, prepared using the classic reactions, have been used for the synthesis of hybrid compounds where hybrids mean containing at least two different kinds of molecules such as for example cardanol and porphyrin, phthalocyanine and fullerene, and so on. Porphyrins, phthalocyanines and macro-cycle molecules have been taken into consideration because of their extensive application in different areas of new materials, chemical technology, medicine, electronics and so on. In addition to this, nowadays there is growing interest also in the development of a new

class of multi-macro-cycles such as multi-porphyrin architectures and arrays due to the easy formation of molecular wires, molecular recognition system, and energy transduction and recently, they have also received attention because of their implications for photo-catalytic reactions [13].

Synthesis of Cardanol Phthalocyanine Hybrids

Recently, new tetra-substituted metal-free and metallo derivatives (Cu, Zn, Ni, Pd) containing a peripheral substituent 3-*n*-pentadecylphenol have been synthesized and characterized [14]. The preparation of the phthalonitrile derivatives, precursors of the phthalocyanines, was accomplished by a simple base-catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with an alcohol or phenol. Thus, as shown in Scheme 9, 4-(3-pentadecyl-phenoxy)-phthalonitrile derivatives **26-29** have been synthesized in 90% isolated yield by reacting 3-*n*-pentadecylphenol derivatives **1, 2, 7** and **8** with 1,2-dicyano-4-nitrobenzene, **25**, in DMSO in the presence of K_2CO_3 . Metallophthalocyanines **30-36** (see Table 2) were obtained refluxing in ethanol the phthalonitrile derivatives **26-29** in the presence of the corresponding metal salt MCl_2 ($\text{M} = \text{Cu, Zn, Pd, Ni}$) and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) for 24 h [14].

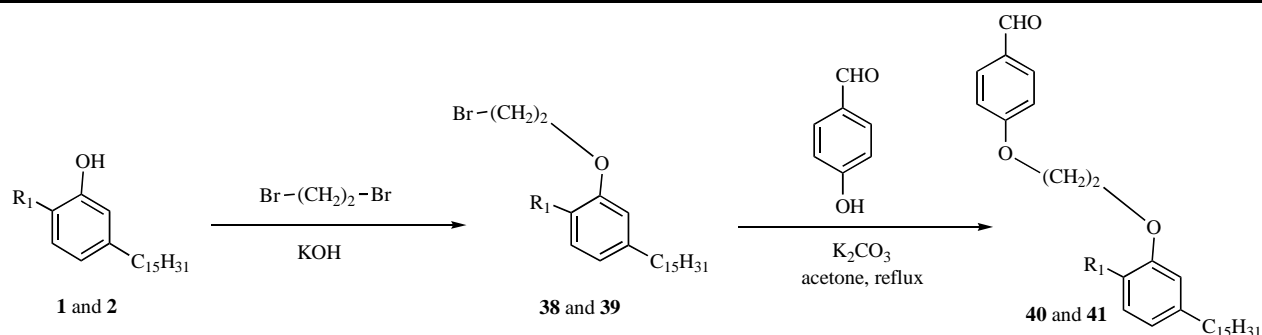
Metal free phthalocyanine **37** was better prepared by fusion of the phthalonitrile derivative **26** and hydroquinone, in a sealed tube, by using a procedure similar to that described by Snow and Jarvis [15]. As expected, most of the phthalocyanine cardanol derivatives have shown important properties such as for example relatively low melting points (within 38-49 °C) and high solubility in organic solvents, due to the long alkyl chains. It must also be pointed out that the com-



Scheme 9.

Table 2. Metal and Metal-Free Phthalocyanine

Cardanol Derivatives	R ¹	R ²	R ³	M	Yield
30	<i>n</i> -C ₁₅ H ₃₁	H	H	Cu	50%
31	<i>n</i> -C ₁₅ H ₃₁	H	H	Pd	40%
32	<i>n</i> -C ₁₅ H ₃₁	H	H	Zn	33%
33	<i>n</i> -C ₁₅ H ₃₁	H	H	Ni	48%
34	<i>n</i> -C ₁₅ H ₃₁	<i>t</i> -butyl	H	Pd	45%
35	<i>n</i> -C ₁₅ H ₃₁	Allyl	H	Cu	30%
36	<i>n</i> -C ₁₅ H ₃₁	H	Allyl	Cu	32%
37	<i>n</i> -C ₁₅ H ₃₁	H	H	(2H)	50%



Scheme 10.

mon feature of the ¹H NMR spectra of MPcs **30-37** is a broadening of the signals when compared with those of the dicyano derivatives **26-29**, probably due to a chemical exchange caused by aggregation-desegregation equilibrium as reported for similar compounds [14].

Synthesis of Cardanol-Porphyrin Hybrids

New lipophilic meso-tetraarylporphyrins bearing cardanol metal-free and metallo derivatives containing a peripheral substituent 3-*n*-pentadecylphenol were also synthesized and characterized. In Scheme 10 is reported the synthesis of precursors for the preparation of the meso-porphyrins. So, 3-*n*-pentadecylphenol, **1**, or 2-*tert*-butyl-5-*n*-pentadecylphenol, **2**, were treated with 1,2-dibromo ethane, under solvent-free reaction conditions, in the presence of anhydrous potassium hydroxide at 70 °C for 6 h to give in good yield **38** and **39**, respectively. In turn, **38** and **39** were then converted into **40** (R₁=H) and **41** (R₁= *tert*-butyl), respectively, by reaction with 4-hydroxybenzaldehyde, in the presence of anhydrous potassium carbonate in acetone under reflux.

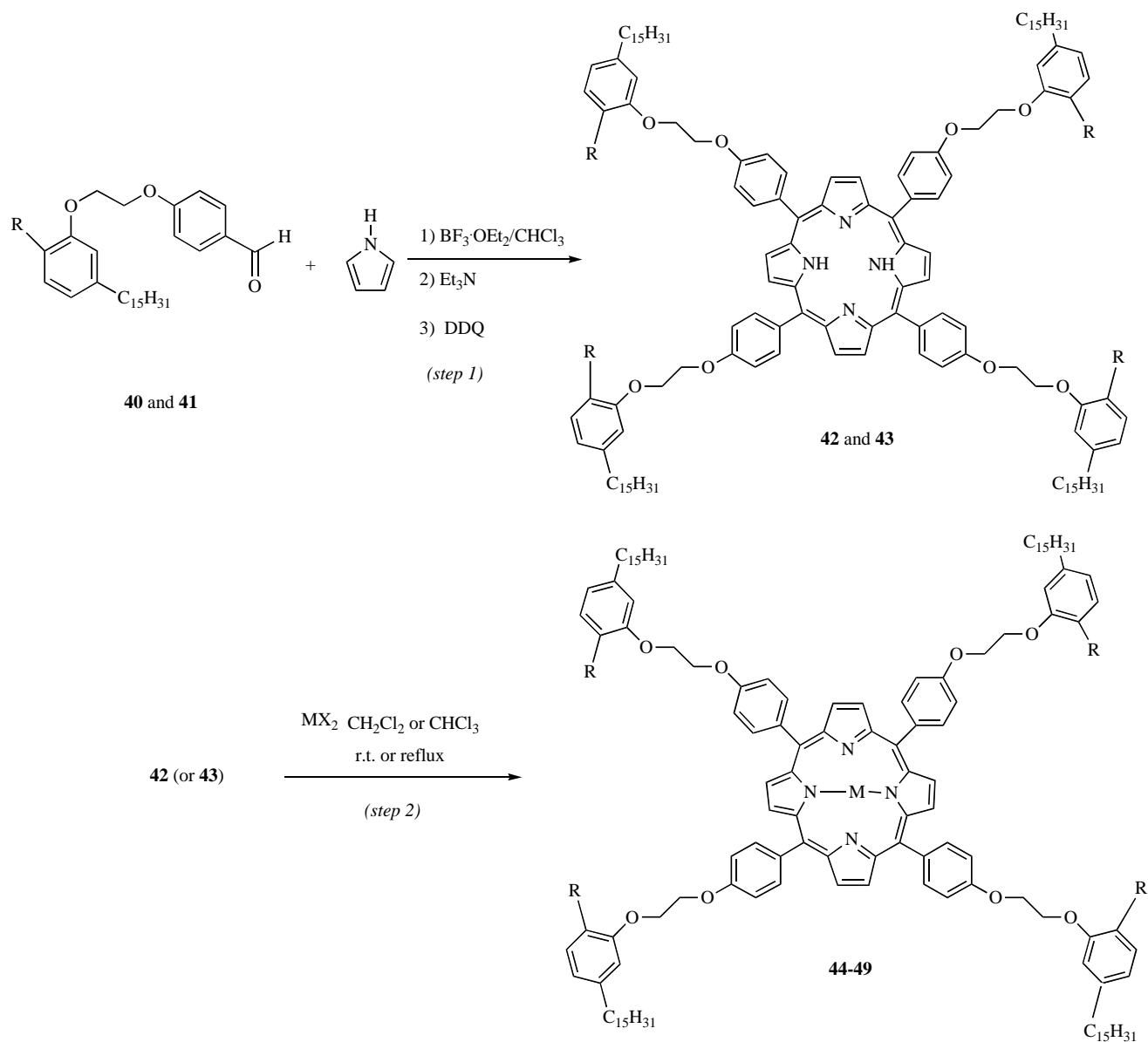
The corresponding meso-tetraarylporphyrins **42** and **43** were obtained by the reaction of **40** or **41**, with pyrrole, as reported in Scheme 11 (*step 1*). In respect to general procedures reported in the literature [16], the yields of meso-tetraarylporphyrins resulted relatively high. **42** and **43** were characterized by FT-IR, UV-vis, ¹H and ¹³C NMR, elemental analyses and LC-MS by using an Electrospray Ionization (ESI) interface. In particular, the ¹H NMR spectra of these compounds exhibited one typical singlet centered at 8.89 ppm (compound **42**) or at 8.91 ppm (compound **43**), being attributable to the eight protons at the β position of the pyrrole moiety, the aromatic protons in the range 8.20-6.80

ppm, the multiplet in the range 4.75-4.50 ppm for the O-CH₂-CH₂-O system, the aliphatic protons in the range 2.70-0.85 ppm and the NH protons as broad singlets centered at -2.73 and -2.70 ppm. The IR spectra of these compounds showed a weak band at 3300 cm⁻¹ characteristic for the NH vibration. As shown in Scheme 11 (*step 2*), the meso-tetraarylporphyrins **42** and **43** were used for the preparation of the corresponding metallo derivatives in nearly quantitative yield, by reactions with CuCl₂, Co(OAc)₂, and Zn(OAc)₂, respectively.

Due to the presence of the long alkyl side-chains, the meso-tetraarylporphyrins **42** and **43** exhibited a good solubility in organic solvents, being 100-300 times higher compared to the unsubstituted porphyrin, together with relatively low melting points. Furthermore, the metalloporphyrin complexes **45**, **47**, and **49** prepared from 2-*tert*-butyl-5-*n*-pentadecylphenol, **43**, showed melting points lower than those both of the corresponding free-base porphyrin **42** and the metalloporphyrin complex **44**, **46**, **48** obtained from 3-*n*-pentadecylphenol, **1** (see Table 3). Based on these results, it is evident that the substituents and the metals in the meso-tetraarylporphyrins **42** and **43** and their metal derivatives **44-49** influence intramolecular interactions and aggregation in the solid state.

meso-Tetra-Arylporphyrin- Cardanol Hybrids with Cardanol Bearing Unsaturated Chain

The new meso-tetraarylporphyrin **50** bearing cardanol and containing unsaturated chain and its metallo derivative was also synthesized and characterized. The unsaturation in the chain in the new hybrid gives different chemical and physicochemical properties from the saturated one. Also, the presence of double bonds on the side chains of cardanolic



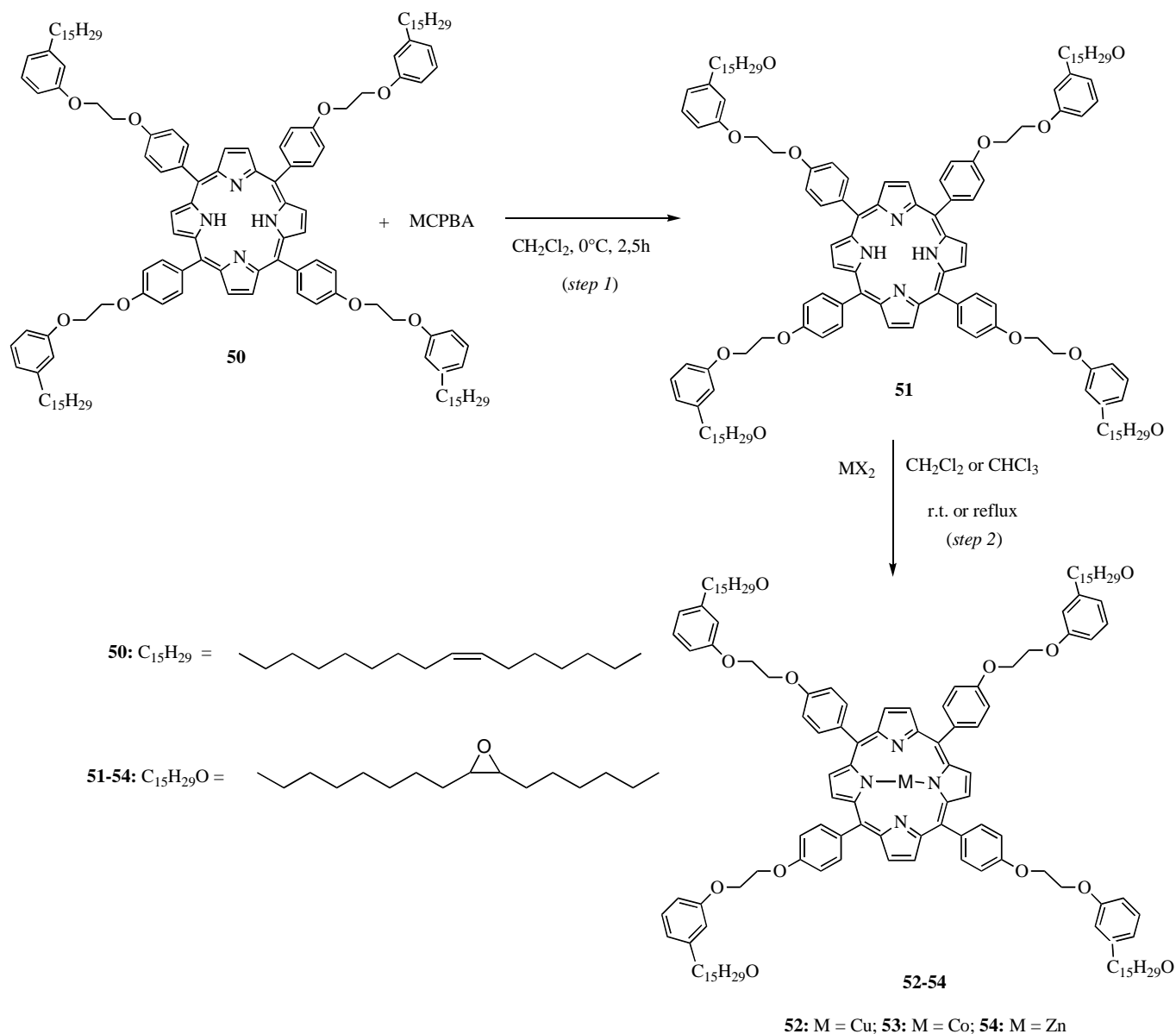
Scheme 11.

Table 3. Metal and Metal-Free Porphyrins 42-49

Compound	R	M	Yield (%)
42	H	(2H)	6
43	t-butyl	(2H)	5
44	H	Cu	95
45	t-butyl	Cu	95
46	H	Co	90
47	t-butyl	Co	90
48	H	Zn	90
49	t-butyl	Zn	90

moiety in the porphyrin molecule permits additional reactions such as the introduction of functional groups (for example bromine, oxirane). So, **50** was reacted with *m*-

chloroperbenzoic acid in dichloromethane at 0°C to give the epoxydized product **51** in nearly quantitative yields (Scheme 12, *step 1*) [17].



Scheme 12.

Compound **51** was characterized by FT-IR, MS, 1H and ^{13}C NMR analysis and all spectra were in agreement with the proposed structure; its 1H NMR spectrum showed the signals corresponding to the epoxy moiety ($\delta = 2.99$ - 3.01 ppm) and to the CH_2 -7 and CH_2 -10 of side chain (as a multiplet in the range 2.84-2.96 ppm); also ^{13}C NMR spectrum exhibited the signal typical of the oxiranic carbon atoms at $\delta = 58$ ppm.

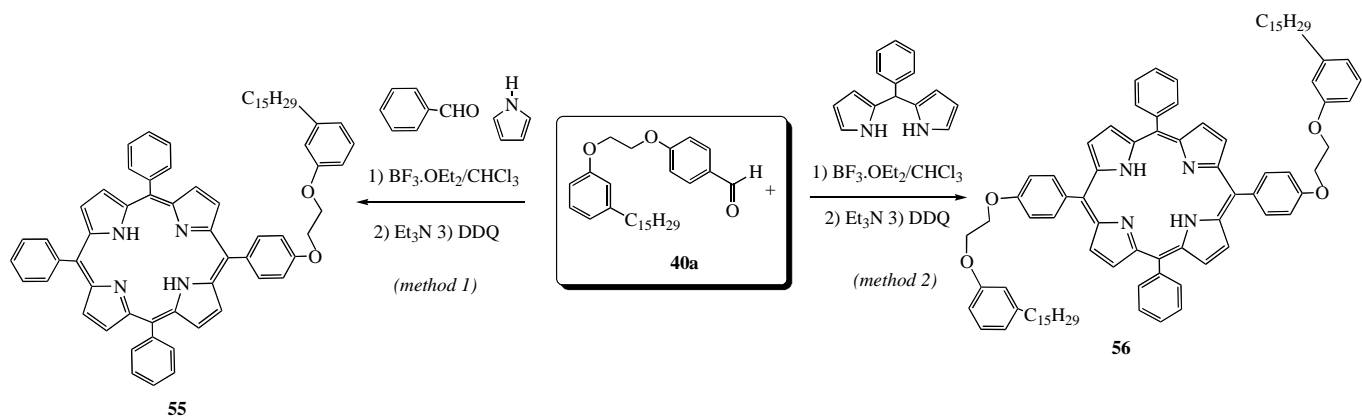
The ESI mass spectrometry was used for the determination of the molecular weight of the **51**. FT-IR spectrum of **51** also exhibited the absence of the peak at 3006 cm^{-1} corresponding to $=C-H$ stretching in vinyl system and the presence of a peak at 822 cm^{-1} due to the epoxy group.

Compound **51** was used in a successive metalation reaction with $CuCl_2$, $Co(OAc)_2$ and $Zn(OAc)_2$ for the preparation of the corresponding metallo derivatives **52-54**, in nearly quantitative yields (Scheme 12, step 2).

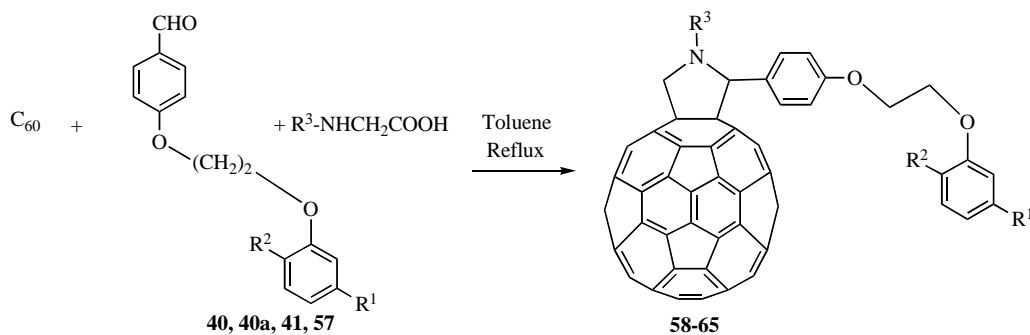
meso-AB₃ and Trans-A₂B₂ Porphyrin-Cardanol Hybrids

meso-AB₃ and trans-A₂B₂ porphyrin-cardanol derivatives bearing cardanol and containing unsaturated chain were also synthesized and characterized.

So, cardanol-based porphyrin 5,10,15-triphenyl-20-mono-[4-(2-(3-pentadec-8-enyl) phenoxy) ethoxy] phenyl porphyrin **55** and 5,15-diphenyl-10,20-di-[4-(2-(3-pentadec-8-enyl) phenoxy) ethoxy] phenyl porphyrin **56** were synthesized by acid-catalyzed condensation of 4-[2-(3-(pentadeca-8-enyl) phenoxy)-ethoxy]-benzaldehyde **40a** respectively by statistic reaction with pyrrole and benzaldehyde (Scheme 13, method 1) or meso-phenyldipyrrolo methane (Scheme 13, method 2). Methods 1-2, in accordance with the Lindsey procedure, were opportunely modified in order to improve the yields [18].

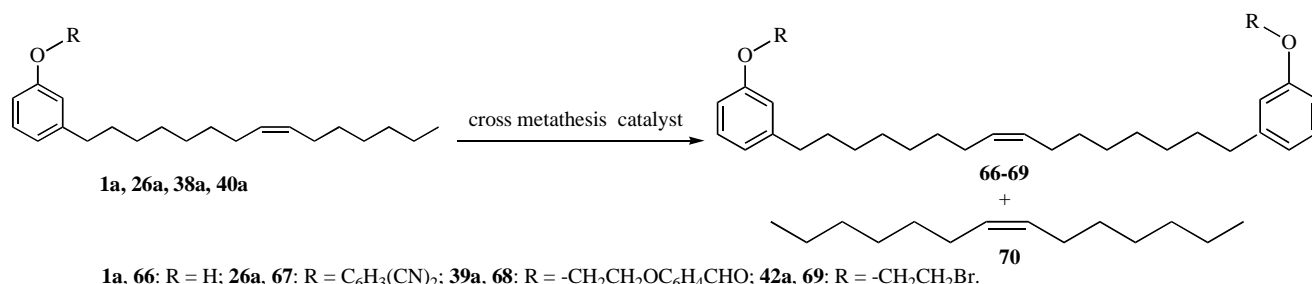


Scheme 13.



58: $R^1 = C_{15}H_{29}$, $R^2 = H$, $R^3 = Me$; 59: $R^1 = C_{15}H_{31}$, $R^2 = H$, $R^3 = Me$; 60: $R^1 = C_{15}H_{31}$, $R^2 = t-Bu$, $R^3 = Me$;
 61: $R^1 = C_{15}H_{31}$, $R^2 = t\text{-amyl}$, $R^3 = Me$; 62: $R^1 = C_{15}H_{31}$, $R^2 = H$, $R^3 = Ph$; 63: $R^1 = C_{15}H_{31}$, $R^2 = t-Bu$, $R^3 = Ph$;
 64: $R^1 = C_{15}H_{31}$, $R^2 = t\text{-amyl}$, $R^3 = Ph$; 65: $R^1 = C_{15}H_{29}O$, $R^2 = H$, $R^3 = Me$

Scheme 14.



Scheme 15.

Synthesis of Cardanol Fullerene Hybrids

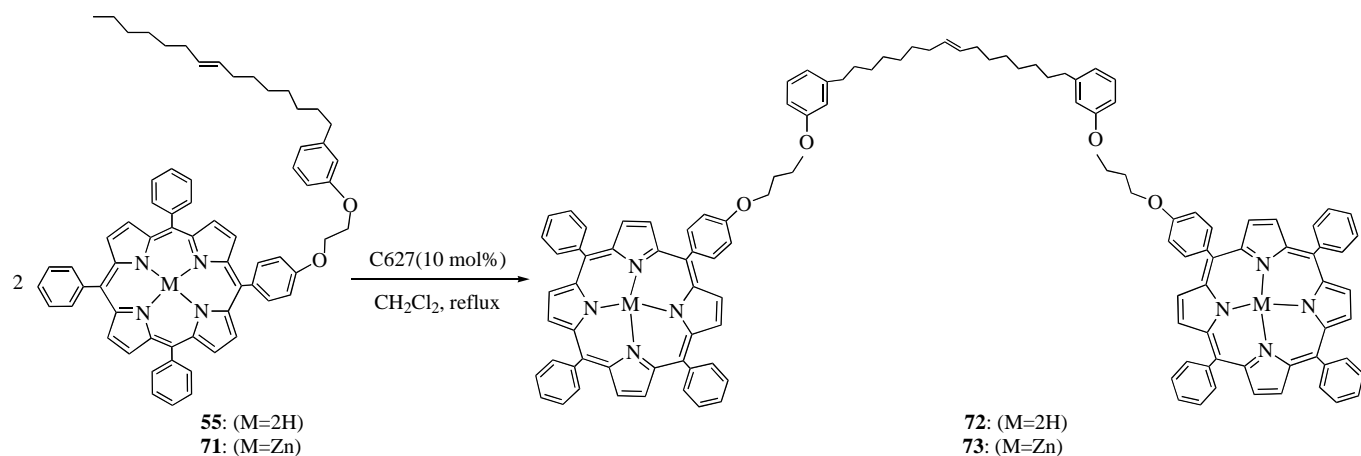
New cardanol based fulleropyrrolidines have also been synthesized and characterized, with cardanol containing both saturated or unsaturated chains using aldehydic precursors of cardanol [19]. Usually, as reported in the literature, the synthesis of the fulleropyrrolidines occurred via condensation of an amino acid (e.g. of *N*-methylglycine, *N*-phenylglycine) with an aldehydic compound and C_{60} through a typical 1,3-dipolar addition of azomethine ylides generated in situ [20]. So, as shown in Scheme 14, the syntheses of the fulleropyrrolidines 60-65 were performed through a cycloaddition to C_{60} of the azomethine ylide (resulting from the decarboxylation of *N*-methylglycine or *N*-phenylglycine in the presence of the aldehydic precursors of cardanol 40, 40a, 41 and 57) [21].

All the products were purified by chromatography and characterized by FT-IR, LC/MS, 1H and ^{13}C NMR analysis. In particular, the 1H -NMR spectra of 58-65 were in agreement with the proposed structures. For example, compound

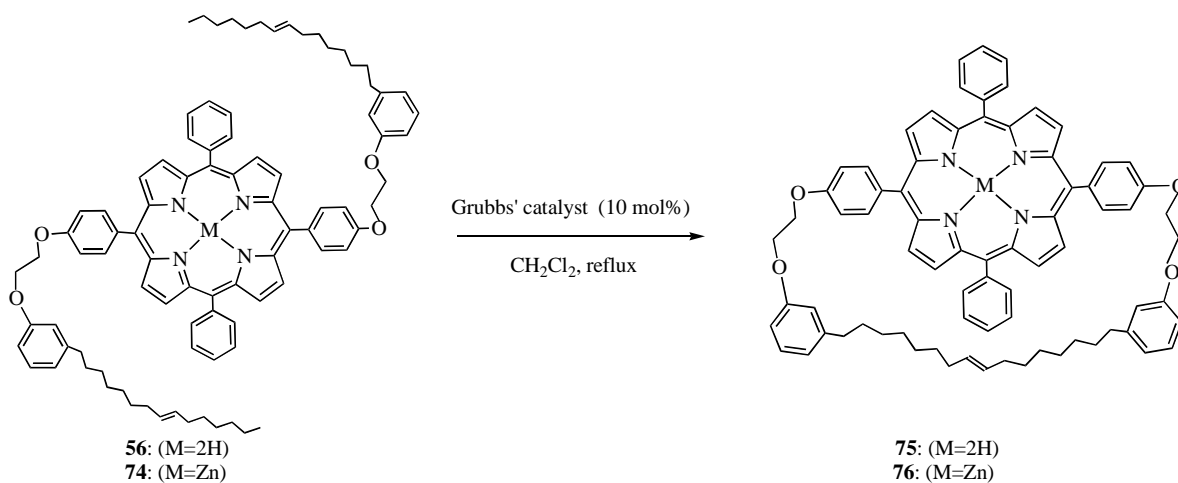
65 showed typical signals of the pyrrolidine (C_{60})-fullerene system: a singlet for H-2 at $\delta = 4.92$ ppm and the AB system for CH_2 -5, two doublets centered respectively at $\delta = 4.27$ ppm and $\delta = 5.00$ ppm with a geminal coupling $J_{AB} = 9.4$ Hz. All the analytical and spectral data obtained for 58-65 were consistent with the formulation of the compounds. Also, most of the compounds showed relatively low melting points and high solubility in the most common organic solvents ascribable certainly to the presence of the long alkyl chains. It is well known that similar fulleropyrrolidine derivatives without adequate substituents are insoluble in organic solvents.

Synthesis of bis-Cardanol Compounds via Metathesis Reaction

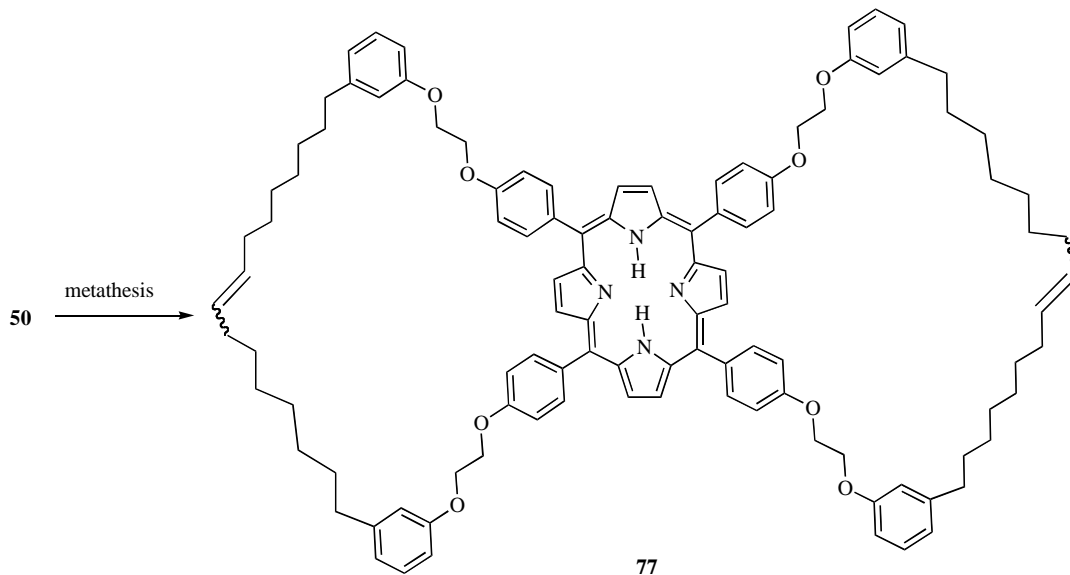
It is well known from the literature that olefin metathesis reaction, by using Grubbs' catalysts, has become a very important way to obtain new olefins by carbon-carbon formation.



Scheme 16.



Scheme 17.



Scheme 18.

For instance, the use of Grubbs ruthenium-based catalyst enables vegetable oils to be efficiently processed into compounds that can serve as renewable sources of petroleum product alternatives as well as fine chemicals, vitamins and nutraceuticals. As shown in the Scheme 15, the reaction of

cross metathesis has been applied to prepare new bis-cardanol based compounds [22].

Quite interesting were also some results obtained in the case of metathesis, which involved the double bonds of two unsymmetrical cardanol derivative such as 57 and 71,

(Scheme 16) in which 72 and 73 were the main compounds [23] and also in the case of ring-closing metathesis (RCM) in which two double bonds contained in the same molecule, such as the case of porphyrin 56 and its zinc complex 74 are involved (Scheme 17) and porphyrins 75 and 76 were the main compounds. Four double bonds contained in the same molecule such as in the case of porphyrin 50 double ring-closing metathesis porphyrin 77 were obtained as the main compounds (Scheme 18) [17, 22].

In conclusion, this review shows how it is possible to use waste, such as cardanol, as a starting material for the preparation of new fine chemicals and new hybrid materials useful to develop new composites and functional materials.

A variety of cardanol compounds such as lactones, bis-lactones, nitro, amino, nitroso, hybrids with porphyrin, phthalocyanine, fullerene and other macrocycles can be prepared and used as building blocks for new materials.

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