Renewable Feedstocks in Chemistry

The United Nations Conference on Environment and Development (UNCED), held in Rio de Janeiro in 1992, provided the fundamental principles (Rio Declaration) and the program of action (Agenda 21) for achieving sustainable development[1]. Agenda 21 addresses the pressing problems of today and also aims at preparing the world for the challenges of this century. It was adopted by more than 170 governments.

Sustainable chemistry is understood as the contribution of chemistry to the implementation of the Rio Declaration and Agenda 21 including its on-going advancements, such as the Johannesburg Declaration of the World Summit of Sustainable Development that was held in 2002[2,3]. Principle 1 of the Rio declaration proclaims: that human beings are at the center of concerns for sustainable development. (http://www.un.org/esa/sustdev/agenda21.htm).

Agenda 21 pointed out – interestingly in chapter 4 *Changing consumption patterns*:

“Reducing the amount of energy and materials used per unit in the production of goods and services can contribute both to the alleviation of environmental stress and to greater economic and industrial productivity and competitiveness.”

Analysis of the production output of the US chemical industry from 1974 - 1997 shows, however, that the energy consumption per unit of emission declined by more than 39% between 1974 to 1988, but that since then it has stagnated, while the total energy consumption from 1974 to 1997 has risen, as a result of the continuous growth of the chemical production, by 80% [4,5]. This leads us to the conclusion that the relatively low-cost, high-return energy investments have already been undertaken. Further gain will require more dramatic changes in process design and in innovative solutions yet to be provided by research and development.

The principles of production and product-integrated environmental protection are increasingly accepted and implemented by numerous enterprises of the chemical industry [6-8]. Basic concepts for an environment-oriented design of chemical products and processes have been developed [9,10]. “Green Chemistry” was proposed as an orientation for chemical industry as well as applied and basic research in chemistry[11].

The basic knowledge of sustainability in chemistry has to be implied already in the education of chemists, chemical engineers and laboratory assistants. Employees in chemical companies must be able to evaluate reactions, processes and techniques with regard to their contribution to sustainable development. In search for new methods for a sustainable chemistry renewable raw materials should become more important[12,13)].

Most products obtained from renewable raw materials are at present not competitive with the products of petrochemistry, a circumstance that will change rapidly when oil resources diminish and the oil price rises. Therefore, it is high time to expand basic research to achieve substitution processes and products. A signal is given by the Biomass Research and Development Act of 2000 on the basis of the recommendations of the National Research Council of the United States on the estimated development of renewable feedstocks up until 2090[14,15)]. In 2030, 25% of the production of organic chemical products is expected to come from renewable feedstocks (www.nas.edu/nrd).

The encouragement of environmentally sound renewable natural resources and their sustainable use is an important aim of Agenda 21. The biomass cycle shows the advantages of renewable resources (Fig. 1). Photosynthesis produces biomass, which delivers renewable feedstocks such as vegetable oil, starch and others. These are processed to give the renewable base chemicals such as fatty acids, glycerol, glucose etc. Further processing results in useful products that can be biologically degraded after utilization to give again carbon dioxide and water. This is the ideal type of biomass cycle producing no additional carbon dioxide. Of course, some process energy is necessary. However, the chemical energy accumulated in the product comes completely from the sun.

In contrast, petrochemicals are derived completely from fossil feedstocks. Most importantly, when renewables are used as base chemicals for organic synthesis, natures synthetic input is used to obtain in one or only very few chemical reaction steps those complex molecules which petrochemically are only accessible in multistep reaction sequences, thus reducing the process energy as well.

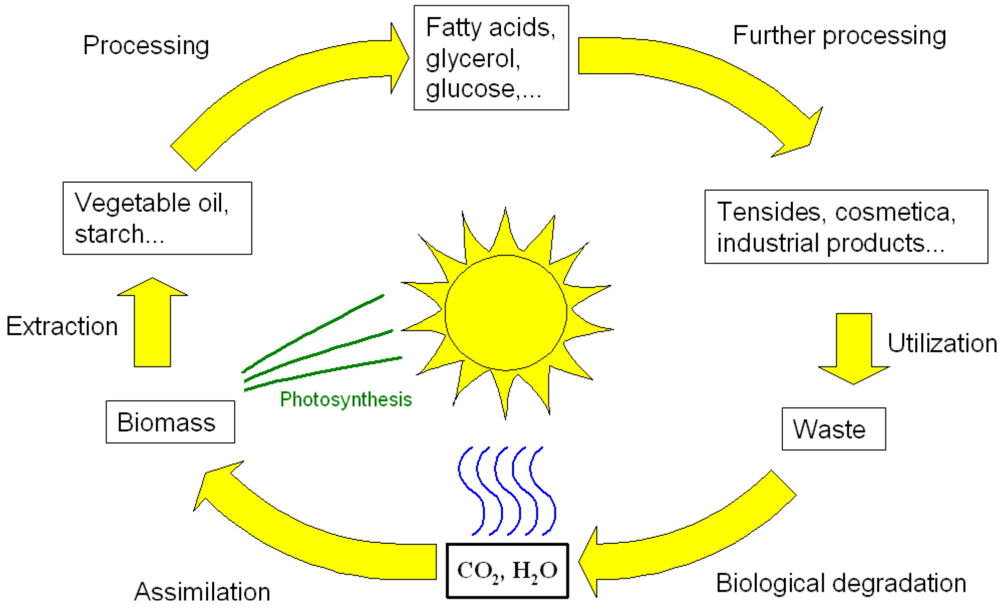


Fig. 1

At present, the share of renewable raw materials in the feedstock consumption of the chemical industry in the USA and in Germany runs to approximately 5 and 8%, respectively. It is assumed that this percentage will increase notably. In the long run, renewables are the only workable solution, and their processing, inter alia, catalytic will make it possible to replace oil and coal as basic feedstocks. Approximately 51% of the renewable raw materials used at present in Germany are fats and oils. Carbohydrates constitute the second largest portion at 43%, while a further 6% is made up of other renewables such as proteins and lignins[3)].

(http://www.fnr.de/de/index.htm).

In contrast to fossil raw materials, renewables are more or less highly oxidized. Therefore, it is clear that for base chemicals that are obtained petrochemically by nonsustainable oxidation reactions, alternatives need to be developed from renewables. Many highly oxidized industrial chemical products based on starch are already available. Further developments are on the way. Alkyl polyglucosides are a good example; they are produced as skin-compatible, environmental benign tensides on a scale of 70.000 t/year[16)].

Furthermore starch is used in the production of binders and adhesives: as reactive component in the production of synthetic polymers, as raw material for biotechnological processes as well as in the area of cosmetics and pharmacenticals[17)]. D-Glucose which is mainly obtained from starch is of special interest. In follow-up reactions it is transformed into building blocks, precursors with industrial applications and specialty chemicals[18)].

In a recently published paper the transformation of carbohydrates to give unsaturated O- and N-heterocycles such as furans, pyrans, pyrazoles, imidazoles and pyrazines is described[19)]. Interesting industrial applications in different areas should be expected for these highly functionalized compounds.

Native oils which are obtained in Europe mainly from rapeseed, sun flower and linseed (fig. 2) are discussed in the following in more detail because they are the most important renewable raw materials together with soybean and flax (fig. 3).

Rape

sun flower

Flax

Fig. 2: Native oil plants

Fig. 3: Oil seeds

Native oils and fats consist of triglyerides (fig. 4) which are obtained by extraction . The fatty acids of the triglycerides are more or less unsaturated. In general triglycerides with a high amount of unsaturated fatty acids are liquid. Up to now nearly all reactions of the oleochemical industry have been carried out at the fatty acid carboxy group, while less than 10% have involved transformations of the alkyl chain [20].

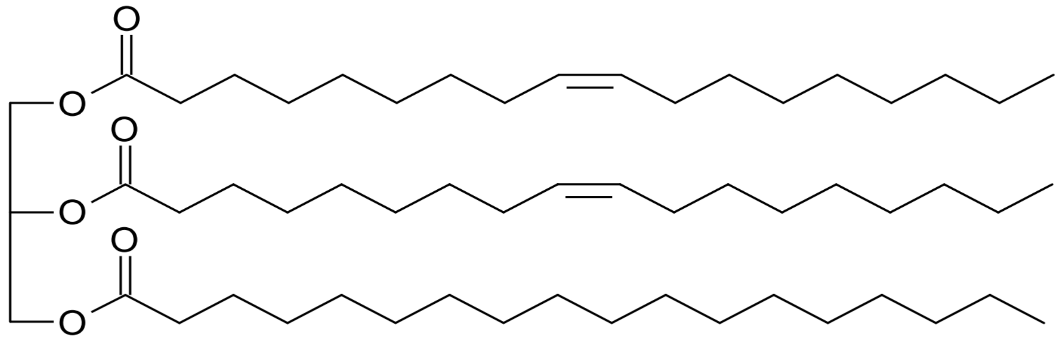


Fig. 4: Example of a triglyceride

The most important oleochemical transformations of the triglycerides are the saponification to give free fatty acids and the transesterification with methanol to give the respective fatty acid methyl esters, which can be hydrogenated to the respective fatty alcohols (fig. 5). Further important base chemicals of the oleochemistry are fatty amines, which are obtained from triglycerides by treatment with ammonia followed by hydrogenation.

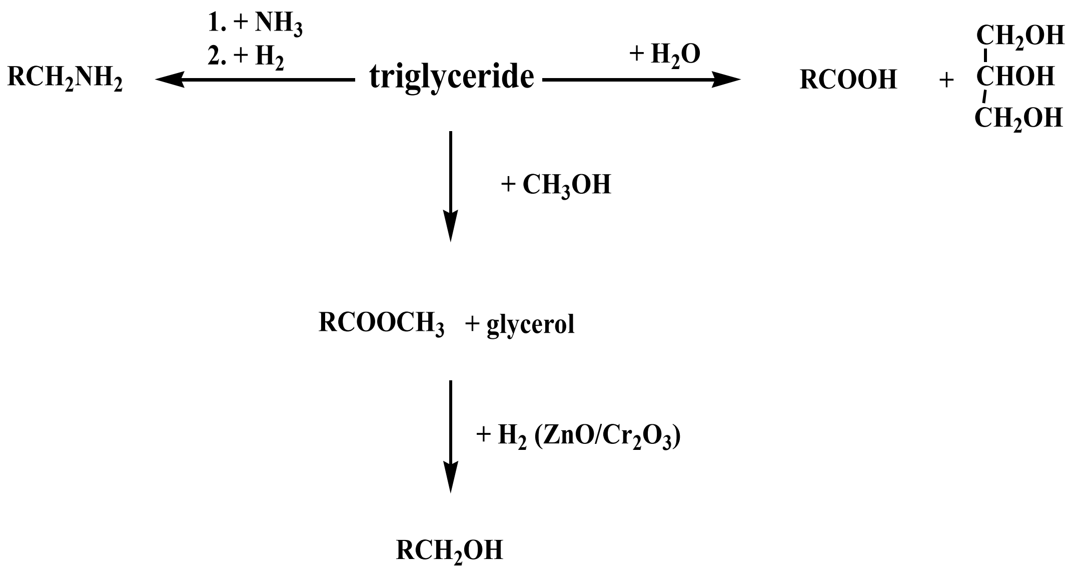


Fig. 5: Oleochemical transformations of triglycerides

When renewables are used as base chemicals for chemical products, Nature's synthetic input is optimally used and high creation of value is obtained. The scheme shows the most important applications for fats and oils at present (fig. 6).

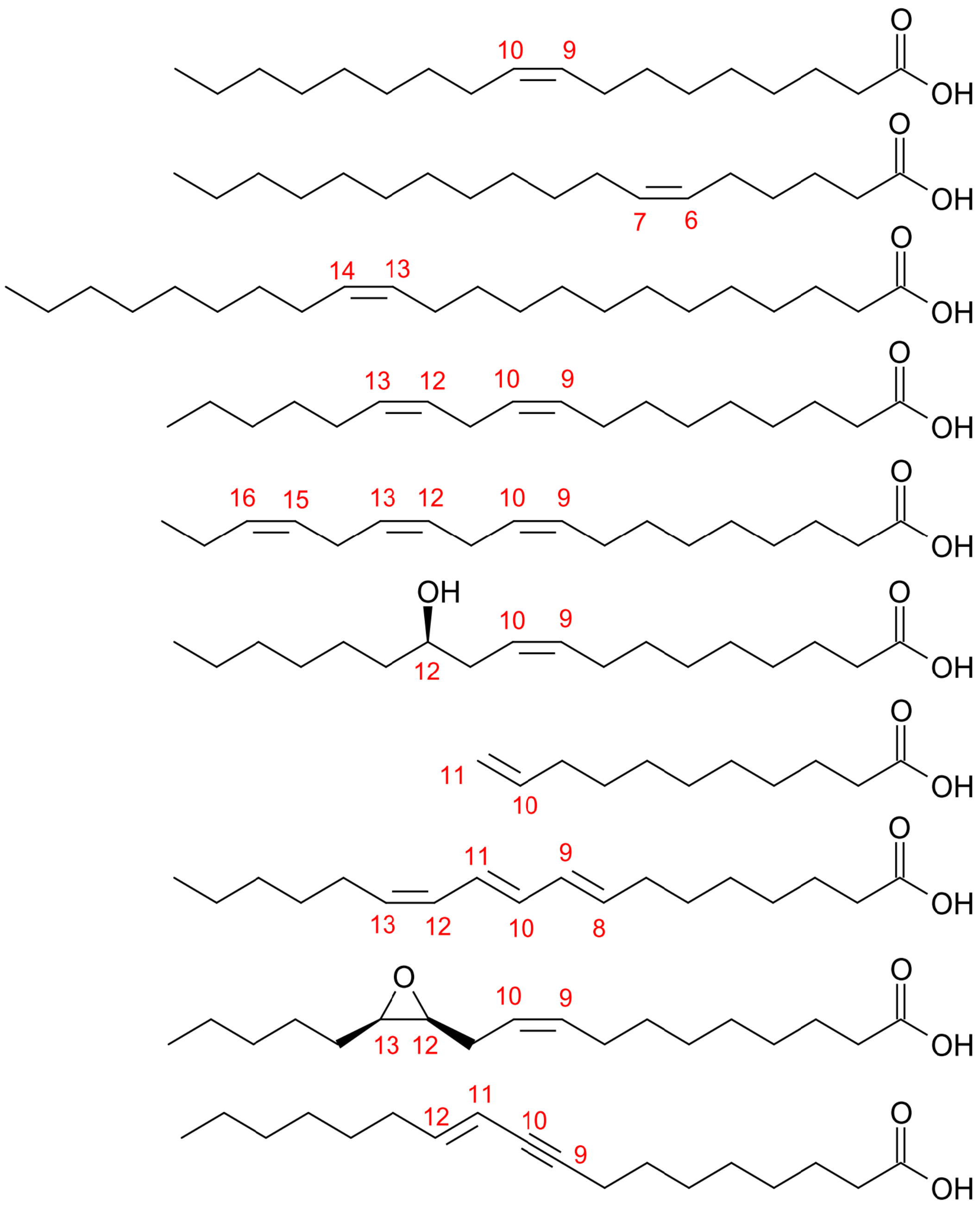
Primary product		Application
Fatty acids / -derivatives	⇒	plastics, metal soaps, detergents and cleaning agents, soaps, cosmetics, alkyd resins, paints, textile-, leather-, paper industry, rubber, lubricants
Fatty acid methyl esters	⇒	cosmetics, detergents and cleaning agents
Glycerol / -derivatives	⇒	cosmetics, tooth paste, pharmaceuticals, food, coatings, plastics, resins, tobacco, explosives, cellulose processing
Fatty alcohols / -derivatives	⇒	detergents and cleaning agents, cosmetics, textile-, leather-, paper industry, mineral oil additives
Fatty amines / -derivatives	⇒	softeners, mining, road work, biocides, textile-, fiber industry, mineral oil additives

Fig. 6: Applications of oils and fats

An important question is whether a product that was produced on the basis of renewable feedstocks is more sustainable than a comparable product which was produced using petrochemical feedstocks. Life-cycle analysis is the scientific instrument which is used for the assessment of the sustainability of a product. It analyzes a product from the gradle to the grave including extraction and processing of raw materials, production, distribution and transport as well as application, consumption and waste management; it analyzes ecological effects and evaluates the turnover of material and energy and the resulting environmental pollution along the path of life.

The "Institut für Technische Chemie und Umweltchemie" of the University of Jena carried out a life-cycle assessment for a new uv-curable coating which was produced from linseed oil without using any organic solvent. In comparison to petrochemically derived coatings the new product showed remarkable advantages of all environmental-relevant criteria as accumulated input of energy, CO_2- and NO_2-emissions as well as consumption of resource.

In rapeseed, sun flower and linseed oil more than 90% of the fatty acids have one or more C,C-double bonds. The olefin-chemistry with unsaturated fatty compounds should give interesting perspectives for the use of native oils.[21,22] Numerous addition reactions have been carried out especially to the C,C-double bond of oleic acid (**1**), petroselinic acid (**2**), erucic acid (**3**), linoleic acid (**4**), and ricinoleic acid (**6**) as well as 10-undecenoic acid (**7**), which is obtained by pyrolysis of ricinoleic acid. Interesting products were also obtained with unusual fatty acids such as linolenic acid (**5**), calendic acid (**8**), vernolic acid (**9**) and santalbic acid (**10**) (fig. 7).



1 2 3 4 5 6 7 8 9 10

Fig. 7: Unsaturated fatty acids

Commercially available epoxidized linseed and soybean oil which are obtained by the Prileschajew reaction are used as substances in interesting follow-up reactions (fig. 8).

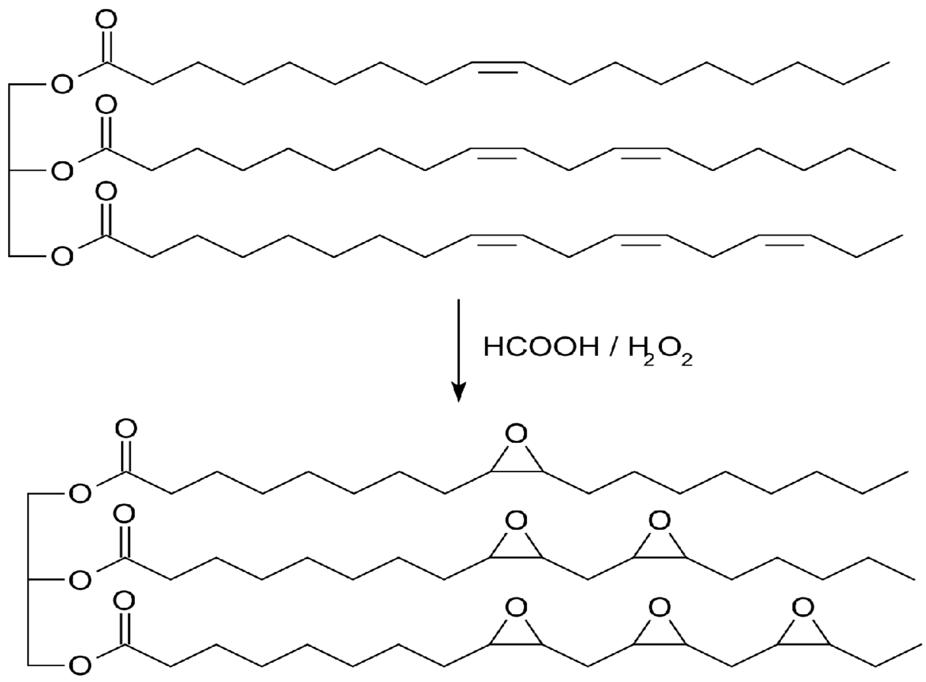


Fig. 8: Epoxidation of plant oils

At present epoxidized oils are used mainly as PVC stabilizers. New applications have been opened by the possibility of photochemically initiated cationic curing. There are also some natural occurring unsaturated vegetable oil epoxides such as vernolic oil which is contained with 40% in the seed of *Vernonia galamensis*. In the presence of a heterogeneous, basic catalyst the oil can be transesterified in a simple reaction with methanol to give methyl vernolate with retention of the oxiran ring. Vernolic acid (fig. 7: 9) is an enantiomerically pure compound of the natural chiral pool and can be used for interesting syntheses of optical active compounds.

Furthermore radical C,C-bond forming addition reactions are of great attractivity especially those which can be performed without organic solvents.

In a copper initiated reaction 2-halocarboxylic acid esters are added to unsaturated fatty compounds such as methyl oleate (fig. 9). The reaction procedure is very simple: the unsaturated fatty compound, the 2-halocarboxylate, and commercial copper powder are mixed without further pretreatment and heated at 100–130 °C under inert atmosphere. The product, a γ-lactone, is obtained in 51% yield.

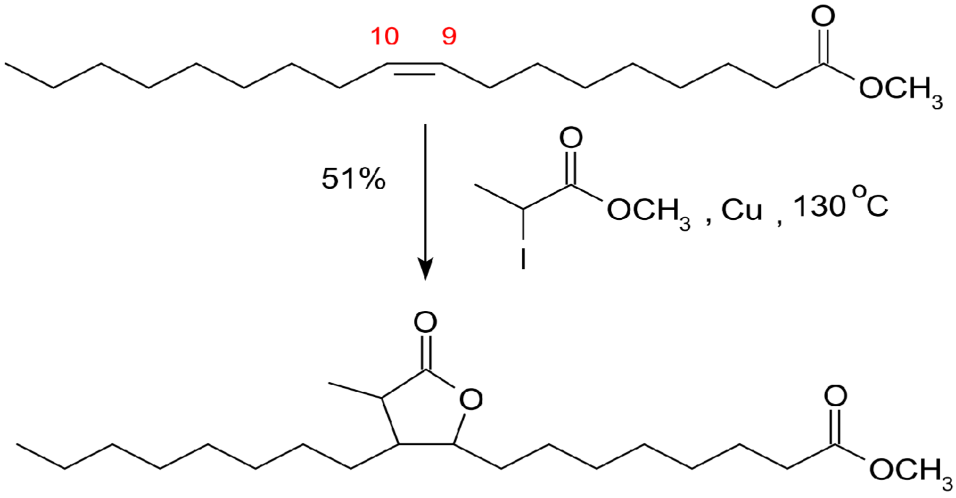


Fig. 9: Copper initiated addition of methyl 2-propionate to methyl oleate

In analogy perfluoroalkyl iodides react with unsaturated fatty compounds (fig. 10) to give perfluoroalkylated products which have interesting surfactant properties.

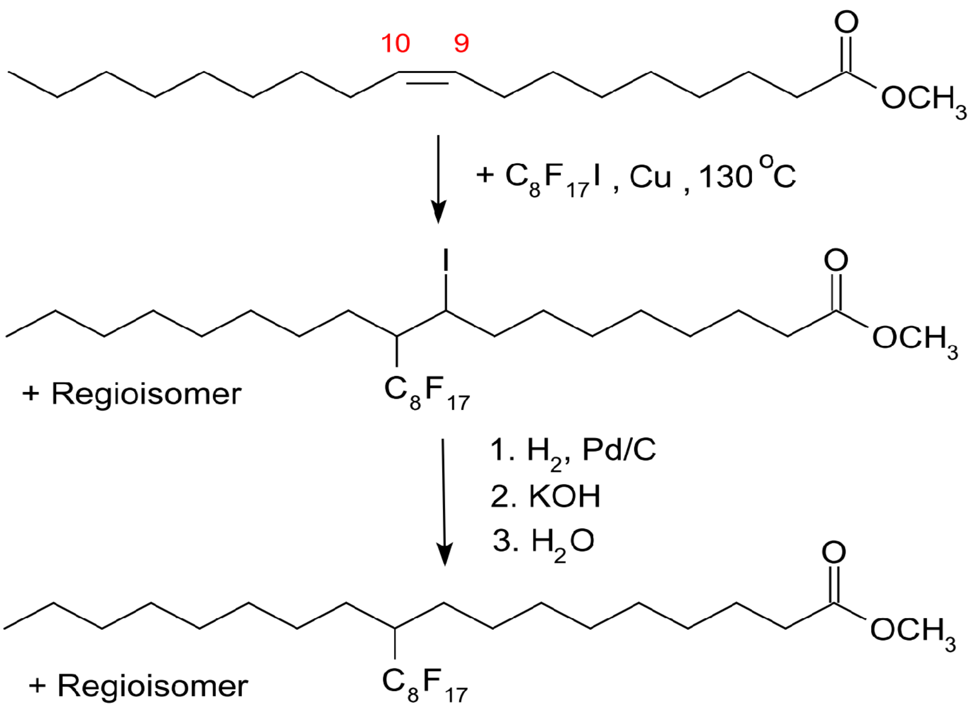


Fig. 10: Copper initiated addition of perfluorooctyl iodide to methyl oleate

Among thermal reactions of unsaturated fatty compounds the ene addition of maleic acid anhydride especially to 10-undecenoic acid methyl ester is of interest (fig. 11). The reaction is carried out at 190 °C and takes place regioselectively at C-11 to give the product as mixture of the (E)- and (Z)-stereoisomers.

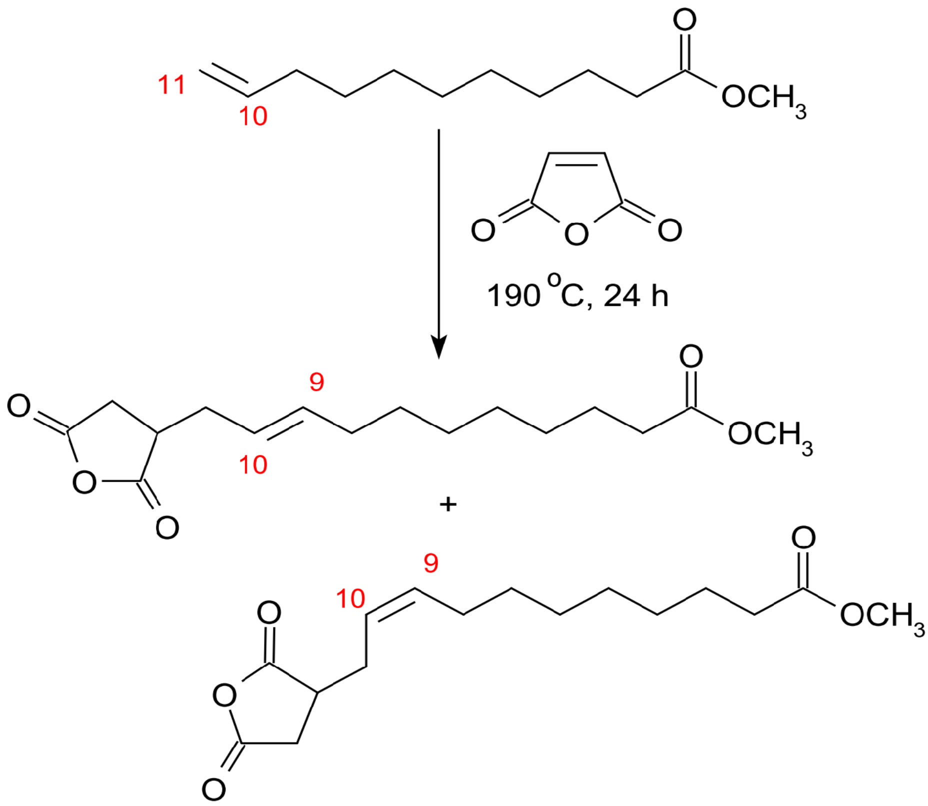


Fig. 11: Thermal ene reaction of methyl 10-undecenoate and maleic acid anhydride

At 100 °C the thermal addition of maleic acid anhydride to calendic acid methyl ester – calendic acid is a polyene fatty acid with three conjugated C,C-double bonds and is the main fatty acid with an amount of 55 – 60% in the seed oil of *Calendula officinalis* – takes place by formation of a Diels-Alder adduct (fig. 12).

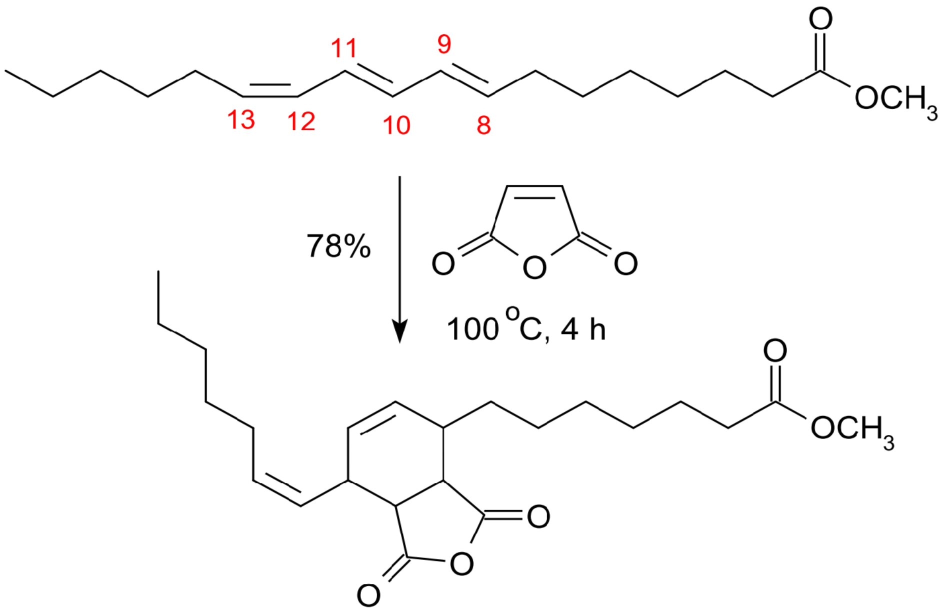


Fig. 12: Diels-Alder reaction of calendic acid methyl ester and maleic acid anhydride

The high regio- and stereoselectivity of the *endo*-Diels-Alder addition to positions C8 and C11 is shown by the X-ray structure analysis (fig. 13).

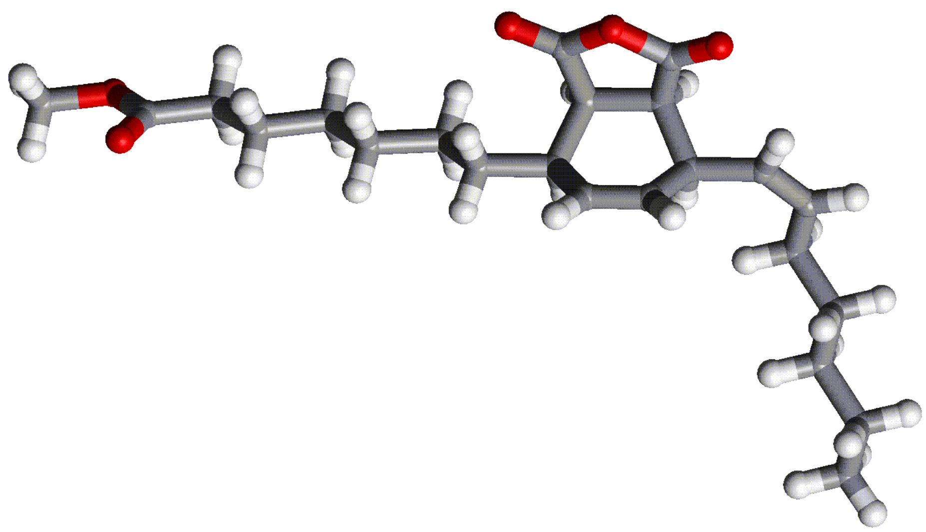


Fig. 13: X-ray structure analysis of the Diels-Alder adduct of calendic acid methyl ester and maleic acid anhydride

Lewis acid induced cationic addition reactions to unsaturated fatty compounds give new functionalized products, too. In the presence of $AlCl_3$ unsaturated fatty acid methyl esters give on reactions with aldehydes alkyl substituted 4-chlorotetrahydropyrans. The respective reaction of methyl oleate and paraformaldehyde affords a 3,5-dialkyl substituted 4-chlorotetrahydropyran derivative which is obtained as a mixture of regio- and diastereomers (yield: 86%). The reaction shows a considerable diastereoselectivity – the ratio of **[1]:[2]** is 3:1 (fig. 14).

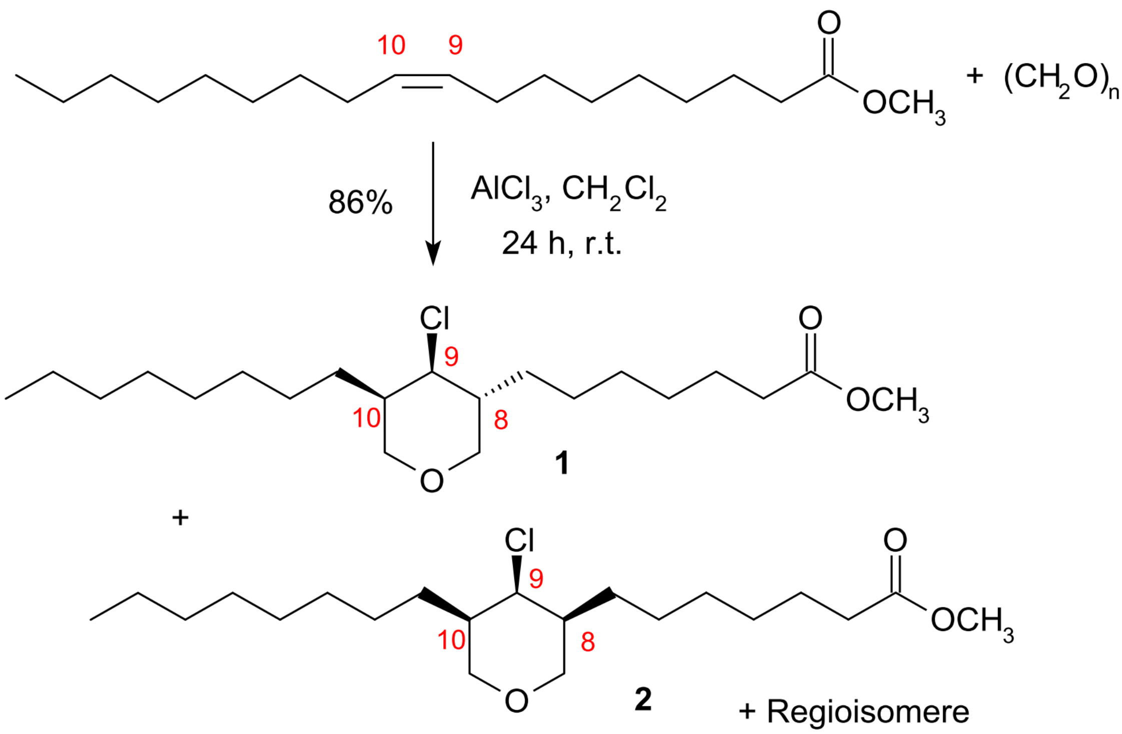


Fig. 14: Addition of paraformaldehyde to methyl oleate in the presence of $AlCl_3$
methyl oleate : paraformaldehyde : $AlCl_3$ = 2 : 4 : 1 => [1] : [2] = 3 : 1

The Ritter reaction is an example for a reaction that takes place by formation of a new carbon-nitrogen bond. The reaction of methyl oleate and acetonitrile in the presence of tin-IV-chloride and water yields the carboxylic acid amide acetamidostearic acid methyl ester (fig. 15). The Lewis acid tin-IV-chloride partially causes **isomerization** of the C,C-double bond, however, the main fraction of the product is obtained as a regioisomeric mixture of 9- end 10-acetamidostearic acid methyl ester. The 7-, 8-, 11- and 12-isomers are formed in small amounts.

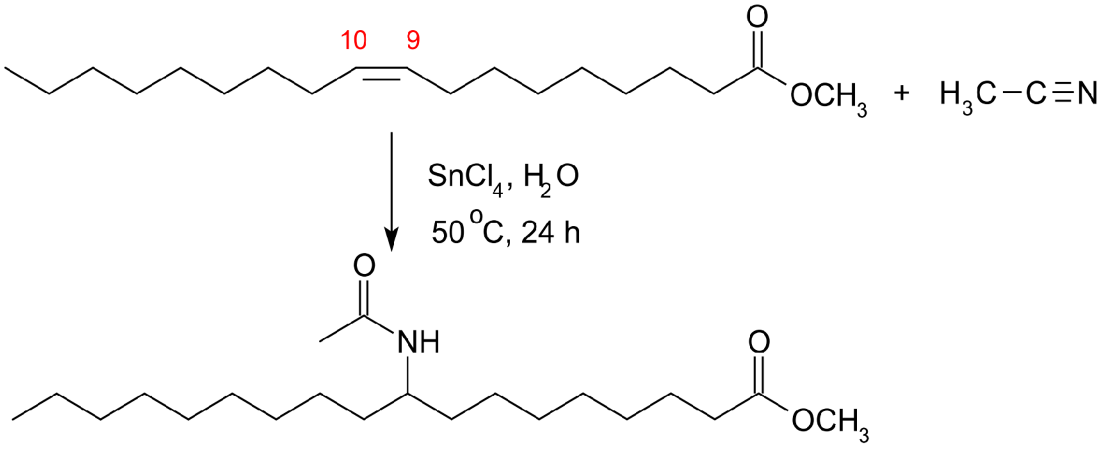


Fig. 15: $SnCl_4$-induced Ritter reaction of methyl oleate and acetonitrile

The $SnCl_4$-induced addition of acrylonitrile to high oleic rapeseed oil gives a highly functionalized oil in 70% yield (fig. 16). This product should be of interest for polymerization reactions and for the production of coatings.

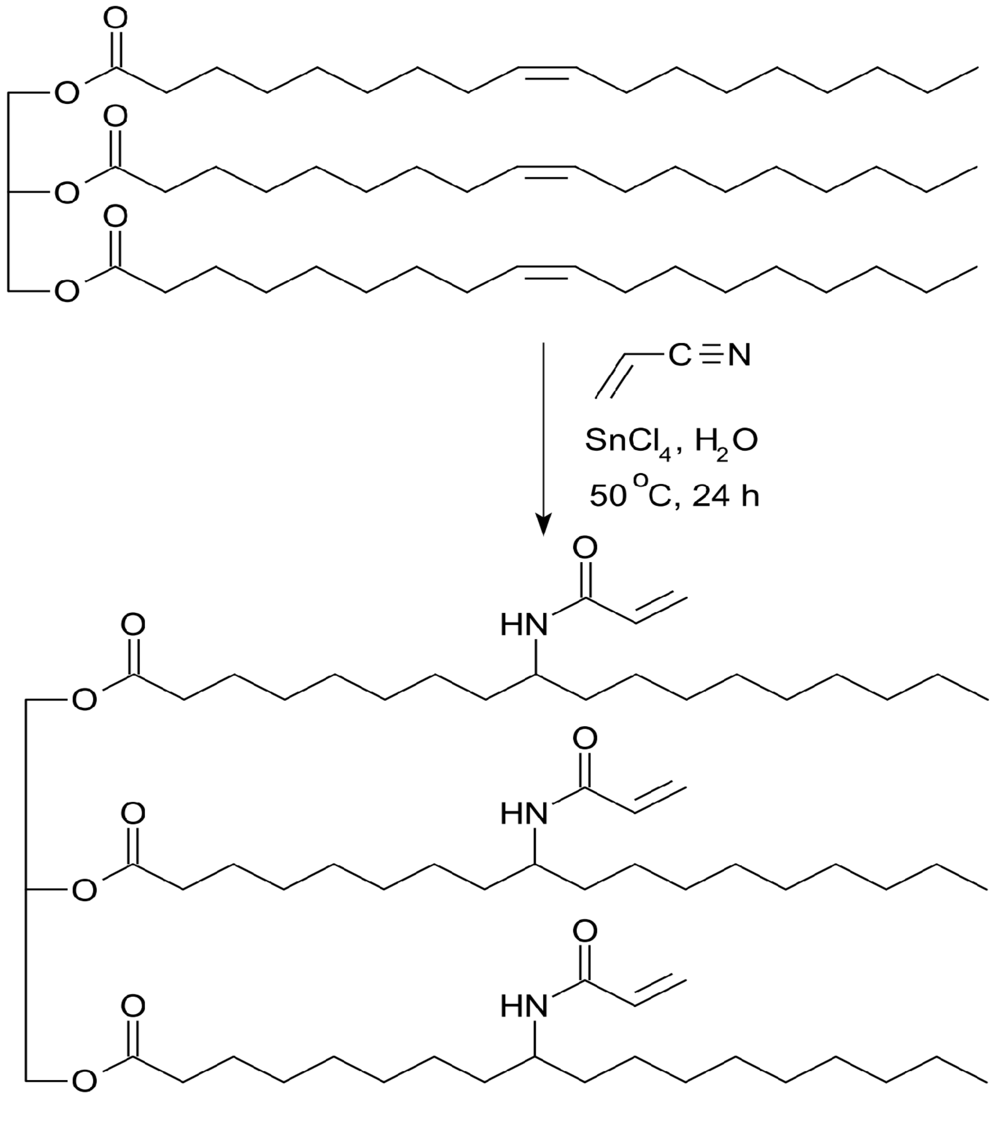


Fig. 16: $SnCl_4$-induced addition of acrylonitrile to high oleic rapeseed oil

The increasing substitution of petrochemical feedstocks by renewable raw materials in the chemical industry is a great challenge for chemists. However, numerous synthetic problems have to be solved and solutions must be found in the near future. Chemists, biotechnologists, and plant breeders are all challenged to continue development of the advances made in recent years and thus prepare the way for oils and fats to be increasingly used as renewable raw materials in the chemical industry.

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