OXIDATION AND OZONOLYSIS

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Middle chain linear molecules with identical or different primary functionnal groups at each end of the chain, are wanted for numerous utilizations (for example for high performance lubricants, for synthetic polymers, for plasticizers).

For that reason, the conversion of natural fatty acids into $\alpha \omega$ difunctionnal molecules with a shorter carbon chain is one of the most interesting features of chemurgy of fats, all the more the other part of the fatty chain is a primary monofunctionnal compound, which has also numerous potential uses.

That conversion which implicates the cleavage of a carboncarbon bond, must be as specific as possible, so much the more the users of difunctionnal molecules require high purity products and, often, above all, molecules of only one chain lenght, free of homologues.

Oxidation is always necessary to break a carbon-carbon bond, except for ricinoleic chain, whose homoallylic structure induces particular and highly specific reactions. A double bond is more easily and more specifically cleaved than a single one. Consequently unsaturated acids are exclusively used as substrates.

SUBSTRATES

Concerning the nature of substrates, two attitudes are possible; both have been taken up in laboratory and pilot plant studies as wellas in industrial realizations. One can either first isolate a monoenic fatty acid in a state of purity as high as possible, and then submit it to the cleavage reaction, or use raw material the total fatty acids of an unsaturated oil with a low content of saturated acids. In the first case if the quantity of cleavage reagents used is limited and the monofunctionnal compo·

und formed well defined, the obtention of a pure monoenic acid is expensive. In the second case the raw material is nearly costless, but as all double bonds are indifferently oxidized, the quantity of cleavage reagent increases with unsaturation, and in additioin the reaction mixture is very complicated; it contains indeed both difunctionnal fragments coming from the cleavage of two consecutive double bonds of the same chain, and monofunctionnal fragments of various chain length according to the position of the last double bond in polyunsaturated fatty acids.

CHEMICAL OXIDATION

Formerly chemical oxidants were used as cleavage reagents; patents litterature proposes for example oxidation of oleic acid, or more exactly of oleine, with either partially diluted sulfochromic acid [2] or nitric acid to which various catalysts are added [1].

Chemical oxidants are expensive, they induce, through side reactions, the formation of impurities which are often difficult to eliminate, and above all they are not sufficiently specific, since the expected difunctionnal compounds are often, if not always, contaminated by shorter chain homologues with one or even two carbons less.

OZONOLYSIS

For nearly twenty five years, chemical oxidation has been supplanted by ozonolysis which is less expensive, more specific and also more versatile.

Ozonolysis is the result of two consecutive, but independant steps. The first, which corresponds to the action of ozone, the trimer of oxygen produced by passing this gas through an electric discharge, is known as ozonation, and leads to the formation of the so-called ozonides. Consequently to the high viscosity of faty ozonides, it is necessary to dissolve or dilute the substrate in a convenient medium. The second step is the decomposition of ozonides, leading to the formation of two fragments of lower molecular weight. If decomposition occurs spontaneously, one of the formed fragments bears an aldehydic group, the other a carboxylic function. When, as it is the case in monoenic fatty acids, the double bond is in the middle of the carbon chain and therefore free from orientation effects, both possible fragments bear indifferently each function. If oxidation phenomena are made possible during decomposition (oxidative ozonolysis), only acids are formed: but on the contrary, in reductive conditions (reductive ozonolysis), only aldehydes appear.

The possibility of generating more or less oxidated functions is not

the only feature of ozonolysis versatility. An other is the possibility to use as substrate not only faty acids, but also fatty derivativese like esters, amides, nitriles, the functionnal group of which is not oxidable by the mixture oxygen/ozone [6].

OZONATION

The actually proposed mechanism for ozonides formation is the following. Ozone adds on to double bounded carbons giving a very unstable cyclic structure which spontaneously breaks into two fragments, each of them bearing at its end a zwitterion; one of these immediately changes into an aldehydic function, the other is more stable and has the possibility to remain unchanged during a short period of time.

In the case of monoenic fatty acids, for the reasons formerly stated, each fragment is indifferently an aldehydic or a zwitterion one. Ozonides result from recombinations of an aldehydic fragment and a zwitterion one. Contrarely to what was initially thought, no solvent cage effect occurs, and fragment coming from non indentic precursors may combine with one another [8].
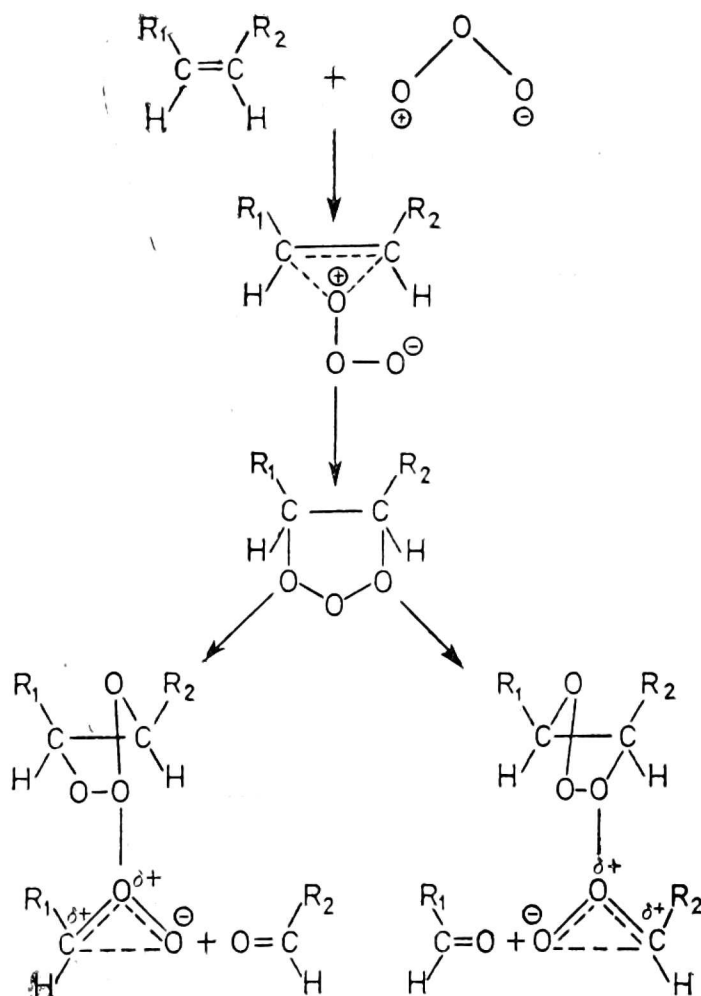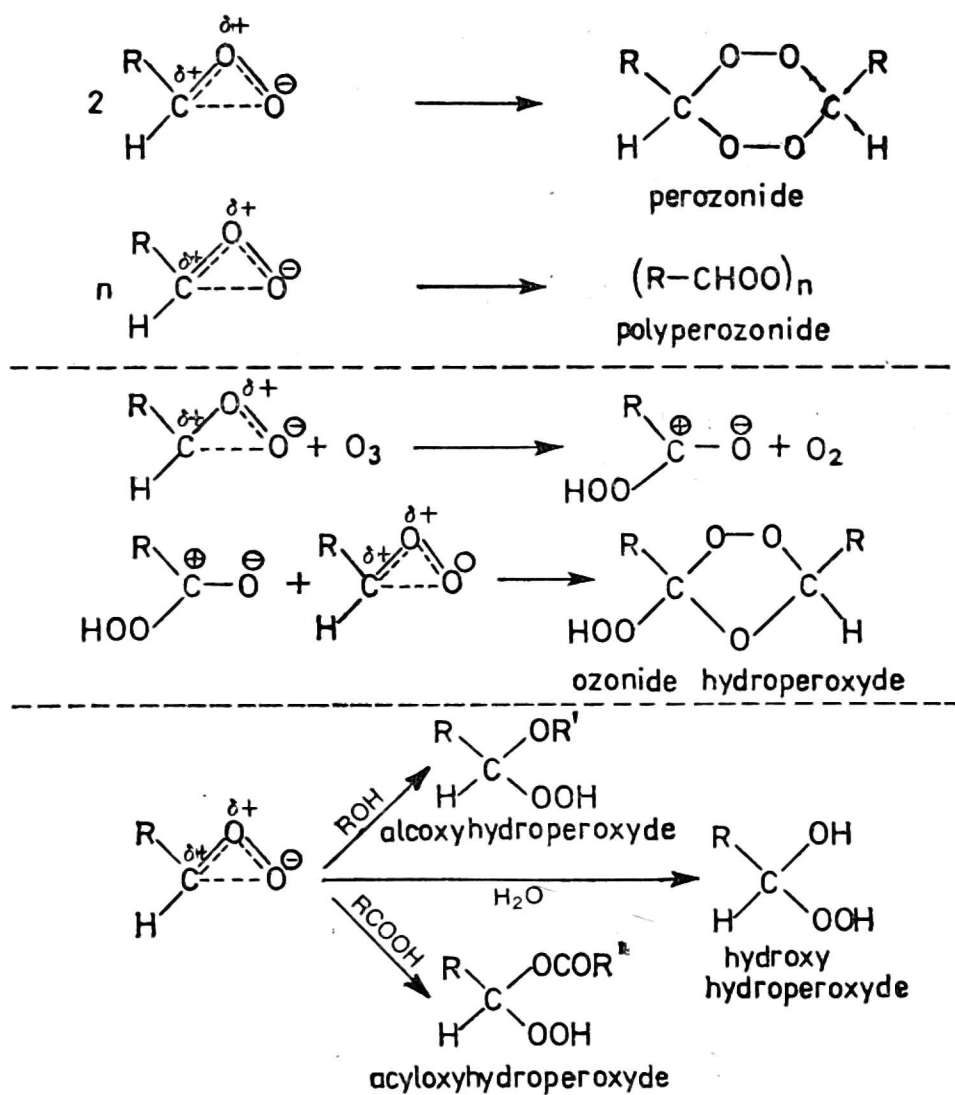

Fig. 1. Formation of ozonides
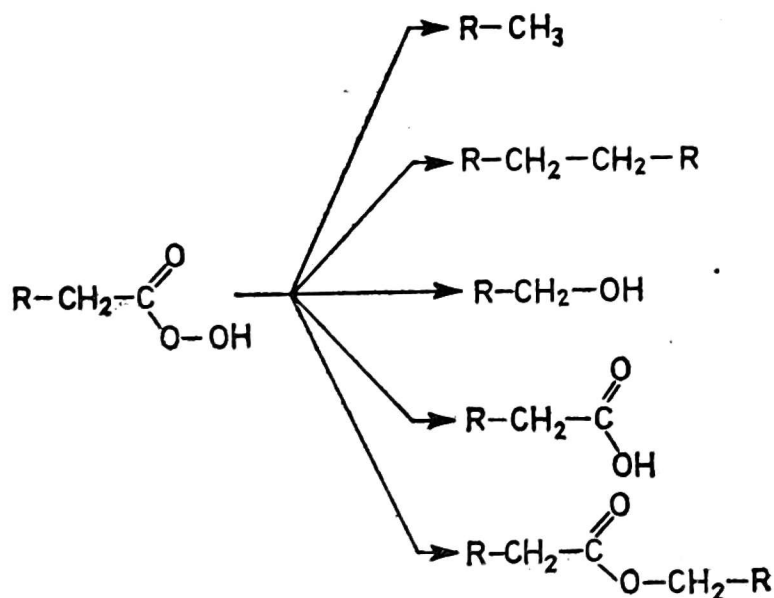
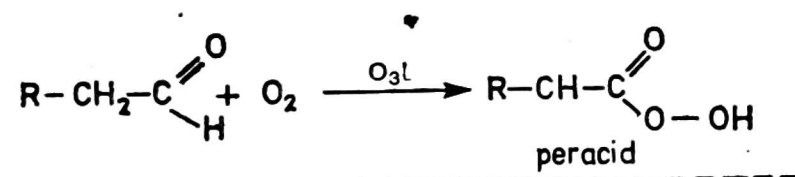Fig. 2. Non normal reactions of zwitterions

Fig. 3. Formation and possible evolutions of peracid

Zwitterions can also take part in several side-reactions: — formation of perozonides or polyperoxides through reactions with other zwitterions — formation of ozonide hydroperoxide after oxidation by ozone — formation of substituted hydroperoxides by reaction with oxygenated molecules, especially in the case of reactive solvents or diluents.

Aldehydic fragments, which consequently cannot be associated with zwitterions, may be oxidized very easily in presence of ozone to form peracids. These are unstable and may be included in several reactions, most of them being radicalar in nature, leaving off carbon dioxid [4]. In such a manner not only acids may be formed but also middle and long chain hydrocarbons, middle chain alcohols and their esters with all the possible acids.

In must be noted here that the presence of water decreases, if not completly suppresses, the formation of high molecular weight esters, which are the most abondant side compounds formed [5, 7].

DECOMPOSITION

Decomposition of ozonides occurs throught a mechanism similar to the one of their formation. The epoxide bridge opens first — the oxidative or reductive reaction, when favoured occurs probably at that moment — and after the peroxide bridge is broken to give the two functionnal fragments.
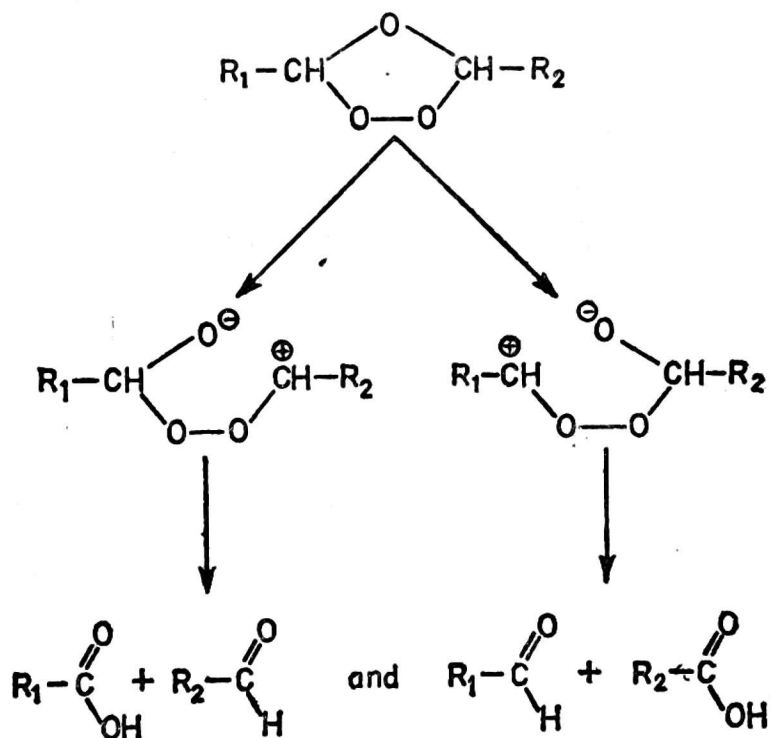

Fig. 4. Decomposition of ozonides

During the decomposition step and according to the conditions of decomposition, the other compounds formed by reactions including zwit-

terions may react in various ways sometimes leading to the expected compounds, sometimes on the contrary to undesirable molecules. Supplementary by-products identical or different to those previously formed, may results principally but no exclusively of the oxidation of the aldehydic fragment, and to consecutive radicalar reactions of the formed peracids.

In spite of the numerous possibilities offered by ozonolysis, the greatest number of laboratory researches and all the pilot and industrial realizations concern only the obtentioin of two compounds:

— azelaic acid and other dibasic acids through oxidative ozonolysis
— methylazelaaldehydate and similar compounds through reductive ozonolysis.

PRODUCTIONS OF DIBASIC ACIDS

To produce dibasic acids, the substrate is always an acid. It is dissolved or diluted for ozonation in a non-reactive solvent like saturated hydrocarbons or chlorinated solvents or in a weak organic acid (acetic acid or higher homologue); alcohols are never used as solvent to avoid esterification.

Non forming ozonide reactions of zwitterion except formation of polyzonides, are not disturbing, since during oxidative decomposition acids groups are regenerated from perozonides, ozonide peroxides and acyloxyhydroperoxides.

Simultaneous decomposition of ozonides and oxidation of aldehydes may be performed in dry conditions by blowing through ozonides (or dissolved ozonides), heated between 90°C and 100°C, a stream of air or oxygen. Wet decomposition-oxidation is also possible: ozonides are suspended in boiling water; either an oxidant like perhydrol is added or a stream of air or oxygen is blown through after addition of a convenient catalyst (silver salt).

As far as the reviewer can see, only one procedure has received an industrial application; this is the one patented by G.C. Goebel *et al.* for Emery Industries [3].

That procedure is a continuous one. The prefered substrate is commercial oleic acid, the substrate is diluted with a final product of the reaction: pelargonic acid in the weight proportion of 2 parts of oleic acid and 1 part of pelargonic acid. A mixture of ozone and oxygen, produced from substantially pure oxygen (99.5⁰/o) is used for ozonation.

Ozonized oxygen and oleic acid diluted with pelargonic acid are reacted counter-currently in an ozone absorber maintained below 45°C. Rate of circulation of oleic acid solution, and ozonized oxygen flow are
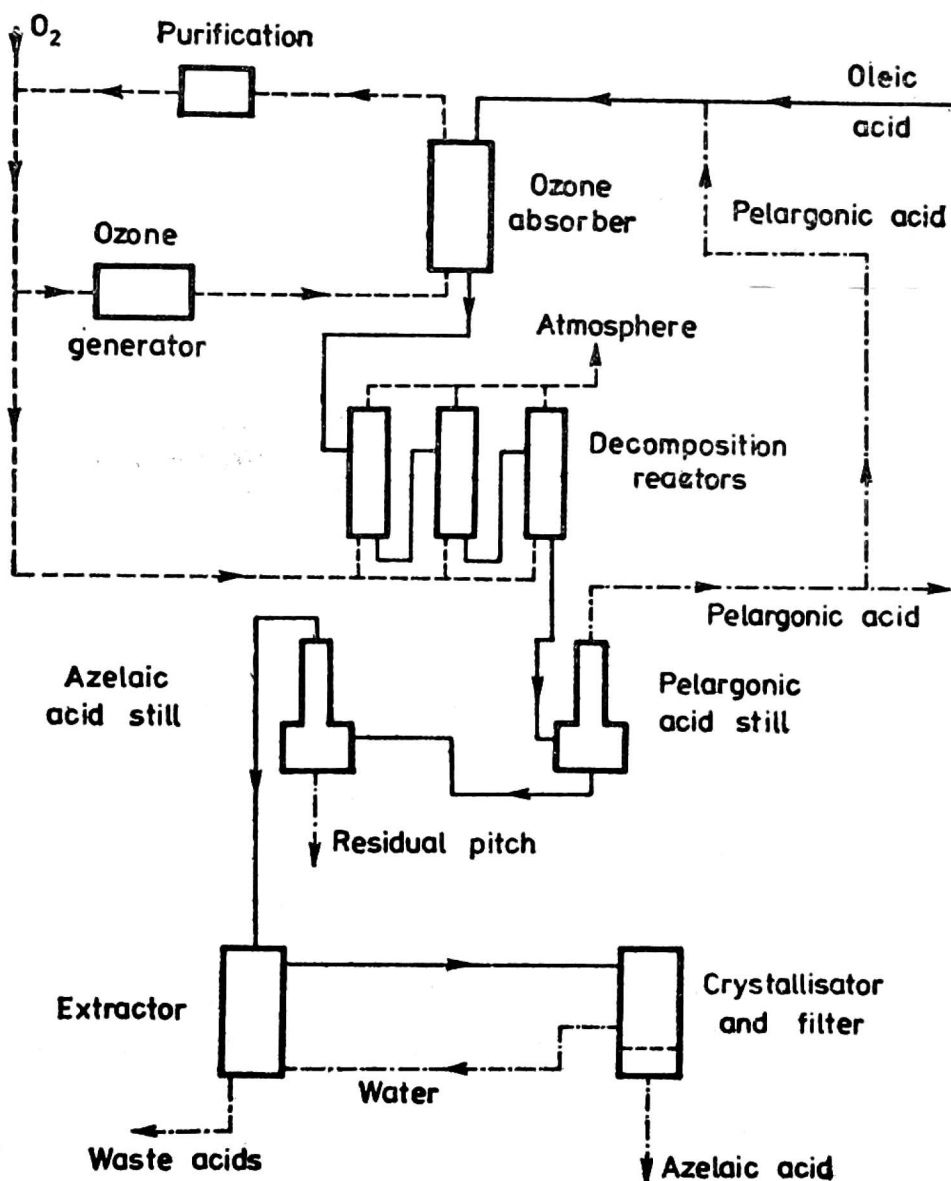
Fig. 5. Industrial obtention of azelais acid

calculated in view to obtain a complete transformation of the double bonds and a nearly quantitative utilization of ozone. The oxygen flowing out the absorber still contain ozone traces; it is then freed from non volatile impurities and recycled.

Ozonides diluted with pelargonic acid, are introduced at the top of a multiple stage decomposition reactor. At the bottom of each stage a part of the purified and recycled oxygen is introduced. The oxidative decomposition temperature is 95°C. Since ozonides decomposition and aldehydes oxidation are exothermic, water cooling of the reactor, at least of the first stage is needed to limit the temperature to the desired value.

The mixed decomposition-oxidation products are stripped under a partial vacum (25 mm) to distillate pelargonic acid. The residue of that first stripping contains azelaic acid and various non volatile by-products. A distillation under a high vacuum (3-4 mm) gives crude azelaic

acid, contaminated with different acidic by-products. Azelaic acid is finally purified by cristallization from boiling water.

According to the patent 100 parts by weight of oleic acid need 28 parts of oxygen both for ozonation, oxidation and probably also for stripping some highly volatile by-products, and give 40 parts of pelargonic acid (yield 72% of theory) and 52 parts of recrystallized azelaic acid (yield 78% of theory).

PRODUCTION OF ALDEHYDIC ESTERS

Ozonolysis of unsaturated fatty esters to produce aldehydic esters and aldehydes, and above all the isolation and purification of final products are difficult due to the oxidability of aldehydic groups.

It is first necessary during ozonation to prevent the formation of zwitterion derivatives which might be susceptible to form, by decomposition, an acidic group in spite of reductive conditions. The actual solution consists in utilizing a reactive solvent, which forms with zwitterions unstable compounds, giving aldehydes by decomposition. Monoalcohols of low molecular weight have been widely proposed. They form easily with zwitterions alcoxyhydroperoxides. Water is a possible participating medium, but as shown by Pryde et al. [10], it must be emulsified in the oily phase, forming a water in oil emulsion, to give satisfactory results.

The hydrogen which is necessary for reduction during decomposition, may be produced in situ by action of acetic acid on zinc dust: numerous examples of reductive decomposition in this way have been given. More satisfactory while less expensive and more efficient is the reductive decomposition by gaseous hydrogen in presence of an hydrogenation catalyst, like Pd/C. According to some authors in the case of reductive decomposition of alcoxyhydroperoxides such a catalyst has to be partially poisoned by pyridine to prevent the formation of esters [9].

Aldehydic esters and aldehydes are too unstable to be directly isolated and purified with acceptable yields. Usually they are transformed into their dimethylacetals, which are stable, volatil and therefore can be easily fractionnated by distillation without excessive losses.

Most of the researches on reductive ozonolysis to produce aldehydic esters have been purchased in Peoria U.S.D.A. Laboratories by Pryde, Cowan and coworkers. Their several years work resulted in a pilot plant study and after optimization in a plant design [11, 12].

The complete proposed process may be summarized as follows.

The esters used are soybean oil total methyl fatty esters, named soyate esters.

Hundred parts by weight of soyate esters are mixed with 130 parts of water. The water in oil emulsion formed is introduced at the top of an ozonolysis reactor at the bottom of which ozonized oxygen is blown. Convenient devices in the reactor permit an efficient contact between the two phases and prohibit the emulsion breaking. Temperature in the reactor increases from 30°C in the lower part to 50°C in the upper one. The oxygen which flows out the reactor is freed from organic vapours and gases by passing through a catalytic burner and then recycled. Dissolved oxygen is stripped of by blowing nitrogen through the water in oil emulsion.

Ozonides obtained at the lower part of the stripper are pumped to a first decanter in which the largest part of water separates and is withdrawn. The wet ozonides are introduced into a fixed bed catalytic continuous hydrogenator in wohich hydrogen is pumped. The catalyst is a Pd/C one. Optimized hydrogenation conditions are 75°C and 2 kg/ /cm²; as reductive decompozition of ozonides is exothermic, the hydrogenator must be cooled.

After cooling, benzene is added to the decomposition mixture; a supplementary quantity of water can consequently be separated in a second decanter. Last traces of water are eliminated by azeotropic distillation of a portion of the benzene.

By addition of sulfuric methanol to the dry crude aldehydes, dimethyl acetals are formed. These, in concentrated benzene solution, are counter-currently washed, first by water, then by aqueous sodium bicarbonate, and finally by water. Washed crude acetals are dried by azeotropic distillation of the residual benzene.

Fractionation by vacuum distillation leads successively to the isolation, in a nearly pure state, of carproaldehyde, pelargonaldehyde and methylazelaaldehydate as their dimethyl acetals. Saturated methylesters present in soyate esters are also separated by distillation from a non volatile residue.

The quantities expected, from 100 parts by weight, of soyate esters, in continuous industrial operation, are: — methylazelaaldehydate dimethyl acetal: 61 part (i e. 80% of the theoritical quantity) — pelargonaldehyde dimethyl acetal: 11 parts (about 70% of the theoritical quantity) — caproaldehyde dimethyl acetal: 10 parts (about 35% of the theoritical quantity).

The main potential use of these aldehydic esters is their transformation in ω amino nonanoic acid, monomer of Nylon 9. The best way to obtain ω amino-nonanoic acid appears to be a catalytic reductive amination, needing several steps which have not yet been completely optimized.

Fig. 6. Proposed industrial scheme for preparation of methylazelaaldehydate diacetals
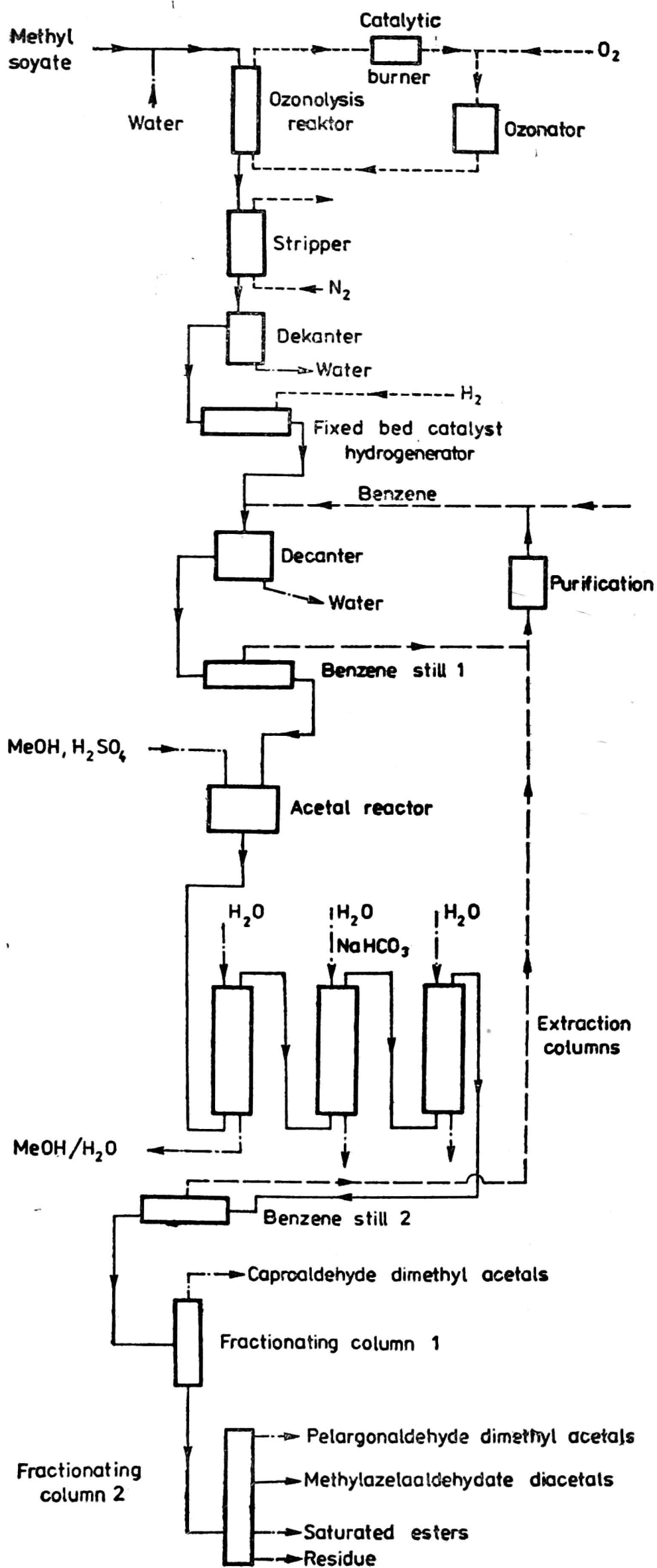
CONCLUSION

As a conclusion ofr this short review, it is possible to say that the productioin of $\alpha \omega$ medium chain difunctionnal compounds by disruptive oxidation of unsaturated fatty acids or derivatives is an industrial reality. For such a reaction, ozonolysis is the best way. Its versatility and its specificity makes of it one of the most fruitful reaction in chemurgy of fats.

If still actually industrial and even pilot plant realizations are in limited number and are restricted to few compounds, this seems more related to economical considerations than to chemical or technological problems; therefore one may hope that in the future a more important part of the past or present laboratory researches will enrich industrial production.

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M. Naudet

OKSYDACJA I OZONOLIZA

Streszczenie

Konwersja naturalnych kwasów tłuszczowych w $\alpha \omega$ dwufunkcyjne cząsteczki z krótszymi łańcuchami węglowodorowymi jest jedną z najbardziej interesujących modyfikacji w chemiurgii tłuszczów.

Praktycznie tylko monoenowe kwasy tłuszczowe mogą być używane jako surowiec. Konieczną reakcją w szczególnym przypadku nieobecności kwasu rycynolo-

wego jest oksydacja, prowadząca do przerwania łańcucha w miejscu podwójnego wiązania. Chociaż chemiczne utleniacze mogą być i były dawniej używane, to obecnie jedynym stosowanym sposobem jest ozonoliza ze względu na jej łatwość wykonania, widoczną specyficzność i dużą wszechstronność.

Podstawowe zasady ozonolizy stanowią:

— mechanizm powstawania i struktura ozonków,

— mechanizm rozpadu ozonków i charakter powstających produktów, zależnie od warunków rozkładu,

— drugorzędne reakcje, które mogą występować zarówno podczas ozonolizy, jak i podczas rozkładu.

Warunki procesu oraz ich wpływ na tworzenie się produktów ubocznych, a w konsekwencji na wydajność przedyskutowano na dwóch szczególnych przypadkach:

1) otrzymywanie kwasów dwukarboksylowych z wolnych kwasów tłuszczowych przez oksydatywną ozonolizę,

2) otrzymywanie aldoestrów lub aminoestrów przez redukcyjną lub aminoredukcyjną ozonolizę.

Podano przykłady zastosowania przemysłowego w skali technicznej i półtechnicznej obu rodzajów ozonolizy.

М. Ноде

ОКСИДАЦИЯ И ОЗОНОЛИЗ

Резюме

Конверсия природных жирных кислот в двухфункционные частицы α, ω, с более короткими углеводными цепями является одной из наиболее интересных модификаций в химиургии жиров.

Практически только моноеновые кислоты могут использовываться в качестве сырья. Необходимой реакцией в особом случае отсутствия рицинолевой кислоты является оксидация ведущая к разрованию цепи в месте двойной связи. Хотя минеральные химические окислители могут использовываться и раньше были используемыми, то в настоящее время единственным используемым способом является озонолиз из-за легкости его проведения, видимой специфичности и значительной всесторонности.

Основными принципами озонолиза являются:

— механизм образования и структура озонидов,

— механизм распада озонидов и характер образующихся продуктов в зависимости от условий разложения,

— второстепенные реакции, которые могут происходить как во время озонолиза, так и во время разложения.

Условия процесса и их влияние на образование повочных продуктов, а тем самым на производительность, обсуждались на примере двух особых случаев, в частности:

1) подучения бикарбоновых кислот из свободных жирных кислот путем оксидативного озонолиза,

2) получения альдоэфиров или аминоэфиров путем восстанавливающего или амино-восстанавливающего озонолиза.

Приводятся примеры промышленного использования в техническом и полутехническом масштабе обоих видов озонолия.