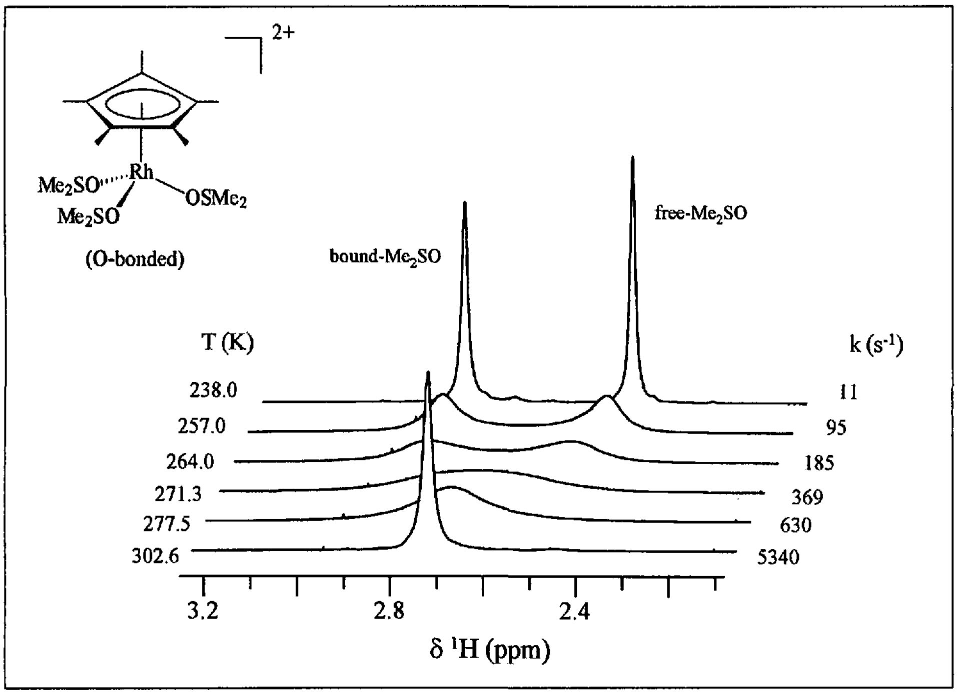

Fig. 3. *Experimental ^1H-NMR (400 MHz) spectra of $[Cp^*Rh(Me_2SO)_3](PF_6)_2$* (0.100 m) *with free Me_2SO* (0.304 m) *in CD_3NO_2 at various temperatures*

These results suggest that increasing the steric environment around the metal center promotes the dissociation process and thus leads to an increase in the rate of solvent exchange whereas increasing the π-acceptor ability of the bound solvent ligand creates a stronger metal–ligand bond and thus decreases the exchange rate.

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Catalytic Opportunities in the Flavor and Fragrance Industry

Hubert Mimoun*

Abstract. Because catalytic processes produce in general less residues than conventional stoichiometric ones, they are advantageous for the environment. This short review will focus on new opportunities for catalysis in the field of terpene transformation, citral and ionones synthesis, and macrocyclic *vs.* aromatic musks.

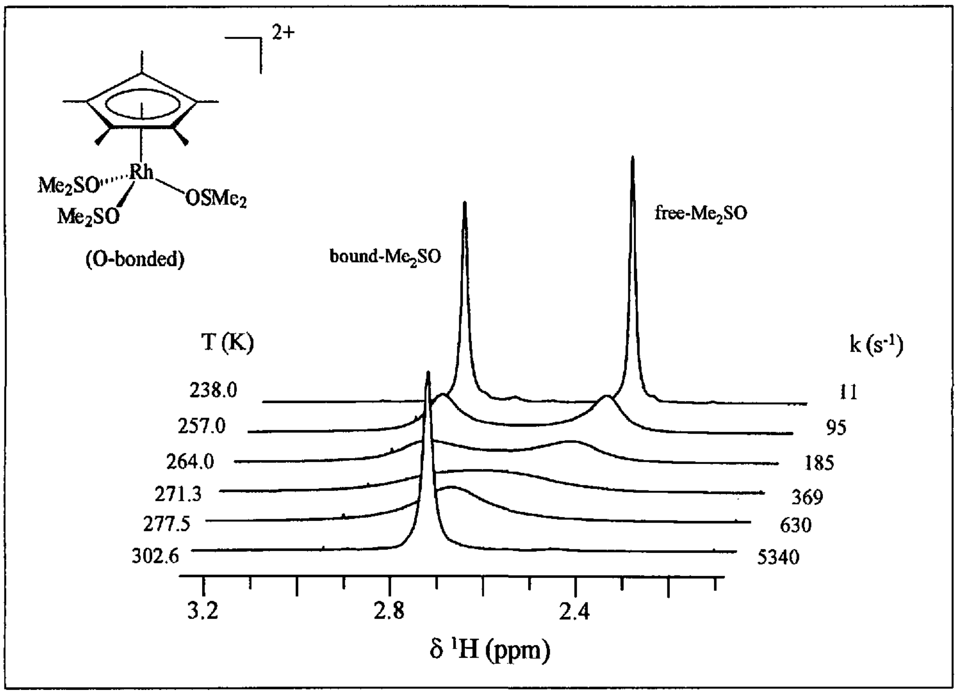
Introduction

Like other chemical industries, the flavor and fragrance (F&F) industry [1][2] has taken up the challenge to reduce cost of waste treatment, thereby using processes more friendly for the environment. Thus, the substitution of conventional organic chemistry processes such as stoichiometric oxidation by permanganates and chromates, reduction by dissolving metals and metal hydrides, *Wittig* condensations (recycling of triphenylphosphine oxide), *Friedel-Crafts* acylation, *etc.* by alternative cleaner, safer, and environmentally friendly alternative technologies are under continuously development. Most of the toxic metals such as chromium, lead, selenium, mercury, cadmium have been removed from industrial processes. The use of reagents such as acrolein, methyl vinyl ketone, phosgene, and dimethyl sulfate is severely limited because of transportation regulations, and/or have to be used at their production site. Chlorinated and aromatic solvents also have very restrictive uses. Perfume producers are also becoming more and more concerned with the biodegradability and innocuity of their products.

Catalysis is now seen as a substitute or a complement to conventional organic processes since it involves higher atom economy, and therefore generates much less waste, as has already been shown in the bulk chemical industry [3].

A further important feature of catalysis is enantioselectivity. Smell and taste involve chiral biological sensors that are sensitive to stereogenic centers in the molecules, and the organoleptic properties of two enantiomers often differ in intensity and quality [4]. For example, (+)-(*S*)-carvone (caraway-like) and (–)-(*R*)- carvone (spearmint-like) have different odors. Thus, enantioselective catalysis is the next frontier for the commercialization of chiral perfumes. This short review will deal with some recent applications of catalysis in the F&F industry, and focus on new opportunities in this area.

**Correspondence*: Prof. Dr. H. Mimoun
Firmenich S.A.
45, Route de la Plaine
CH–1283 La Plaine-Geneva



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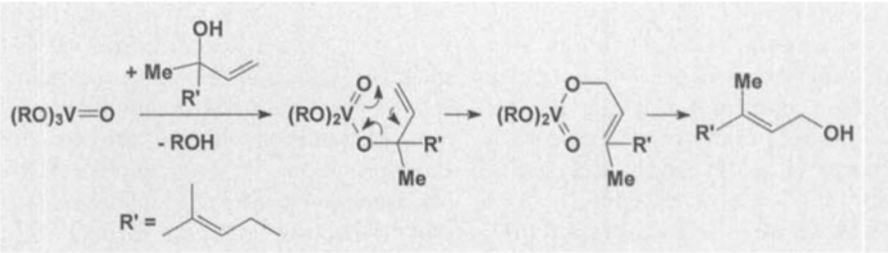
**Correspondence*: Prof. Dr. H. Mimoun
Firmenich S.A.
45, Route de la Plaine
CH–1283 La Plaine-Geneva

1. Fragrances from α-Pinene and β-Pinene

α-Pinene (*ca.* 18000 t/year), β-pinene (*ca.* 12000 t/year) and Δ_3-carene (*ca.* 1000 t/year) are the main inexpensive monoterpenes that are extracted from turpentine, a very important raw material in the F&F industry.



(1)

1.1. *Fragrances from* α-Pinene

Scheme 1 shows some of important fragrances manufactured from **α-pinene**. Hydration of α-pinene affords terpine hydrate which is dehydrated to **α-terpineol** ((+)-isomers). Epoxidation by peracetic acid gives α-pinene epoxide which rearranges to **campholenic aldehyde** in the presence of catalytic amounts of Zn salts. Campholenic aldehyde is a very important intermediate used for the manufacture of **sandalwood** fragrances, *e.g.*, *Sandalore®* (*Givaudan*), *Bacdanol®* (*IFF*), *Brahmanol®* (*Dragoco*), *Polysantol®* (*Firmenich*)[5]. Catalytic hydrogenation of α-pinene gives mainly *cis*-pinane which can be pyrolyzed to **dihydromyrcene**, from which **dihydromyrcenol** can be obtained by hydration in the presence of H_2SO_4. Autoxidation of pinane to the hydroperoxide, followed by hydrogenation to **pinanol**, is carried out in large scale by *SCM* in its Colonel's Island plant (Georgia, USA) [6]. Pinanol is then pyrolyzed to **linalool**, which can be rearranged to **geraniol** in the presence of trialkyl oxovanadates $VO(OR)_3$. Catalytic hydrogenation of geraniol affords **citronellol**.

The allylic rearrangement of linalool to geraniol deserves particular attention, since it is an ene-like reaction involving the vanadium-oxo bond V=O as a partner (*Eqn. 1*) [7].

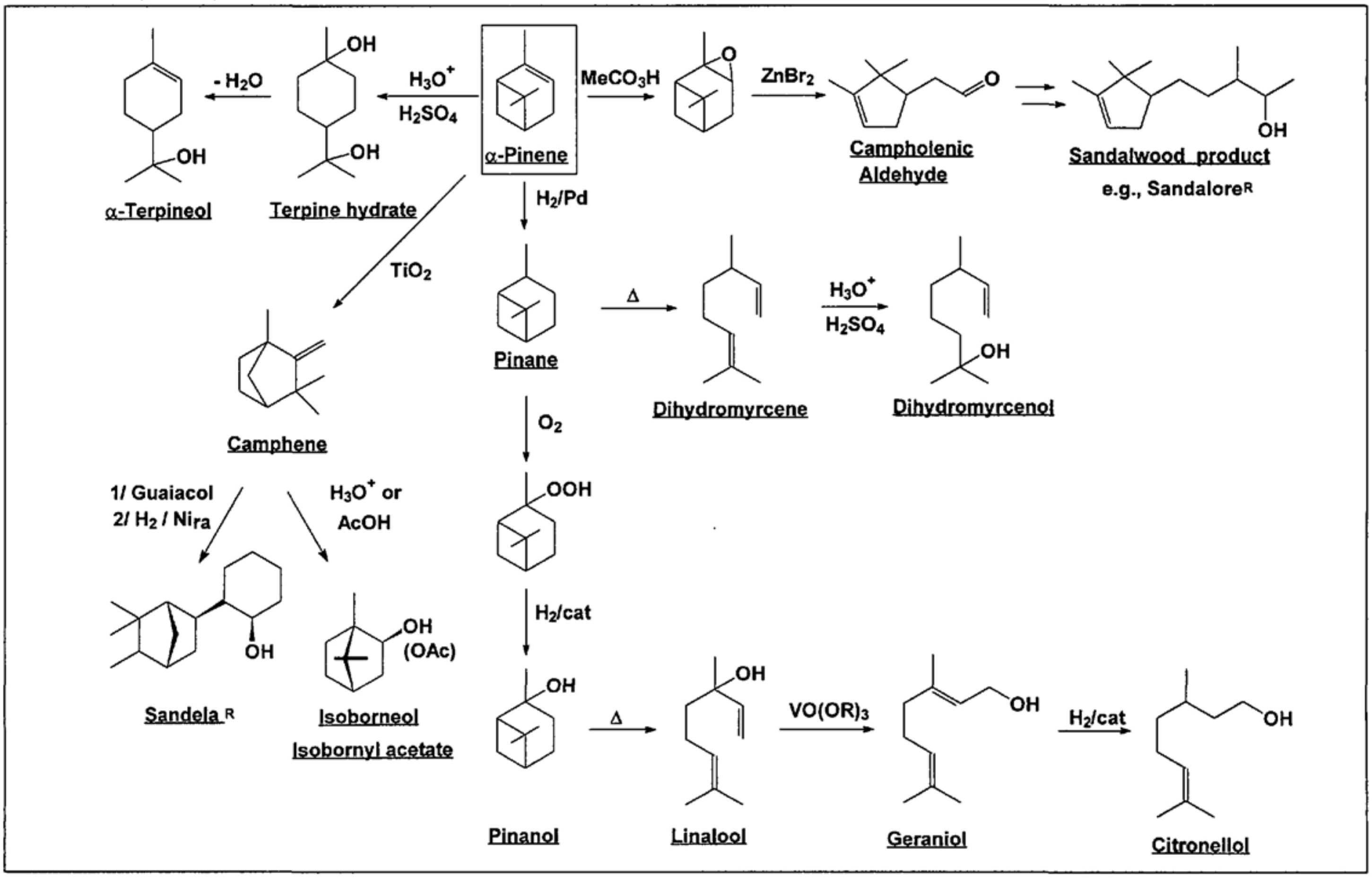
α-Pinene rearranges to **camphene** in the presence of TiO_2. Camphene can be acetylated to **isobornyl acetate**, or condensed with guaiacol and catalytically hydrogenated to give **isocamphylcyclohexanol** a sandalwood fragrance commercialized under the trade name of *Sandela®* (*Givaudan*), *Santalex-T®* (*Takasago*), or *Sandel H&R®* (*Haarmann & Reimer*) [8].

Nonselective and polluting hydration of terpenes by H_2SO_4 has been recently greatly improved by the use of hydrophobic Beta and USY zeolites with high Si/Al ratios. Thus, α-pinene and camphene were hydrated to α-terpineol and isoborneol, respectively, with selectivities as high as 70 and 90% [9].

1.2. *Fragrances from β-Pinene and Myrcene*

Except for the synthesis of **Nopol** and **Nopyl acetate** by a *Prins* condensation with formaldehyde, **β-pinene** is mainly used in industry as its rearrangement product, **Myrcene,** which is obtained by pyrolysis (*Scheme 2*). *Diels-Alder* reaction of myrcene with acrolein gives ***Acropal®***, whereas reaction with 3-methylpent-3-en-2-one followed by cyclization gives isocyclenone, also known as ***Iso E Super®*** (*IFF*), which displays a pleasant woody amber note [10]. Myrcene can also be hydrated to **myrcenol** through its cyclic

Scheme 1. *Fragrances from α-Pinene*



sulfone. Myrcenol is condensed with acrolein to give *Lyral*® (*IFF*) [11], which has a lily-of-the-valley odor. An alternative synthesis of **geraniol** involves the 1,4 addition of HCl to myrcene to give geranyl chloride which is then hydrolyzed by alkali.

(–)-Menthol is a widely used F&F ingredient (*ca.* 5000 t/year) which has both a natural (from peppermint and spearmint oil) and a synthetic origin. It is industrially produced, *inter alia*, by hydrogenation of thymol, followed by separation and resolution of the menthyl benzoates enantiomers [12]. *Takasago* has recently disclosed a process for the manufacture of (–)-menthol (1000 t/year) involving *a*) the addition of diethylamine to myrcene catalyzed by lithium; *b*) the enantioselective isomerization of **diethylgeranylamine** to an enamine in the presence of $[Rh(BINAP)_2]^+$ catalyst; *c*) the hydrolysis of the dieneamine to **(*R*)-citronellal**; *d*) the cyclization of (*R*)-citronellal to **(–)-isopulegol** in the presence of catalytic quantities of $ZnBr_2$; and *e*) the hydrogenation of (–)-isopulegol to (–)-menthol (*Scheme 2*) [13]. The key step of this process is the isomerization of diethylgeranylamine to the diethyl enamine of citronellal which is achieved with 96% enantiomeric excess (ee) and a turnover number (TON) of 400 000. This is carried out in the presence of a chiral rhodium complex $[Rh((S)\text{-}BINAP)_2]^+$ containing the atropisomeric chiral diphosphine ligand 2,2'-bis(diphenylphosphino)-1,1'-binaphtyl (BINAP). *Tagasago* also commercializes other fragrances derived from this BINAP technology such as (+)- and (–)-citronellol and (–)-7-hydroxycitronellal [14].

A further application of catalysis in the transformation of myrcene is the industrial synthesis by *Rhone Poulenc* (*RP*) of **geranylacetone** in which methyl acetoacetate is added to myrcene in the presence of a H_2O-soluble rhodium tris(*m*-sulfonatoylphenyl)phosphine trisodium salt (TPPTS) complex [15]. The biphasic liquid-liquid process allows for an easy separation of the organic products by decantation and the recycling of the aqueous catalytic solution without significant loss of activity. Geranylacetone is an important intermediate in the F&F industry but is mainly used by *RP* for the synthesis of isophytol and tocopheryl acetate (vitamin E, *ca.* 10000 t/year world market).

2. Citral and Ionones

Citral [16] is a key intermediate in the F&F industry as well as in the vitamin A synthesis. It allows the synthesis of α- and β-ionone and methylionones after aldol condensation with acetone or methyl ethyl ketone followed by acid-catalyzed cyclization [17]. It is also used as intermediate in the synthesis of Rose ketones (α-, β-, and γ-Damascones, Damascenone) and numerous woody and amber fragrances [5].

The different approaches by the three main vitamine A producers, *F. Hoffmann-La Roche* (*HLR*), *BASF*, and *Rhone-Poulenc* (*RP*) to the synthesis of citral and **β-ionone** are shown in *Scheme 3*.

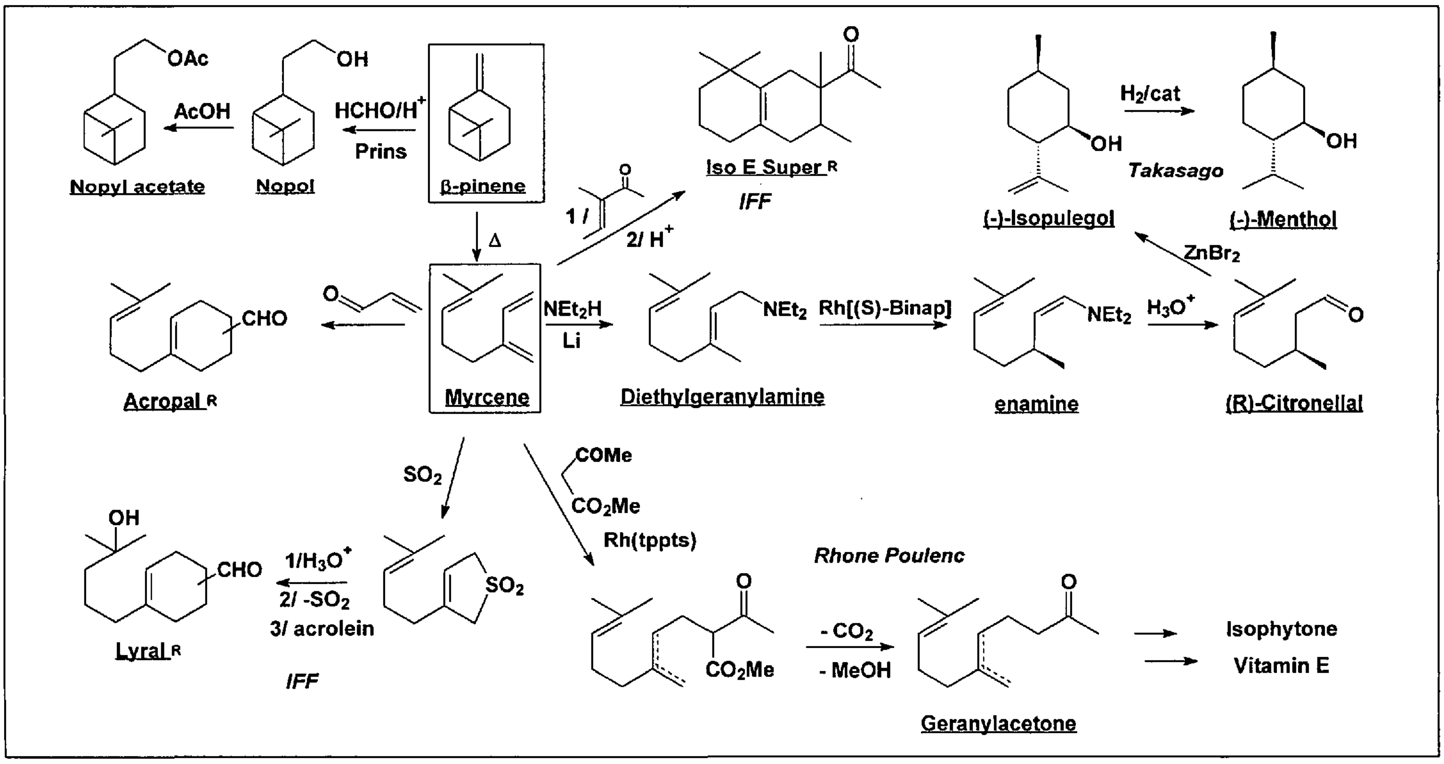
The *HLR* process involves the ethynylation of **methyl heptenone** to **dehydrolinalool**, followed by *Saucy-Marbet* addition of methyl isopropenyl ether and rearrangement to **pseudoionone** [18]. Citral can be made *via* a *Meyer-Schuster* [19] or trialkyl-vanadate rearrangement of dehydrolinalool.

The *BASF* and *RP* processes differ in the choice of the starting materials used for the synthesis of **prenol** and **prenal,** the two building blocks used in the manufacture of citral.

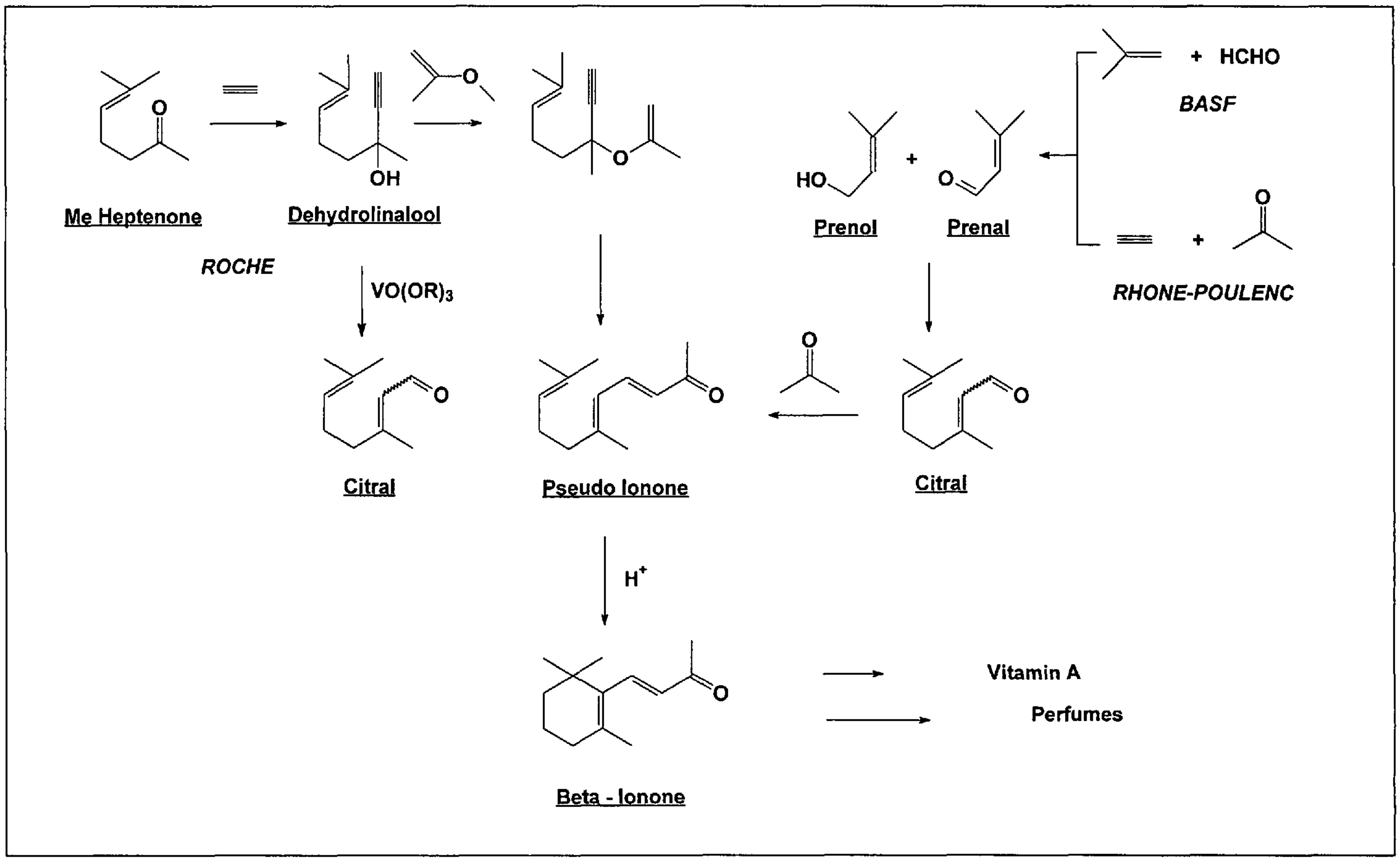
The *BASF* process is a triumph of catalysis in the synthesis of fine chemicals and involves both atom economy and environmentally friendly technology. Ene condensation of isobutene and formaldehyde in the gas phase at 280° affords isoprenol [20]. In a continuous process, the isoprenol is first isomerized to prenol over a supported palladium catalyst, then oxidized to prenal with a 95% yield at 500° and a millisecond residence time over a fixed bed containing a supported Ag catalyst [21] (*Eqn. 2*). Two moles of prenol and one mole of prenal condense to prenal diprenyl acetal, which loses one mole of prenol, and rearranges in a *Claisen-Cope* sigmatropic reaction to give citral (*Eqn. 3*) [22][23].

The *Rhone-Poulenc* route involves ethynylation of acetone to **2-methylbutyn-2-ol**, followed by rearrangement of

Scheme 2. *Fragrances from β-Pinene and Myrcene*



Scheme 3. *Citral and β-Ionone*

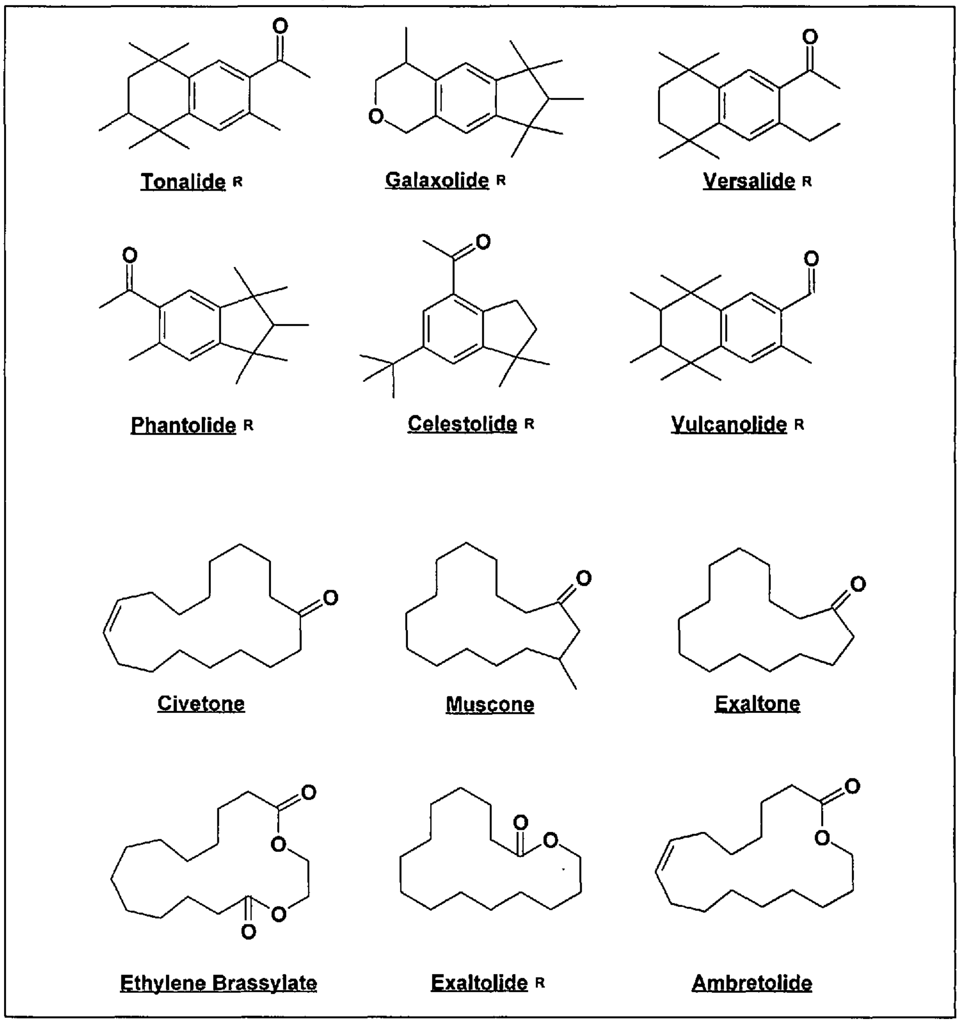


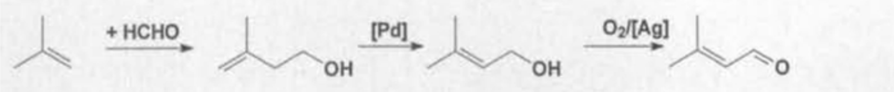
methyl butynol to prenal in the presence of trialkyl vanadate or $Ti(OR)_4$-CuCl catalysts [11][24]. Prenal can then be selectively hydrogenated to prenol in the presence of H_2O-soluble catalyst made from $RuCl_3$ and TPPTS (*Eqn. 4*) [25].

3. Macrocyclic *vs.* Aromatic Musks

Aromatic musks (*Scheme 4*) such as ***Tonalide***® (*PFW, Givaudan*), ***Galaxolide***® (*IFF*), ***Versalide***® (*Givaudan*), ***Phantolide***® (*PFW*), ***Celestolide***® (*IFF*), and ***Vulcanolide***® (*Firmenich*) are widely used (world market; *ca.* 7000 t/year) both in fine perfumery and household soaps and detergents. Their success can be attributed to their excellent odor and fixative properties, as well as their moderate cost and outstanding stability [26][5]. They are generally synthesized by acid-catalyzed cycloalkylation of petrochemical aromatic starting materials, *p*-cymene, α-methylstyrene, or (*tert*-butyl)benzene with olefins such as isoamylene, neohexene, dimethylbutenes, and isoprene, followed by *Friedel-Crafts* acylation [21]. These alkylations are carried out in the presence of $AlCl_3$ or H_2SO_4/AcOH [27]. Better yields have been recently obtained in the presence of sulfonated resins or polysiloxanes *Deloxan*® ASP catalysts [28]. As an illustrative example, the synthesis of

Scheme 4. *Aromatic and Macrocyclic Musks*





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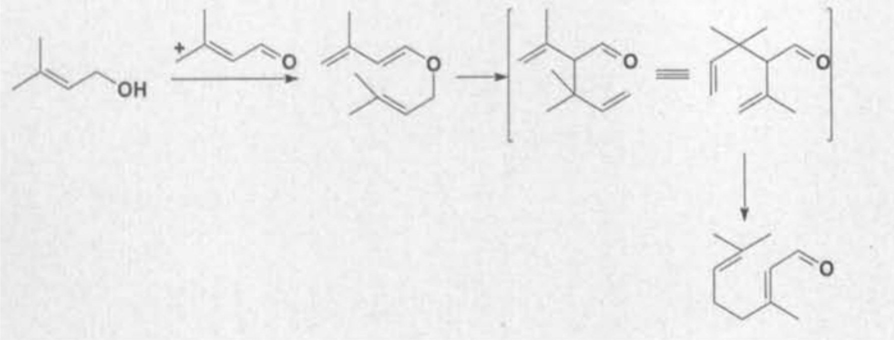

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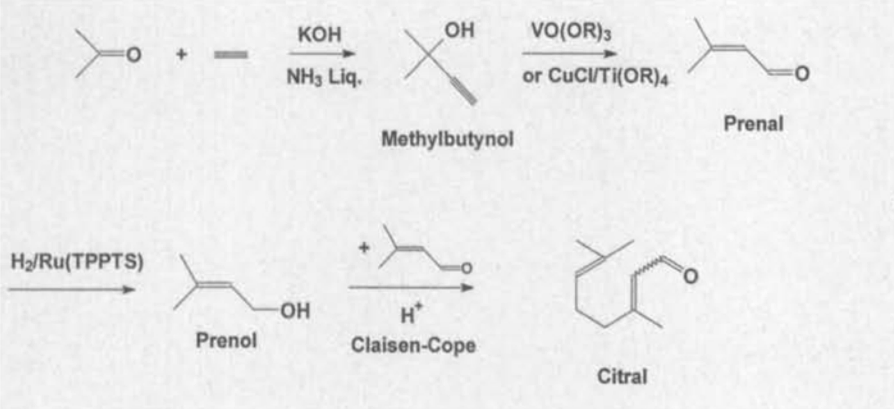

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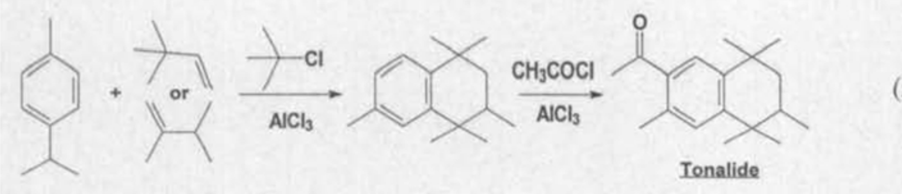

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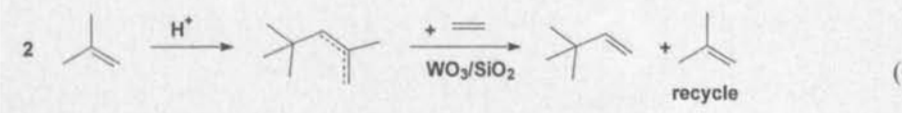

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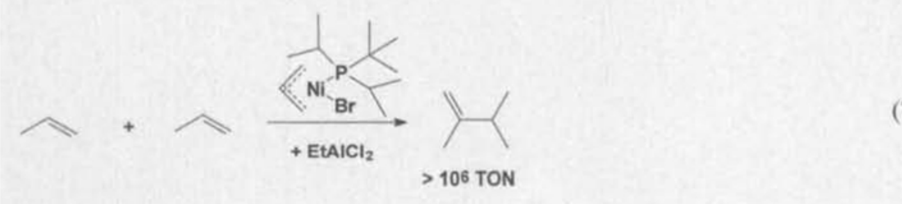

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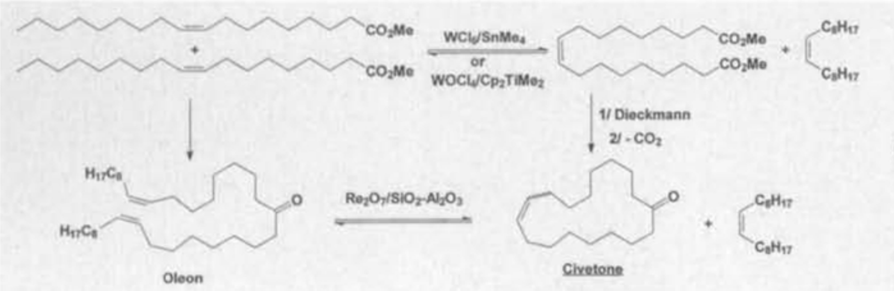

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Tonalide from *p*-cymene, neohexene, or 2,3-dimethylbutene, and acetyl chloride is shown in *Eqn. 5*. Neohexene is prepared on a large scale by *Phillips Petroleum* by cross-metathesis of 2,4,4-trimethylpent-2-ene (diisobutene) with ethylene in the presence of WO_3/SiO_2 (*Eqn. 6*) [29].

Dimerization of propylene to 2,3-dimethylbut-1-ene (*Eqn. 7*) can be achieved with excellent selectivity and very high turnover numbers (> 10^6) in the presence of a mixture of $[NiBr(\eta^3\text{-allyl})P(iPr)_2(^tBu)]$ and $EtAlCl_2$ as catalyst [30].

The high stability and lack of biodegradability of aromatic musks makes their future development questionable for environmental reasons [31], and they are progressively sought to be substituted by natural-identical macrocyclic musks such as **Civetone** (civet cat), **Muscone** (musk-deer), ***Exaltone®*** (muskrat), ***Exaltolide®*** (angelica root oil), and **Ambrettolide** (ambrette seeds) [32]. Since their discovery by *Ruzicka* some 70 years ago [33], these macrocyclic musks have been the object of considerable studies, and many synthetic routes have been published [26][34][35]. Although most industrial syntheses involve ring-enlargement reactions from cyclododecanone [26][36], ring-closing metathesis (RCM) has recently emerged as an attractive alternative catalytic route for the synthesis of macrocyclic musks [37].

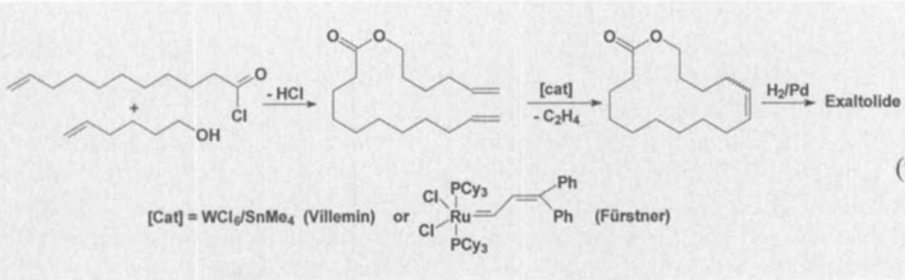
Civetone can be prepared from metathesis of inexpensive methyl oleate in the presence of $WCl_6/SnMe_4$ (50% based on the theorical yield of 50%) [38] or $WOCl_4/Cp_2TiMe_2$ (87% yield) [39] catalyst, followed by *Dieckmann* condensation and decarbomethoxylation. In an alternative route, methyl oleate is converted to **Oleon** (yield 80%) which is metathesized to Civetone in the presence of $Re_2O_7/SiO_2\text{-}Al_2O_3$ catalyst [40] (*Eqn. 8*).

An elegant synthesis of ***Exaltolide®*** from undec-10-enoyl chloride, an inexpensive derivative of castor-oil pyrolysis, and hex-5-enol was carried out by *Villemin* [41]. The resulting dienic ester was closed by RCM with the elimination of ethylene in the presence of $WCl_6/SnMe_4$. The yield of the RCM step was recently substantially improved to 79% by *Fürstner et al.* [42] in the presence of the *Grubbs* [43] functional-group-tolerant ruthenium-carbene catalyst (*Eqn. 9*).

RCM access to macrocyclic musks appears, therefore, to be very promising despite insufficient turnover numbers, and the fact that high dilution conditions are required to avoid intermolecular reactions.

Conclusion

As can be seen the future of catalytic processes in the F&F industry looks very promising and development of such systems will be driven by the need for clean, safe, and environmentally friendly technologies. Both heterogeneous (selective oxidation, cyclization) and homogeneous catalysis (metathesis, carbonylations, ox-



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idations, enantioselective reactions, alkylations) will be increasingly used in these selective alternative processes.

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New Directions towards the Understanding of Physico-Chemical Processes in Aquatic Systems

Christine Couture, Charles-Philippe Lienemann, Denis Mavrocordatos, and Didier Perret*

Abstract. Some applications of Analytical Electron Microscopies (AEM) for the characterization of colloids in natural waters are presented. These techniques go much beyond the basic level of morphological observation and render possible to gain detailed physico-chemical information difficult to obtain by conventional analytical methods. Hence, AEM appear as a challenging necessity for understanding the colloid-mediated transport of toxics in the environment.

1. Introduction

Because of the ever increasing demand on water resources, efforts have been directed during the last decades towards water sanitation, and in the development of models for predicting the response of water systems to anthropogenic constraints.

This paper briefly describes our research, which is focused on the microscale characterization of colloids in aquatic systems, and on the understanding of their transformation processes, their reactivity, and their role in the scavenging of toxic trace elements and nutrients.

**Correspondence*: Dr. D. Perret
Institut de chimie minérale et analytique
Université de Lausanne
BCH
CH–1015 Lausanne