

Ms. Fedak: Our next speaker, Dr. Jacques Sibeud, was graduated from the University of Lyon with a degree in chemical engineering in 1949 and with a PhD in chemistry in 1952.

After starting with Rhone-Poulenc in France, the parent company of Rhodia, he was transferred to the United States in 1955 to start up Rhodia's first plant in New Brunswick. As technical director and director of operations there, he supervised the firm's

first production of coumarin, alpine violet, isobornyl acetate, and other products. Later, as vice president, R & D, Dr. Sibeud served on the Rhodia team which conceived, built, and started the Freeport, TX, plant where Rhodia manufactures terpene products, using a series of original processes.

Now vice president-technical, Dr. Sibeud is responsible for corporate research, development, and engineering for Rhodia Inc.

More Perfume Materials from Isoprene

Dr. Jacques Sibeud, Rhodia Inc.

When I told our chemical research director, Peter Gradeff, that I intended to give a talk at the American Society of Perfumers' Symposium, his first comment was rather blunt: "Do you really believe that perfumers would appreciate a lecture in chemistry?" My answer was simple: "Perfumers do buy our research on aroma chemicals. It is essential that we—chemists, engineers—tell them what we are doing and what we can do for their industry."

The aroma chemical industry has undergone some fundamental transformations in the last twenty-five years. Of course, these changes have affected the direction of our research and have imposed new requirements in the choice of our new processes.

1. Until the late 1950s most aroma chemicals were derived from essential oils. The demand for larger quantities of these products at lower prices has compelled the industry to search for more abundant and cheaper raw materials. Most aroma chemicals are now made from acetylene, isoprene, acetone, phenol, and α and β pinenes. Any new processes should be based on readily available synthetic raw materials at a stable price.

2. Twenty years ago, most of the aroma chemicals were produced batchwise in relatively small, unsophisticated, multipurpose units. The high-volume aroma chemicals are now manufactured in large, integrated units. This type of installation is very expensive. To keep capital expenditure at an acceptable level, processes have to be simple and include a minimum number of steps, even at the price of greater raw-material consumption. This accent on simplicity has become a very important consideration in the choice of a process.

3. Chemists and engineers, when developing new processes for aroma chemicals, have to become sensitive to the very special problems of our industry.

For instance, chemists should understand that an aroma chemical does not have to be extra pure but must have an acceptable odor. However, impurities will affect odors. These impurities should be identified, their formation understood, and their effects recognized. Some impurities should remain in the final product; others must be eliminated. Fortunately, remarkable advances in analytical chemistry have provided us with the tools to resolve these problems.

Engineers should be aware that most aroma chemicals are heat sensitive and may acquire, if mistreated, a "burnt or still" odor, which may be very difficult to eliminate either by redistillation or recrystallization. Fortunately, chemical engineering has made some substantial progress, especially in regard to vacuum distillation so important in our field of activity. It is possible now to build a vacuum distillation column equivalent to 50-100 theoretical plates, functioning below 3 mm of Hg vacuum, with a pressure drop of less than 10 mm.

Reboilers with a very small temperature differential between the heating fluid and the product to be evaporated could be designed to minimize the effect of overheating. I feel strongly that basic olfactory training of all chemists and engineers involved in manufacturing aroma chemicals is a necessary requirement for success.

These general principles represent part of the experience acquired at Rhodia in designing, building, and operating large production units for aroma chemicals, such as coumarin and terpene chemicals. And these principles have guided Rhodia's research in developing new processes for aroma chemicals.

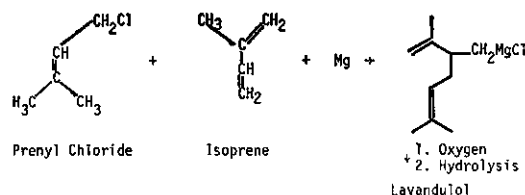
The terpene chemicals which Rhodia produces in its Freeport plant are made from isoprene. Of course, we had been very interested in developing

our isoprene chemistry. One of the chemicals which had attracted attention was lavandulol, a C_{10} terpenic alcohol, which is found in small amounts in several essential oils, such as lavender and lavandin. As you probably know, lavandulol has a most interesting odor, green rosy, herbaceous, decisively different from linalool and geraniol. The odor of its acetate is also interesting, altogether sweet and fruity but rather fresh. Lavandulol is available commercially, but its high price has, so far, limited its usage in perfumery. Our perfumers and our marketing department agree that a substantial market could be developed for lavandulol at a proper price level.

Lavandulol was isolated from *lavandula vera* oil and was identified by Schinz and his co-workers in 1942, although in 1935 Ruzicka and Roethlisberger had obtained some racemic lavandulol mixed with other isomeric alcohols. Schinz and his co-workers proposed two syntheses for lavandulol, but neither was suitable for low-cost, large-scale production.

More recently, several other syntheses were proposed, none of which were attractive enough for large-scale production. The goal was to develop a process comprising one or two steps at most, and utilizing readily available raw materials. We felt that a normal starting point for this synthesis should be prenyl chloride, an intermediate produced in large quantities at our Freeport plant. The most direct route to lavandulol was to combine prenyl chloride with another suitable C_5 molecule. This means essentially condensing prenyl chloride either with itself or with other C_5 compounds, such as prenyl alcohol or isoprene.

One of our researchers, Dr. H. Ramsden, found that it was possible to use a modified Grignard reaction and directly condense prenyl chloride and isoprene with magnesium to obtain lavandulyl magnesium chloride. Lavandulyl magnesium chloride can be readily oxidized with air or oxygen and hydrolyzed to yield lavandulol. This reaction is covered by two U.S. patents granted to Rhodia Inc., U.S. No. 3,819,733, June 25, 1974, and U.S. No. 3,856,867, December 24, 1974.



The process is simple. Isoprene and prenyl chloride, in equimolar proportions, are added to a suspension of magnesium turnings in boiling tetrahydrofuran. When the magnesium has reacted, the mass is cooled to 30°C and oxidized by bubbling air through it. After hydrolysis and solvent recovery, lavandulol is isolated by vacuum distillation. The yield of this reaction is not very high: 40%; however, raw materials are relatively inexpensive and readily available. Lavandulol is obtained in only two steps. The technique of employing large-scale Grignard reactions is somewhat delicate but is

now well known and does not present any insurmountable difficulties.

One of the most arduous problems we had to resolve was the identification of the other C_{10} alcohols formed in addition to lavandulol and to determine their influence as trace impurities on the lavandulol odor. The separation of lavandulol from these isomeric C_{10} alcohols by vacuum distillation is not easy. However, as mentioned earlier, we know how to build vacuum stills which combine high efficiency with low pressure drop. This kind of equipment affords a good separation of lavandulol with a minimum of degradation.

This new process will permit manufacture of lavandulol in a relatively simple manner for marketing at a reasonable price. Lavandulol and its acetate should become very useful raw materials for fine fragrances.

While pursuing research on terpene chemicals, we became interested in a completely different field of chemistry, namely, catechol and its derivatives. Our parent company in France, Rhone-Poulenc, had pioneered a new oxidation process for phenol which yielded both hydroquinone and catechol. The aroma chemicals industry has little interest in hydroquinone but the availability of catechol at a reasonable price has already affected the manner in which some aroma chemicals are produced.

From the 1920s to the late 1940s, the starting raw material for vanillin synthesis was guaiacol, a phenolic ether closely related to catechol. Guaiacol was made from phenol via a complicated and expensive process. In the late 1940s, it was found that vanillin could be manufactured at a lower cost from wood lignin, a by-product of the paper industry. Within a few years, vanillin made from guaiacol disappeared from the market.

However, it is relatively simple to manufacture guaiacol from catechol by reacting this diphenol with either dimethyl sulfate or methyl chloride. Guaiacol obtained through this process is cheaper. It has become, again, an attractive raw material for vanillin, and vanillin will be produced from guaiacol in the very near future. When we realized that guaiacol would be produced on a large scale, we decided to investigate if other chemicals derived from guaiacol, in addition to vanillin, could be of interest to the fragrance industry.

Eugenol appeared as a logical candidate. Eugenol is used in large amounts. It is one of the last important aroma chemicals derived from an essential oil, clove leaf oil. Until now the relatively high cost of guaiacol had discouraged any attempt to manufacture a synthetic eugenol except possibly in the Soviet Union. Several syntheses for eugenol are described in the literature, the most recent being found in two U.S.S.R. patents.

U.S.S.R. patent No. 117,492 describes the C-allylation of guaiacol with allyl chloride using a copper catalyst to obtain eugenol. A special grade of powdered copper is employed. The eugenol fraction obtained is composed of 59% eugenol, 30% meta-eugenol (5-allyl, 2-methoxyphenol) and 10% ortho-eugenol (6-allyl, 2-methoxyphenol).

U.S.S.R. patent No. 166,019 suggests that guaiacol can be allylated using cuprous chloride in sodium chloride solution, removing the hydrochloric acid formed with a sodium acetate solution. The yield of para-eugenol is about 45%. The reaction product is composed of 70% para-eugenol, and 30% meta- and ortho-eugenols combined. Meta- and ortho-eugenols have a rather unpleasant odor, phenolic, harsh, burnt. Eugenol must be free of ortho- and meta-isomers to have an acceptable odor.

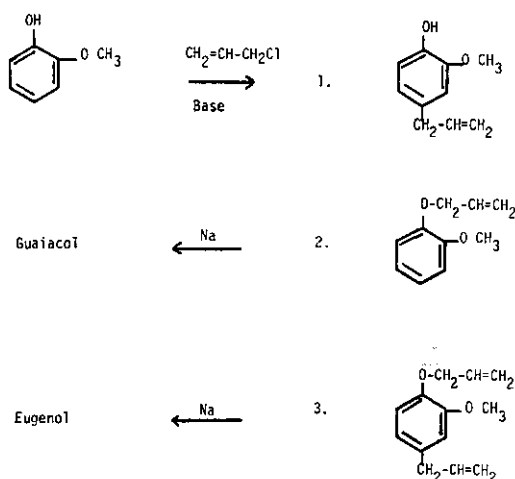
Separating the eugenol isomers by distillation, especially the meta-isomer from the para-isomer, is nearly impossible. Vacuum distillation with a 45-plate column of a mixture containing 60% para-eugenol and 40% meta- and ortho-eugenols yields a product which is only 90% pure.

At first, we investigated the route followed by the Russians. We quickly reached an impasse. It became clear to us that any acceptable eugenol process should provide a crude product without meta-eugenol. Meta- and para-eugenol could not be separated except by lengthy and costly procedures. Attempts to use a Claisen-type transposition failed for the same reason. We realized that to be successful we had to discover a completely new kind of reaction.

Two of our researchers, Dr. DeSimone and Dr. Ramsden, found that guaiacol could be allylated with an allyl halide or an allyl sulfate or sulfonate, in the presence of an alkali or alkaline earth metal hydroxide in aqueous solution. The reaction proceeded at room temperature. Unfortunately, in addition to the C-allylation, the process resulted in some allylation of the guaiacol free hydroxyl group. A fair amount of guaiacol allyl ether was formed along with smaller amounts of eugenol allyl ether. There was no problem in separating these two ethers from the eugenol and unreacted guaiacol. They are insoluble in dilute caustic soda solution; eugenol and guaiacol are soluble. However, to have a viable process, it was essential to convert guaiacol allyl ether and eugenol allyl ether back to guaiacol and eugenol.

It was found that guaiacol allyl ether and eugenol allyl ether could be cleaved by treatment with sodium in boiling heptane or xylene, resulting in formation of the sodium guaiacolate and sodium eugenate which could be acidified, giving guaiacol and eugenol.

Combinations of these two reactions, allylation of guaiacol in alkaline medium and cleavage of the



ethers formed besides eugenol, gave us the eugenol process we sought. This process is simple and comprises only two steps. Raw materials are easily available. It produces a crude eugenol free of meta-isomer. Concentration of the ortho-isomer in crude eugenol varies from 15% down to 5%. Best results are obtained when barium hydroxide is used as condensing agent. In that case, the true yield is 76.7%; the direct yield 28.6%; and the crude eugenol contains only 5% of ortho-isomer.

Separation of ortho- and para-eugenol requires a very efficient distillation column, but it is possible to design and build such a column.

Synthetic eugenol is comparable to the best grade of eugenol derived from clove leaf oil. Of course, its odor is completely devoid of any terpenic undertone. It should satisfy the most demanding perfumers and flavor chemists. On December 30, 1975, Rhodia was granted U.S. patent No. 3,929,904 covering this new eugenol process.

Obviously, we consider these two processes for producing lavandulol and eugenol substantial contributions to the efforts of our industry to improve and broaden the supply of aroma chemicals. It is clearly in the interest of the fragrance industry to understand and encourage such efforts. We should all realize that the new Toxic Substances Control Act, which Congress is about to pass, will increase considerably the cost of developing new aroma chemicals. The new law may reduce the number of such chemicals drastically. Closer cooperation between the fragrance and the aroma chemical industries will now be even more important in order to maintain a healthy level of innovation in areas of mutual interest.

Past presidents of the American Society of Perfumers are (from left, front) Vincent Ellis, Edward Shuster, Ernest Shiffan, Harry Cuttler, Stanley Rutkowski, Morrison Patterson (from left, back) Henry Weiner, Jacques Masson, Raoul Panta-leoni, and John Funesti.

Ms. Fedak: Ed Blaumeiser is our next speaker. As manager of fragrance planning and evaluation for Avon Products, Inc., a position he has held for over three years, Mr. Blaumeiser is responsible for all fragrance planning for Avon, both domestically and internationally.

Before joining Avon in 1972, Mr. Blaumeiser was men's fragrance coordinator for International Flavors and Fragrances. He is a member of the Society of Cosmetic Chemists. Educated at Seton Hall University and at the New School for Social Research, Mr. Blaumeiser also holds a diploma in fine arts.

Design and Creation of a Successful Major Fragrance

Edward Blaumeiser, Avon Products Inc.

This discussion of the design and creation of successful major fragrances will deal with the subject from the standpoint of fragrance planning and evaluation by a major marketer. I see this as a creative process, not as a science, but as an art—an artistic process which should have as its end not only a work of beauty, but a fine product which will make a major contribution to the profit picture of its marketer.

Even before we get to the actual subject of fragrance creation, however, certain questions come to mind.

For instance: "Why market yet *another* new fragrance?"

Some responses occur immediately: First, to meet the changing needs and moods of an ever-changing consumer. Second, to add excitement and newness to the fragrance marketplace. Third, to answer an existing consumer need which is not currently being met by any other fragrance. Fourth, to increase the marketer's share of the total fragrance market.

"How can one assure the success of the new fragrance?" becomes the next obvious question when we recall the enormous number of new fragrance introductions last winter. It is now quite apparent that simply being new is by no means enough to insure a fragrance's place in the market, or even to gain it sufficient consumer interest to lead to a meaningful purchase volume. Any new introduction must, of course, make a statement in terms of its type of fragrance and the impression it gives. It must, however, certainly do a good deal more than just that. This fragrance must be an expression of its wearer, and it must in some way reflect the world and times in which it exists. In order to understand some other important aspects of this fragrance introduction, we must consider the fragrance's function—indeed, the function of any fragrance. This we can call the "promise," or the "emotional benefit." As we all know, the response to

fragrance is very basic and fundamental. The sense of smell is the first to awake after birth. It subliminally influences our thoughts, actions, reactions, and desires to an enormous degree all through our lives.

Each year we understand more and more just how enormous these effects can be. The most direct and obvious way in which a fragrance fulfills its promise is by being an enhancement of one's self. This enhancement should be immediately apparent to the wearer—and very quickly thereafter to those surrounding her. The fragrance becomes a sharing of that self with others.

As a fragrance amplifies the impression made on others, there is an increase not only in the *degree* of the impression, but in the *type* of impression. An exotic and sultry woman can increase her desirability, her warmth, her femininity, her sensuousness, immensely, by wearing an appropriate fragrance. By the same token, a vivacious, alive girl, who wants to express her love of life and her vitality, can find no means which will do more to convey these feelings than a fresh, vibrant, and crisp fragrance.

The effect of fragrance is not just in the words which the copywriters use or in the promotional material produced by the artists. There is something intrinsically distinctive about any really successful creative fragrance, and there *must* be this uniqueness if the fragrance is to be a success with its wearers as well as from the standpoint of continuing sales.

More and more we find that fragrances can actually be expressions of the times in which we live. The popular fragrances of the day mirror the life currents of our society. When there is a groundswell of desire on the part of the people generally for a more lavish and a more opulent way of life, then we find many fragrances that are rich, heady and complexly sensuous. As the pendulum of attitudes