

THE CHEMISTRY OF ESSENTIAL OILS AND RELATED PRODUCTS

Introduction

The basic reason for having this symposium is the great interest which essential oils and related products have received in the past and which they command at present. This interest is justified, because these products are truly "essential" to our culture and civilization.

While essential oils find a variety of applications, their most appreciated properties are their odors. Thus, as it is well known, these materials are used to give fragrance to a great number of diversified products and they contribute extensively to "flavor," which is a combination of odor and taste.

Many items which we are using in our daily life are first evaluated by their appearance and odor. In these instances fragrance is not an additive to such products, but it is one of their essential parts.

An example to illustrate this point is "soap," which would lose much of its attractiveness without fragrance. This fact is also applicable to many more consumer articles such as all kinds of lotions and other cosmetics, room sprays, etc.

Essential oils are products of agriculture. They are the volatile essences of botanicals such as flowers, buds, twigs, leaves, barks, roots, and the rind of certain fruits which are the source of citrus essential oils. Volatility is a prerequisite for odor perception; thus, essential oils are the scent carriers of these floral materials.

In chemical terms these natural products consist of an extensive number of diversified chemical entities which can be divided into two main groups, terpenoids and nonterpenoids.

Both of these groups comprise hydrocarbons and oxygenated components such as aldehydes, ketones, acids, alcohols, esters, etc., of the aliphatic, cyclic, acyclic, and aromatic series.

The chemistry of essential oils consists of: separation or isolation of the individual components of essential oils; structural identification of these materials; synthetic duplication of these components in order to confirm a chemical structure or to produce commercially these materials; establishment of the biogenetic pathway of the production of such constituents in plants to prove the validity by appropriate procedures, such as the study of photosynthesis; and study of the influence of agricultural conditions on yield and composition of essential oils.

As in many other branches of organic chemistry, the rapid progress of essential oil chemistry, which we have witnessed in the recent decades, is the result of the spectacular advances made in structure determination. This was made possible by physicochemical methods such as the chromatographic separation techniques, combined with ir, nmr, mass, X-ray diffraction, and some of their sophisticated improvements. By the application of these methods a great number of essential oil components were isolated and their exact three-dimensional chemical structures were established.

Simultaneously, the sensory properties and value of these constituents as "aroma" chemicals and their specific contributions to the fragrance of essential oils could be evaluated. Such assays were and are important in deciding whether duplication of such isolates on a commercial scale are desirable.

The other question is a strictly economical consideration, namely whether nature, in such selected cases, is a more expensive or a less expensive producer than the organic chemical industry.

There are also specific differences between the performances of nature and the chemical industry to be considered. For example, nature produces mixtures of chemicals, such as essential oils, whereas the com-

mercial synthesis is aimed at the production of a single chemical.

One of the most powerful motivations to duplicate specific natural isolates by synthetic methods is the fact that such items have established uses. Under favorable economical conditions they are valuable products of commerce. Examples are linalool, geraniol, and menthol.

Uncontrollable, unfavorable events in nature can justify the synthetic production of specific items. However, only synthetic processes which can compete under all conditions with agriculture will have a permanent place in our economy. Adverse agricultural conditions during one year can change to the opposite the next year. In such cases improved harvests would be the cause of lower prices which could make synthetic production economically uninteresting.

There are several factors which are important to the agricultural aspects of essential oils. Climatic conditions: The cultivation of essential oil-bearing plants is dependent on climatic conditions. Thus, the cultivation of the parent plants of specific essential oils is limited to certain areas of the globe. Availability of land: Even where favorable climatic conditions prevail, only those plants will be cultivated which promise the highest financial return. These are not necessarily essential oil-bearing plants.

Land, which was previously used for agriculture, is in some instances unavailable for this purpose, due to the utilization for other objectives such as housing or the erection of industrial plants. What may be expected from agricultural science is the utilization of advances made and to be made in soil conditioning, the combatting of insect pests and plant diseases, improved planting and harvesting methods, equipment improvements, etc. These should result in higher yield and quality of essential oils in general.

Novel essential oils and more robust plants have been produced by hybridism (Lavandin algeris) and this approach remains a future possibility.

In spite of the great strides which organic synthetic chemistry has consistently and continuously made (for example, modification and modernization of such classical methods as the Grignard and the Friedel-Crafts reactions and the many useful novel preparative methods) agriculture still holds her own and remains the producer of a great part of organic chemicals used as perfume and flavor materials. Examples are "eugenol" and "safrole," which is used in the production of "heliotropine."

On the other hand, the chemical industry was able to compete successfully with agriculture and has produced synthetic duplications of natural isolates at consistent quality and lower prices than previously obtained from agriculture. Examples are methylsalicylate, thymol, vanillin, linalool, and geraniol.

Many isolates of essential oils are per se important and used for diversified applications. There are many of such essential oil constituents which are today not at all synthetically produced because nature is still the less expensive producer.

It can be expected, however, that the search for better and more economical synthetic methods aimed at the duplication of such natural products will go on and on as long as organic chemistry will progress.

Organic chemistry had its beginning by the systematic investigation of natural products. Essential oils are among them. Thus, it can be stated that essential oils were vital to organic chemistry and vice versa. If anything should or could be added to this statement it is that this interdependence has grown stronger and

Continued on next page

stronger in the past and at present. Judging from the literature, essential oils and their constituents are widely used as research media and research topics by organic chemists and by chemists devoted to the biochemistry and the physiology of plant life. These facts explain why this symposium was organized by the Division of Organic Chemistry, jointly with the Division of Agricultural and Food Chemistry of the American Chemical Society.

It is also necessary to mention what products related to essential oils stand for. This relationship can be either chemical in nature, as it is well demonstrated by terpenes and steroids (both of these products are biologically formed from mevalonic acid) or it can be based on similar applications. Products are considered related to essential oils if they are used for a similar application as essential oils. This application can be in perfumery, flavor, or in other fields such as pharmaceuticals.

These chemicals distinguish themselves furthermore from the natural products, i.e., essential oils, by being purely synthetic. This means that they were not found in nature.

In the past many interesting molecules, not existing in nature, but having odor and/or flavor value, have been synthesized, mainly by the following approaches. Serendipity: Examples of such chemicals are hydroxycitronellal and the nitromusks. As long as we cannot pinpoint and describe the odor of molecules by their chemical structures, it can be assumed that in the future some chemicals having odor and/or flavor value, which were most probably prepared without having this property in mind, will be found or detected by incident. The intuitive empirical approach (sometimes referred to as the "Dynamic" approach): This approach is widely used by industry. It is practiced most successfully by chemists highly experienced in their field. There is no rule by which this approach can be guided. Molecular modification: This is a highly effective and widely practiced approach, not only in the aroma industry but also in other industries; e.g., the pharmaceutical industry [Molecular

Modification in Drug Design, Advances in Chemistry Series, 45 (1964), American Chemical Society]. As its name indicates, this method modifies existing molecules having either proven value or it modifies molecules which do not have value but where modification is assumed to be beneficial. Simple and successful molecular modifications are "ethyl vanillin," which has more odor-flavor potency than the natural "vanillin." In analogy, "ethyl maltol" is a stronger odor-flavor chemical than "maltol."

In both of these cases the molecules were modified by replacing a methyl with an ethyl group. However, to improve the odor of even "somewhat related" molecules by replacing a methyl group with an ethyl group is not a rule.

There were several approaches made to correlate structure with odor and some progress was accomplished, particularly in specific areas such as "musks."

To predict the type of odor or odor intensity of many novel chemicals is, at present, speculative and difficult. In this connection it should be remembered that only identical chemicals have identical odors and even slight variations in chemical structure or configuration are in many instances sufficient to change an odor profile.

The correlation of odor and structure is being actively pursued in many laboratories and it can be expected that some of these research approaches will be eventually successful. The symposium is divided into five sessions, according to related topics. The symposium presents a cross section of today's standing of the chemistry of essential oils and related products with aspects of pure and applied chemistry, academic and industrial research. Both areas are of equal importance and neither can exist without the other. They are interdependent.

KURT KULKA, Symposium Chairman
Fritzche Dodge & Olcott, Inc.
New York, N.Y.

Part One of a Two-Part Symposium

Sensory Properties and Applications of Derivatives of

1-Phenyl-2,2-dialkyl-1,3-propanediols

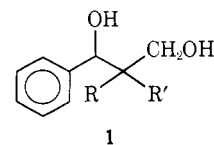
Kurt Kulka,* Odd Hansen, and Ronald A. Joseph

1-Phenyl-2,2-dialkyl-1,3-propanediols were prepared by reacting aromatic aldehydes with isobutyraldehyde and related aliphatic aldehydes under alkaline conditions. In the course of this process the aldol is formed which reacts with an additional mole of the aliphatic aldehyde in a crossed Cannizzaro reaction. Certain derivatives of these diols such as esters, acetals, and ketals have diversified and interesting

odors which make them useful in perfume compositions. In addition to the easily recognizable olfactory properties of these novel chemicals, specific acetals, ketals, and methylcarbamates of this chemical family are promising synergists for insecticides. Monocarbamates of these diols are of interest as pharmaceuticals.

This presentation is concerned with a group of diols and some of their derivatives which are related to essential oils. This relationship is based on the common application of essential oils and the chemicals under discussion as perfume materials.

The basic structure of these diols is as follows

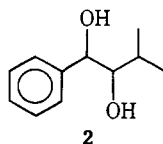


where the aromatic ring can be substituted, as will be dem-

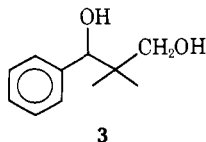
Research Laboratories, Fritzche Dodge & Olcott, Inc.,
New York, New York 10011

onstrated later in this paper, and R and R' are the same or different alkyl radicals.

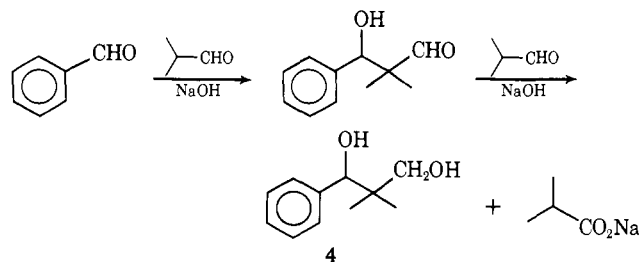
Historically, the condensation of isobutyraldehyde with benzaldehyde was first reported in 1890 by Swoboda and Fosseck who assumed the reaction product to be phenyl-isopropylethylenediol.



In 1896, Lieben advanced experimental evidence that this assumption was erroneous and reported the correct structure of this chemical to be 2,2-dimethyl-1-phenyl-1,3-propanediol.



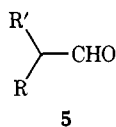
It is interesting to note that in Lieben's experiments 2 mol of isobutyraldehyde were reacted with 1 mol of benzaldehyde and 1 mol of alcoholic potassium hydroxide. These proportions correspond to today's accepted mechanism for the above reaction, namely that benzaldehyde condenses with isobutyraldehyde in molecular equivalents under alkaline conditions to give a hydroxyaldehyde which, in the presence of sodium or potassium hydroxide, reacts in a crossed Cannizzaro reaction with another mole of isobutyraldehyde as follows



to give the diol and a salt of isobutyric acid.

While related condensations of isobutyraldehyde with aliphatic aldehydes and their reaction products have received some attention in the past, the reaction of isobutyraldehyde with aromatic aldehydes was neglected.

There were two main reasons which prompted us to revive this reaction by condensing isobutyraldehyde and other aliphatic aldehydes having the structure

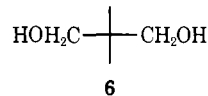


where R and R' are the same or different aliphatic chains with a variety of aromatic aldehydes. They are an anticipated broad spectrum of application possibilities for these novel diols and basic economical considerations.

ANTICIPATED USAGE OF THESE NOVEL PRODUCTS

In putting this reaction into practice, we visualized a great variety of novel diols which would lend themselves readily to esterification and dioxane derivatives such as acetals and ketals. We could assume that among the variety of these

novel chemicals at least some of them would have interesting sensory properties. This assumption, although intuitive and empirical, is based on previous experience. This previous experience is both of a general nature and of a specific nature. We have previously described (Kulka, 1966b) novel acetals and ketals prepared from the aliphatic diol 2,2-dimethyl-1,3-propanediol



and some of these chemicals have received acceptance in perfumery. There are some obvious similarities between this aliphatic diol and the diols under discussion.

It is a fact that similar research concepts are among the various approaches industry applies today to obtain novel chemicals for evaluation and possible usage. We also believe that this basic philosophy has, and will have, its place in industrial research as long as chemistry remains an experimental science.

To predict the odor type or odor intensity of such novel chemicals is, however, speculative and difficult. In the past there were several approaches made to correlate structure with odor and some progress was made, particularly in specific areas such as "musks." It should, however, be remembered that only identical chemicals have identical odors, and even slight variations in chemical structure or configuration are, in many instances, sufficient to change an odor profile. The final judgment concerning merit of such novel chemicals can be made only by experts devoted to this specific task. Extensive experimentation is necessary to prove or disprove the value of novel aroma chemicals.

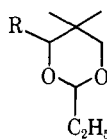
BASIC ECONOMICAL CONSIDERATIONS

The following considerations are of importance and favorable: (1) The availability of isobutyraldehyde in com-

Table I. 1,3-Diols from Aromatic Aldehydes and Isobutyraldehyde

R	Properties	Yields
	Mixture of three isomers Meta isomer predominates Heavy sirupy liquid bp 131° C/1 mm	88%
	mp 59-60° C	79%
	mp 89-90° C	80%
	mp 107-108° C	70%
	mp 113-114° C	80%

Table II. Acetals from Propionaldehyde



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R	Odor	bp/mp	n^{20}_D	Yields
 20	Walnut	108–110° C/3 mm	1.5035	97%
 14	Hyacinth, green	123° C/3 mm	1.5042	55%
 21	Fruity, wine, melon	118–123° C/2 mm	1.5116	75%
15	Nutty	140–143° C/3.5 mm	1.4978	88%
16	Coumarin, heliotropin	147–149° C/1.3 mm mp 58–59° C		75%
18	Indefinite	mp 76–77° C		97%

mercial quantities at reasonable prices by the production of isobutyraldehyde from isopropylene by oxonation and by other modern processes (Hagemeyer and DeCross, 1953); (2) The availability of aromatic aldehydes under similar favorable conditions; (3) Simplicity of the reaction. The production of the various diols is a simple one-step process which, from an industrial point of view, is ideal; (4) High yields and high purity. Relatively high yields were obtained and the purification of the diols is readily accomplished by distillation and/or recrystallization. Thus, no difficulty is encountered in scaled-up production of these diols of consistent quality.

Some of the physical properties and yields for five of such novel 1,3-diols obtained by a crossed Cannizzaro reaction from aromatic aldehydes with isobutyraldehyde (Kulka, 1962, 1963, 1966a) are tabulated in Table I. As expected, these diols are odorless.

Among the derivatives of these diols, two groups of acetals which we have prepared from propionaldehyde and iso-

butyraldehyde are recorded with their odor characteristics, physical properties, and yields in Tables II and III.

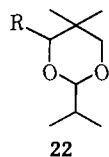
In general terms it can be stated that some of these acetals have interesting and useful odor characteristics.

We have also prepared the dimethyl ketals of some of these diols, as shown in Table IV.

Several of these materials are of definite usefulness in perfumery.

We have also observed a rather unexpected phenomenon, and that is that the ketals of two of these diols, prepared with methyl amyl ketone, have rather weak odors, whereas the ketals obtained from methyl hexyl ketone exhibit some interesting possibilities as shown in Tables V and VI.

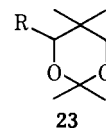
Table III. Acetals from Isobutyraldehyde



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R	Odor	bp	n^{20}_D	Yields
20	Woody, cedar, tobacco	113° C/2 mm	1.4980	76%
14	Cherry	116° C/2 mm	1.4936	65%
21	Woody, slightly anisic	131–135° C/1 mm	1.5052	65%
15	Nutty, opopanax	134–136° C/1 mm	1.4952	88%
16	Fatty, green, apple, jasmin	161° C/4.5 mm	1.5126	91%
18	Leather, labdanum, olibanum	165° C/2 mm	1.5506	84%

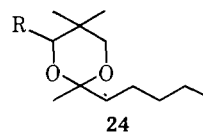
Table IV. Dimethyl Ketals



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R	Odor	bp/mp	n^{20}_D	Yields
20	Floral and amber note	107–108° C/4 mm mp 61–62° C		90%
14	Leather, amber, green	116° C/3 mm	1.5040	75%
15	Indefinite	126° C/2 mm	1.5026	57%
21	Green, anisic	120° C/1 mm	1.5111	85%
16	Banana, fig, fruity	mp 67.5–69.5° C		65%

Table V. Ketals from Methyl Amyl Ketone

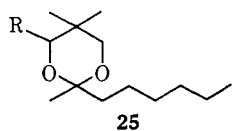


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R	Odor	bp	n^{20}_D	Yields
20	Weak	124–125° C/1 mm	1.4968	91%
14	Weak, slightly green	133–135° C/1 mm	1.4974	77%

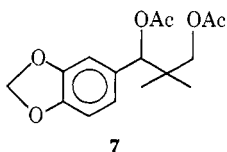
Table VI. Ketals from Methyl Hexyl Ketone

R	Odor	bp	n_D^{20}	Yields
20	Jasmin, green	140–141° C/2 mm	1.4941	80%
14	Jasmin, green, mushroom	134–135° C/0.4 mm	1.4956	70%



ESTERS

Among the various diacetates which we have prepared, the one having a methylenedioxy group on the ring was found to have the most obvious merit in perfumery. This



diester has a rather strong, basically floral odor reminiscent of root beer and anise. Some of the diesters, including those having no substituents on the ring (prepared from benzaldehyde and isobutyraldehyde), were labeled as having rather weak odors. These results prove the influence of ring substitution on the odor or odor intensity of this group of diesters.

Evaluating these results, it can be stated that some of these novel chemicals will find their way into perfume compositions. As expected, this cannot be said of the rest of these chemicals which we have prepared so far and tested in the course of this project.

The stereochemistry of these chemicals is under investigation, and our results will be reported in a separate communication. We realize the importance of this investigation, particularly because one theory of olfaction states that stereochemical features of a molecule are determinative factors of odor. Such a project, in our case, is rather extensive. The great number of acetals, ketals, some of the diesters, and isomers which can be involved, and the separation, identification, and evaluation of their sensory properties, have to be considered.

There remains an almost infinite number of derivatives of such diols which could be prepared and made available for evaluation.

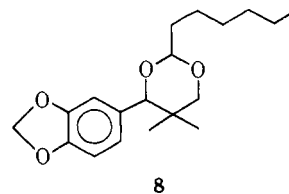
From the structural examination of these novel diols, certain similarities with the structures of chemicals having established definite usage becomes evident. Based on this observation, one can take an "educated guess" that some of the diols reported here will lend themselves well as building blocks in the synthesis of novel products having, in all probability, other important applications than just odor.

One of these possibilities is in pesticide chemistry, one of the significant branches of agricultural chemistry.

It is well known that the presence of a methylenedioxyphenyl group is a basic requirement in giving a chemical synergistic activity with insecticides such as pyrethrum. There are many compounds prepared for this application, the activity of which is mainly based on the presence of the above group in the molecule.

A rather extensive literature on this subject gives witness to the importance of this objective. One of the most recent and most complete essays dealing with this item is by John E. Casida: "Mixed Function Oxidase Involvement in the Biochemistry of Insecticide Synergists," (Casida, 1970).

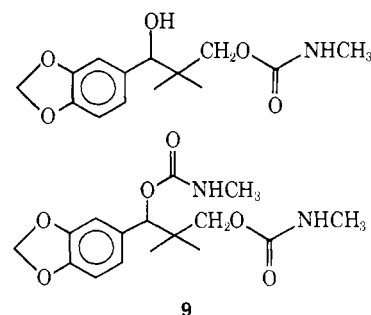
We were interested whether our assumption was correct and have prepared the heptaldehyde acetal of 2,2-dimethyl-1-(3,4-methylenedioxyphenyl)-1,3-propanediol:



Testing by an outside laboratory specializing in such assays proved that this chemical has indeed very significant synergistic properties with pyrethrum and allethrin insecticides.

The possibility of preparing and testing other acetals and ketals of this and similar diols, whereby, for example, the gem-dimethyl group is replaced by other aliphatic chains, is indeed inviting, and such structural variations could pave the way to even more potent synergists.

Another possibility in this field is offered by the condensation products of isocyanates, e.g., methyl isocyanate with the above-mentioned diol or other diols of this project to give either the mono- or dimethyl carbamate.



Metcalf and Fukuto (1965) state that carbamic esters of aromatic and heteroaromatic systems frequently possess insecticidal activity. This action is explained by the result of the inhibition of acetylcholinesterase, probably by the transfer of the carbamoyl group to an active site of the enzyme.

In our specific case, the methylenedioxyphenyl group might be beneficial to the activity of such methyl carbamates.

Still another aspect of utilizing these diols is in the synthesis of novel pharmaceuticals. Such incidents are not quite the exception because many so-called "aroma chemicals" are used as building blocks in the preparation of pharmaceuticals.

The interesting structural arrangements of these diols, which are indicative for this specific application, are hereby given.

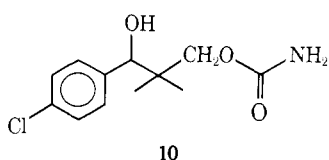
The 1,3-Diol Structure Having a Gem-Dialkyl Group on the 2 Carbon. Such molecular arrangements are present in several pharmaceuticals, e.g., in some of the so-called "tranquilizers" such as "Meproamate."

The Aromatic Ring with its Various Possibilities of Substitution. Some of these substituents are credited with exerting specific pharmacological activity.

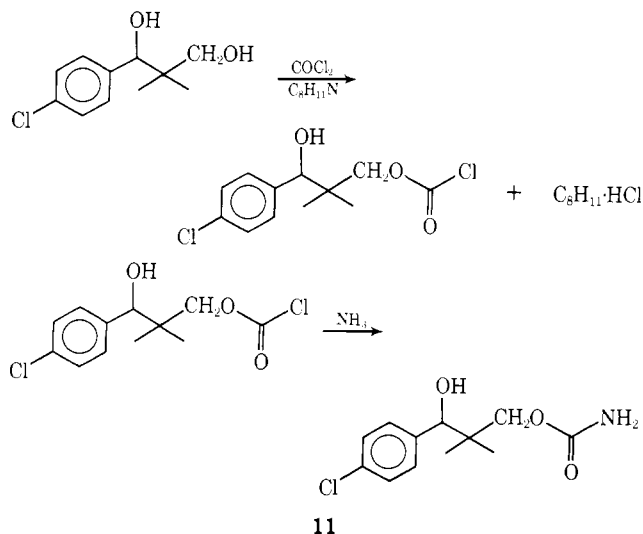
THE METHYLENEDIOXYPHENYL GROUP. This group is usually found in alkaloid molecules. There is relatively extensive literature dealing with the influence of this group on the pharmacological activity of products, *e.g.*, an essay by A. A. Newman: "The Occurrence, Genesis and Chemistry of the Phenolic Methylene-Dioxy Ring in Nature," (Newman, 1962).

A HALOGEN ON THE RING. The action of halogens is on the ring explained by Burger (1960) as follows: "Depending on their electrochemical nature, halogens exert a pronounced influence on the biological behavior of organic compounds. Halogens substituted in nonconjugated positions ("negative halogens") usually increase both useful and toxic properties of active compounds but not at the same rate. The rate in toxicity is often negligible and many medicinal chemists look upon halogen substitution, especially chlorination, as a reasonable means of stepping up activity and widening the margin of safety in a given series."

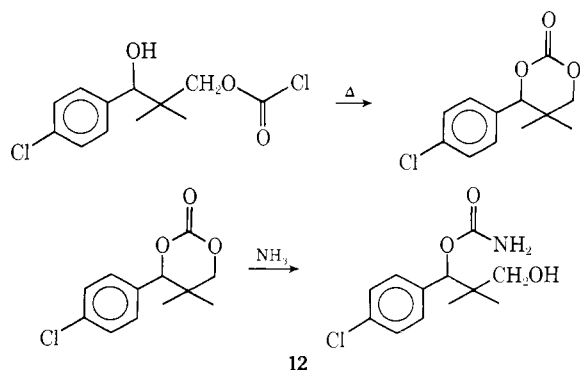
Based on such consideration we have prepared the monocarbamate by the reaction of the diol with phosgene in the



presence of dimethylaniline to obtain the monochloroformate which on reaction with ammonia produces the monocarbamate of the primary hydroxyl group of the diol.



The monochloroformate, on heating or standing at room temperature overnight, will cyclize to the cyclic carbonate. This carbonate on reaction with ammonia gives the carbamate of the secondary hydroxyl group of the diol.



Extensive animal testing with these products gave very encouraging results, and further testing as required is in progress.

It is unfortunate that because of the very rigid and expensive testing procedures which are required, our efforts are presently limited to just one compound. There remains, however, the aspect that molecular modification of these chemicals could result in even more powerful pharmaceuticals and other valuable materials.

EXPERIMENTAL

Synthesis of 1-Phenyl-2,2-dialkyl-1,3-propanediols. To a solution of 3.3 mol of potassium hydroxide in 700 ml of methanol was added a solution of 3 mol of the aromatic aldehyde and 6.5 mol of the aliphatic aldehyde (isobutyraldehyde) and 200 ml of methanol over a period of 4.5 hr at a temperature of 10–16° C. This reaction mixture was agitated overnight at room temperature, acidified with acetic acid, and approximately 800 ml of methanol was stripped off by distillation. The reaction mass was washed with water, separated, and the desired product was obtained by fractional distillation in vacuum.

Synthesis of Acetals of 1-Phenyl-2,2-dialkyl-1,3-propanediols with Propionaldehyde and Isobutyraldehyde. To a solution of 1 mol of the diol and 1.1 mol of the aliphatic aldehyde in 250 ml of benzene is added 0.5 g of *p*-toluenesulfonic acid (as the catalyst). The solution is refluxed with a water entraining system until the theoretical amount of water formed in the reaction is collected. The reaction mass is cooled and made slightly alkaline with a 5% aqueous sodium hydroxide solution. The organic part is separated from the aqueous layer and washed with 2 × 250 ml of water. The solvent is removed by distillation, and the reaction product is obtained by fractional distillation through a 1.5-ft Vigreux column.

Synthesis of Dimethyl Ketals of 1-Phenyl-2,2-dialkyl-1,3-propanediols. 1 mol of the diol is combined with 1.3 mol of 2,2-dimethoxypropane. The mixture is dissolved in 520 ml of toluene. To this solution is added 0.5 g of methanesulfonic acid (as the catalyst). The reaction mixture is heated and the formed methanol is removed as an azeotrope with toluene boiling at 63.8° C through a 1-ft Vigreux column. After the theoretical amount of methanol has been removed, the reaction mixture is cooled to room temperature, washed with 100 ml of a 3% aqueous sodium hydroxide solution, and 2 × 150 ml of water. The aqueous part is separated from the organic part which is fractionated through a 14-in. Vigreux column.

Synthesis of Methyl Amyl Ketals and Methyl Hexyl Ketals of 1-Phenyl-2,2-dialkyl-1,3-propanediols. First, the dimethyl ketals of methyl amyl ketone and methyl hexyl ketone were prepared by standard procedures. Then, 0.3 mol of the diol was combined with 0.5 mol of one of the above mentioned ketals. The mixture was dissolved in 250 ml of toluene and 0.2 g of *p*-toluenesulfonic acid (catalyst) was added. The reaction mixture was heated, and the formed methanol was removed by distillation through a 0.5-ft Vigreux column as an azeotrope with toluene, boiling at 63.8° C. After the theoretical amount of methanol was stripped off, the reaction mixture was cooled to room temperature and washed with 500 ml of a 3% aqueous sodium carbonate solution, then with 2 × 250 ml of water. After separation from the aqueous layer, the organic part was fractionated through a 0.5-ft Vigreux column.

SUMMARY

We have described *one* research aspect or approach practiced by the essential oil and aroma chemical industry. We have demonstrated the usefulness of this technique by reporting the results of its application. The "Chemistry of Essential Oils and Related Products" is not an isolated part of chemistry. Many of these natural and synthetic products have, in addition to odor and/or taste, other valuable properties which make them useful in other fields where chemistry is applied.

LITERATURE CITED

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