

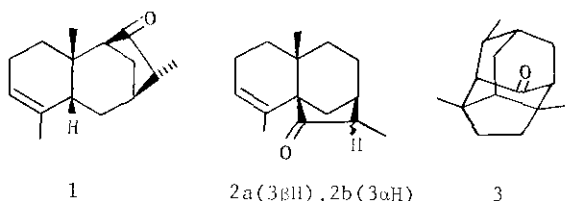


Chemistry/Technology Section Synthesis and Substitutes for Essential Oils

This begins a partial listing of the abstracts of papers tentatively scheduled to be presented at the **9th International Congress of Essential Oils**. The balance of the abstracts will be published in our report issue of April/May **Perfumer & Flavorist**.

558

Unique tricyclic eudesmenones transformed from santanolide, S. Inayama, H. Hori, A. K. Singh, T. Kawamata, T. Shibata, Keio University, and Y. Iitaka, Tokyo University, Japan



A fragrant tricyclic eudesmenone (1) and its inodorous ring isomers (2) were obtained together with tetracyclic adamantanone (3) by an unusual reaction of 3-deoxyhexahydro-*l*- α -santonin with hot phosphoryl chloride. The structure, conformation and absolute configuration of 1, 2a and b and 3 were all established by spectroscopic especially CD/RD determinations and X-ray diffractions of 1 and 3 as well as 10 α , 11 α -epoxides of 2a and 2b. The proposed reaction pathway for this unique cyclization-skeletal rearrangement from the eudesmanolide to 3 through 1 and/or 2a, b was rationalized by heat of formation based on a semi-empirical MO calculation.

704

The effect of structural modifications on the odour of jasmone analogues, Charles S. Sell, PPF International, England

Jasmone and methyl jasmonate are well known and organoleptically important constituents of the essential oil, concrete and absolute of jasmine (*Jasminum grandiflorum*). Because of the commercial value of the jasmine oils and extracts, a great deal of research has been carried out on these two materials in terms of synthesis of the compounds per se and analogues of them. Typical analogues which have become well established synthetic perfumery chemicals are dihydrojasmone, 2-hexylidenecyclopentanone and methyl dihydrojasmonate. Variations to the structures of the natural materials have been made in terms of carbon chain length on the 2-position of the cyclopentanone nucleus, the presence/absence/stereochemistry of the double bonds in the ring and in the side chain and substituents on the 3-position of the nucleus. In contrast, the effect of substitution and cyclisation of the side chain has received virtually no attention, only a few materials having been reported which possess branched or cyclic side chains. Following investigations into the effects of side chain substitution on the odour of 2-alkylcyclopentanones, it has been found that appropriate substituents can radically alter the odour character of the materials within this series. These observations will be described and the structure/odour cor-

relations defined as closely as possible.

699

Generation of novel sandalwood odorous compounds via hydroformylation of alpha- and beta-pinene, R. W. Trenkle and B. D. Mookherjee, International Flavors and Fragrances Inc., United States

Hydroformylation of α - and β -pinene yielded a series of homo-terpenic aldehydes which on condensation with ethyl methyl ketone produced a mixture of unsaturated ketones possessing interesting odor. These ketones were further reduced to saturated and unsaturated alcohols having sandalwood odor. The structure and odor properties of the individual ketones and alcohol will be discussed.

655

8-Hydroxymethyl-8-methylcamphene and the Bamford-Stevens reaction of some isocamphanylalkanones, Gerhard Buchbauer, Helga Ch. Rohner and Jutta Zehetner, University of Vienna, Austria

In the first part of this paper this synthesis of 8-Hydroxymethyl-8-methyl-camphene, the methyl homologue of Patchenol[®], is described. Grignard reaction of 1-(3,3-Dimethyl-2-exo-norbornyl)-ethanone with CH_3Br followed by dehydration of the intermediate tert. alcohol yields 8,8-Dimethylcamphene which upon SeO_2 oxidation was converted to the title compound.

In the 2nd part the synthesis of some isocamphanylkenes by the Shapiro-Heath modification of the Bamford-Stevens reaction of the tosylhydrazones of the corresponding 1-(3,3-Dimethyl-2-exo-norbornyl) alkanones is described. In connection with earlier results, it is shown, that 8-substituted camphene compounds cannot be prepared by dehydration of prim. or sec. isocamphanyl-alkylcarbinols (with the exception of the certainly not careful pyrolysis methods) or deoxygenation of their oxidation products, but is possible if the hydroxyl group is tertiary and either connected with the isocamphane nucleus in position 2 or with the -C-atom of the side chain.

705

Electrophilic addition reactions of isolongifolene, H.R. Ansari and N. Unwin, Bush Boake Allen, respectively, United States and England

Isolongifolene, an acid-catalysed isomerisation product of Sesquiterpene Longifolene, provides an interesting model for stereochemical studies. The addition of electrophiles such as protonated formaldehyde (Prins Reaction), Bromine, Chlorine and Hypochlorous acid to 3,4-double bond generates a variety of reactivities leading to: (a) Stereospecific entry of the reactants; (b) Skeletal rearrangements of Wagner-Meerwein type and (c) Transannular and other types of proton eliminations. Products from Prins Reaction have woody-ambery odor and are of particular commercial interest. The formation of the products isolated is rationalized in terms of steric hindrance and the nature of the active intermediates involved in transition state.

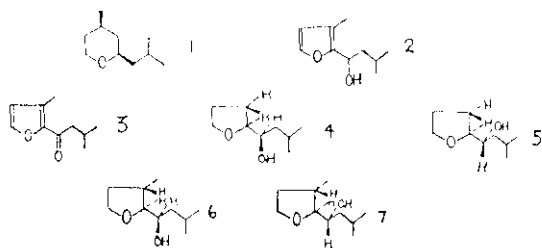
574

Synthesis of cis-dihydro-rose oxide and related stereochemistry, Liu Chu-tsin, Chang Ji-xian and Chou

Zu-liang, Shanghai Institute of Organic Chemistry, China

A new method of synthesis of *cis*-dihydro-rose oxide (1) (analogue of fragrance rose oxide) from a natural product elsholtzia oil is presented. Besides the stereochemistry of the catalytic hydrogenation of elsholtziol (2) and elsholtzione (3), the catalytic dehydration of two diastereoisomeric tetrahydroelsholtziols (4) and (5) are also discussed.

The probable mechanism and stereochemistry of the catalytic hydrogenation of 2 is discussed. The configurations of the four diastereoisomers of tetrahydroelsholtziol, 4, 5, 6 and 7, have been determined with the aid of GC, IR and conformational analysis.



Stereochemical study of catalytic dehydration-rearrangement reactions of 4 and 5 to form dihydropyran system confirms that these reactions follow a transelimination process as suggested by Doscotes and Laily. The antielimination mechanism of catalytic dehydration for 4 and 5 are presented.

542

Novel approach to the synthesis of the C₁₃ degraded carotenoids from isophorone, Tetsuya Kato and Hisao Kondo, Toray Industries, Inc., Japan

The synthesis of the C₁₃ degraded carotenoids including theaspirone, dihydroedulan, and blumenol C is described. 1-Trimethylsilyloxy-3,5,5-trimethyl-1,3-cyclohexadiene (1), generated from isophorone via an enolization/trimethylsilylation sequence, undergoes Diels-Alder reaction with methyl vinyl ketone providing 7-acetyl-3,5,5-trimethyl-1-trimethylsilyloxybicyclo [2.2.2]oct-2-ene (2). Hydrolytic removal of the trimethylsilyl group of (2) followed by retroaldol type cleavage leads to 4-(2,6,6-trimethyl-4-oxo-2-cyclohexenyl)-2-butanone (3). The diketone (3) can be used as a versatile intermediate for the synthesis of the C₁₃ degraded carotenoids. For example, the diketone (3) was converted to dihydroedulan by reduction with NaBH₄ and subsequent cyclization with formic acid.

628

Cyclocitral and derivatives, Dr. L. Janitschke and Dr. W. Hoffmann, BASF Laboratory, West Germany

Cyclocitral and structural analogues which are possible degradation products from carotinoids are well known as plant constituents. Due to the fact of their high reactivity they are key intermediates for synthesis of valuable natural products. Starting from citral a new synthesis of α - and β -Cyclocitral will be reported. Besides this an original access to oxocyclocitral has been found. Cyclocitral and oxocyclocitral are starting materials for valuable constituents of essential oils such as Megastigmatrien,

670

Dehydration studies of alpha- and beta-ionol, Frank B. Whitfield and Galina Sugowdz, Government Research Organization (CSIRO), Australia

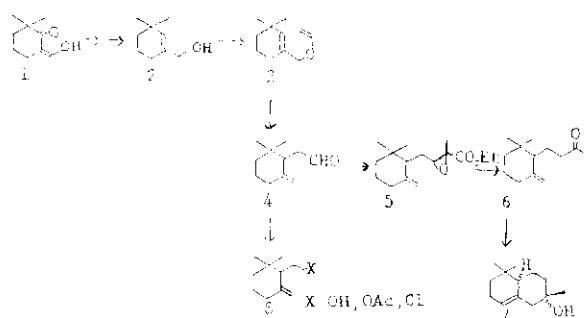
α -Ionol (1) when heated under reflux (230°) for 30 min with hexamethylphosphoric triamide gave in 86% yield (1'E)-6-(buta-1',3'-dienyl)-1,5,5-trimethylcyclohex-1-ene (2). Under similar conditions β -ionol (3) gave in 20% and 40% yields respectively (6E,2'E)- and (6Z,2'E)-6-(but-2' enylidene)-1,5, 5-trimethylcyclohex-1-ene (4a) and (4b), together with 14% of (1'E)-1-(buta-1',3'-dienyl)-6,6-dimethyl-2-methylene cyclohexane (5) and 6% of 1,1,6-trimethyl-1,2,3,4,5,6-hexahydronaphthalene (6). By comparison, when the alcohol (1) was reacted with 5% toluene-p-sulfonic acid in benzene at 20° for 120 h the triene (2) was obtained in only 20% yield while (3) under the same conditions gave after only 10 min and in 84% yield the trienes (4a,b). However, at 80° and in the presence of this acid, the alcohols (1) and (3) gave after 6 h and 4 h respectively and in 60% yield a complex mixture of dehydration products including 1-butyl-2,3,6-trimethylbenzene (7), 1-butyl-2,4,6-trimethylbenzene (8), 1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene (9) and 1,1,4,4-tetramethyl-4,5,6,7-tetrahydroindane (10). Minor products obtained at 80° included 1,1,4,4-tetramethyl-2,4,5,6-tetrahydro-1H-indene (11) and 1,4,4,7a-tetramethyl-4,5,6,7-tetrahydro-7aH-indene (12). The trienes (1) and (4a,b) when reacted

with toluene-p-sulfonic acid at 80° for 6 h and 4 h respectively also gave the compounds (7,8,9,10) in about 60% yield. Reaction pathways are suggested for the formation of all identified compounds and the aroma and flavour properties of several of these compounds briefly described.

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Novel synthesis of γ -homocyclogeraniol, dihydro- γ -ionone and their derivatives, Tsuneo Kawanobe, Kunio Kogami, Kazuo Hayashi and Masanao Matsui, T. Hasegawa Company, Ltd., Japan

Syntheses of γ -homocyclogeraniol 4, dihydro- γ -ionone 6 and their derivatives 7,8, known as the volatile constituents of ambergris, were carried out according to scheme:

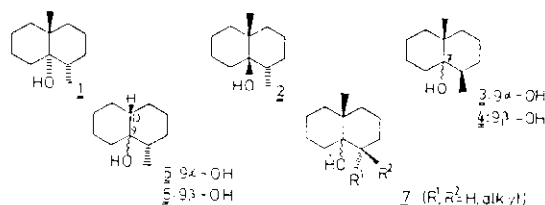


Claisen rearrangement was employed to synthesize γ -homocyclogeraniol 4 by utilizing vinyl ether 3 of the allylic alcohol 2 obtained from hydroxymethylene cyclohexanone 1. Subsequent Darzens reaction of the aldehyde 4 gave glycidate 5, which was hydrolysed and then decarboxylated to give dihydro- γ -ionone 6. The two compounds 4 and 6 were further converted to their derivatives 8 and α -ambrinol 7.

547

Stereospecific syntheses of geosmin, its stereoisomers and homologues, E. J. Brunke, C. H. Kappey and E. Klein, Dragoco GmbH, West Germany

Geosmin (1), the main odor component of the garden soil, is one of the strongest fragrance chemicals, which are known today. We describe a new stereospecific total synthesis of geosmin (1) as well as stereo-controlled syntheses of the stereoisomers 2-4, the desmethyl derivatives 5,6 and the higher homologues 7. The compounds 1-7 possess odor properties of the earthy type



with different intensity and odor quality. The odor valuation of compounds 2-7 in comparison with 1 leads to a better knowledge on chemical structure and earthy odor.

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Recent advances in the development of macrocyclic musk compounds since 1970, Shozo Abe, Soda Aromatic Company, Ltd., Japan

Following earlier review on macrocyclic musks, part 1: review on progress from discovery up to now (The Koryo, No. 96, Sept. 19-27, 1970) and part 2: recent advances in the development of macrocyclic musk compounds (The Koryo, No. 101, March, 53-74, 1972) and Cosmetic and Perfumery, Vol. 88, June, 67-86, 1973), the author attempts to review the general trend of macrocyclic musks in the last 10 years or so. The author presents new macrocyclic musks and odors, advances in the synthesis of macrocyclic ketone, lactone and diester musks and the others since 1970. Reports and patents during the last 12 years or so are classified and starting materials and feature of synthetic method are discussed from all approaches to research for the recent tendency in the synthesis.

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Synthesis of angelic acid esters, essential components of Roman chamomille oil and their organoleptic properties, Masanobu Naruto, Hisao Kondo, Masaru Kobayashi, Toray Industries, Inc.; Go Hata, Soda Aromatic Company, Ltd.; and Ikua Sakai, Toray Research Center, Japan

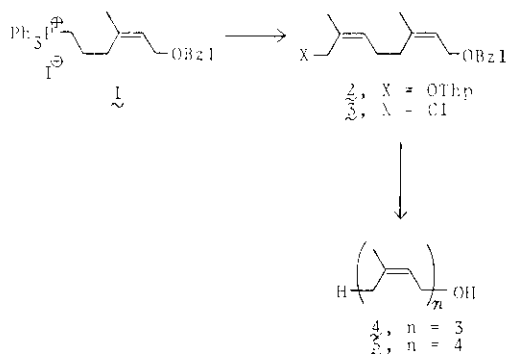
Several angelic acid esters are well known as main components of Roman chamomille oil, but their efficient

synthetic method has not been developed. The authors describe their commercially available synthetic method and their organoleptic properties. Isomerization of methyl tiglate (MTG) to methyl angelate (MAG) was effectively catalyzed by p-toluenesulfonic acid (PTSA). The mixture of MTG and PTSA was heated at the boiling point and formed MAG, which has lower boiling point (about 10°C) than MTG, was continuously distilled off through high performance column. In the above condition, any migration of double bond was not observed. Various angelic acid esters were obtained by transesterification between MAG and alcohols catalyzed by $Ti(OBu)_4$ or $R_2Sn(RCOO)_2$. Their organoleptic properties were examined.

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Synthesis of (Z,Z)-farnesol and (Z,Z,Z)-nerylnerol,
Kikumasa Sato, Osamu Miyamoto, Seiichi Inoue, Fumio Furusawa and Yasusuke Matsushashi, Yokohama National University, Japan

Cisoid terpenoids are often found in many essential oils, but a general synthetic strategy for polyolefinic cis isoprenoids has scarcely been reported. We report here a synthesis of all cis-polyprenols using a regioselective C-C bond formation between a terpenoid terminal and a cisoid monoterpene building block, stereoselective synthesis of which has now been established by means of a novel Wittig reaction. The key C_{10} building block 3 was synthesized stereoselectively ($Z/E = 98/2$) by the reaction between tetrahydropyranolxyacetone and a phosphonium salt 1, prepared from nerol by the known procedure, followed by hydrolysis and chlorination. Treatment



of anion of prenyl- or neryl-sulfone with 3, followed by reduction with lithium/ethylamine yielded the title compounds 4 and 5. Utilities of the key building block 3 for the synthesis of some other natural polyprenols will also be discussed.

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Electrochemical methods of synthesis of some aroma chemicals, J. Gora, E. Smigielski, Technical University of Lodz, and W. S. Brud, Pollena-Aroma, Poland

The development of utilisation of electrochemical methods of synthesis for preparation of aroma chemicals and their semiproducts is discussed according to authors' own research and some literature data. The following applications are presented:

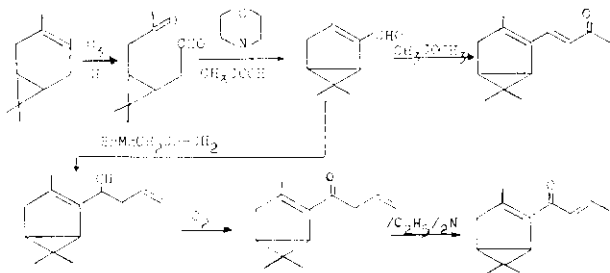
- indirect electrolytic oxidation (rose oxide from citronellol, carboxylic acids from alcohols),
- electrochemical reductions (alkylhydroxyperoxides to

alcohols, ozonides to carbonyl compounds or alcohols, alkyloxiranes and carbonyl compounds to alcohols),
 —Kolbe synthesis applied to preparation of macrocyclic musks,
 —electrochemical methods of functionalisation of alkenes: alkoxylation, acylation, chlorination.

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New aroma chemicals from 3-carene, J. Podlejski, Lodz Technical University, Poland

3-carene is one of two main components of Polish turpentine. Its use in synthesis of new aroma chemicals according to following scheme is presented:



Analytical data and odor characteristics of the products and intermediates are discussed.

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Relative menthenes reactivity in chlorination reaction, V. V. Bazyl'chik and V. I. Staninetz, Chuvash State University, USSR

Chlorination of menthenes is of great interest from the point of view of their comparative reactivity, and the investigation of the reaction products composition gives the possibility to evaluate common regularities of menthenes properties in electrophilic addition reactions. Besides, the exposure of possible use of this reaction as a preparative method for production of little known functional derivatives of menthene series is of great importance.

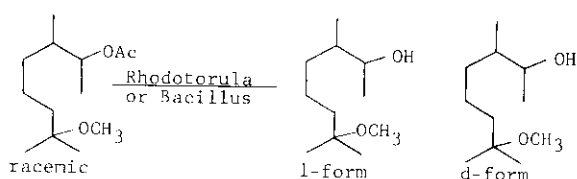
Investigation of *o*- and *p*-menthenes reactivity by competing reactions method were in the limits of one order, and were higher in comparison with the rate of cyclohexene chlorination. Menthenes having tetra-substituted double bonds, such as *o*-1-menthene and *o*-2-(8)-menthene are the most readily chlorinated. Stereoisomeric *o*-8-menthenes are more difficult to react, in comparison with their modifications of *p*-menthane structure. These distinctions can be explained by electronic and space reasons. Formation of 1-methyl-2-(3-chlorine-1-propenyl) cyclohexane and 1-methyl-2-(1-chlorine-1-propenyl)

cyclohexane in 5:1 proportion, observed at trans-o-8-menthene chlorination shows that the process is principally directed at the anomalous chlorination, that is, the production of unsaturated chlorides. o-1-Menthene chlorination is accompanied with a skeletal rearrangement.

510

Enantioselective microbial hydrolysis of racemic 8-methoxyelgenole acetate by *Rhodotorula mucilaginosa* and *Bacillus subtilis spec.*, J. Gora and A. Monkiewicz, Lodz Technical University, Poland

The possibilities and conditions of the shown process were investigated. The relationship between Chirality and odour of enantiomeric 8-methoxyelgenoles was determined.

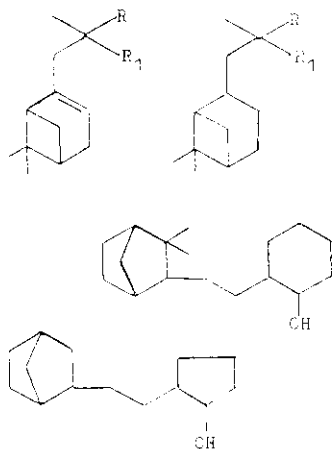


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Synthesis of some new sandalwood-type aroma chemicals from alpha-pinene or camphene, J. Gora,

L. Markowicz, J. Gibka, Technical University of Lodz, and M. Pilecki and W. S. Brud, Pollena-Aroma, Poland

New aroma chemicals with the shown general structures were prepared and relationship between structure and odour examined. Some of these compounds have strong characteristic odour of sandalwood.



$R = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$

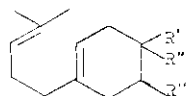
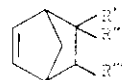
$R_1 = -\text{CHO}, -\text{CH}_2\text{OH}, -\text{C} \equiv \text{N}, -\text{CH}(\text{OH})\text{CH}_3, -\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$

513

Application of Diels-Alder reaction in synthesis of aroma chemicals, J. Podlejski, M. Sikora, W. Sadowska, Lodz Technical University, and M. Pilecki, Pollena-Aroma, Poland

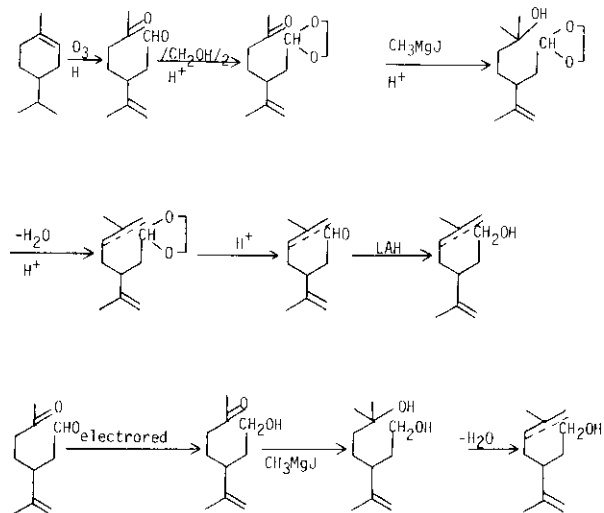
With use of catalysed and non-catalysed Diels-Alder reaction a group of aroma chemicals was prepared. Myrcene and cyclopentadiene were used as starting materials which were condensed with mesityl oxide, crotonic aldehyde, acrylonitrile and methyl acrylate. The following products were obtained and olfactorily evaluated.

$R' = R'' = \text{CH}_3, R''' = \text{COCH}_3$
 $R' = \text{CH}_3, R'' = \text{H}, R''' = \text{CHO}$
 $R' = R'' = \text{H}, R''' = \text{CN}$
 $R' = R'' = \text{H}, R''' = \text{COOCH}_3$
 $R' = \text{CH}_3, R'' = \text{H}, R''' = \text{CH}=\text{CHCOCH}_3$
 $R' = \text{CH}_3, R'' = \text{H}, R''' = \text{CH}=\text{CHCOC}_2\text{H}_5$
 $R' = \text{CH}_3, R'' = \text{H}, R''' = \text{CH}=\text{C}(\text{CH}_3)\text{COCH}_3$



$R' = R'' = \text{CH}_3, R''' = \text{COCH}_3$
 $R' = \text{CH}_3, R'' = \text{H}, R''' = \text{CHO}$
 $R' = R'' = \text{H}, R''' = \text{CN}$

Methods of synthesis of homolavandulol, J. Podlejski, J. Kula, Lodz Technical University, and W. S. Brud, Pollena-Aroma, Poland



Synthesis of homolavandulol was elaborated from limonene obtained in deterperation of sweet orange oil.

Studies into the photochemical transformations of acyclic monoterpenoids, R. K. Baslas, Rohilkhand University, India

Studies into the photochemical transformations of few acyclic monoterpenoids have been made. In the present communication the photochemical transformations of Citral, citronellal, Rohdenal, Citronellol, Geraniol and Linalool have been described. Under different condition of photo irradiations the formation of various compounds from these transformations have been discussed viz from

1. Citral into one monocyclic aldehyde, one bicyclic aldehyde, four monocyclic alcohols and one bicyclic four membered oxy compound.
2. Citronellal into one bicyclic five membered oxy compound.
3. Rohdenal into one bicyclic five membered oxy compound.
4. Citronellol into Rose oxide.
5. Geraniol into one Rose oxide type compound.
6. Linalool into one four membered oxy compound and one five membered oxy compound.

The mechanism of various transformations have also been suggested.