[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
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The Structures and Mechanisms of Formation of Some Cyclogeraniolenes

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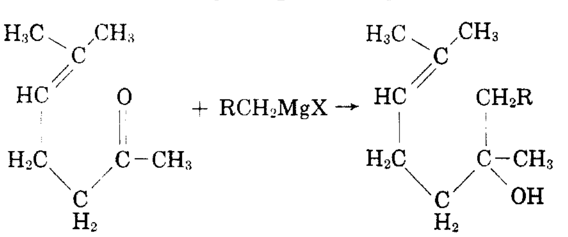
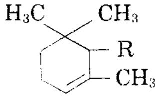
Several olefinic tertiary alcohols have been prepared from 2-methylhepten-2-one-6. Cyclodehydration of these alcohols with anhydrous oxalic acid gave substituted cyclohexenes. Evidence is presented for their structures and mechanisms of formation.

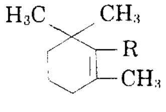
Escourrou in 1926 reported the preparation of a series of cyclogeraniolenes by heating the appropriate unsaturated tertiary alcohol with anhydrous oxalic acid.[1]

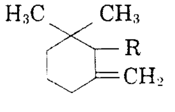
The alcohols were prepared from methylheptenone and the necessary Grignard reagents.



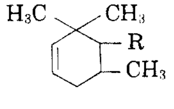
The dehydration of these alcohols could lead to the formation of any of the five isomeric cyclogeraniolenes.


α


β


γ


δ


ε

It was reported that the predominant isomer in each case was the γ-isomer.[1] This conclusion was based on the quantities of formaldehyde formed by ozonolysis.

More recently it has been reported that the composition of methylcyclogeraniolene ($R = CH_3$) prepared by the method of Escourrou was the following:

α-methylcyclogeraniolene, 30%
γ-methylcyclogeraniolene, 20%
ε-methylcyclogeraniolene, 50%[2]

The evidence upon which these assignments were made was based upon an interpretation of the Raman spectra of these compounds together with some chemical information. The conclusion that the ε-isomer is the main constituent rests entirely on the presence of the 1663 cm.$^{-1}$ line in the Raman spectrum, a line that cannot be considered definitive at present.[3] Furthermore the 1663 cm.$^{-1}$ appears to lie outside of the range for cyclohexenes containing only a disubstituted olefin group (as in the δ- and γ-forms) but within the range for cyclohexenes which contain a trisubstituted olefin group (as in the case of the α-isomer).[4]

The work of Dupont[2] has shown that methyl cyclogeraniolene does not consist solely of the γ-isomer. The structure of other alkyl cyclogeraniolenes is left in doubt since Escourrou assigned γ-structures to them also. Since the evidence for the structures of the cyclogeraniolenes as obtained from cyclodehydration reactions does not appear to be very conclusive, it was decided to examine the structures of cyclogeraniolenes in general, of methylcyclogeraniolene in particular, and to study their mechanisms of formation.

A series of five alcohols was prepared from methylheptenone and the Grignard reagents of methyl iodide, ethyl bromide, *n*-propyl bromide, isopropyl bromide, and *n*-butyl bromide. The alcohols were then dehydrated to the corresponding alkyl cyclogeraniolenes by the method of Escourrou.[1]

Ozonolysis of methylcyclogeraniolene resulted in the formation of three fractions: a small amount of oil soluble in sodium bicarbonate; a small amount of formaldehyde; and a relatively large amount of a neutral oil. The formaldehyde presumably came from the γ-isomer and based upon its dimedon derivative accounted for 2% of the original methylgeraniolene mixture. The only compound isolated from the neutral oil was 3,3-dimethyloctadione-2,7 which was isolated as its disemicarbazone. Since this compound was reported previously,[5] it was readily identified. This diketone obviously came from the β-isomer and from the amount of disemicarbazone isolated it accounted for 21% of the original. It is interesting to note that the β-isomer had been reported missing previously.[3] Furthermore large quantities of formaldehyde were not liberated

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[1] Escourrou, *Bull. soc. chim.*, [4], **39,** 1126, 1460 (1926); [4] **43,** 1227 (1928).

[2] Dupont, Dulou, and Desreux, *Bull. soc. chim.*, [5], **6,** 93 (1939).

[3] Dupont and Dulou, *Compt. rend.*, **201,** 219 (1935).

[4] Chiurdoglu and Guillemonat, *Bull. soc. chim.*, [5] **5,** 1626 (1938).

[5] Fischer, Lardelli, and Jeger, *Helv. Chim. Acta*, **34,** 1585 (1951); Cheeseman, *et al.*, *J. Chem. Soc.*, 1521 (1949).

as reported by previous workers. The very small bicarbonate-soluble fraction could not be identified through the formation of a derivative.

An attempt was made to convert the methylcyclogeraniolenes to the corresponding glycols by the performic acid method.[6] A considerable amount of an unidentified monoketone was obtained along with a glycol or a mixture of glycols. The formation of the ketone may be attributed to a pinacolinic rearrangement.[7]

An investigation of the infrared spectra of the alkyl cyclogeraniolenes was next carried out. The one serious disadvantage of infrared spectroscopy as applied to this problem is the lack of characteristic absorption bands associated with tetrasubstituted olefins. The β-forms of the alkyl cyclogeraniolenes are tetrasubstituted olefins and hence cannot be identified by infrared spectroscopy. This is not serious in the case of β-methylcyclogeraniolene since it may be identified by other means. The other isomers can be distinguished by their infrared spectra since they represent different double bond types.

Model compounds were prepared which represented the three cycloölefinic types: (1) for the terminal methylene type, methylenecyclohexane; (2) for the *cis*-disubstituted type, cyclohexene; and (3) for the trisubstituted, 1-methylcyclohexene. Assignments were made for the various olefinic bands and these bands were compared with those of methylcyclogeraniolene. This comparison is given in Table I.

TABLE I

INFRARED BANDS[a] FOR THE MODEL CYCLIC OLEFINS AND THE METHYLCYCLOGERANIOLENES

Type	Olefin	C—H Stretching	C=C Stretching	C—H in Plane Deformation	C—H out of Plane Deformation
cis-Disubstituted	Cyclohexene	3.30 μ	6.065 μ	7.18 μ	s 13.91 μ
	MCG	2.96	Absent	Absent	w 13.92
Trisubstituted	1-Methylcyclohexene	Absent	w 5.97	m 7.47	s 12.56
	MCG	Absent	w 5.98	m 7.20	m 12.40
Terminal methylene	Methylene cyclohexane	m 3.24	m 6.06	7.05	s 11.24
	MCG	Absent	w 6.06	Absent	w 11.24

[a] s = strong; m = moderate; w = weak.

These data indicate that ε-methylcyclogeraniolene is present to a very small extent if present at all. The presence of the α-isomer is assured by the infrared data while the γ-isomer could be present in small amounts only. It would appear from these data and the data from the ozonolysis experiments that methylcyclogeraniolene, as prepared by the method of Escourrou, consists mainly of α- and β-methylcyclogeraniolenes with a small amount of the γ-form and little or no ε-isomer.

There remains the possibility that some of the bands might arise from other species such as open chain ten-carbon atom diolefins which might be formed from the dehydration of the starting alcohol. That little if any of this type was present was shown by the following work. Methylcyclogeraniolene was fractionally distilled and separated into three fractions. The boiling point range, 48.8–54.7° (12 mm.), and the refractive index range, n_D^{25} 1.4547–1.4647, show that methylcyclogeraniolene is not homogeneous. The calculated molar refractivities, 45.78–45.83, for the three fractions are close to the theoretical value of 45.71 for ten-carbon cyclic olefins. Furthermore, the hydrogenation numbers for these fractions indicated the absence of any open-chain diolefin. Finally, the infrared curves of the hydrogenated fractions were almost identical. If an open chain isomer were present to any extent, the curves should have shown some significant differences.

The data thus far indicate that methylcyclogeraniolene, as prepared by Escourrou, consists of large amounts of the β-isomer, smaller amounts of the α-isomer, and very small amounts of the γ-isomer.

Cyclogeraniolene, ethylcyclogeraniolene, dimethylcyclogeraniolene, and *n*-propylcyclogeraniolene were also prepared from the corresponding olefinic alcohols by treatment with oxalic acid according to the method of Escourrou. The hydrogen numbers of these compounds were within one per cent of the theoretical value for a cyclic monoölefin. The molar refractivity values agreed well with those calculated for the corresponding cyclic monoolefins.

The infrared spectra of these compounds had characteristics in common with methylcyclogeraniolene. The low intensity of the 11.24 μ bands indicated that only small amounts of the γ-isomers were present. The infrared bands of higher intensity appeared at approximately the same wave lengths

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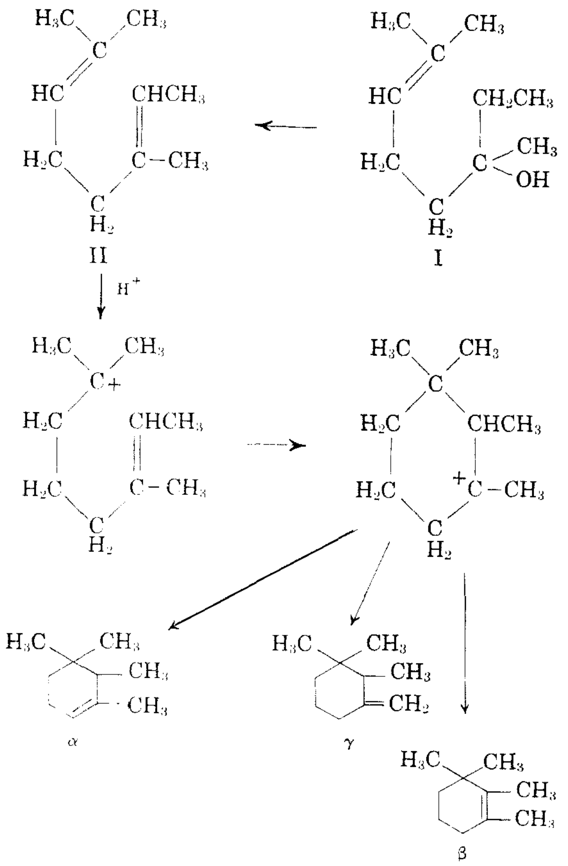
(6) Roebuck and Adkins, *Org. Syntheses*, **28**, 35 (1948).

(7) It had seemed originally that oxidative cleavage of the glycols might lead to the formation of identifiable dicarbonyl compounds. Due to the difficulties encountered, these cleavages and the rearrangements are being investigated as a separate project.

Bands in the range 12.5–12.6 μ indicated the presence of a trisubstituted olefin type, probably the α-isomer. These bands were of high intensity for cyclogeraniolene and dimethylcyclogeraniolene and of moderate intensity for ethylcyclogeraniolene and *n*-propylcyclogeraniolene. The absence of absorption bands in the regions where cyclohexene absorbs indicated the absence of the disubstituted olefin types, the δ- and ε-isomers. It seems probable that cyclogeraniolene, ethylcyclogeraniolene, and *n*-propylcyclogeraniolene consist of mixtures of the α-, β-, and γ-isomers similar to methylcyclogeraniolene. Dimethylcyclogeraniolene is the only member studied in which there is no possibility for a β-isomer.

Mechanism of formation of methylcyclogeraniolene. Escourrou had suggested that the alcohol is first dehydrated to a diolefin which then undergoes cyclization. In order to substantiate this theory, in the present study, dihydromyrcene (II) was cyclized under the same conditions as was dihydrolinalool (I). Both anhydrous oxalic acid and oxalic acid and water were used to effect the cyclization and in both cases the resulting methylcyclogeraniolene had the same physical and infrared characteristics. The following mechanism is proposed as being in good agreement with the data.



Eight hyperconjugative structures can be written for the β-methylcyclogeraniolene, six for the α-isomer, and three for the γ-form. On this basis the relative amounts formed should be as follows, β > α > γ. The experimental results support this assumption. Other factors contribute to this order also. For example, the small amount of the γ-isomer might well be due to the well-known instability of an exocyclic double bond attached to a six-membered ring. The dehydration of 1-isopropyl-1-cyclohexanol gives mainly 1-isopropyl-1-cyclohexene and only a small amount of isopropylidenecyclohexane.[8] If hyperconjugation were the only factor here, isopropylidenecyclohexane would be the predominant isomer. The instability of the exocyclic double bond has been attributed to the unfavorable conformation of the groups attached to the exo-carbon atom with respect to the ring hydrogen atoms.[9]

The other cyclogeraniolenes are undoubtedly formed in the same manner as the methylcyclogeraniolenes.

EXPERIMENTAL

Distillations. The Todd distillation apparatus was used for most of the distillations.

Infrared. A Perkin-Elmer Model 21 Spectrometer was used.

Syntheses of tertiary alcohols from 2-methylhepten-2-one-6. Methylheptenone was treated with the Grignard reagents from methyl iodide, ethyl bromide, *n*-propyl bromide, isopropyl bromide, and *n*-butyl bromide, respectively, according to the method of Escourrou.[1]

2,6-Dimethylhepten-5-ol-2, yield 81%, b.p. 79°/13 mm., n_D^{25} 1.4461.

3,7-Dimethylocten-6-ol-3 (*Dihydrolinalool*), yield 91%, b.p. 90°/12 mm., n_D^{25} 1.4528.

4,8-Dimethylnonen-7-ol-4, yield 85%, b.p. 104°/13 mm., n_D^{25} 1.4515.

2,3,7-Trimethylocten-6-ol-3, yield 19%, b.p. 103°/11.5 mm., n_D^{25} 1.4555.

5,9-Dimethyldecen-8-ol-5, yield 78%, b.p. 99°/7 mm., n_D^{25} 1.4538.

Preparation of cyclogeraniolenes from the tertiary alcohols. The tertiary alcohols were heated with anhydrous oxalic acid, according to the method of Escourrou[1] to give the following cyclogeraniolenes.

Cyclogeraniolene, yield 68%, b.p. 30–31°/12 mm., d^{25} 0.7885, n_D^{25} 1.4446, hydrogen number 0.99.

Methylcyclogeraniolene, yield 70%, b.p. 52–53°/12 mm., d^{25} 0.8350, n_D^{25} 1.4600, hydrogen number 1.00.

Ethylcyclogeraniolene, yield 75%, b.p. 70–71°/13 mm., d^{25} 0.8420, n_D^{25} 1.4600, hydrogen number 1.00.

Dimethylcyclogeraniolene, yield 69%, b.p. 71–72°/13 mm., d^{25} 0.8314, n_D^{25} 1.4604, hydrogen number 1.01.

n-Propylcyclogeraniolene, yield 72%, b.p. 80–82°/11.5 mm., d^{25} 0.8394, n_D^{25} 1.4660, hydrogen number 1.00.

Ozonolysis of methylcyclogeraniolene. The Wellsbach, Model-23, ozone generator was used for this work. Ethyl acetate was used as the solvent. To the resulting ozonide solution was added an equal volume of water and excess zinc dust. The mixture was refluxed for two hours while passing a slow stream of nitrogen through the flask. The exit vapors were passed through two chilled traps containing a dimedon solution. After standing for two days, the precipitate was removed and recrystallized from water, m.p. 189–190°. A mixture melting point determination with an

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[8] Mosher, *J. Am. Chem. Soc.*, **62**, 5 (1952).

[9] Brown, *et al.*, *J. Am. Chem. Soc.*, **76**, 470 (1954).

authentic sample of the dimedon derivative of formaldehyde showed no depression. The amount of formaldehyde obtained by this method accounted for 2% of a terminal methylene compound in methylcyclogeraniolene.

The ethyl acetate layer from above was extracted with a sodium bicarbonate solution and then was washed with water. The ethyl acetate was removed under reduced pressure, leaving a light-yellow, viscous oil. This oil gave a positive test with 2,4-dinitrophenylhydrazine, a positive iodoform test, and negative tests with Tollen's and Fehling's reagents. The oil was treated with semicarbazide hydrochloride under the usual conditions and a semicarbazone was obtained. After recrystallization from water it melted at 200–201°.

Anal. Calc'd for $C_{12}H_{24}N_4O_2$: C, 50.67; H, 8.51; N, 29.55. Found: C, 50.85; H, 8.48; N, 29.40.

A mixture melting point determination with the semicarbazone of 3,3-dimethyloctadione-2,7 showed no depression. The 3,3-dimethyloctadione-2,7 was prepared from 4-[2′,6′,6′-trimethylcyclohexen-1-yl]-2-methylbuten-2-al-1[10] by the procedure of Fischer, *et al.*[11] The amount of semicarbazone obtained from the yellow oil accounted for 21% of the β-isomer in the methylcyclogeraniolene.

PREPARATION OF MODEL INFRARED COMPOUNDS

Cyclohexene. Analytical grade cyclohexene was fractionated in the Todd distillation apparatus and the fraction boiling at 83° with a refractive index of 1.4450 at 25° was used for the infrared work.

1-Methylcyclohexen-1. This compound was obtained from 1-methylcyclohexanol-1 by heating with 50% sulfuric acid until no more organic material distilled. The oily layer from the distillate was washed with bicarbonate solution, dried over calcium chloride, and fractionally distilled through a Todd column, b.p. 109°, n_{D}^{25} 1.4910.

Methylenecyclohexane. Methylenecyclohexane was prepared from cyclohexylcarbinol by the methyl xanthate procedure devised by Tschugaeff[12] and adapted for this purpose by Roberts and Day,[13] b.p. 102.5°, n_{D}^{25} 1.4504.

Preparation of dihydromyrcene. This hydrocarbon was prepared from linalool by the method of Chablay.[14] After fractionation a sample was obtained which had the following constants: b.p. 57.5°/13 mm., d^{25} 0.7706, n_{D}^{25} 1.4471.

Cyclization of dihydromyrcene. Method (1). The hydrocarbon was heated with oxalic acid plus one equivalent of water. The mixture was worked up by the method of Escourrou. *Method (2).* Dihydromyrcene was distilled over anhydrous oxalic acid through a small packed column. The distillate was washed with a bicarbonate solution, dried over magnesium sulphate, and fractionally distilled. The two products obtained from these methods had the same physical constants and infrared spectra as did methylcyclogeraniolene.

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(10) Cheeseman, *et al.*, *J. Chem. Soc.*, 1521 (1949).

(11) Fischer, Lardelli, and Jeger, *Helv. Chim. Acta*, **34**, 1585 (1951).

(12) Tschugaeff, *Ber.*, **32**, 3332 (1899).

(13) Roberts and Day, *J. Am. Chem. Soc.*, **72**, 1226 (1950).

(14) Chablay, *Ann. chem.*, **194**, 8 (1917).