CCXXXI.—*Synthesis of 1:1:3-Trimethylcyclohexene (cycloGeraniolene).*

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SOME years ago Tiemann and Semmler (*Ber.*, 1893, **26**, 2708) prepared from the aldehyde citral (geranial) an open-chain hydrocarbon, C_9H_{16} , named by them geraniolene. The constitution of this substance (I) follows from that of citral, which was established by Barbier and Bouveault in 1896 (*Compt. rend.*, **122**, 393).

When geraniolene is shaken with a 60 per cent. solution of sulphuric acid, an isomeric change takes place, the open-chain hydrocarbon being converted into a mixture of two cyclic hydrocarbons, α - and β -cyclogeraniolene (II and III), in which mixture the α -variety is present in larger quantity:

The constitutional formulæ of these hydrocarbons were ultimately determined by Tiemann (*Ber.*, 1898, **31**, 816, 881; 1900, **33**, 3711) from a study of their oxidation with potassium permanganate, the products isolated being two ketonic acids, *isogeronic* (IV) and *geronic* (V) acids, together with *as*-dimethylsuccinic acid and $\beta\beta$ -dimethylglutaric acid.

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The formation of the two modifications of *cyclogeraniolene* was ascribed to the addition of two molecules of water to the molecule of *geraniolene* which were subsequently eliminated. According to Tiemann, hydroxyl groups became attached to the carbon atoms bearing methyl groups, so that the first stage in the reaction consists in the formation of a compound of formula VI; this is succeeded by ring-formation due to elimination of a molecule of water and subsequent union of the two carbon atoms marked *:

It is obvious that the second molecule of water may be eliminated from the compound (VII) in two different ways, and the formation of the two modifications of *cyclogeraniolene* is thus explained:

A third hydrocarbon having the formula:

is a possibility, but no evidence of its presence is recorded.

Tiemann did not actually isolate either of the hydroxy-compounds VI or VII, but a synthesis of 1:1:3-trimethyl*cyclohexan*-3-ol (VII) has now been effected by a method which leaves no doubt as to its constitution, and it is found that this alcohol can be readily converted into *cyclogeraniolene*, thus affording confirmation of Tiemann's supposition.

The starting point was 1:1-dimethyl*cyclohexan*-3-one (VIII), prepared by the action of reducing agents on 5-chloro-1:1-dimethyl- Δ^4 *cyclohexen*-3-one (Trans., 1907, 91, 81). When this ketone is treated with an ethereal solution of magnesium methyl iodide and the product decomposed with water, trimethyl*cyclohexanol* (IX) is obtained as a well-defined, crystalline substance, melting at 72.5°

Fuming hydrobromic acid converts the alcohol into 3-bromo-1:1:3-trimethyl*cyclohexane* (X), which, when treated with alcoholic potassium hydroxide, loses the elements of hydrogen

bromide in two ways, giving rise to the same mixture of hydrocarbons as described by Tiemann.

The work of Tiemann on the preparation of *cyclogeraniolene* was repeated by Wallach (*Annalen*, 1902, **324**, 97), who prepared the nitrosate of α -*cyclogeraniolene*, and proved that it was transformed by the action of alkalis into the oxime of 1:1:3-trimethyl- Δ^2 -*cyclohexen-4-one*. The identity of the hydrocarbons described in the present communication with *cyclogeraniolene* has been established by preparing this crystalline nitrosate, and from it the above-mentioned oxime; further, by oxidising the hydrocarbons with potassium permanganate, when the products isolated were *as*-dimethylsuccinic acid, *isogeronic* and *geronic* acids, the two latter being identified as their semicarbazones, melting at 195° and 164° respectively.

EXPERIMENTAL.

Thirty grams of 1:1-dimethylcyclohexan-3-one (*Trans.*, 1907, **91**, 81), dissolved in an equal volume of ether, were gradually added to a Grignard reagent prepared from 33 grams of methyl iodide and 5.7 grams of magnesium turnings in 100 c.c. of dry ether. The ethereal solution was gently boiled on a water-bath for one hour, cooled, and poured into a concentrated solution of ammonium chloride, to which ice had been added. The ethereal layer was separated, the saline solution extracted three times with ether, the mixed ethereal liquids washed, dried over potassium carbonate, and evaporated, when a solid residue (23 grams = 70 per cent. of the theoretical amount) was obtained, which, after drying on porous plate, was recrystallised from dilute alcohol and analysed:

0.1061 gave 0.2965 CO₂ and 0.1209 H₂O. C = 76.21; H = 12.66.

C₉H₁₈O requires C = 76.06; H = 12.67 per cent.

1:1:3-Trimethylcyclohexan-3-ol is readily soluble in the cold in all the ordinary organic solvents, and may be crystallised from dilute alcohol or dilute acetone, from which it separates in beautiful four-sided, elongated prisms, having a characteristic, strongly camphoraceous odour, and melting at 72.5°.

3-Bromo-1:1:3-trimethylcyclohexane.

Trimethylcyclohexanol, in quantities of 10 grams at one time, were sealed up with 50 c.c. of a solution of hydrogen bromide (saturated at 0°) in small soda-water bottles, which were heated in a boiling-water bath for one hour. The mixture was poured

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into water, extracted three times with ether, the ethereal solution washed with a solution of sodium hydrogen carbonate, then with water, dried, evaporated, and the residue distilled under diminished pressure, when, after two distillations, 11.5 grams passed over constantly at 88°/20 mm.:

0.1527 gave 0.1375 AgBr. Br=38.31.

C₉H₁₇Br requires Br=39.02 per cent.

Bromotrimethylcyclohexane is, when freshly prepared, a faintly yellow liquid boiling at 88°/20 mm., which, especially on exposure to air, evolves fumes of hydrogen bromide and rapidly decomposes, becoming green, and finally black. The rapidity with which this decomposition takes place accounts, no doubt, for the low result for bromine quoted above.

1:1:3-Trimethyl-Δ³- and -Δ²-cyclohexenes. α- and β-cyclo-Geraniolene,

Thirty grams of potassium hydroxide were dissolved in a little water, and added to 35 grams of bromotrimethylcyclohexane dissolved in 150 c.c. of absolute alcohol. The whole was heated on the water-bath for one hour, cooled, poured into water, and extracted four times with ether; the ethereal solution was washed, dried, and evaporated, and the residue distilled, when the following fractions were collected: 110—136°=2 grams; 136—142°=13 grams; 142—150°=3 grams. The fraction 136—142° was twice redistilled over sodium and analysed:

0.1244 gave 0.3971 CO₂ and 0.1430 H₂O. C=87.06; H=12.77.

C₉H₁₆ requires C=87.10; H=12.90 per cent.

Trimethylcyclohexene (cyclogeraniolene) is a colourless, refractive liquid, possessing a pronounced terpene-like odour. It boils at 137—140°/760 mm., and has a density of 0.8085 at 15°/15°.

This hydrocarbon has also been prepared by the action of dehydrating agents on trimethylcyclohexanol (potassium hydrogen sulphate at 130—140°, and zinc chloride at 160—170°) and by shaking trimethylcyclohexanol with dilute sulphuric acid (D 1.67) for several hours at the laboratory temperature. If this latter action is prolonged for several days, the principal product is a polymeric modification of the hydrocarbon boiling at 165—170°/30 mm.

When dissolved in glacial acetic acid and treated with amyl nitrite and nitric acid according to the directions of Wallach

(*loc. cit.*), the mixture of trimethylcyclohexenes, prepared by any of these methods, yielded the crystalline nitrosate of 1:1:3-trimethyl- Δ^3 -cyclohexene, melting at 103–104°, which by the action of sodium methoxide was transformed into the oxime of 1:1:3-trimethyl- Δ^2 -cyclohexen-4-one, melting at 128°.

The hydrocarbon was oxidised with potassium permanganate as described by Tiemann (*Ber.*, 1900, **33**, 3711), when the residue obtained on working up the product partly solidified on keeping. It was spread on plate, and the residue crystallised from water, when it melted at 140°. The identity of this substance with *as*-dimethylsuccinic acid was proved by the mixed melting-point method, and by preparing from it an anilic acid, which melted at 186°.

The porous plate (see above), on extraction with ether, yielded an oil which was dissolved in alcohol and treated with a solution of semicarbazide acetate. After some time a solid was deposited, melting at 185–192°, which crystallised from alcohol, in which solvent it is only sparingly soluble, in feathery needles, melting and decomposing at 198°. (Found, N=18·46. $C_{10}H_{18}O_3N_3$ requires N=18·34 per cent.) These data prove the substance to be the semicarbazone of *isogeronic* acid.

On concentrating the mother liquor from the above semicarbazone, a further quantity of crystals was obtained in glistening lamellæ, melting, after recrystallisation, at 163°. (Found, N=18·37. $C_{10}H_{18}O_3N_3$ requires N=18·34 per cent.) The substance was therefore the semicarbazone of *geronic* acid (compare Tiemann).

It appeared to be of interest, in connexion with other work which is in hand, to try the action of Grignard reagents, other than magnesium methyl bromide, on dimethylcyclohexanone, but the results are most disappointing, as with increase in the molecular weight of the alkyl group, the yields of the products decrease rapidly, and further work in this direction has been abandoned for the present.

1:1-Dimethyl-3-ethylcyclohexan-3-ol, prepared by the action of magnesium ethyl bromide on 1:1-dimethylcyclohexan-3-one, is a colourless, refractive liquid, boiling at 94°/30 mm., and possessing a penetrating, camphoraceous odour:

0·1363 gave 0·3851 CO_2 and 0·1552 H_2O . C=77·05; H=12·65.

$C_{10}H_{20}O$ requires C=76·93; H=12·82 per cent.

The alcohol is readily converted by the action of fuming hydrobromic acid into 3-bromo-1:1-dimethyl-3-ethylcyclohexane (b. p. 105–106°/22 mm.), from which substance hydrogen bromide is eliminated by potassium hydroxide to give a mixture of isomeric 1:1-dimethyl-3-ethylcyclohexenes:

0.1210 gave 0.3848 CO_2 and 0.1425 H_2O . $\text{C}=86.73$; $\text{H}=13.09$.

$\text{C}_{10}\text{H}_{18}$ requires $\text{C}=86.95$; $\text{H}=13.04$ per cent.

Dimethylethylcyclohexene is a colourless, refractive liquid, boiling at $156^\circ/760$ mm.

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