

CCCLXV.—*Olefinic Terpene Ketones from the Volatile Oil of Flowering Tagetes glandulifera. Part II.*

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THE structures assigned by Jones and Smith to $\gamma\eta$ -dimethyl- Δ^2 -octen- ϵ -one and tagetone, the two olefinic terpene ketones isolated from the volatile oil of *Tagetes glandulifera* (J., 1925, **127**, 2530), depended primarily on the identity of the saturated ketone—the common product of their reduction—and of the ketonic acid resulting from oxidation of the former with $\gamma\eta$ -dimethyloctan- ϵ -one and β -isovaleryl- α -methylpropionic acid, respectively.

The saturated ketone and the ketonic acid have now been synthesised by the ketonic hydrolysis of the products of interaction of ethyl sodioisovalerylacetate with (a) *sec.*-butyl iodide, and (b) ethyl α -iodopropionate.

The properties of $\gamma\eta$ -dimethyl- Δ^2 -octen- ϵ -one and tagetone have been further examined. Agitated for 2 hours with 70% sulphuric acid at about 100°, $\gamma\eta$ -dimethyl- Δ^2 -octen- ϵ -one undergoes profound

decomposition with production of methyl ethyl ketone, methyl isobutyl ketone, and isovaleric acid. The reaction, no doubt, involves hydrolysis of $\gamma\gamma$ -dimethyl- Δ^8 -octen- ϵ -one, formed by the shifting of the double bond of the original ketone to the β -position. The isomeric ketone could not, however, be isolated during the course of the reaction. Although tagetone is almost entirely resinified by heating with alcoholic potash, methyl isobutyl ketone, presumably a product of its hydrolysis, is formed in small quantity. No evidence of ring condensation in the ketones was obtained.

The tendency of tagetone to pinacol formation is marked. The pinacol and the substance $C_{10}H_{18}O$ previously obtained by the action of sodium in moist ether (*loc. cit.*) are also produced with zinc and acetic acid as reducing agent; zinc dust and alcoholic potash gave rise only to the pinacol, which is the sole product also of electrolytic reduction (*loc. cit.*).

The substance $C_{10}H_{18}O$ has now been proved to be an alcohol, which it is proposed to designate tagetol. Its density (0.8524) is somewhat low in comparison with that of tagetone (0.8803), a fact probably to be accounted for by partial polymerisation of the latter during distillation. Compared with tagetone, both tagetol and the pinacol are stable substances, distilling under reduced pressure with but little resinification. Tagetol reacts readily with acetic and phthalic anhydrides, but on regeneration from the liquid acid phthalate suffers considerable loss by resinification. Attempts to dehydrate tagetol with a view to the production of an olefinic terpene were but partly successful; heated at 180° with potassium hydrogen sulphate, the alcohol was mostly recovered unchanged, whilst the quantity of hydrocarbon produced by warming with phosphoric oxide was too small to permit of its characterisation.

The preservation of the two ethylenic linkings of tagetone during reduction, as shown by the analysis and the iodine value (336, equivalent to four atoms of iodine) of tagetol, indicates that the former does not function as an $\alpha\beta$ -ketone, and lends support to the view (*loc. cit.*) that tagetone is to be regarded as comprising, in its main reactions, the group $\cdot CO \cdot CH_2 \cdot C(:CH_2) \cdot CH : CH_2$ in preference to the alternative $\cdot CO \cdot CH : CMe \cdot CH : CH_2$. As, however, the latter group provides equally well for the fundamental property of capacity for enolisation, it is possible that the structure of the ketone is fully and more correctly represented by the tautomeric systems $\cdot CO \cdot CH_2 \cdot C(:CH_2) \cdot CH : CH_2 \rightleftharpoons \cdot C(OH) : CH \cdot C(:CH_2) \cdot CH : CH_2 \rightleftharpoons \cdot CO \cdot CH : CMe \cdot CH : CH_2$, whilst $\cdot CH(OH) \cdot CH_2 \cdot C(:CH_2) \cdot CH : CH_2$ and $\cdot CH(OH) \cdot CH : CMe \cdot CH : CH_2$ represent derived isomeric tagetols.

The characteristics recently ascribed to the volatile oil of *T. minuta* (*Bull. Imp. Inst.*, 1924, **22**, 3, 279) in conjunction with the

observation already made (Part I, *loc. cit.*) in reference to the oil of *T. petula* would indicate that tagetone or allied ketones are common to or characteristic of the flower oils of the genus *Tagetes*.

It is proposed to continue, as opportunity offers, the examination of the reactions of tagetone and tagetol.

EXPERIMENTAL.

Synthesis of $\gamma\eta$ -Dimethyloctan- ϵ -one.—Ethyl isovalerylacetate (25 g.) was heated under reflux on the water-bath with a solution of 3.4 g. of sodium in 150 c.c. of absolute alcohol and 27 g. of *sec.*-butyl iodide for 8 hours; the alkaline reaction had then disappeared. The excess of alcohol was expelled, and *ethyl sec.-butylisovalerylacetate*, b. p. $133^{\circ}/24$ mm. (Found: C, 68.4; H, 10.3. $C_{13}H_{24}O_3$ requires C, 68.4; H, 10.5%), and the unchanged isovalerylacetic ester were recovered by extraction with ether and separated by fractional distillation. The former (15 g.) was boiled for 15 hours with 300 c.c. of 10% alcoholic potash. (Hydrolysis by this reagent or by dilute sulphuric acid [1 : 3] appears to take place with difficulty.) $\gamma\eta$ -Dimethyloctan- ϵ -one was then isolated by steam distillation and, after fractional distillation, had b. p. $187^{\circ}/760$ mm., d_{4}^{25} 0.8190, n_D^{20} 1.4190—constants agreeing closely with those of the reduction product of the ketones of the flower oil, to which the constitution of $\gamma\eta$ -dimethyloctan- ϵ -one was assigned (*loc. cit.*) (Found: C, 76.6; H, 12.7. $C_{10}H_{20}O$ requires C, 76.9; H, 12.8%). The semicarbazones of the synthetic and the reduction product melted singly and in admixture at 91.5° .

Synthesis of β -isovaleryl- α -methylpropionic Acid.—A solution of 3.4 g. of sodium in 150 c.c. of absolute alcohol was heated under reflux with 25 g. of ethyl isovalerylacetate and 33 g. of ethyl α -iodopropionate until neutral (8 hours). The product (22 g.), isolated by extraction with ether and distillation, had b. p. 167 — $169^{\circ}/26$ mm. (Found: C, 61.4; H, 8.6. $C_{14}H_{24}O_5$ requires C, 61.7; H, 8.8%). On being boiled for 48 hours with alcoholic potash, it gave β -isovaleryl- α -methylpropionic acid, b. p. 169 — $170^{\circ}/24$ mm. (Found: C, 62.4; H, 9.3%), the semicarbazone of which did not depress the m. p. (166°) of the semicarbazone of the ketonic acid obtained by the oxidation of $\gamma\eta$ -dimethyl- Δ^{α} -octen- ϵ -one. (The m. p. was recorded in Part I, *loc. cit.*, as 165° . The purest sample melts at 166° .)

Decomposition of $\gamma\eta$ -Dimethyl- Δ^{α} -octen- ϵ -one with 70% Sulphuric Acid.—A well-agitated mixture (20 g.) of $\gamma\eta$ -dimethyl- Δ^{α} -octen- ϵ -one and 100 c.c. of 70% sulphuric acid was heated under reflux on the water-bath for 2 hours, and the product steam-distilled. The distillate was extracted repeatedly with ether, and the extract shaken

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with dilute alkali solution. The alkaline extract, on acidification and steam-distillation, gave a small quantity of *isovaleric* acid, which was identified by means of the silver salt and the anilide, m. p. 110—111°.

The residual ethereal extract, on distillation, gave two main fractions consisting essentially of methyl ethyl ketone (semicarbazone, m. p. 135°) and methyl *isobutyl* ketone (semicarbazone, m. p. 132°), respectively. A third small fraction (2 c.c.), collected at 180—190°/760 mm., was mainly composed, apparently, either of the original ketone or an isomeride, but the quantity available was too small for identification.

Owing to the small amount of $\gamma\eta$ -dimethyl- Δ^8 -octen- ϵ -one occurring in the essential oil, it was not possible to investigate this reaction further.

Decomposition of Tagetone by Alcoholic Potassium Hydroxide.—On steam distillation of the resinous mass resulting from treatment of 50 g. of tagetone under reflux with boiling alcoholic potash, a small amount (approx. 2 c.c.) of methyl *isobutyl* ketone was obtained. It was identified by means of its semicarbazone, m. p. 132°.

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