LXXX.—*Some Derivatives of Humulene.*

BY ALFRED C. CHAPMAN, F.I.C.

IN a former communication to the Society on the essential oil of hops (Trans., 1895, **67**, 54), I described the preparation from the oil, by fractional distillation, of a new sesquiterpene for which the name humulene was suggested. In the paper referred to, the chief physical constants of this hydrocarbon were given and a crystalline nitrosochloride melting at 164—165° was described, as also a well-crystalline nitrol-piperide (m. p., 153°), obtained by acting on the nitrosochloride with an excess of piperidene. Since the publication of this paper, I have made a further study of humulene, and have succeeded in preparing from it the following compounds.

Hydrochloride of Humulene Nitrol-piperide.

On passing dry hydrogen chloride into a solution of the nitrol-piperide in ether, a dense, white, curdy precipitate immediately falls;

this was collected and recrystallised either from boiling water or from alcohol. From the former solvent, it crystallises in hard nodular masses.

0.245 gave 0.0985 AgCl. $\text{Cl} = 9.95$.

$\text{C}_{15}\text{H}_{24}\text{NO}\cdot\text{NC}_5\text{H}_{10}, \text{HCl}$ requires $\text{Cl} = 10.01$ per cent.

The platinumchloride of this salt was prepared by mixing alcoholic solutions of platonic chloride and of the salt. It crystallises from alcohol in reddish needles which melt at $187\text{--}189^\circ$, at the same time undergoing considerable decomposition.

0.3297 gave 0.062 Pt. $\text{Pt} = 18.80$.

$(\text{C}_{15}\text{H}_{24}\text{NO}\cdot\text{NC}_5\text{H}_{10})_2, \text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 18.79$ per cent.

Humulene Nitrolbenzylamine.

On heating humulene nitrosochloride with an excess of benzylamine almost to the boiling point of the latter, a very vigorous action occurred, the mixture becoming almost solid. On adding sufficient alcohol to dissolve the whole of the products, then a little water, and allowing the solution to stand, the nitrolbenzylamine crystallised out in considerable quantity. It was purified by recrystallisation from boiling alcohol, from which it separates in bunches of very small needles, radiating from a centre. It melts at 136° .

0.200 gave 14.0 c.c. moist nitrogen at 7° and 757 mm. $\text{N} = 8.35$.

$\text{C}_{15}\text{H}_{24}\text{NO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ requires $\text{N} = 8.24$ per cent.

On dissolving this compound in dry ether and passing hydrogen chloride into the solution, a white granular precipitate of the hydrochloride formed; this is more soluble in ether than the corresponding nitrolpiperide compound. It was purified by recrystallising it several times from boiling water. It melts at $187\text{--}189^\circ$, but at this temperature undergoes some decomposition.

0.197 gave 0.0745 AgCl. $\text{Cl} = 9.34$.

$\text{C}_{15}\text{H}_{24}\text{NO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5, \text{HCl}$ requires $\text{Cl} = 9.42$.

Humulene Nitrosate, $\text{C}_{15}\text{H}_{24}\text{N}_2\text{O}_4$.

A mixture of 5 volumes of humulene, 5 volumes of amyllic nitrite, and 8 volumes of glacial acetic acid was cooled in a freezing mixture to about -15° . To this solution, a well-cooled mixture of equal volumes of nitric acid and glacial acetic acid was added little by little, with constant shaking; there was considerable evolution of heat and a white crystalline substance soon formed, the mixture becoming almost solid. Alcohol was now added, and after the contents of the tube had been allowed to remain in the cold for about an hour

the substance was collected with the aid of a pump, and washed with cold alcohol. The air-dried substance was found to be practically insoluble in alcohol and ether, but fairly readily soluble in benzene, chloroform, and glacial acetic acid on warming. It crystallises best from hot benzene in the form of extremely small colourless needles, often forming rosettes on the side of the containing vessel. It melts at 162—163°, but at this temperature there is considerable blackening and escape of gas.

0.112 gave 0.085 H₂O and 0.251 CO₂. C = 61.07; H = 8.40.

0.204 „ 16.2 c.c. moist nitrogen at 6° and 750 mm. N = 9.53.

C₁₅H₂₄N₂O₄ requires C = 60.81; H = 8.11; N = 9.46 per cent.

When this compound was heated with piperidine, the elements of hydrogen nitrate were removed and the nitrolpiperide before described, melting at 153° was obtained as in the case of the nitrosochloride.

It is interesting in this connection to note that Wallach (*Annalen*, 1894, 279, 392) has described an analogous compound obtained from caryophyllene. This nitrosate appears to resemble the one just described in its crystalline form and solubility, but melts at 148—149°. On boiling the nitrosate with an alcoholic solution of sodium ethoxide, no visible action occurred, but on heating the compound with the same solution in a closed vessel to the boiling point of water, it gradually disappeared, and was replaced by a dense precipitate of sodium nitrate. After filtering and evaporating the alcohol, a gummy mass remained which would not crystallise either from alcohol or ether, and which decomposed when distilled under a pressure of 20 mm.

Nitrosite of Humulene, C₁₅H₂₄N₂O₃.

To a mixture of equal volumes of humulene and light petroleum, a concentrated aqueous solution of sodium nitrite was added and the mixture thoroughly cooled; a volume of glacial acetic acid equal to that of the humulene taken was then added little by little with frequent shaking. The upper hydrocarbon layer rapidly acquired a deep blue colour, which, on standing for some time, became somewhat green. From this green layer, deep blue needles soon separated, which, after some hours, were collected and purified by one recrystallisation from boiling alcohol, from which solvent it separated in the form of magnificent, blue needles.

Two separate preparations gave the following results on analysis.

0.2085 gave 18.5 c.c. moist nitrogen at 18° and 762 mm. N = 10.24.

0.207 „ 17.8 „ „ „ at 15° and 756 mm. N = 10.04.

C₁₅H₂₄N₂O₃ requires N = 10.00 per cent.

The oily mother liquors from which the above crystals were obtained deposited a further quantity of needles of a paler colour than the above, and the mother liquors from these in turn deposited needles, which, after crystallisation from alcohol, were colourless. This compound, which could only be obtained in small quantity, gave the following numbers on analysis.

0.203 gave 17.5 c.c. moist nitrogen at 18° and 758 mm. $N = 9.93$.

$C_{15}H_{24}N_2O_3$ requires $N = 10.00$ per cent.

From this it appears that the white compound is isomeric with the blue, the latter being the nitroso- the former the isonitroso-derivative of humulene. This conclusion is borne out by determinations of the melting points of the two compounds given below, and by the almost complete conversion of the blue into the white by the long-continued boiling of its alcoholic solution.

Several preparations of the blue compound, purified by one crystallisation from alcohol, melted at about 120°, the effect of each subsequent recrystallisation from the same solvent being to very considerably increase its melting point and to render the substance paler in colour. The melting point of several preparations of the white compound obtained both from the original mother liquors and also by the boiling of an alcoholic solution of the blue compound, was 166—168°, at which temperature it underwent some decomposition, melting to a brownish liquid. The blue crystals also undergo some decomposition when heated to their melting point, forming a greenish liquid.

As an example of the effect of boiling alcohol on the blue compound, I may give the following numbers.

A preparation of the blue needles, after one recrystallisation from alcohol, melted at 120—121°. A second recrystallisation from the same solvent raised the melting point to 140°, the crystals obtained being much paler in colour. They were then dissolved in alcohol and boiled for several hours; the needles which separated on cooling had only a very faint blue tinge and melted at 165—168°. Two other experiments gave similar results, although the final melting point was not quite so high.

The blue nitrosite dissolves readily in hot alcohol, glacial acetic acid, ether, and chloroform, giving in all cases blue solutions, but is practically insoluble in light petroleum. Of the few blue solid nitroso-compounds at present known, the nitrosochloride of tetramethylethylene described by Thiele (*Ber.*, 1894, **27**, 455) is, perhaps, the most interesting, since, as Tilden has pointed out (*Trans.*, 1894, **65**, 324), it must be a true nitroso- and not an iso-nitroso-compound, as there is no hydrogen directly united to the two ethylenic carbon

atoms. It is, of course, well known that many other compounds containing the NO group, though colourless when crystallised, are blue when melted or when in solution, such as the pseudonitrols, nitrosobenzene, &c., and Tilden (Trans., *loc. cit.*) has suggested that the blue or green colour, which is so frequently observed when nitrosyl chloride and nitrous anhydride unite with unsaturated hydrocarbons, is to be regarded as an indication of the formation of a true nitroso-compound as the first step in the process, the colourless compound which afterwards separates out being probably an oxime. The experiments above described afford strong proof of the correctness of this suggestion.